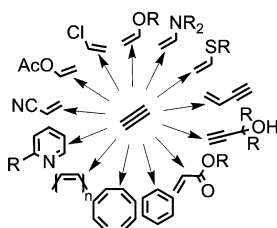# Catalytic Reactions of Acetylene: A Feedstock for the Chemical Industry Revisited

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CONTENTS

1. INTRODUCTION

With the start of the industrial production of acetaldehyde by acetylene hydration in 1916, acetylene became one of the most important raw materials for coal-based chemistry in the first half of the 20th century. However, the move from coal chemistry to petrochemistry made ethylene and propylene incomparably more important than acetylene. Similar to most of the acetylene-based processes, the production of acetaldehyde from acetylene was replaced in favor of an olefin-based process, the Wacker oxidation, in the late 1950s. This happened because of the more energy efficient and hence cheaper production of olefins as well as their easier handling compared with acetylene. Nevertheless, it should be kept in mind that acetylene is more reactive and often requires fewer process steps, leading to a higher overall selectivity.[1,2]

Since then it has repeatedly been discussed, mostly concomitant with an increase in the oil price, whether acetylene could become an important feedstock for the chemical industry again.[3−9] However, this has not happened to date, and the use of acetylene is still restricted to locations or processes with specific conditions. Nevertheless, the current discussion shows that with the development of new technology this might become reality.[10,11]

Although any prediction about oil production in the future bears uncertainty, there is agreement that coal and natural gas, important raw materials for acetylene manufacture, will last longer than oil. This might be seen as an indication that the role of acetylene could become important again. Also the shale gas boom, which decreased the price of natural gas in the USA, can favor both the production of olefins[12] and that of acetylene. While olefins are in higher demand at the present date, since they are the preferred feedstocks in many applications, future development of new acetylene-based processes could encourage the production of acetylene from shale gas.

Because of the desire for diversification and independence, it is advisable to reconsider acetylene as a possible feedstock for the chemical industry, and thus, the development of novel technology for the use of it would expand our options. China with its huge hard coal reserves can be seen as a pioneer in this direction. As one of the most important and fastest growing

markets as well as production sites for chemical industry, China is increasing its acetylene production, especially for vinyl chloride monomer (VCM) manufacture.[13,14] From this economic point of view, it is imperative to develop new technology for acetylene production and conversion.

Another driver for the use of acetylene as an alternative feedstock has recently been discussed by researchers of Evonik Industries:[15] With increasing amounts of fluctuating power in the electricity grid from wind and solar energy, especially in Germany, but also in other countries, there is a need for large consumers of electrical energy that can cope with fluctuating conditions. Acetylene can be produced from natural gas or other carbon-containing feedstocks in an electric arc furnace; hydrogen and carbon black are obtained as byproducts. Such plants require very significant amounts of electrical energy (on the order of several hundred megawatts of electrical energy for a large-sized plant) and can thus have a substantial load-leveling influence: In times of normal electricity supply and demand, the power plant associated with the acetylene plant would produce the electrical energy for operation of the arc furnace. If the power plant is based on a gas turbine, the hydrogen in the product stream from the arc can alternatively be used as a chemical feedstock or as additional fuel for the gas turbine. In times of surplus electricity production from renewable resources, the power plant would be shut down and the electricity would be purchased from the grid; in times of high demand of electrical energy, the arc furnace would be shut down (this is possible with short time constants) and the electricity from the power plant would be sold to the grid. In combination with low methane prices, as is the case in the USA presently because of the shale gas boom, and/or in cases where gas-fired power plants suffer from insufficient operation hours, as, for example, is increasingly the case in Germany, such schemes could become cost-competitive relative to the conventional chemical production routes.

Besides the economic factors, it should also be seen that acetylene is a fascinating molecule that shows interesting reactivity patterns, which will be shown throughout this review. Despite this, it has not been as extensively studied as ethylene in the past decades. With the industrial chemical production moving from acetylene as the major feedstock to olefins, a fact that is thoroughly covered in the work of Tedeschi,[16] research and development efforts have strongly decreased since the 1960s. However, chemical technology, with respect to catalysts, reactor technology, engineering, separation, and other factors, has very much advanced. Thus, there appear to be new opportunities to revisit acetylene chemistry and technology and explore novel options for the conversion of this interesting molecule. Consequently, increasing interest from academic researchers can be observed over the last years.

In this review, the term acetylene is used in its narrow sense and refers exclusively to C_2H_2; all other organic molecules bearing a triple C–C bond are termed substituted alkynes or higher alkynes. In the literature, one often refers to "acetylenes" in the latter cases. The reactions of substituted alkynes, which are of great interest in synthetic chemistry and have been more intensely investigated, partly because of the easier handling of substituted alkynes, are beyond the scope of this review. The interested reader is referred to some of the numerous existing reviews concerning addition reactions to substituted alkynes,[17–20] cycloaddition of substituted alkynes,[21,22] reactions where alkynes function as nucleophiles,[23,24] azide–alkyne cycloaddition reactions,[25] Pauson–Khand reactions,[26] and

alkyne metathesis.[27] While some of these reactions may serve as a source of inspiration for reactions applied to acetylene itself, others may only produce interesting products when applied to substituted alkynes. If one considers how substituents induce steric and electronic effects that alter the reactivity of the triple bond, the broad knowledge base available for substituted alkynes is often not directly transferable to acetylene.

This review will first give an overview about the production and especially the handling of acetylene. Afterward, the different reactions acetylene can undergo will be described. Many of these reactions were either discovered or greatly improved by the work of Walter Reppe. However, this is generally considered to be textbook knowledge and will thus only be discussed on a basic level. At the end it will be shown why acetylene can nowadays be seen as a field with several dark spots and a lot of possibilities for new discoveries and improvements.

2. PRODUCTION AND USE OF ACETYLENE

2.1. General Considerations

For the completeness of this review, the production of acetylene has to be included. However, the discussion contained herein is very brief; for a detailed, recent account on this topic, the interested reader is referred to Ullmann's Encyclopedia of Industrial Chemistry,[28] and older references are also available.[16,29] Although it is speculative to expect that acetylene will again become a major platform molecule, it is and will be an indispensable raw material for modern society.[2,28] Besides the use of CaC_2 for the desulfurization of pig iron and the production of the fertilizer $CaCN_2$, acetylene is important for construction work. It enables higher flame temperatures than most combustible gases, which is crucial for welding, especially in remote areas (e.g., for pipeline construction).[30]

However, for the production of base chemicals, alternative routes often exist. As a consequence, the decision for or against acetylene-based production is determined by costs. A major contribution is the energy price, which does not favor acetylene and shows the big drawback compared with olefin-based routes. The high energy needed for its production makes acetylene much more expensive than olefins, although acetylene-based routes often require fewer production steps and show high overall product selectivity. In cases where production is achieved with amortized plants or the supply of oil is insecure, along with abundant hard coal reserves, acetylene can be used for the production of chemicals in an economically sound manner. Also in the production of chemicals such as butynediol, where alternative processes are scarce, production is dominated by acetylene routes. Additionally, in the synthesis of fine chemicals, where acetylene is just a small part of the desired product and therefore plays only a minor role in feedstock costs, acetylene is used as a reactant.[2,28]

The reason why acetylene is expensive is of thermodynamic origin. As the formation of this molecule is highly endothermic, with a standard free enthalpy of formation of 226 kJ/mol, its synthesis requires high temperatures. In contrast to alkanes and olefins, the standard free energy of formation decreases with increasing temperature. In consequence, the formation of acetylene starting from methane begins at around 1000 K. However, at 2000 K carbon and H_2 are still more stable by about 100 kJ/mol, which leads to the decomposition of acetylene. Among the hydrocarbons, methane can be

considered as the most stable one, which means that starting from higher alkanes or olefins thermodynamically favors acetylene formation at lower temperatures compared with methane.[28,31]

2.2. The Calcium Carbide Process

The classical CaC_2 process is described first because it considerably differs from cracking processes. As the thermodynamic situation in this process is somewhat different, rapid quenching is not necessary. It produces acetylene as the only hydrocarbon and uses exclusively coal as a carbon source. In the first reaction step, CaC_2 is formed by the reaction of quicklime and coal at around 2000 °C. Although it is possible to combust coal with oxygen in the presence of CaO, the applied procedure is the melting of CaO with coke in an electrothermal shaft furnace.[32] This first reaction step also produces a stoichiometric amount of CO, which can be converted to synthesis gas by the water gas shift reaction. In the second step, CaC_2 is reacted with water to produce acetylene and $Ca(OH)_2$. Water can be added in large excess (wet generator) or almost stoichiometrically (dry generator). The second type is usually preferred. However, the main issue is the dissipation of the heat of reaction. In order to remove impurities and ensure sufficient product quality, the produced gas is subjected to several scrubbing operations. Dry generators can have a capacity of 5 t of acetylene per hour.[28]

2.3. Cracking Processes

Cracking processes can be distinguished by the method of heat supply. Three different types exist: partial combustion, electrothermic cracking, and thermal cracking with heat carriers. Although the Dow partial combustion cracking process (PCC) and the advanced cracking reactor process (ACR) of Kureha, Chiyoda, and Union Carbide are interesting representatives of the third type, only the first two types will be described in more detail because just these types operate on a commercial scale. Furthermore, the PCC and ACR are mainly developed for producing olefins.[28]

2.3.1. Partial Combustion. Partial combustion processes can practically make use of almost any carbon -containing feed. However, the availability and ease of handling favor the use of natural gas. In any partial combustion process, the fuel and a defined amount of oxygen are preheated, mixed, and injected into a reaction chamber. In the reaction chamber, a portion of the hydrocarbons is burned, and the temperature increases to approximately 1200 °C, which leads to thermal cracking of the remaining hydrocarbons. The formed radicals, mainly H and CH_3, can recombine and terminate or undergo chain reactions that produce among others acetylene.[31] From there, the reaction mixture is rapidly quenched, most commonly with water. From the thermodynamic considerations discussed at the beginning of this section, it is clear that the desired products are thermodynamically not favored, and hence, short residence times (in the range of milliseconds) and rapid quenching are necessary.[31] The most common partial combustion process is the BASF (or Sachsse−Bartholome) process, which mainly differs from other partial oxidation processes by the design of the burner and not by the process steps and principles.[33,34]

To achieve a hydrocarbon conversion that is independent of gas mixing, respectively diffusion, the gases are premixed. This allows residence times smaller than the decay time of acetylene. Uniform mixing is important because high local oxygen concentrations cause preignition. In order to save oxygen and fuel, the gas mixture is preheated, which also gives higher flame

temperatures and consequently results in higher propagation speeds. After leaving the reaction chamber, the gas mixture gets cooled by a spray of a cooling agent. Depending on the feed and the reaction conditions, the product distribution can differ; however, typically the gas after the reactor contains around 50% H_2, 30% CO, 7% acetylene, and some methane. The usual capacities of a burner are 1 t of acetylene per hour.[28]

A special partial oxidation process for the conversion of heavy residues from oil refining is the submerged flame process. It was abandoned in 1973, and typical capacities are similar to the Sachsse−Bartholome process. As the main difference, because of the different feed composition and cracking temperature, the cracked gas contains around 6% acetylene, 7% ethylene, 29% H_2, and 42% CO.[35]

2.3.2. Electrothermal Processes. Electrothermal processes have the advantage that the heat for the reaction is not supplied by burning a portion of the hydrocarbons, which can decrease the consumption of hydrocarbons by up to 50%. However, as the thermal efficiency of electricity production is in general lower than direct heat generation, electrothermal processes are economically and ecologically favorable only if cheap or renewable electricity is supplied. Other advantages of electrothermal processes are their easy and robust design and the fact that the arc can be turned off and on immediately.[2,28] These features favor the use of electrothermal processes under conditions of high levels of fluctuating renewable power in the grid, a situation that is expected to be encountered increasingly in the future.

The most prominent electrothermal process, the Hüls arc process,[6] preferentially uses natural gas as a feed. However, upon modification liquids and solids can also be converted. The general requirements for high temperature and short residence time have to be met as well. The arc furnace consists of an anode and a cathode, a reaction chamber, and a quench unit. The anode and cathode are made of carbon steel and cooled by water. They operate with a direct current of 1200 A, which creates an electric arc with a length of around 1.2 m.[6,28] The gas is tangentially injected into the arc, where it is cracked, and it resides there for a few milliseconds. After the gas leaves the arc, its temperature is still around 1800 °C, which makes rapid quenching necessary. This can be done either by prequenching with hydrocarbons, increasing the ethylene yield, or by direct quenching with water. The rate of temperature decrease is as high as 10^6 K s^{-1}. The capacity per furnace (a plant can consist of up to 20 furnaces) is also in the range of 1 t acetylene per hour. Normally the gas contains 15% acetylene, 7% ethylene, 58% H_2, and 14% unconverted methane as major components.[28]

In conclusion, the use of the CaC_2 process is preferred where coal is available as a cheap feedstock for electricity generation and the process itself. Partial oxidation processes are preferred when hydrocarbons are available but electricity is expensive, and electrothermal conversion of hydrocarbons is used if both hydrocarbons and electricity are cheap.[6] The product stream of the CaC_2 process consists of stoichiometric but separated amounts of CO and acetylene, whereas the other processes produce a mixture of gases in which acetylene is present in amounts up to 15% depending on the detailed process conditions.[28]

3. HANDLING OF ACETYLENE

3.1. General Considerations

It was already shown in the previous section that the production of acetylene requires excellent engineering knowledge. However, its handling, especially under pressure, also needs a sound basis in high-pressure engineering technology. The reason why special care has to be taken can also be ascribed to thermodynamics and the high energy content of the unstable molecule. The most important rules for working safely with acetylene are the subject of this section. Readers are referred to more detailed descriptions of the safety aspects of acetylene handling[16,29,36,37] before working with this compound.

As several types of reaction, such as carbonylation, vinylation, and cyclization, were introduced by Reppe and tested or used on an industrial scale in the first half of the 20th century, a substantial amount of important and useful information about handling of acetylene can be found in Reppe's original work.[38,39] Furthermore, the Technische Regeln für Acetylenanlagen and Calciumcarbidlager (TRAC) of the government of the Federal Republic of Germany states clear rules about handling acetylene in a safe manner.[36] With the beginning of 2013 the TRAC is no longer legally binding,[40] but the rules can still be used as a source of knowledge.[41] Handling on an industrial scale is beyond the scope of this review, but it should be mentioned that it is possible to work with pressurized acetylene safely on a large scale and that this has been done for years (e.g., for the manufacture of butynediol and methyl vinyl ether).[42]

Although there are clear rules, as has just been mentioned, it is difficult to guarantee absolute safety of experiments. This can be seen, for example, by comparing the stability pressures of acetylene given by Reppe and the Bundesanstalt für Materialprüfung (BAM), where the results of the BAM give lower values because of the use of different ignition methods.[43−45] Hence, the experimentalist should always be careful and perform experiments only in a cubicle that is sufficiently armored against blasting of the equipment.

There are three major issues of which one should be aware when working with acetylene: (1) its high reactivity toward oxygen; (2) its high tendency to form explosive acetylides; and (3) its thermodynamic instability and the tendency to decompose into the elements.

3.2. Acetylene Mixtures with Oxygen

Concerning issue (1), the presence of oxygen or air has to be excluded, as explosive mixtures of air and acetylene are formed between 2.5 and 82 vol % of air in acetylene and the energy required for decomposition is strongly influenced by the presence of oxygen.[46] In the case of deflagration, the pressure increase would be 11-fold. In the case of mixtures of pure oxygen and acetylene, the upper explosive limit is extended to 93% oxygen in acetylene and the pressure increase is 50-fold.[28] In laboratory use, this issue can be overcome by excessive purging with inert gas. However, the connection to the acetylene bottle has to be secured by a flame arrester and not only by a check valve in any case.[47,48]

3.3. Materials

The formation of explosive acetylides can be avoided by the proper choice of suitable materials, which does not allow the use of copper- or silver-containing equipment, since the acetylides of these elements are especially problematic. In the

case of copper, the TRAC restricts the use of materials containing more than 65% Cu.[36] However, as other suitable materials exist, one should completely avoid the use of brass or other materials containing metals that form reactive acetylides. This rule might also exclude the use of some catalysts that contain copper, which could be converted to copper acetylide under the reaction conditions. If using copper as a component in the catalyst is intended (it is a good catalyst for several acetylene-based conversions), one should be aware of the possibility of forming explosive copper acetylide. However, in a wet state copper acetylide is not prone to explosion.[39]

The materials used for reactors and other equipment in contact with gaseous acetylene should be either steel that does not contain any alloy components except carbon or highly alloyed stainless steel. The last recommendation goes back to the observations of Reppe, made during the scale-up of butynediol synthesis to industrial production. As free formic acid is formed under the reaction conditions, corrosion-resistant materials are required. Consequently, stainless steel was used, and it was realized that only highly alloyed steels (V4A, which corresponds to 1.44XX according to the EU norm, and the 316 steels according to the AISI norm) do not favor the formation of cuprene.[39] The same holds for 1.4571 steel, which has in addition low amounts of Ti as an alloy component.[49]

3.4. High-Pressure Equipment

The use of pressurized acetylene in an advanced setup requires a compressor, as the available equipment allows just releasing acetylene with a relative pressure of 1.5 bar from the gas bottle. However, the good solubility of acetylene in several solvents (e.g., methanol) provides the possibility to investigate certain reactions with an acetylene pressure higher than 1.5 bar, even if it is taken from a typical container. This can be done by introducing acetylene in an autoclave that contains a suitable solvent at the temperature of a dry ice/methanol bath. A concentration of acetylene up to 4 mol/L in methanol can be reached in this way.[49] The achievable concentration depends on the solvent used.[50] This procedure for using pressurized acetylene at pressures up to 50 bar for reactions has been used in our laboratory without problems.

Because of the high solubility of acetylene in the solvent even at high temperatures, the pressure of gaseous acetylene does not give clear information about the amount of acetylene in the system without knowledge of the solubility of acetylene under the applied conditions. The amount of acetylene fed into the reactor system is thus best determined by the use of a mass flow controller during charging of the autoclave.

High-pressure acetylene can be obtained with compressors, which have to fulfill the general specifications described in this section. In addition, these compressors should operate with a low stroke speed in order to avoid a sudden pressure increase, although in an oxygen-free atmosphere there is little concern about decomposition upon a pressure surge.[39,46]

Even at atmospheric pressure, acetylene can decompose if the energy supplied for ignition is sufficiently high.[44] Therefore, the most important design rule for the equipment used is a pressure tolerance up to at least the pressure $P*$ given by eq 1, which is based on the measurement of the pressure increase upon acetylene decomposition:[28,36]

$$P* = 11P + 10 \text{ bar} \tag{1}$$

where P is the maximum working pressure in bar. This means that if one wants to work under an acetylene pressure of 25 bar,

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the whole setup needs to be able to tolerate a pressure of almost 300 bar. This requires the installation of safety valves and min−max manometers to ensure that the pressure in the system does not exceed the given limit. The use of short pipes with a small inner diameter is advisable because the detonability limits are strongly dependent on these parameters.[51,52] This provides an additional safety margin for laboratory work because the diameter of pipes typically used there lies below that of pipes used in the decomposition tests.

Furthermore, one also has to account for the temperature (i.e., the condensation curve) in order to avoid condensation and the formation of liquid acetylene, which is considered as a serious danger. This means that the temperature of the acetylene has to be monitored and the compression needs to be stopped if the temperature falls below a certain value at a given pressure. Although exclusively liquid acetylene without any gas phase was claimed to be not prone to decomposition,[53] this is difficult to ensure, and condensation should be avoided in any case.[28]

The use of a solvent or dilution with other gases helps to decrease the tendency for decomposition.[38,43,54] In the case of dilution with other gases, this effect is related to the heat capacity of the gas. The beneficial effect of reacting acetylene in a solvent is maintained only if no separate gas phase is formed.[28]

With respect to laboratory use, it has to be mentioned that the acetylene released from the bottle always contains acetone (in rare cases, DMF is used as a solvent).[28] According to this, all materials, especially those used for sealings, should be able to withstand exposure to acetone, and the acetylene needs to be purified by passing it over an adsorbent of suitable size or polarity (e.g., zeolite A and alumina[55] or zeolite 13X[56]).

4. REACTIVITY OF ACETYLENE

This section shall serve as a basis for the following descriptions of the different reactions, group these into certain types, and give an overview of the general reactivity aspects of acetylene and the role of acids/bases and nucleophilicity/electrophilicity therein. Scheme 1 gives an overview of the possible reactions of acetylene.

At the beginning of the review the strongly endergonic nature of acetylene with an enthalpy of formation of 226 kJ/mol was mentioned. While this is a disadvantage for the production of the compound, it is an advantage in further

**Scheme 1. Reaction Classes of Acetylene**

reactions, since even with highly unreactive molecules such as water or carbon dioxide, overall reactions always tend to be thermodynamically favored.

Acetylene would therefore be expected to have very high reactivity. Given this high value of the enthalpy of formation, it is very difficult to imagine reactions with acetylene that would not be exothermic. Its high reactivity is confirmed by the ease with which acetylene decomposes to form coke and hydrogen. However, harnessing the potential of acetylene to produce useful chemicals in a selective manner is not as easily done as might be expected from thermodynamic considerations alone. A very good example of this is the cyclotrimerization of acetylene to benzene. Although the reaction itself is very exothermic and forms a stable molecule, temperatures around 600−700 °C are required for it to proceed in the absence of a catalyst.[57] An appropriate catalyst can, however, strongly facilitate this reaction and lead to benzene formation at room temperature[58] or even at temperatures below 0 °C, as was observed for niobium and tantalum pentahalogenides.[59] This example shows that although certain reactions of acetylene might have high activation energies, suitable catalysts can cause an immense acceleration of the desired reaction.

The first reaction class that will be discussed is the electrophilic addition of Brønsted acids to the triple bond of acetylene. These reactions need suitable metal catalysts (Hg, Au, Cu) to guide the reaction into the desired way because the typically used acidic environment poses a serious challenge. In the presence of acid catalysts, most authors report that polymerization reactions occur, which in the end are responsible for deactivating the catalyst by blocking access to the active sites. This will also be discussed in the further sections. The formation of polymeric compounds is also a major issue in the hydration of acetylene with mercury catalysts in acidic media, a reaction that has been performed on an industrial scale.[60] On the other hand, the reaction of acetylene with methanol on a ZnO/SiO$_2$ catalyst to produce methyl vinyl ether has been suggested to proceed on acidic sites of the catalyst, which are formed after 48 h of activation on stream.[61] This shows that acid catalysis might still be of interest in acetylene chemistry, but for this the acid-site structure and acidity must be controlled properly. This acid catalyst is even more interesting because vinylation is usually performed under basic conditions.

Base-catalyzed reactions of acetylene are more frequently encountered, since the protons of acetylene are relatively acidic for a hydrocarbon ($pK_a = 25$), and thus, the molecule can be activated by bases. Vinylation (i.e., nucleophilic addition of alcohols, thiols, and amines to the triple bond) and ethynylation (i.e., nucleophilic addition of an acetylide anion to a carbonyl group) both belong to this category. It is interesting to note that in basic media acetylene can react with nucleophiles, as in the case of vinylation, but in spite of this, acetylene is a poor electrophile. This becomes apparent when one considers that ethynylation reactions occur under milder conditions than vinylation. Also, in spite of the fact that carbonyl compounds can themselves be deprotonated to form enolate anions (the equilibrium constants for this reaction are often several orders of magnitude higher than that for the deprotonation of acetylene), in the presence of a carbonyl compound the ethynylation of the carbonyl compound is the preferred reaction pathway. Vinylation of the enolate anion has been suggested to explain the formation of methylenediox-obicyclooctanes in the reaction of ketones with acetylene in the
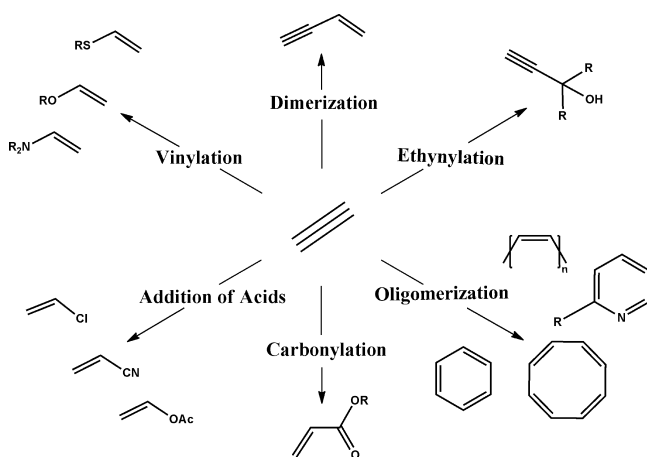
KOH in dimethyl sulfoxide (DMSO) system at 80 °C at an acetylene pressure of 12−14 bar,[62] but this is a rather rare example where vinylation of an enolate might occur. In other words, the ethynylation and vinylation reactions are distinguished from each other by the fact that in the former acetylene can find another electrophile with which to react, whereas in the latter acetylene is forced to function as an electrophile because of the lack of a more suitable option. It is noteworthy that while the nucleophilic addition of an acetylide anion to acetylene leading to vinylacetylene seems to be a plausible reaction under basic catalysis, this product has been reported only with the Nieuwland catalyst.[63] This shows again how a metal catalyst can modulate the reactivity of acetylene. The Cu catalyst facilitates the deprotonation of acetylene by coordination to the triple bond, which is known from the Sonogashira cross-coupling reaction, and consequently forms the nucleophilic Cu acetylide. Deactivation of catalysts by pore blocking, polymer formation, or coking is less frequently observed under basic conditions than in acidic media, suggesting that the tendency for reaction of acetylene with itself is less favored under basic conditions.

Although acid−base catalysis can offer some possibilities for producing useful compounds from acetylene, it is often metal species that catalyze the more interesting transformations of acetylene. Some reactions of acetylene catalyzed by metal ions in solution have already been mentioned. Still, there is a lot of room for improvement in catalyst selectivity and activity as well as in understanding of the reaction mechanisms. One impressive transformation observed only with metal catalysts is the carbonylation reaction. This was first achieved by reacting acetylene, carbon monoxide, and water or an alcohol with nickel carbonyl or nickel salts.[64] Recently a very active catalyst system for carbonylation consisting of palladium acetate, 2-pyridyldiphenylphosphine, and methanesulfonic acid has been reported.[65,66] The most fascinating aspect of this system is that the presence of the 2-pyridyldiphenylphosphine ligand is essential for the catalyst to function: using 4-pyridyldiphenylphosphine instead of 2-pyridyldiphenylphosphine drastically reduces the activity, as was observed in the carbonylation of propyne.[67] This example shows very well the level of precision that might be required in order to make acetylene react in the desired way, but it demonstrates on the other hand that a properly chosen catalyst could direct reactions of acetylene probably to any target molecule. For most reactions of acetylene, however, such a catalyst has not yet been reported.

The cyclotrimerization of acetylene itself, catalyzed by Ni and Co complexes, is quite an impressive transformation. However, the accidental discovery that cobalt complexes that catalyze the cyclotrimerization reaction can also catalyze the reaction of two acetylene molecules and one nitrile molecule to form a pyridine molecule[68] shows just how varied the reaction possibilities of acetylene are and how careful analysis of a reaction gone in an unexpected way can lead to new discoveries, especially with a molecule as reactive as acetylene.

In view of the great number of possible thermodynamically viable transformations of acetylene, it is imperative to underline the need for catalyst selectivity and specificity with respect to a desired reaction. Especially required are catalysts that avoid the decomposition of acetylene or the formation of polymers that would block access to the active sites. Achieving this might not be straightforward and trivial. However, examples where this has been accomplished are available. In the following, we will discuss the reactions leading to a number of important products

that can be obtained from acetylene, especially focusing on the developments in the post-Reppe era.

5. ADDITION OF BRØNSTED ACIDS

5.1. Vinyl Chloride

Poly(vinyl chloride) (PVC) is an important raw material for many applications because of its outstanding properties and the possibilities to modify them. In particular, the excellent resistance to chemicals and weathering is remarkable and makes PVC a good material for use in housing, for example.[69] Consequently, the production of VCM is expected to increase further, especially in emerging markets, with their high demand for new residential buildings. In the context of this review it is interesting that China, the largest consumer of VCM, has been producing VCM predominantly by the hydrochlorination of acetylene since the beginning of VCM manufacture.[14] This is a result of the fact that China owns vast coal reserves, making acetylene a relatively cheap feedstock compared with imported oil.[13]

Compared with ethylene-based production of VCM, the hydrochlorination of acetylene has the advantage of involving a single reaction step, whereas the ethylene-based processes include several reaction and separation steps.[2,14] This is often associated with the need for chlorine recovery from hydrochloric acid. This shows that in cases where acetylene is an available and cheap feedstock, the hydrochlorination reaction is particularly interesting.[2]

The hydrochlorination of acetylene (Scheme 2) has been strongly influenced by Hg and Au catalysis, as developed in the

Scheme 2. Solid Catalysts for Hydrochlorination of Acetylene
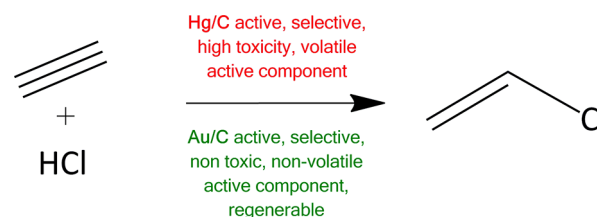
work of Hutchings. In his well-recognized publication from 1985, he correlated the catalytic activities of several metal chlorides with their standard electrode potentials. For efficient catalysis, the catalyst needs to be able to form compounds with acetylene and HCl. In addition, the catalytic activity increases with increasing standard reduction potential, so Au is more active than Pd and Hg. The support of choice is activated carbon, as other compounds with acidic functionality tend to form polymeric deposits on the surface.[70]

However, the industrial process still makes use of $HgCl_2$ supported on activated carbon as a catalyst with a $HgCl_2$ loading of around 10 wt %.[14] The reaction is realized by passing an almost stoichiometric gas mixture of acetylene and HCl at temperatures from 140 to 200 °C over the catalyst. The applied pressure lies slightly above atmospheric pressure with a gas hourly space velocity in the range of 100 h^{-1}. Under these conditions, the reaction occurs in a hot spot zone that moves through the reactor with time on stream.[71]

The problem associated with the Hg-based catalyst is rapid deactivation because of the loss of the active component. This is caused by the high volatility of $HgCl_2$ itself as well as its

reduction to volatile metallic mercury under the applied conditions. Consequently, the lifetime of the catalyst inventory is only around 120 days.[56]

Mechanistic studies of the hydrochlorination over $HgCl_2$ catalysts have been restricted to kinetic models, and to our knowledge there has been no contribution since the 1980s.[72] However, those studies suggest that the mechanism of the hydrochlorination over $HgCl_2$ catalysts is dependent on temperature. Up to 135 °C, a Langmuir–Hinshelwood model agrees well with the experimental data. Above this temperature, the determined activation energy decreases from 40 to 10 kJ/mol. It is suggested that above 135 °C the reaction proceeds via an Eley–Rideal mechanism, where HCl is adsorbed on the catalyst and gas-phase acetylene reacts by collision with the HCl–catalyst complex. Although the authors determined effectiveness factors and showed that no mass transfer limitations exist, the value of the activation energy seems to be unexpectedly low. Other explanations could not be ruled out because of experimental limitations.[72] In view of the aforementioned hot spots, an isothermal kinetic model might be too simple to deduce a clear mechanism. Modern computational methods could help to considerably improve the mechanistic understanding of this reaction.

In recent years, academic researchers have lost almost all of their interest in $HgCl_2$ as a catalyst, so new developments in this field are scarce. In industry the use of catalysts with low mercury content has been attempted. To achieve this, $HgCl_2$ is selectively deposited in the mesopores of the carbon support. This approach makes better use of the $HgCl_2$ because evaporation from macropores is decreased and carbon deposits in micropores do not reduce the accessible amount of $HgCl_2$.[73]

Acetylene hydrochlorination with gold-based catalysts uses conditions similar to those already mentioned for $HgCl_2$. The catalysts are prepared by incipient wetness impregnation of activated carbon with a solution of $HAuCl_4$ in aqua regia. The dried material shows Au particles with sizes of 5 nm. However, it was shown by XPS that the active state is Au(III). Compared with $HgCl_2$, the activity, on a molar basis of metal, is higher by an order of magnitude.[74] In contrast to $HgCl_2$, deactivation occurs not because of loss of the active component but mainly because of the reduction of Au(III) to lower valence states. At temperatures up to 100 °C coke deposition also contributes to deactivation, whereas particle growth and sintering seem to be negligible.[75,76]

In addition to low concerns with respect to toxicity as opposed to mercury compounds, a great advantage of Au is that the activity of the deactivated catalyst can be fully restored without significant loss of gold by treating it in boiling aqua regia.[77,78] Besides this, online reactivation with, for example, HCl is also possible.[79] Although a comparison between different publications is difficult, as the used conditions vary, it seems that the space time yield and the rate of deactivation are comparable for Au and $HgCl_2$ catalysts,[56,74,77] as can also be seen in Table 1. This raises the question of why Au catalysts have not yet been introduced as a drop-in solution in existing processes.

The mechanism of acetylene hydrochlorination has been investigated by experiments with higher alkynes and by DFT calculations.[80–82] The use of higher alkynes as reactants shows that the addition of HCl follows the Markovnikov rule. Furthermore, using DCl as a reactant revealed that HCl adds to the alkyne in an anti configuration.[82] The DFT calculations do not unambiguously point to a certain reaction pathway.

Table 1. Comparison of Catalytic Activities for HCl Addition to Acetylene (from ref 74)

metal	metal loading (wt %)	initial rate $(mol_{HCl}\ mol_{metal}^{-1}\ h^{-1})$	average decay rate (% conv. h^{-1})
Hg	8.8	78.3	8.8
Au	1	461.0	6.0

However, the models used rely either on $AuCl_3$[81,82] or Au_2Cl_6[80] as active site, which might not correctly describe an Au(III) site on a gold-based nanoparticle.

Other metals play a minor role in the gas-phase hydrochlorination of acetylene because their activities are inferior than those of $HgCl_2$ and Au or they deactivate faster. $PdCl_2$ on carbon, for instance, shows a similar activity compared with Hg-based catalysts but a higher rate of deactivation because of coke formation.[83]

In order to increase the activity and catalyst lifetime, gold was alloyed with other noble metals. In general this did not significantly increase the activity. Furthermore, if the activity was in fact increased, the catalyst deactivated much more rapidly. Most likely this happened because of the oligomerization activity of the alloyed metal and the formation of coke associated with it.[84]

Alloying with Cu[81] or La[85] seems to be more promising with respect to increased stability. At the same level of activity as observed for pure gold, the deactivation rates were significantly decreased. This should be further investigated and the origin of the improved performance should be explored, since this could provide guidelines for a more targeted optimization of this catalyst system.

Alternatively, it is also possible to perform the hydrochlorination in the liquid phase. The major advantage of a liquid-phase process is the excellent temperature control for this highly exothermic reaction. However, there are only few examples of work in liquid phase. One study made use of ionic liquids as solvents and metal chlorides as catalysts.[86] The most active catalysts are copper(II) chloride, hexachloroplatinic acid, and tetrachloroauric acid. They operate under temperature, space velocity, and feed composition conditions similar to those for the well-investigated gas-phase processes. Compared with these, the conversion for $CuCl_2$ at a space velocity of 100 h^{-1} and a temperature of 180 °C is around 40% at a selectivity greater than 90%, which would make recycling of unconverted gases necessary. Nevertheless, this study suggests that there exist possible ways to circumvent the problems associated with the $HgCl_2$ process. The patent literature also gives examples of the preparation of VCM in the liquid phase using homogeneous catalysis.[87,88] These systems consist of group VIII metal chlorides in a mixture of an aliphatic solvent and fatty amines and operate at temperatures from 150 to 200 °C.

In an attempt to combine the advantages of homogeneous and heterogeneous catalysis, a supported liquid-phase catalyst composed of $RhCl_3$ dissolved in N-methylpyrrolidone supported on activated carbon was reported for the hydrochlorination of acetylene at 170 °C.[89] The activity of this system was superior compared with those of known catalysts. Unfortunately, the reported data are insufficient for a detailed validation of the study, and to our knowledge no subsequent work has been published, which is surprising given the excellent reported performance of the system with respect to both activity and deactivation behavior.

5.2. Acrylonitrile (Addition of Hydrogen Cyanide)

Addition of hydrogen cyanide to acetylene was one of the methods used to obtain acrylonitrile before the propylene ammoxidation (SOHIO) process was introduced in the 1960s.[90] The addition reaction is carried out by passing a mixture of acetylene and hydrogen cyanide through a concentrated solution of CuCl, NH$_4$Cl, and HCl. This process produces around 15 g of acrylonitrile per liter of solution per hour.[29] Since this catalyst solution is very similar to the Nieuwland catalyst system,[63] it is not surprising that vinyl-acetylene, divinylacetylene, chlorobutadiene, cyanobutadiene, and other impurities are also formed. These render the obtained acrylonitrile much less suitable for polymerization than acrylonitrile obtained from the SOHIO process.[91] With increasing oil prices, this reaction might be of interest for producing acrylonitrile in areas rich in coal and/or natural gas, but for that purpose new catalyst systems need to be developed to avoid the formation of side products that could affect the polymerization process of the obtained acrylonitrile.

5.3. Vinyl Acetate (Addition of Acetic Acid)

The first production process for vinyl acetate on an industrial scale was the addition of acetic acid to acetylene. The reaction was initially carried out in the liquid phase with mercury catalysts at 60−100 °C, but this approach was later replaced by a gas-phase process. In the gas-phase process, zinc acetate supported on carbon is used as a catalyst, and a gas mixture of acetylene and acetic acid is reacted on this catalyst at temperatures in the range of 160−220 °C.[92] This was the main route for producing vinyl acetate before the 1960s, when ethylene acetoxylation became economically more attractive. Even so, the acetylene-based process still accounts for 20−30% of the world's production of vinyl acetate. Although it is not of foremost industrial importance, the addition of acetic acid to acetylene is an attractive process in regions where cheap acetylene can be obtained.

Like many other reactions of acetylene, this reaction has not received much interest from the academic community during the last 50 years. Several kinetic studies have been published, and they suggest that with increasing temperature the rate-limiting step changes from acetylene adsorption at low temperature[93] through an intermediate temperature window to acetic acid adsorption at high temperature.[94] With a mixture of deuterated acetic acid (CD$_3$COOH) and acetylene it was shown that undeuterated vinyl acetate is formed first and that the formation of deuterated vinyl acetate starts only after a period of time, indicating that acetate anions are first removed from the catalyst by reaction with acetylene and afterward regenerated by acetic acid from the gas phase.[95]

Improvements in catalyst performance and stability could make the addition of acetic acid to acetylene economically more attractive, since only about 70 g of vinyl acetate per liter of catalyst per hour is produced. However, since the reaction is exothermic with an enthalpy of reaction of 116.5 kJ/mol, too high an activity of the catalyst could cause heat transfer problems. This in turn would require the construction of new plants for the production of vinyl acetate that use reactor concepts allowing for better heat removal, instead of using the already existing plants. It has been reported that using a carbon support with a higher content of carboxyl groups can improve the productivity of the catalyst.[96] A high concentration of these functional groups on the carbon support of the zinc acetate catalyst can increase the activity by around 15−20%.[97]

However, as the demand for vinyl acetate has not increased dramatically enough to justify new investments, not much effort has been spent on the development of new catalyst generations.

5.4. Acetaldehyde (Acetylene Hydration)

The hydration of acetylene catalyzed by neutral or acidic aqueous solutions of mercury salts was first reported in 1881 by Mikhail Kucherov. This reaction has been used industrially for the production of acetaldehyde, especially in areas of the world where acetylene was easy to obtain.[60] The drawbacks of this process are the use of toxic mercury salts, the reduction of mercuric salts during the reaction, and the formation of polymeric species that deactivate the catalyst.[98] Typically temperatures of 90−95 °C are used in this process, and reduction of the mercury salts can be overcome by adding iron(III) sulfate to reoxidize the reduced mercury.

Acetylene was also used in a different process to produce acetaldehyde in Germany during the Second World War. The first step of this process consisted of vinylation of methanol with acetylene in a basic medium to produce methyl vinyl ether, and this was followed by hydrolysis of the ether in an acidic medium to release methanol and acetaldehyde.[29]

The hydration of acetylene was also attempted on zeolites exchanged with ions such as Ag$^+$, Zn^{2+}, Cd^{2+}, and others at temperatures between 100 and 200 °C. These studies were carried out at atmospheric pressure with an excess of water and with all reactants in the gas phase. Although these catalysts were initially active for acetylene hydration, most of them deactivated quickly because of the formation of polymers that blocked the active sites.[99−101] The only catalysts that did not suffer from deactivation in these studies were the metal-exchanged clinoptilolites.[99] It has been suggested that this is a consequence of their smaller pore size, which supposedly does not allow the formation of polymers.

The worldwide demand for acetaldehyde has decreased over the last years, mainly because acetaldehyde oxidation to obtain acetic acid is being replaced by methanol carbonylation.[60] With this in mind, it might not be very attractive to produce acetaldehyde from acetylene, except in regions where acetylene is available at a very low price. However, the reaction itself may be worth studying in order to get more insight in the reactivity of acetylene.

6. ETHYNYLATION

The addition of alkynes to carbonyl compounds in basic media to form propargylic alcohols (Scheme 3) was a known reaction

Scheme 3. Catalysts for Ethynylation Reactions
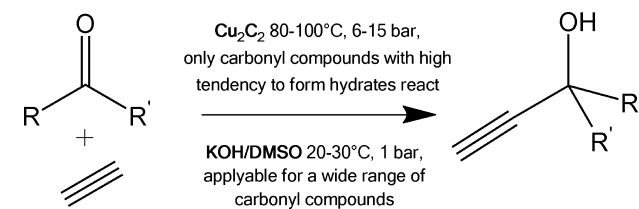
at the time of Reppe, having first been reported by Alexei Favorskii as far back as the early 1900s. The merit of Reppe's work, however, lies in the development of a process for the addition of acetylene to formaldehyde to obtain 1,4-butynediol with propargyl alcohol as a side product.[29,102] The process can be forced to produce higher amounts of propargyl alcohol if a higher ratio of acetylene to formaldehyde is used. The catalyst

developed for this process consists of copper oxide and bismuth oxide supported on silica, but it is actually the copper acetylide formed during the reaction that catalyzes the reaction. The bismuth oxide acts as a promoter by inhibiting the formation of metallic copper, which would catalyze the formation of cuprene and clog the reactor. The process is carried out by passing a solution of aqueous formaldehyde and a flow of gaseous acetylene under pressure over the catalyst. The 1,4-butynediol obtained from this process has been used for further transformation to 1,4-butanediol, tetrahydrofuran (THF), butadiene, and also pyrrolidone. The ethynylation of aldehydes other than formaldehyde was also found to be catalyzed by copper acetylide, although at a lower rate, whereas for the ethynylation of ketones, alkaline hydroxides or other basic compounds are preferred. According to Reppe, the reactivity of a carbonyl compound toward the copper acetylide catalyst increases with the increasing ability to form hydrates.[103]

The process for obtaining 1,4-butynediol has not changed much since its invention. Catalyst compositions of 3−6% bismuth oxide and 10−20% copper oxide on silica are used, and the reaction is carried out at 80−100 °C and acetylene pressures of up to 6 bar (up to 15 bar when propargyl alcohol is the desired product) with a 30−50% formaldehyde solution in water.[104] The demand for 1,4-butynediol is quite high since it is used among other things in the most widely applied industrial process for THF manufacture. Despite this, not much effort has been invested in understanding the copper-based catalyst and further improvement.

However, there is one significant development of the ethynylation reaction that has been made since the work of Reppe, namely, the use of alkaline bases suspended in polar aprotic solvents (e.g., DMSO). This increases the basicity of the system because of the high affinity to the cation and the lack of an acidic proton that would react with the OH$^-$ anion. However, much of this work has been published only in the Russian language. Some reviews exist on this topic, which suggest that this might be a promising alternative to the copper acetylide-catalyzed process. The ethynylation of carbonyl compounds with KOH in DMSO takes place at temperatures between 20 and 30 °C, and in many cases atmospheric pressure is sufficient to carry out the reaction.[105] With this catalyst system, much better yields of propargyl alcohol are obtained than with the copper acetylide catalyst, where the main product is 1,4-butynediol.[106] In the described ethynylation experiments, usually the number of moles of KOH used is roughly on the same order of magnitude as the number of moles of reactants,[107] and the reaction times required to obtain yields above 50% are on the order of hours. The synthesis of secondary[108] and tertiary[109] propargyl alcohols from aldehydes and ketones, respectively, with KOH in DMSO as the catalyst has also been reported, demonstrating the wide range of substrates that can be ethynylated using this system. If the ethynylation of carbonyl compounds is attempted under acetylene pressure and at temperatures around 90 °C in the KOH/DMSO system, it is possible in one pot also to vinylate the OH group of the alcohol formed in the ethynylation reaction.[110] Further reactions may also be possible, such as ethynylation at both ends of the acetylene molecule as well as vinylation of the resulting diol.[111]

Since the ethynylation reaction of other carbonyl compounds also is a useful synthetic tool that can generate an asymmetric carbon atom possessing both OH and alkyne functional groups in its proximity, attempts to perform this reaction in an enantioselective manner have been made. A very promising example of enantioselective ethynylation has been reported in which the reaction was carried out in toluene with zinc triflate, ethyldiisopropylamine, and (+)-N-methylephedrine. Enantiomeric excesses as high as 98% were reported.[112]

A recent patent of BASF claims the use of acetylene dissolved in the formaldehyde solution mixed with an organic solvent without the formation of a continuous gas phase, thus reducing the risks associated with the use of pressurized acetylene.[113] This patent claims also the use of copper oxide/bismuth oxide supported on silica as the catalyst for the ethynylation reaction. The productivities described in the patent are on the order of 4 g L_{cat}^{-1} h^{-1} for propargyl alcohol and on the order of 40 g L_{cat}^{-1} h^{-1} for 1,4-butynediol. Performing reactions of acetylene under pressure in the absence of a continuous gas phase is also not a recent invention; it was reported more than 50 years ago.[114]

7. VINYLATION

As vinyl ethers are interesting starting materials for polymers, Reppe was looking for methods to obtain vinyl ethers and discovered that vinyl halides react with alkoxides to give the desired vinylation products. This was surprising because at that time it was believed that under those reaction conditions elimination should occur, resulting in acetylene formation. With this in mind, Reppe also attempted the reaction of alcohols with acetylene in the presence of basic catalysts. This led to the discovery that vinyl ethers can be readily produced from the reaction of alcohols with acetylene under pressure at temperatures above 120 °C in the presence of bases. Prompted by this finding, he also tested the addition of sulfur or nitrogen nucleophiles to acetylene, leading to the discovery that thiols, primary amines, and secondary amines also add to acetylene (Scheme 4), resulting in the formation of the corresponding

Scheme 4. Vinylation Reactions
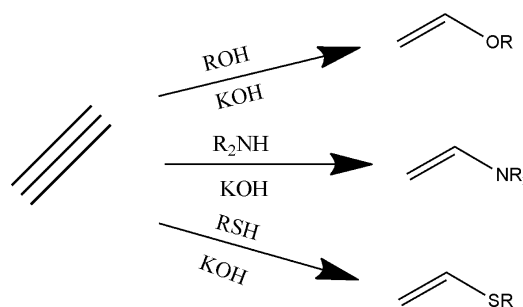
vinylation products.[29,115] These reactions presented an easy way to produce a wide range of vinyl compounds, which were promising precursors for new polymeric materials at that time. Poly(vinyl pyrrolidone) is probably the most important polymer discovered by Reppe in the course of these studies.[116]

A continuous industrial process for preparing vinyl ethers used in Germany during the Second World War has been described.[29] The reactor consists of a tower with a diameter of 1.2 m and a height of 10 m that is filled with an alcoholic solution of KOH, through which gaseous acetylene is passed. The pressure, temperature, and KOH concentration depend on the type of alcohol used in the vinylation reaction. To obtain methyl vinyl ether, the conditions used were around 160 °C, 20 bar, and 20% KOH in methanol. The reported productivities were around 500 kg of vinyl ether per hour with this reactor. This corresponds to about 40−50 g of ether per liter per hour.

The base-catalyzed vinylation of alcohols with acetylene is unique compared with most of the other reactions of acetylene developed before the 1960s in that it is still being used nowadays as the main industrial process for the production of vinyl ethers.[117] Consequently, it is one of the more studied reactions of acetylene. Nevertheless, the currently used industrial catalysts are still alkaline bases, as in the early days of this process.

An interesting approach for industrial production of vinyl ethers is the use of flow reactors where no continuous gas phase is allowed to form. With this concept it is possible to work under pressures from 1 to 50 bar and temperatures up to 300 °C. The productivities obtained using such a setup for producing methyl vinyl ether using KOH as a catalyst are as high as 70 g L^{-1} h^{-1}.[42]

In the gas−liquid vinylation of alcohols with the catalyst dissolved in the liquid phase, advances have been made by using alkaline hydroxides in aprotic coordinating solvents such as DMSO or hexamethylphosphoramide (HMPA). These solvents have the advantage that they coordinate to the cation, thus making the base soluble in them, but as they have no acidic hydrogen, they do not neutralize the OH$^-$ anion. This is the reason why they are called "superbasic catalytic systems". This concept has already been introduced above in the description of the ethynylation reaction. For such reactions, temperatures between 70 and 140 °C are used with acetylene pressures between 1 and 20 bar and amounts of base ranging from 10 to 100 mol % with respect to the alcohol. The system uses oversaturated solutions of anhydrous alkaline hydroxides in DMSO, and the undissolved base serves to remove the water from the solvent. Of the alkaline hydroxides, CsOH was shown to perform best, but a more convenient way to run this reaction is using CsF and NaOH or LiOH to generate CsOH in situ because anhydrous CsOH is not readily available.[41] With this catalytic system it is also possible to perform the reaction with only 3 mol % base for certain alcohols.

The impressive aspect of the CsF/NaOH in DMSO system is not necessarily the observed increase in catalytic activity for vinylation of alcohols but the much better yields obtained in the vinylation of polyols with more than three carbon atoms between the OH groups. Thus, the vinylation of 1,4-butanediol using acetylene at atmospheric pressure and 100 °C in DMSO with 20 mol % CsF/NaOH affords the divinyl ether in 86% yield, whereas with 20 mol % KOH only a 10% yield of divinyl ether was obtained under the same conditions.[118] In a different study it was shown that it is possible to catalyze this reaction with potassium alkoxides in aromatic solvents in the presence of crown ethers to solubilize the alkoxide. With this system better results than with potassium alkoxides in alcohols were achieved.[119]

N-Vinylation reactions under similar conditions catalyzed by KOH in DMSO or with crown ethers as cocatalysts are also possible under similar conditions, and some recent studies were published on the vinylations of caprolactam[120] and mela-mines.[121]

The vinylation of potassium thiolates in aromatic solvents in the presence of crown ethers at atmospheric pressure and 70 °C has also been reported.[122,123] A very interesting type of sulfur vinylation proceeds when acetylene is reacted under pressure at 100−110 °C with sodium sulfide, H$_2$S, or elemental sulfur in DMSO in the presence of KOH and water, from which divinyl sulfide is obtained. The properties and reactions of this compound have been extensively reviewed.[124,125]

One very intriguing transformation has been observed in the reaction of ketoximes with acetylene in the KOH/DMSO system. The resulting product is surprisingly not the O-vinylation product one might expect, but rather one in which a new pyrrole ring is formed (Scheme 5). This is now known as

Scheme 5. The Trofimov Reaction
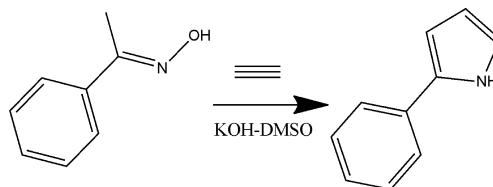
the Trofimov reaction, and it is a useful synthetic pathway for the production of aryl pyrroles that allows a wide range of aryl substituents on the pyrrole ring.[126] It also gives the possibility of further vinylation of the resulting pyrrole to produce 1-vinyl pyrroles in a one-pot reaction.[127] It is also noteworthy that the O-vinylation product can be isolated with diaryl ketoximes, where the pyrrole ring cannot form.[128] With careful control of the reaction conditions, O-vinyl ketoximes of other ketones can also be isolated before they transform into pyrroles.[129] Amidoximes have also been shown to react to form O-vinyl amidoximes.[130]

Vinylation reactions are of great interest from both the academic and industrial points of view because of their potential to generate vinyl monomers from substances containing groups capable of nucleophilic addition to acetylene. Numerous studies on this subject by the group of Boris Trofimov have revealed the synthetic versatility of the vinylation reaction to prepare vinylated compounds that are not readily accessible through other synthetic pathways. Some of these compounds are depicted in Scheme 6. Unfortunately, a

Scheme 6. New Vinyl Monomers Accessible by the Use of Superbasic Catalytic Systems
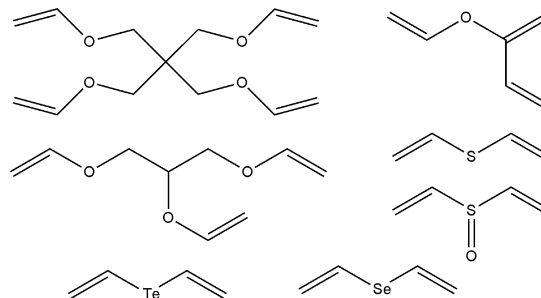
great number of these studies were reported in publications available only in the Russian language, making them less accessible to a substantial fraction of researchers, and thus, they have received less attention than they deserve. The reviews on the subject of acetylene reactions in basic media written by Trofimov and co-workers present an overview on this topic.[105,106,131] An interesting application of the vinylation of OH groups that has been recently reported uses sugars to give chiral compounds containing vinyl groups.[132] These compounds might be useful for the synthesis of polymers presenting chiral functionality starting from readily available chiral materials. Also, the vinylation of cellulose to produce polymers that can be further modified because of the reactive

vinyloxy groups has been reported. For this reaction, the KOH in DMSO catalytic system is used.[133] A further proof of the versatility in terms of substrates that can be vinylated using this catalytic system is the vinylation of cholesterol.[134]

In Reppe's work,[29,115] attempts to react acetylene with alcohols in the gas phase at temperatures between 150 and 350 °C over solid catalysts such as soda lime, sodium zincate, or alkali hydroxides supported on carbon were also mentioned, but not many details about this process were given. The reason for this is probably rapid catalyst deactivation that prevented commercial use at that time. A study dating from 1963 using KOH supported on MgO or CaO showed that these catalysts are active for vinylation of alcohols with acetylene in the vapor phase, with conversions of up to 70% at space velocities around 50−100 h^{-1}, atmospheric pressure, and temperatures of 180−260 °C.[135] However, these catalysts have lifetimes of around 24 h, with deactivation most likely occurring because of loss of KOH from the catalyst. Recently a system that is more stable in the gas-phase addition of methanol to acetylene has been reported. It consists of a ZnO/SiO$_2$ catalyst that after activation for 48 h in the feed stream presented conversions of around 50% at space velocities between 350 and 700 h^{-1}, atmospheric pressure, and temperatures between 200 to 270 °C, while its activity remained stable for several months.[61] Since this catalyst also produces 1,1-dimethoxyethane, the addition product of methyl vinyl ether and methanol, it is believed that the reaction actually proceeds through an acid-catalyzed mechanism. Regardless of whether the reaction is acid- or base-catalyzed, it is remarkable that the catalyst enables the reaction between gaseous acetylene and gaseous methanol without deactivation.

8. DIMERIZATION

The dimerization of acetylene can be seen as a combination of vinylation and ethynylation, as each of the two molecules of acetylene involved can be seen to undergo either one or the other reaction. After the first report on this reaction by Nieuwland,[63] the dimerization was used for the production of vinylacetylene by DuPont for the manufacture of chloroprene,[136] which served in the manufacture of polymers with properties analogous to isoprene rubber. The catalyst for this reaction consists of a very concentrated aqueous solution of CuCl and KCl or NH$_4$Cl. Gaseous acetylene is reacted with this solution, resulting in vinylacetylene and divinylacetylene as the main products. Further reaction of vinylacetylene with hydrochloric acid produces chloroprene. Since the 1960s, the manufacture of chloroprene has been accomplished by chlorination of butadiene followed by isomerization of the resulting 1,4-dichloro-2-butene to 1,2-dichloro-3-butene and dehydrochlorination in a basic environment to yield chloroprene.[137] After the replacement of the vinylacetylene-based process for the manufacture of chloroprene, the production of vinylacetylene was not of industrial interest anymore, and thus, the Nieuwland catalyst system has not been studied much, although there are still very few known catalyst systems that can selectively produce linear oligomers of acetylene while avoiding the formation of cyclic ones, such as benzene.

After the year 2000, interest in the Nieuwland catalyst has been reignited, and some studies have been focused on elucidating the structure of the catalyst and the mechanism of the reaction. It has been shown that ammonium or potassium ions are essential for the function of the catalyst, as the activity is much lower if these are replaced by other alkaline ions.[138] Also, the same study showed that a K/Cu ratio corresponding

roughly to that in the salt KCuCl$_2$ is responsible for the function of the catalyst, and a slight excess of potassium over the 1:1 ratio was found to be beneficial. This salt has the highest solubility among the K$_n$CuCl$_{n+1}$ salts and even a higher solubility than KCl.

Studies using deuterated water for the catalyst solution have shown that an exchange between the protons of acetylene and the deuterium atoms in the water takes place faster than the dimerization reaction. This means that deprotonation is not rate-limiting for this reaction.[139,140] Mechanistic studies using isotopically labeled compounds and in situ NMR measurements indicated that the active intermediate is a copper acetylide complex [Cu−C≡CH] and that vinylacetylene is formed after insertion of an acetylene molecule into the Cu−C bond.[140,141]

The stability of the Nieuwland catalyst was also revisited in a recent study, which proposed that the loss of activity over time is because of loss of HCl from the system. The stability can be improved if the acidity is properly controlled and if HCl is continuously added to the system.[142] It has been reported that using organic solvents instead of water and quaternary ammonium chlorides instead of KCl or NH$_4$Cl can improve catalytic activity. Thus, for an acetylene space velocity of 200 h^{-1}, the aqueous catalyst system reached around 7% conversion, while in DMF the conversion was over 20% under the same conditions.[143] The stability of the catalyst in an organic solvent can also be improved by continuously supplying HCl to the system.

Improvements in the catalyst for the dimerization of acetylene are still desirable, especially in terms of activity, selectivity at high activities, and stability. The recently rekindled interest in this reaction seems to suggest that as oil prices are increasing and oil-derived feedstocks are becoming more expensive, it is possible that dimerization of acetylene could once again serve as a source of chloroprene rubber and possibly other materials as well.

9. CARBONYLATION

The reaction of acetylene with carbon monoxide and water to yield acrylic acid was first observed by the Reppe group in an attempt to make use of the carbon monoxide obtained as a side product from the manufacture of calcium carbide in the production of acetylene.[64,144] When instead of water other compounds with displaceable hydrogen atoms such as alcohols, thiols, or amines were used, the corresponding esters, thioesters, or amides were obtained (Scheme 7).

Reppe described two ways to perform these reactions. One relies on Ni(CO)$_4$ as a stoichiometric source of CO under an acetylene pressure from 1 to 12 bar at temperatures of 40−50

Scheme 7. Carbonylation Reactions
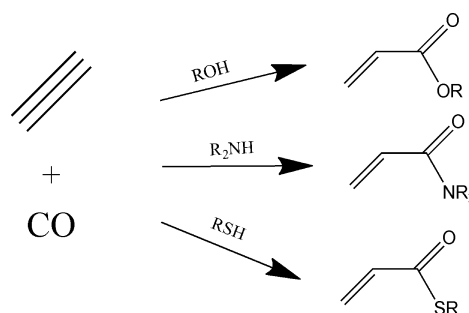
°C in the presence of acids. The other possibility is a catalytic route that proceeds under 30 bar pressure of CO and acetylene in a 1:1 ratio. The catalysts are generated from salts of nickel or other metals that form carbonyls at temperatures above 130 °C. A density functional theory (DFT) study of this mechanism, considering the active intermediate in these reactions to be a nickel carbonyl hydride with the formula $HNi(CO)_2X$, where X^- is a halide anion, showed[145] that for the considered mechanism the formation of the nickel carbonyl hydride species is the most energy-intensive endothermic step. The subsequent steps of acetylene insertion into the Ni−H bond and CO insertion into the $Ni-CH=CH_2$ bond are both exothermic. However, to the best of our knowledge, experimental evidence for this mechanism has not yet been provided.

It is worth mentioning that when iron pentacarbonyl in aqueous or alcoholic solution was used as a source of CO at temperatures around 80 °C and acetylene pressures of around 25 bar, hydroquinone was obtained. This reaction is favored by the presence of bases.[146]

Industrial processes based on acetylene carbonylation were the main source for obtaining acrylic monomers until the 1960s but were afterward replaced by propylene oxidation.[147] After industry lost interest in this method for the production of acrylic acid, the carbonylation of acetylene has not enjoyed much attention over the last 50 years, but there are still some efforts in this field worth mentioning.

Inspired by the work of Reppe, Bhattacharyya et al.[148−150] carried out detailed studies of the carbonylation of acetylene to produce acrylic acid and acrylates using Fe-, Co-, and Ni-based catalysts in batch reactors under pressure of CO and acetylene at temperatures around 200 °C. From the data reported in these studies, one can calculate the turnover frequency (TOF) of the catalysts used, and these are at best on the order of 10 turnovers per hour.

Recently, acetylene carbonylation leading to acrylic monomers has received interest again as a synthesis pathway that is independent of petroleum-derived feedstocks. The nickel acetate copper bromide system dissolved in a THF/water mixture in a batch reactor at 200 °C has been studied by Tang et al.[151] for the production of acrylic acid. This system showed catalytic activity comparable to that of the nickel salts reported by Bhattacharyya et al.[148−150]

In the search for better acetylene carbonylation catalysts, Tang et al.[65,66] also used a molecular Pd-based catalyst for this reaction. This was inspired by a highly active catalyst system that had been developed by Drent et al.[67,152] for the carbonylation of propyne to produce methyl methacrylate. The system is based on palladium acetate and 2-pyridyldiphenylphosphine in an acidic medium and is typically used at temperatures around 60 °C. In the carbonylation of acetylene[65,66] this catalyst has shown TOFs as high as 2500 h^{-1}. This finding demonstrates that substantial improvements of the carbonylation reaction are possible if the developments in alkyne chemistry from the last 50 years are taken into account. Even so, there is a lot of room for improvement since all of the reported catalysts for this reaction are homogeneously dissolved in the medium and thus present difficulties in catalyst recovery and product separation.

Aside from the carbonylation of acetylene to yield acrylic acid or its derivatives, other variations of the carbonylation reaction with acetylene have been studied. The homogeneously catalyzed carbonylation of allyl halides with nickel carbonyl and acetylene in alcohols, which can also be considered as a coupling of acetylene with the allyl chloride and subsequent carbonylation of the resulting alkyne, to give a 2,5-dienoic acid ester has been reported.[153] However, the products of this reaction are of interest only for synthetic chemistry and not for bulk industrial production.

Another variation of the carbonylation reaction can be used for the production of maleic or succinic anhydride. It is catalyzed by $PdBr_2/LiBr$ dissolved in acrylonitrile, as reported by Bruk and co-workers[154−156] The reaction has been studied in a gas flow atmospheric pressure reactor at 40 °C. This is interesting because it shows that successive carbonylation of the resulting acrylate is possible under the same reaction conditions. However, the reported system has TOFs on the order of only tens of turnovers per hour.

Carbonylation in general is dominated by liquid-phase processes and molecular catalysts.[147,157] Carbonylation of acetylene in the gas phase has not been reported to date.

## 10. OLIGOMERIZATION AND POLYMERIZATION

10.1. Cyclotrimerization

10.1.1. Cyclotrimerization at Atmospheric or Higher Pressure. The cyclotrimerization of acetylene to yield benzene was first observed by Berthelot in 1866 upon heating acetylene to temperatures "around the softening point of glass".[57] However, it was Reppe who showed that this reaction can be performed at temperatures around 70 °C in the presence of nickel carbonyl phosphine complexes, such as $Ni(CO)_2(PPh_3)_2$, dissolved in aromatic solvents at acetylene pressures around 10 bar.[146,158] Even with these improvements, obtaining benzene from acetylene was never commercially relevant, and the cyclotrimerization reaction was of interest only when substituted alkynes were used as starting materials in order to produce substituted benzenes. It is worth mentioning that with higher pressures of acetylene styrene is also obtained as a side product.[158] Although obtaining styrene directly from acetylene seems like an interesting process, at least from a scientific point of view, appropriate reaction conditions and catalysts for this reaction have not been reported to this day.

The cyclotrimerization of substituted alkynes has become an established technique in the synthesis of larger molecules,[21] while cyclotrimerization of acetylene has not received much attention as a preparative technique. A study focusing on substituted alkynes showed that the donor properties of the ligand in a nickel phosphine catalyst influence the activity of the catalyst: the better the electron donor properties of the ligand, the higher the reaction rate. The IR frequency of the alkyne triple bond coordinated to the Ni center was correlated with the Tolman electronic parameter of the phosphine ligand. Additionally, the authors investigated the influence of the alkyne substituents on the shift of the IR frequency of the triple bond. It was also shown that at 35 °C under ambient pressure, 42 760 turnovers of acetylene to benzene can be achieved in 3 h using nickel(II) ethylhexanoate, tricyclohexylphosphane, and sodium borohydride in hexane.[159] However, this study also underlines the difference between mono- and disubstituted alkynes, showing that under almost identical conditions using the previously mentioned catalytic system, 1,4-dimethoxy-2-butyne gives the trimerization product whereas propargylic alcohol gives the tetramerization product. Thus, transferring the experience made with one alkyne to another one is not straightforward.

One recent study showed an iron bis(imino)pyridine complex activated with methylaluminoxane to be highly active in the cyclotrimerization of acetylene at ambient temperature and pressure with over 1000 turnovers per hour, although small amounts of polyacetylene were also obtained.[58] While specific products might be favored in catalyzed oligomerization reactions of acetylene, in many cases trimerization, tetramerization, further oligomerization, and polymerization (Scheme 8) occur simultaneously, albeit at different rates.[58,160] Finding a system that favors exclusively one of these pathways is a quite delicate matter.

Scheme 8. Oligomerization Reactions

Side product of many reactions of acetylene, especially oligomerizations
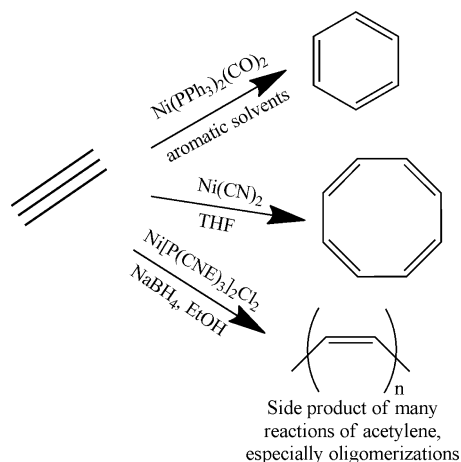
10.1.2. Cyclotrimerization under Ultrahigh Vacuum Conditions.

The trimerization is an intriguing reaction because it brings three molecules together to form a single molecule. It is very exothermic with about 599 kJ of heat released per mole of benzene produced, but in the absence of a catalyst it has also a very high activation energy, calculated to be in the 250−335 kJ/mol domain.[161] As such, it has been the object of fundamental and theoretical studies.

These studies show some general features of acetylene chemistry and report some interesting observations that might be transferred to ambient- and high-pressure applications. Some of these studies were specifically conducted to transfer the conclusions from ultrahigh vacuum (UHV) to ambient conditions[162] or in order to extend the experiments from single-crystal surfaces to model catalysts[163,164] as well as to continuous flow conditions.[165] These studies not only give valuable information about the reactivity of acetylene but also show that acetylene cyclotrimerization is a suitable reaction to assess the pressure, material, and complexity gap between surface science and catalysis.

A rather general observation, which holds for almost any surface, is the high tendency of acetylene, once adsorbed, to form coke. Evaluating this by temperature-programmed desorption (TPD) shows that only a part of the acetylene is ultimately converted to benzene. For example adsorption of acetylene on Pd(111) and successive heating produces a 25% yield of benzene based on acetylene. However, using desorption methods, such as laser-induced thermal desorption, which allows for rapid heating and suppresses consecutive reactions, shows that 50 K below the desorption onset in TPD acetylene is quantitatively converted to benzene.[166] This incidentally suggests that benzene is a precursor for coke

formation. Coking is also one of the major drawbacks under ambient conditions for almost all reaction classes. However, it is interesting to notice that there are differences with respect to coke formation on different surfaces. Consequently, surface science studies might give some hints for reducing deactivation by coke formation.

Under UHV conditions, Pd(111) is more active for benzene formation than the other crystal planes of Pd, whereas at ambient pressure also Pd(100) shows a comparable activity.[162] On Cu surfaces, the reaction produces less coke and is less structure-sensitive with respect to activity. However, Cu(111) shows a different selectivity, also producing butadiene and cyclooctatetraene (COT), whereas over Cu(100) and Cu(110) benzene is formed exclusively.[167−169] This is surprising because, as already discussed above, metallic copper is a good catalyst for the formation of cuprene.[39]

The mechanism for the reaction seems to be similar for Pd and Cu. In a rate-limiting step, two acetylene molecules form a C_4H_4 intermediate. Subsequent addition of another acetylene leads to the formation of benzene.[170−172] The C_4H_4 intermediate can also explain butadiene formation, which is observed on some surfaces. Additionally, for the formation of benzene on Pd(111), a critical surface coverage of acetylene is required for the onset of benzene formation.[173,174]

In contrast to Pd, Pt and Ni are inactive for the cyclotrimerization of acetylene. Instead, Pt and Ni dehydrogenate acetylene and form hydrogen and carbon. Upon alloying with Sn, the amount of coke formed can be decreased in favor of benzene formation. This becomes significant when going from the formal Pt_3Sn surface alloy to Pt_2Sn. In addition, similar to Cu(111), the platinum−tin alloys also produce butadiene.[175,176]

In the same manner, depositing Pd on Au leads to an increased activity up to a coverage of 0.6 monolayer of Pd on Au. These materials do not consist of a homogeneous alloy; instead, Pd islands are formed on the Au surface. The different reactivity is mainly attributed to morphology but also to ensemble effects, which enable product desorption at lower temperature.[177] Au(core)/Pd(shell) particles were tested in a continuous flow reactor at 1.5 bar and showed a stable product yield for 3 h. The authors are aware of possible influences by mass transfer at the high conversions they used for some experiments. Besides benzene, as the major product, they also observed different butenes and n-hexane.[165]

Studies of acetylene cyclization on Pd films on Ta,[178] Au on Pd,[179] reduced $TiO_2(100)$,[180,181] and Pd/W(211)[166] have also been conducted.

Other studies focusing on model supported catalysts also confirmed the results obtained with single crystals. On the basis of the knowledge of structure sensitivity of the reaction obtained in Pd single-crystal studies, Pd nanoparticles supported on thin-film Al_2O_3 were investigated. They showed increased activity as soon as they approached a size of approximately 4 nm, which can be explained by the contribution of different crystal planes to the reaction. Particles with sizes above 4 nm do not significantly change in the composition of their crystal planes with increasing size.[164] The structure sensitivity was also shown by deposition of size-selected Pd clusters on MgO. However, this study also showed dramatic effects of an electronic nature: charge transfer from defect sites of the support can activate a single Pd atom for the cyclotrimerization of benzene.[163] After an increase in the cluster size to 7 atoms an additional mechanism for the formation of

benzene opens up, and benzene desorbs at two different temperatures. Furthermore, in the case of size-selected Pd clusters, the selectivity can be tuned toward benzene, butadiene, or butene.[182] Besides Pd clusters, only Cu clusters produced a significant amount of benzene, and other transition metals were observed to be rather inactive.[183]

10.2. Cyclotetramerization

It is quite obvious that acetylene cyclotrimerization and cyclotetramerization are linked. This can also be seen from the surface science studies just described, where COT can be detected as a byproduct in some cases.

The cyclic oligomerization of four acetylene molecules to produce COT was first observed by Reppe in an attempt to produce 3-hexyne-1,6-diol from acetylene and ethylene oxide using $Ni(CN)_2$ as a catalyst. Instead of the desired product, it was observed that the reaction had produced a mixture of hydrocarbons with compositions corresponding to the formulas C_8H_8, $C_{10}H_{10}$, $C_{12}H_{12}$, and $C_{10}H_8$.[29] Of these, C_8H_8 was present in the largest amount and was determined to be COT by comparison of its properties with those of COT synthesized by Willstätter.[184] The production of COT was performed in 4–5 L autoclaves filled with 2 L of THF, 20 g of $Ni(CN)_2$, and 50 g of CaC_2, pressurized with acetylene to 15–20 bar, and heated to 60–70 °C. Reaction times of 30–60 h were used, and 320–400 g of COT was obtained.[160] It is interesting to note that both the cyclotrimerization and the cyclotetramerization are catalyzed by nickel compounds, although the former occurs mostly in aromatic solvents whereas the latter predominates in cyclic ether solvents such as THF.

This reaction has been used for industrial production of COT and has also sparked the interest of synthetic organic chemists, especially as a tool for obtaining substituted COT from higher alkynes. Thus, efforts have been invested in understanding the mechanism of the reaction.[185,186] These studies have shown that the reaction proceeds through either a stepwise coupling mechanism (Scheme 9), a concerted
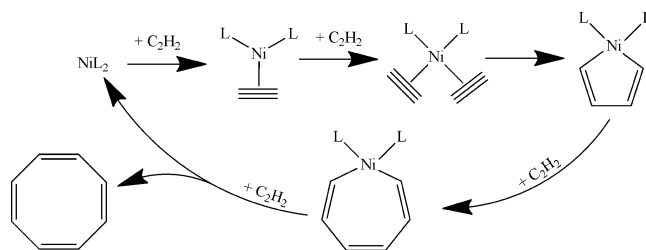
**Scheme 9. Concerted Mechanism for COT Synthesis**
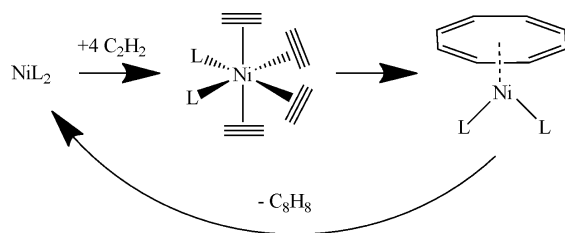
mechanism (Scheme 10), or a binuclear mechanism (Scheme 11);[187,188] although the mechanism is still not fully understood,[189] there is strong evidence for the binuclear mechanism.[187]

Nowadays COT is no longer produced on an industrial scale, and commercial prices for this compound are quite high. The preferred industrial reaction for obtaining eight-membered-ring products is the dimerization of butadiene to produce cyclooctadiene, catalyzed by molecular nickel catalysts. Most of the cyclooctadiene obtained is hydrogenated to cyclooctene, which in turn is subjected to ring-opening polymerization.[190] With this in mind, it might be worthwhile to invest more efforts in making the COT synthesis from acetylene more efficient for industrial applications in regions where acetylene can be obtained with low cost. Also, in order to obtain cyclooctene for

Scheme 10. Stepwise Mechanism for COT Synthesis

Scheme 11. Binuclear Mechanism for COT Synthesis
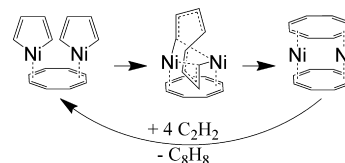
ring-opening metathesis polymerization, the hydrogenation of COT to cyclooctene would have to be investigated. Another possibility that the COT molecule offers is ring-opening metathesis polymerization, as reported in a study by Klavetter and Grubbs,[191] to obtain polyacetylene, a conducting polymer, with potential applications in advanced electronics.

10.3. Pyridine Synthesis

The [2 + 2 + 2] cycloaddition reaction of two acetylene molecules and one nitrile molecule leading to pyridines, which has become an established technique in organic synthesis, has been developed as a catalytic reaction starting from the 1970s by Wakatsuki and Yamazaki[192,193] and at the same time by Bönnemann and co-workers.[68,194,195] The notable features of these reactions are that they used acetylene pressures of up to 60 bar in the presence of nitriles and homogeneous cobalt catalysts. Temperatures up to 200 °C were used, and with some catalysts TOFs as high as a few thousands per hour based on formed pyridine were observed.[196]

As this reaction was considered for the industrial production of pyridines, it was well-investigated over the years, and a high level of understanding was achieved. This reaction provides an illustrative example of how understanding the correlation between structure and activity can improve a reaction.[195−197] Nevertheless, industrial production has not been realized to date, and nowadays the reaction of alkynes with nitriles is of interest mainly in organic synthesis for obtaining pyridines with several substituents.[198]

In principle, several metals, usually also active for cyclization of acetylene, catalyze the formation of pyridines from acetylene and nitriles, but Co proved to be the best and consequently most-studied transition metal.[199] Typical catalysts have the general formula $XCoL_2$, where X is often a cyclopentadienyl-derived system and L a readily displaceable ligand such as an olefin. Catalysts can also be generated in situ by the reduction of Co salts in the nitrile solution. Because of difficulties in the synthesis, systems with phosphines as ligands were only investigated in the beginning.[68]

The reaction mechanism is depicted in Scheme 12. The ligands L are removed, for example by increasing the temperature, before the catalytically active core complex CpCo is formed. The subsequent addition of two molecules of acetylene leads to the formation of a cobaltacyclopentadiene moiety and the formal increase of the oxidation number of the

Scheme 12. Mechanism of Pyridine Synthesis from Acetylene and Nitriles, Showing the Acetylene Cyclotrimerization as a Possible Side Reaction
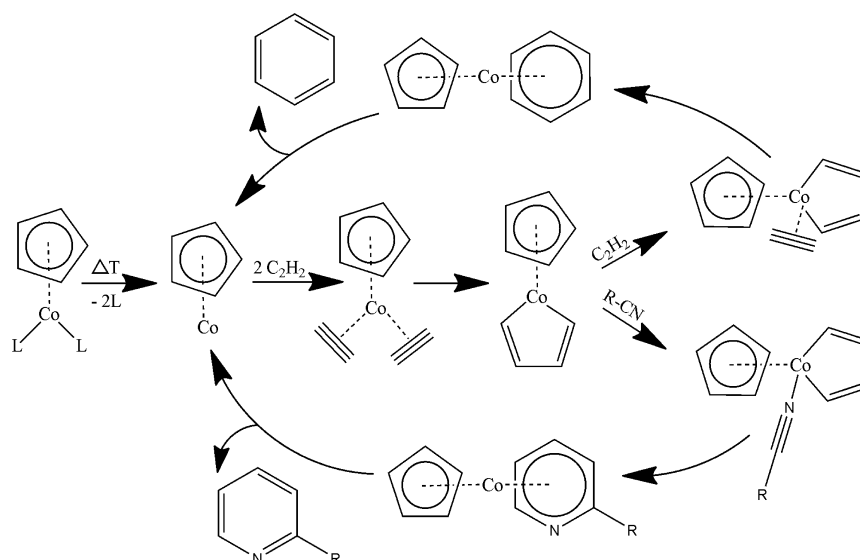
Co from I to III. The nitrile stabilizes this intermediate via the nitrogen and is incorporated into the cobaltacyclopentadiene, followed by subsequent liberation of the pyridine derivative and the CpCo. Also, mechanisms based on azametallacycles as intermediates and an intermolecular reaction of the cobaltacyclopentadiene with the nitrile have been suggested; however, recent DFT studies[200,201] showed that the mechanism depicted in Scheme 12 is the energetically most favored one. The scheme also shows the major difficulty, namely, the chemoselectivity to carbo- or heterocycles. In studies with substituted alkynes a bicyclo intermediate is also discussed.[199]

As can be seen in the scheme, the ligand L is not present in the catalytic cycle but is displaced before the cycle is entered. Improvements in catalytic activity by changing the ligands thus require changes in X. However, L plays a role in the starting behavior of the catalyst. In cases where L strongly binds to Co (e.g., L = CO), temperatures above 100 °C have to be applied in order to start the catalytic reaction. This may be problematic in the synthesis of reactive products such as 2-vinylpyridine, which will cause polymerization of acrylonitrile as well as vinylpyridine. The role of L was illustrated by using complexes having the same ligand X but different ligands L in the reaction of propyne with propionitrile. Comparison of these catalysts showed that although catalysis starts at different temperatures, where L is removed from the Co, the activity after initiation is the same. Consequently, using strongly coordinating ligands L will cause blocking of the active Co sites and thus poisoning of the catalyst.[196]

The difficulty in developing improved catalysts by the establishment of structure−activity relationships for reactions with acetylene can be seen in the fact that after five years of research on pyridine synthesis, Bönnemann and his co-workers concluded that the chemoselectivity to carbocycles or heterocycles is subject to the substrate used and especially the concentration, that is, a low steady-state concentration of acetylene favors the formation of the pyridine derivative.[68] However, around 10 years after their first report on the synthesis of methylpyridine from acetylene, they could impressively show the dependence of the catalytic activity on the proper choice of the ligand X.[196] A considerable amount of

their work was dedicated to the cyclization of propyne with propionitrile as a test reaction. In their studies, they first compared the η^3-allyl−Co core complex, formally having 12 valence electrons, with the η^5-CpCo core complex with 14 valence electrons. Although η^3-cyclooctenyl−CoCOD showed higher activity than CpCoCOD, the chemoselectivity of the CpCo was much higher to pyridines. In further experiments, the influence of various substitutents on the Cp ring was elucidated. They found that electron-withdrawing groups on the Cp ring increase the catalytic activity as well as the chemoselectivity to pyridines. The correlation between the activity and the chemical shifts of the ^{13}C and ^{59}Co NMR resonances proved this influence.[197] Consequently, the investigation of η^6-borinato−Co complexes showed even higher activity and selectivity compared with the investigated cyclopentadienyl-derived complexes. Some of these catalysts were afterward also tested for the reaction of nitriles with acetylene and there as well showed extraordinary behavior compared with the known systems.[195]

One of these catalysts, η^6-1-phenylborinato−CoCOD (Scheme 13), also allowed the synthesis of unsubstituted

Scheme 13. η^6-1-Phenylborinato−CoCOD
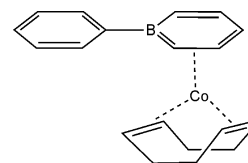
pyridine from HCN and acetylene with a TON greater than 100, a remarkable achievement considering the ligand strength of cyanide and the aforementioned blocking of the metal center with strong ligands.[195]

Using other cyanosources yields other heterocycles (e.g., pyridones in the case of isocyanates), albeit often associated with lower catalyst stability because of the coordinating power of the heteroatoms.[68] Also, irradiating a Co(I) catalyst in water under ambient pressure produces pyridines.[202]

Several reviews of the synthesis of pyridines from substituted alkynes and nitriles have underlined the importance of ligand design to achieve reasonable activity and selectivity. The interested reader is referred to these reviews[199,203,204] and another reference[205] for a discussion about mechanistic aspects.

10.4. Acetylene Polymerization

The subject of polyacetylene is an extremely vast one, and a comprehensive review of it is beyond the scope of this chapter. Herein some of the more significant developments in the field are mentioned.

The first attempt to polymerize acetylene was made by Natta et al. in 1958 using Ti(OBu)$_4$−AlEt$_3$ polymerization catalysts invented for the polymerization of olefins.[206] The obtained material was, however, insoluble in all solvents and detailed characterization proved to be very difficult. Nevertheless, the promise of a material that would combine both the malleability of plastics with the electrical conductivity of metals spurred more attempts at the synthesis of polyacetylene. Luttinger showed that nickel salts in the presence of a reducing agent such as NaBH$_4$ with tris(2-cyanoethyl)phosphine in a solvent such as ethanol can also catalyze the polymerization of acetylene.[207] This method has the advantage that it does not require the exclusion of moisture. Compared with the catalytic system used by Rosenthal and Schulz[159] for trimerization of acetylene consisting of a nickel salt, tricyclohexylphosphane, and sodium borohydride, which produces mainly benzene, the main difference is the phosphine ligand used, showing that the ligands, through electronic effects, determine which path (oligomerization or polymerization) is favored.

The method of Shirakawa and co-workers for obtaining films of polyacetylene by carrying out the polymerization at the surface of a solution of the Ziegler catalyst in toluene provided a way to obtain polyacetylene in a form that is easier to characterize.[208,209] The discovery of this method also led to the idea of doping polyacetylene to improve its properties.

Naarmann et al.[210] reported a method for preparing polyacetylene by polymerizing acetylene in a viscous medium like silicone oil in the presence of the Ziegler catalyst, which produced films of polyacetylene that could be stretched up to 5−6 times their initial size and, after doping with iodine, presented higher electrical conductivities per unit weight than metallic copper. It is noteworthy that polymerization of acetylene has also been reported with titanocene complexes without the need for triethylaluminum to initiate the reaction.[211,212] Recently, efforts have been made to obtain polyacetylene with a helical structure by carrying out the polymerization with the Ziegler catalyst in liquid-crystalline media because of the possibly interesting magnetic and optical effects that such structures might present.[213]

Polyacetylene is not the only known conducting polymer,[214] and the polymerization of acetylene is not the only way of obtaining polyacetylene, as it can also be made by ring-opening metathesis of COT[191] or by an elimination reaction from other polymers.[215] However, in order to develop conducting polymers for broad bulk commercial applications, substantial progress is still required. Since probably the cheapest possible starting material for a conducting polymer is acetylene, be it by direct polymerization or tetramerization to COT and ring-opening metathesis of the latter, the area of conducting polymers presents many opportunities for applying acetylene chemistry on a large scale.

11. ACETYLENE HYDROGENATION

The selective hydrogenation of acetylene to ethylene is a reaction of great practical importance, not as a method for the preparation of ethylene but for removal of small amounts of acetylene from ethylene. The ethylene obtained from steam cracking can contain up to 2% acetylene as an impurity. Because acetylene acts as a poison for the ethylene polymerization catalysts, it first needs to be removed from the feedstock in order to obtain polymer-grade ethylene. One way to do this is to recover the acetylene and sell it as a separate product. The other one is to selectively hydrogenate acetylene to ethylene. The catalyst must be capable of selectively converting acetylene to ethylene in a feedstock containing sometimes more than 98% ethylene so that the resulting concentration of acetylene is below 1 ppm, and this ideally should be done without hydrogenating any of the ethylene to ethane. Typical conditions for this reaction are 20−35 bar pressure, temperatures ranging from 25 to 100 °C, and 1.5- to 2-fold excess of hydrogen with respect to acetylene.[216] The most intensively studied catalysts for this transformation are based on palladium. Various supports and numerous metal or metal oxide promoters have been investigated for this reaction, and these catalysts as well as details of the catalytic process have been reviewed elsewhere.[217,218]

12. GAS TO LIQUID (GTL) APPLICATIONS

With oil becoming more expensive and oil resources becoming less available, there is a high motivation to study the possible use of alternative sources for fuels. While the Fischer−Tropsch process and the Mobil methanol to gasoline (MTG) process can serve to produce fuel-range hydrocarbons from natural gas or coal via syngas formation, more efficient processes via acetylene can be imagined, since acetylene can also be produced from both coal and natural gas. This approach has the advantage that it avoids the syngas formation step, which is very expensive and needs to be run on a very large scale in order to be profitable.[219] Although GTL applications will surely lead to cyclization and oligomerization products, the context is quite different with respect to scale and requirements. Hence, GTL is discussed in its own section. Studies on the oligomerization of acetylene into fuel-range products started nearly 30 years ago, but their number is quite limited.

The first of these studies focused on solid acid catalysts, since these were also used in the MTG process. It has been shown that acetylene reacts on H-ZSM-5 at temperatures between 250 and 500 °C and space velocities between 3900 and 15 000 h^{-1} to produce a wide range of aromatics with 6 to 13 carbon atoms with high selectivity. However after 1 h on stream the catalysts deactivate because of coke formation. Using acetylene diluted with helium increases the catalyst life, but considerable deactivation still occurs. It was shown that at higher Si/Al ratios conversion of acetylene is lower, but catalyst deactivation is less pronounced.[220] Metal-loaded zeolites with Ni, Pd, or Pt have also been tested in the reaction of methane and acetylene at 400 °C. A wide range of products is obtained, most of which have more than six carbon atoms, but in this case as well, deactivation of the catalyst occurs after a few hours.[221]

Fluorinated alumina was also studied as a catalyst for acetylene oligomerization. The temperatures used were in the range of 300 to 400 °C with space velocities in the range of 800 to 1200 h^{-1}, and the products obtained were aliphatics and aromatics in the C1−C15 range.[222] Rapid deactivation of these

catalysts also occurred because of coking, which could be diminished to some extent by increasing the fluorine content of the catalyst. This decreased the number and density of acid sites but along with this also the catalytic activity. Decreasing the concentration of acetylene in the feed also delayed the deactivation.[223,224] While these studies present a good overview of the possible transformations of acetylene over solid acid catalysts and the nature of the catalyst deactivation, neither a stable catalyst nor continuous operation conditions that avoid catalyst deactivation were described.

A catalyst system for the oligomerization of acetylene that was stable for over 100 h was reported by Timmons and co-workers using nickel supported on a mixture of H-ZSM-5 and alumina. For this system to function without deactivation, it was necessary to add to the acetylene feed a hydrogen donor such as water. The reaction proceeds at 350−400 °C at a space velocity around 2100 h^{-1} and produces mostly paraffins, although the product distribution can be controlled to some extent by adjusting the $H_2O:C_2H_2$ ratio and the nickel amount in the catalyst. Even so, the highest selectivity to aromatics that can be obtained at full acetylene conversion is around 33%. Acetaldehyde is believed to be an intermediate in this reaction.[225,226]

A recent study of acetylene oligomerization in the presence of hydrogen over nickel supported on silica catalysts showed that a conversion of nearly 100% can be achieved at 140 °C using a mixture of 25% acetylene in hydrogen at a space velocity of 5000 h^{-1}, with nearly 50% selectivity to oligomers, the major side product being ethylene. The catalyst was stable for at least 5 h under the reaction conditions. The major products identified were branched and linear alkenes with 4−10 carbon atoms.[227] These studies demonstrate the complexity and high number products that can be obtained when acetylene reactions are studied. Considering this multitude of possible reactions of acetylene alone, it is not surprising that there are not many reports of solid catalysts that can selectively favor one reaction pathway of acetylene in the gas phase.

The oligomerization of acetylene in the liquid phase with AlEt$_3$, analogous to the *Aufbaureaktion* of ethylene, which produces ethylene oligomers by successive ethylene insertions into the Al−C bond, was first attempted by Wilke,[228] but it was observed that for acetylene only the first insertion takes place with ease, and higher oligomers were considered to be only the product of the combination of two aluminum species and not of further insertion. Recently this reaction has been revisited with the aim of developing a way to obtain fuel-range acetylene oligomers. It was found that further insertions of acetylene can take place, but only very slowly, and their products can be observed only by sensitive analytical techniques. The reaction itself proceeds too slowly for practical applications and it is also stoichiometric with respect to AlEt$_3$, but these studies have shown how differently acetylene behaves compared with ethylene, the former producing branched oligomers whereas the latter leads to linear species.[229−231] It was shown, however, that by using an efficient acetylene polymerization catalyst, namely, an iron bisiminopyridine complex with methylalumi-noxane as a cocatalyst, the polymerization reaction can be forced to produce oligomers by adding a chain-transfer agent such as ZnEt$_2$. The reaction produces mostly C4−C8 oligomers, with traces of higher oligomers present, but it has the disadvantage of being stoichiometric with respect to ZnEt$_2$.[55] Further studies are still required to make the liquid-phase oligomerization of acetylene a truly catalytic reaction.

13. NOVEL APPROACHES

After the above descriptions of the different reactions in detail, this last section shall emphasize why there is great potential for new approaches to convert acetylene to valuable products.

13.1. Homogeneous Catalysis

Many reactions of acetylene are effected by homogeneous catalysis, but the catalysts employed are often simple metal salts instead of designed molecular catalysts, which are nowadays routine in many industrial processes. This could be because of the fact that many important ligand classes (e.g., NHCs[232−234]) and reactions (e.g., metathesis[235−238]) as well as concepts of modern metal−organic catalysis (e.g., cone angle,[239] bite angle,[240,241] and Tolman electronic parameter[239]) were developed after the shift from acetylene to olefins as the main chemical feedstock. The new concepts have been applied only to a limited extent in acetylene chemistry, for example in the work of Rosenthal and Schulz,[159] where a catalyst with impressive activity for cyclotrimerization of acetylene was developed. Also Pörschke synthesized and characterized several nickel complexes with acetylene that are possible intermediates in the oligomerization of acetylene. In these studies it was also mentioned that the complexes are active for the formation of benzene from acetylene. However, no systematic structure−activity relationship has been established.[242−244] Also, for the Co-catalyzed synthesis of substituted pyridines from propyne and propionitrile, a correlation between ligand structure, spectroscopy, and catalytic activity was demonstrated, and the knowledge was subsequently transferred to the reaction of acetylene with nitriles.[196] Alkyne complexes might also be seen as a source of inspiration for developing new catalytic reactions based on known stoichiometric reactions, such as the reaction of an alkyne with CO$_2$ to produce an unsaturated acid.[245−248]

An impressive example of what can be achieved by the application of nowadays well-established concepts like the use of hemilabile ligands is the carbonylation of propyne, respectively acetylene, with a Pd 2-pyridyldiphenylphosphine complex.[67] By the use of this ligand, the catalytic activity compared with simple nickel salts is increased by 3 orders of magnitude.

Furthermore, the knowledge about substituted alkynes, a well-developed field in metal−organic catalysis, can be seen as a pool of tools that are waiting to be applied to the parent compound acetylene itself, although, as previously mentioned, one should not expect this knowledge to be fully applicable to acetylene.[198,249,250]

In conclusion, current state-of-the-art homogeneous catalysis has not yet been applied to all of the reaction classes, for example, addition reactions to acetylene. Also in the field of carbonylation and oligomerization, respectively cyclization, which is dominated by homogeneous catalysis, not all of the concepts have been applied to explaining the reactivity patterns of acetylene.

13.2. Heterogeneous Catalysis

As discussed throughout the description of the different reactions, the processes used in industry, such as the syntheses of VCM and VAM, are still operated with the catalysts developed originally for these conversions. This is also reflected in the catalytic activities, which are rather low in comparison with more modern, non-acetylene-based processes.

Most of the catalysts make use of activated carbon (a mainly microporous material) as a support. In view of the common problem of coking and pore blocking, mesoporous carbon

materials[109,251−255] could improve the stability of the catalysts. Furthermore, basic supports could be interesting for vinylation and ethynylation reactions, which are dominated by base catalysts. For instance, attempts made by Reppe and others using basic catalysts, such as alkali supported on MgO, were not successful because of rapid deactivation.[135] However, knowing that it is difficult to produce stable high-surface-area mesoporous basic supports such as MgO,[256−258] it can be assumed that today's knowledge concerning the synthesis of basic materials can be used to extend the vinylation chemistry to solid catalysts.

It was shown in UHV that certain reactions such as cyclotrimerization are structure-sensitive. This suggests the use of proven concepts like alloying or selective poisoning.[259] The use of bimetallic particles for acetylene chemistry is still in its infancy. First attempts have already shown that such materials can help to reduce coke formation and improve stability.[165] As done for other reactions, fundamental studies should be used in this context to clearly reveal the active sites and allow for a directed design of catalysts. The use of catalysts for the selective hydrogenation of acetylene where Cu, Co, or Pb is added to Pd can be seen as an example where selective poisoning is already realized.[260]

Several reactions in acetylene chemistry are performed with molecular catalysts. Consequently, the use of solid single-site catalysts could also be extended to the reactions of acetylene.[261] This field can surely be stimulated by the use of heterogenized molecular catalysts.[262] Because of the low reaction temperatures of several acetylene transformations, polymers are suitable candidates for designed catalysts.[263] The use of polymeric supports in reactions of acetylene has already been reported in the ethynylation reaction using cross-linked polyethers impregnated with potassium hydroxide to form a structure resembling that of a potassium hydroxide complex with a crown ether.[264,265]

13.3. Reaction Technology

Improvements in reaction technology can also contribute to making progress in acetylene chemistry. A common characteristic of acetylene reactions is their exothermicity. Consequently, microreactor technology can be used to improve temperature control in acetylene conversion and help to avoid hot spots and deactivation of catalysts by coking.

Even more can be achieved in terms of safety: acetylene is certainly a reactant for which special care has to be taken. As mentioned in the section about safety and handling, using piping with small diameter decreases the tendency toward self-decomposition. Consequently, microreactor technology might allow easy handling of acetylene in the laboratory without the use of costly high-pressure devices.[108,266]

It is worth mentioning that traditional reaction technology has also made considerable progress in achieving improved temperature control. Some concepts for obtaining uniform temperature in the whole reactor, such as the use of fluidized bed reactors instead of fixed bed reactors, are already under investigation in acetylene chemistry.[267]

14. CONCLUSION

The aim of this review was to introduce the state of the art in acetylene handling and to give an overview of the different reaction classes of acetylene. Conversions starting with acetylene are rather underdeveloped compared with many other fields in catalysis, which offers the possibility for significant improvement by applying modern concepts, new materials, and state-of-the-art process technology. In order to reduce our society's dependence on oil-derived feedstocks, acetylene could serve as a platform molecule that can be transformed into various base chemicals. This should not be seen as a step back to coal chemistry but rather a step toward a diversified chemical industry where acetylene is a valuable molecule that can be selectively transformed to materials guaranteeing our prosperity.

AUTHOR INFORMATION

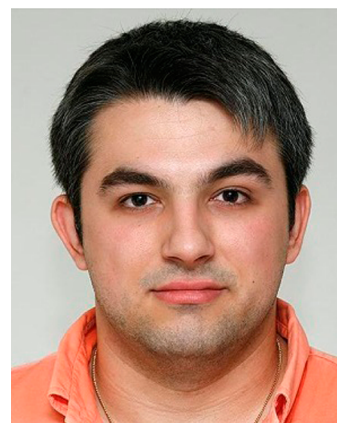### Corresponding Author

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Notes

The authors declare no competing financial interest.

Biographies

Ioan-Teodor Trotuş was born in Galaţi, Romania, in 1988. He participated in the International Chemistry Olympiad in 2006 and 2007, where he received a bronze and a silver medal, respectively. He received his B.Sc. in 2010 and his M.Sc. in 2012 from the University of Bucharest. He then started work on his Ph.D. thesis under the supervision of Professor Ferdi Schüth at the Max Planck Institut für Kohlenforschung in Mülheim an der Ruhr. The topic of his thesis involves the study of catalytic reactions of acetylene and the development of new catalysts to improve the performance of these reactions.

Tobias Zimmermann was born in Pforzheim, Germany, in 1986. He received his M.Sc. (Physical Chemistry) from the Technische Universität München in 2010 with high distinction. Afterwards he

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Professor Ferdi Schüth was born in 1960 in Warstein and is married and the father of two daughters. He studied chemistry and law at the Westfälische Wilhelms-Universität (Münster). He received his doctorate in chemistry in 1988 and passed the First State Exam in Law in 1989. After five years as a scientific assistant at the Johannes-Gutenberg-Universität (Mainz), in 1995 he became Professor of Chemistry. From 1995 till 1998 he worked as Professor for Inorganic Chemistry at the Johann-Wolfgang-Goethe-Universität (Frankfurt). Since 1998 he has been Director at the Max-Planck-Institut für Kohlenforschung (Mülheim an der Ruhr). Professor Schüth has received several awards, and he is a member of numerous editorial boards and committees, including vice chairman of Dechema, vice president of DFG, honorary professor at the Dalian University of Technology (China), and founder of the hte AG (now fully acquired by BASF SE). His research fields include energy, biomass conversion, crystallization processes, synthesis of catalyst materials, catalysis, zeolites, ordered mesoporous materials, and hydrogen storage materials. Professor Schüth has about 350 publications and approximately 30 patents or patent applications.

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