Enhanced Selectivity in the Hydrogenation of Acetylene due to the Addition of a Liquid Phase as a Selective Solvent

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Enhanced Selectivity in the Hydrogenation of Acetylene due to the Addition of a Liquid Phase as a Selective Solvent

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S *Supporting Information*

ABSTRACT: The selective hydrogenation of acetylene is usually a gas-phase reaction. In this work, a liquid phase was introduced as a selective solvent to improve the selectivity to ethylene by coupling absorption to the reaction. The catalyst was 0.01% Pd supported on a low surface area silica. *N*-methyl-2-pyrrolidone (NMP) was used as a selective solvent, and decane was used as a nonselective solvent for comparison. The liquid-phase hydrogenation was carried out in a stirred flat bottom flask operated in gas continuous and liquid batch mode, and the gas-phase hydrogenation was carried out in a fixed bed reactor. The selectivity to ethylene in the gas-phase hydrogenation was 50−70%. In contrast, the highest selectivity to ethylene in the NMP liquid-phase hydrogenation was increased to 96%, while in decane it had the same value as in the gas phase. In NMP, a low reaction temperature below 80 °C did not give a high selectivity to ethylene because the relatively high ethylene solubility in NMP led to deep hydrogenation and the high acetylene solubility caused more oligomerization. Good catalyst stability was obtained under the optimized conditions of a relatively low space velocity, H_2:C_2H_2 ratio above 10, and reaction temperature above 80 °C. Significant deactivation also occurred in NMP under other conditions due to oligomerization.

1. INTRODUCTION

Ethylene is a major raw material in the petrochemical industry. It is primarily used as a chemical building block for the production of plastics. Most ethylene is produced by the steam cracking of naphtha. To prevent catalyst poisoning in the polymerization process, acetylene impurities in the C_2-cut must be reduced to below 5 ppm.[1] The selective hydrogenation of acetylene to ethylene is used in industrial processes to remove trace amounts of acetylene in ethylene.

The industrial process of the selective hydrogenation of acetylene uses a gas-phase reaction with supported Pd or Pd−Ag catalysts in a fixed bed reactor. The gas-phase hydrogenation produces a considerable amount of ethane. For example, in the front-end hydrogenation process, the selectivity to ethane is ~110% on Pd/Al_2O_3 and is ~60% on PdAg/Al_2O_3 at a high conversion near 100%.[2] In the tail-end process, the selectivity to ethane is 60−70% on both Pd/Al_2O_3 and PdAg/Al_2O_3.[3]

Different methods have been investigated to suppress ethane formation, which include enhancing the dispersion of palladium,[4−7] adding a second metal to form bimetallic catalysts,[2,8−14] utilizing the strong metal−support interaction,[15−22] and introducing an inhibiting gas such as CO[23,24] and NO_x.[3,25−29]

The liquid-phase hydrogenation has been reported to give a better performance than the gas-phase hydrogenation when a proper liquid was used.[30−33] The first study on the liquid-phase hydrogenation of acetylene was reported by Edvinsson et al. in 1995.[30] In that study, they found that heptane formed a liquid film on the catalyst layer in a monolith reactor, which improved catalyst stability by removing green oil from the catalyst. Shitova et al. studied the hydrogenation of acetylene in *N*-methylpyrrolidone (NMP) in the presence of CO[33] and observed that by introducing NMP as the liquid phase, the

selectivity to ethylene was increased to 90% at a high acetylene conversion of 96%.

Acetylene has high solubility in polar solvents, such as acetone, NMP, dimethylformamide (DMF), and some ionic liquids,[34] while ethylene has a much lower solubility in these solvents. The selective solubility factor of acetylene to ethylene is about 9 in DMF, and is 45 in 1,3-dimethylimidazolium methylphosphite ([DMIM][MeHPO_3]).[35] It has been shown that an ionic liquid as a catalyst coating gives a better catalytic performance for the selective hydrogenation of acetylene because it reduces the complete hydrogenation of acetylene to ethane and also C_4 species formation.[31,32] These catalysts were described as solid catalyst with an ionic liquid layer (SCILL), and they also improved the selective hydrogenation of citrial.[36,37] With the ionic layer on the surface of SCILL catalysts, the reaction on SCILL is similar to that in the liquid phase.

Although the use of some liquids has been shown to give better catalyst stability or selectivity to ethylene, there is still room for further improvement. In addition, the underlying mechanism is not yet clear. Although catalyst stability was improved by using heptane, the selectivity to ethylene was not enhanced and the highest selectivity to ethylene was 80% at a low acetylene conversion of 30%.[30] In NMP, the selectivity to ethylene was below 20% over the Pd/Sibunit catalyst without cofeeding CO.[33] For the SCILL catalysts, the presence of the ionic layer significantly decreased catalytic activity.[32]

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This work aimed to further improve the selectivity to ethylene while maintaining a high activity in the liquid-phase hydrogenation of acetylene. The reaction was carried out in NMP using 0.01 wt % Pd supported on a low surface area silica (LSA-SiO$_2$). Our previous work showed that Pd/LSA-SiO$_2$ gave a higher selectivity to ethylene than when other supports were used.[22] Under the optimized reaction conditions, a high selectivity to ethylene of 96% was obtained at an acetylene conversion of 96%.

Another consideration in this work was that the selective hydrogenation of pure or highly concentrated acetylene can be an alternative approach to produce ethylene. The oil crises have made the steam cracking of naphtha a less economical route to produce ethylene. A promising alternative route for the production of ethylene is to use natural gas as feedstock. As the price of natural gas is expected to dramatically decrease due to its projected production from shale gas and methane hydrate,[38] cheap acetylene would become available from the partial oxidation process.[39] Then, the selective hydrogenation of acetylene will be economical for the production of ethylene. However, the hydrogenation of pure or highly concentrated acetylene is very different from the removal of trace acetylene from ethylene. The gas-phase process in a fixed bed reactor is not suitable since the reaction requires the removal of a huge amount of reaction heat. A slurry reactor for liquid-phase hydrogenation has very good heat-transfer capability, and it should be used to give a uniform temperature profile.[40]

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. The 0.01%Pd/LSA-SiO$_2$ catalyst was prepared by the incipient wetness impregnation method. A low surface area silica (LSA-SiO$_2$, surface area < 1 m^2/g, Beijing Yi Li Fine Chemicals Co., Ltd.) was used as the support. An aqueous precursor solution of H$_2$PdCl$_4$ was prepared by dissolving the desired amounts of equimolar PdCl$_2$ (99.9%, Alfa Aesar) and HCl (AR, Sinopharm) in deionized water. After impregnation of the precursor solution into the support, the catalyst was dried at 100 °C for 1 h and then calcined at 400 °C for 4 h after increasing the temperature at a rate of 5 °C/min.

2.2. Catalyst Characterization. The crystalline phase of the catalysts was characterized from 20 to 80° 2θ by a Bruker Advance D8 X-ray diffractometer with Cu Kα (λ = 1.5418 Å) monochromatic radiation. The samples were dried and ground before being loaded onto the X-ray diffraction (XRD) instrument. The surface area of the support was determined by Brunaer−Emmett−Teller (BET) method using N$_2$ adsorption−desorption on an Autosorb-1-C instrument. Transmission electron microscopy (TEM) measurements were performed using a JEM-2010 microscope (JEOL Ltd., Tokyo, Japan) operated at 120 kV. The catalyst samples were prepared for imaging by grinding and the suspension of ~1 mg of the reduced catalyst in ~5 mL of acetone. A pipet was then used to collect the sample from the top of this suspension. Two drops of this solution were dropped onto a lacey support film and dried for 0.5 h before the TEM observation. Scanning electron microscopy (SEM) measurements were performed using a JSM 7401F (JEOL Ltd., Tokyo, Japan) instrument operated at 3.0 kV.

2.3. Acetylene Hydrogenation. The selective hydrogenation of acetylene in the gas phase was carried out in a fixed bed reactor of 5 mm i.d. and 600 mm length. This is shown in Figure S1 in the Supporting Information. The catalyst was

mixed with quartz particles in a ratio of 1:9 (0.5 g of catalyst and 4.5 g of quartz particles). The catalyst was reduced with 4% H$_2$ balanced by N$_2$ at 200 °C for 1 h and then cooled to the reaction temperature. The temperature was monitored by a K type thermocouple placed in the catalyst bed. The liquid-phase hydrogenation of acetylene was carried out in a semibatch flat bottom flask. The liquid was stirred with a magnetic stirrer, and the temperature was controlled by an oil bath. The other parts were the same as in the gas-phase apparatus. The reduced catalyst and 80 mL of NMP (Sinopharm) were placed in the flask. Experiments on the effect of stirring speed showed that under a low space velocity of 3600 mL/(g$_{cat.}$ h), the acetylene conversion increased with increasing stirring speed until 600 revolutions per minute (RPM). In all of the following experiments, a stirring speed of 700 RPM was used to eliminate the effect of gas−liquid mass-transfer limitation. The gas feed was a C$_2$H$_2$/H$_2$ (1:4−1:40) mixture at a total flow rate of 30−200 mL/min. The corresponding space velocity was GHSV = 3600−24000 mL·g$_{cat.}$$^{-1}$·h^{-1}. The outlet stream was analyzed online by a gas chromatograph equipped with a flame ionization detector (FID; GC 7900, Techcomp Ltd.) and a HP-Al/S PLOT column (Agilent, 30 m × 0.53 μm). The carbon balance was above 95% by accounting for the carbon atoms in the gas phase. The concentrations of other species in the gas phase are too low for quantitative determination. The acetylene conversion and selectivity to the products were calculated as follows, with o for outlet and i for inlet:

$$\text{acetylene conversion} = \frac{C_2H_2(i) - C_2H_2(o)}{C_2H_2(i)} \quad (1)$$

$$\text{ethylene selectivity} = \frac{C_2H_4(o) - C_2H_4(i)}{C_2H_2(i) - C_2H_2(o)} \quad (2)$$

$$\text{ethane selectivity} = \frac{C_2H_6(o)}{C_2H_2(i) - C_2H_2(o)} \quad (3)$$

C$_4$ species selectivity
$$= 2\frac{\sum C_4H_{10}(o) + \sum C_4H_8(o) + C_4H_6(o)}{C_2H_2(i) - C_2H_2(o)} \quad (4)$$

2.4. Solubility Measurement. The solubilities of acetylene and ethylene were measured isothermally from pressure decay observations using an apparatus similar to that used by Palgunadi et al.[35] This is shown in Figure S2 in the Supporting Information. Two stainless steel vessels were used as the equilibrium cell (EC) and gas reservoir (GR). The EC was placed in an oil bath with a magnetic stirrer, and the GR was at room temperature. Both vessels were equipped with a thermocouple and a pressure gauge (0.4% in precision). The volumes of the two vessels with their tubes and fittings, V_{EC+TF1} and V_{GR+TF2}, were determined by the displacement of water with nitrogen gas (V_{EC+TF1} = 283 mL, V_{GR+TF2} = 291 mL).

The solubility was calculated with the following equation:

$$\text{solubility} = \frac{\text{tot gas input (mol)} - \text{residual gas (mol)}}{\text{amt solvent (kg)}} \quad (5)$$

where the amount of gas was determined by the ideal gas law. An oil bath was used to control the temperature from 20 to 100 °C.

3. RESULTS AND DISCUSSION

3.1. Catalyst Characterization. The surface area of the LSA-SiO$_2$ support was measured by BET method to be less than 1.0 m^2/g. The XRD pattern of the catalyst is shown in Figure 1a. LSA-SiO$_2$ gave very sharp peaks, indicating that it
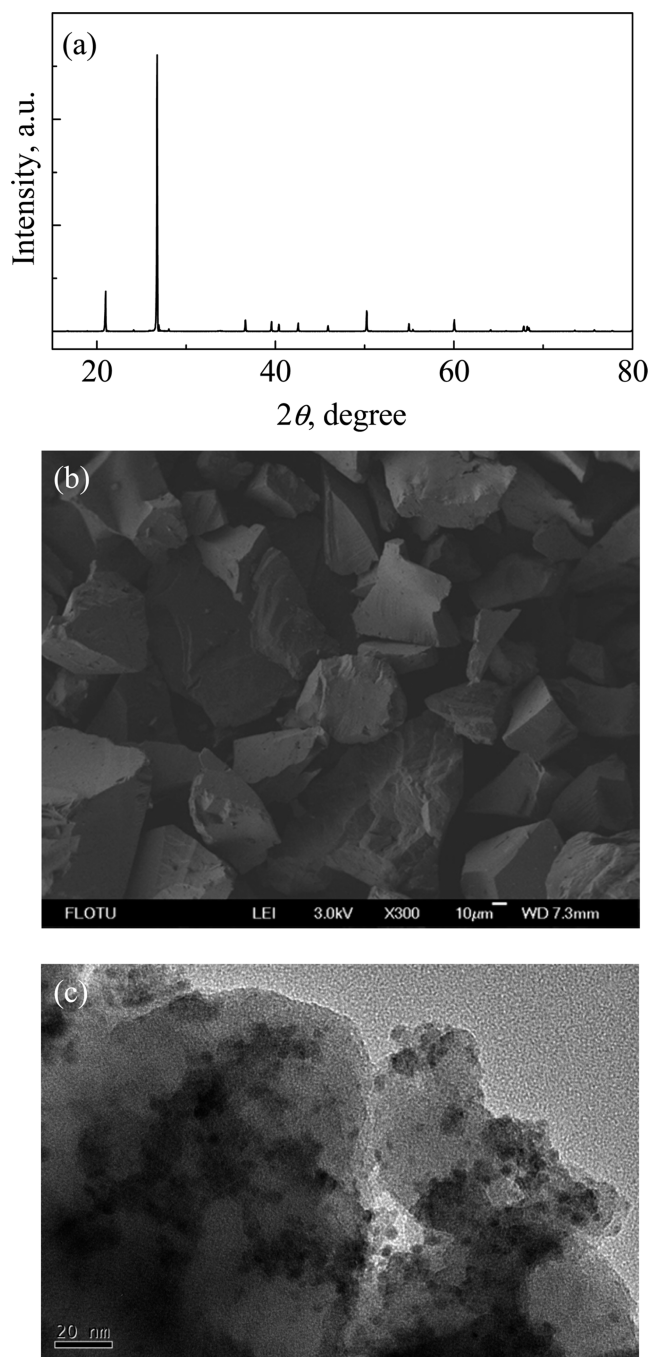

Figure 1. Characterization of the 0.01%Pd/LSA-SiO$_2$ catalyst: (a) XRD pattern; (b) SEM image; (c) TEM image.

comprised large crystalline grains. Palladium peaks were not seen due to the low loading. The SEM image is shown in Figure 1b. The particle size of the support was 20−100 μm. The support has a relatively flat surface without pores. Its TEM image is shown in Figure 1c. This showed that the sizes of most Pd particles were 5−8 nm.

3.2. Effect of Reaction Temperature. The conversion of acetylene in the liquid-phase hydrogenation was similar to that in the gas-phase hydrogenation, except for a slight decrease in acetylene conversion above 80 °C. This is shown in Figure 2.
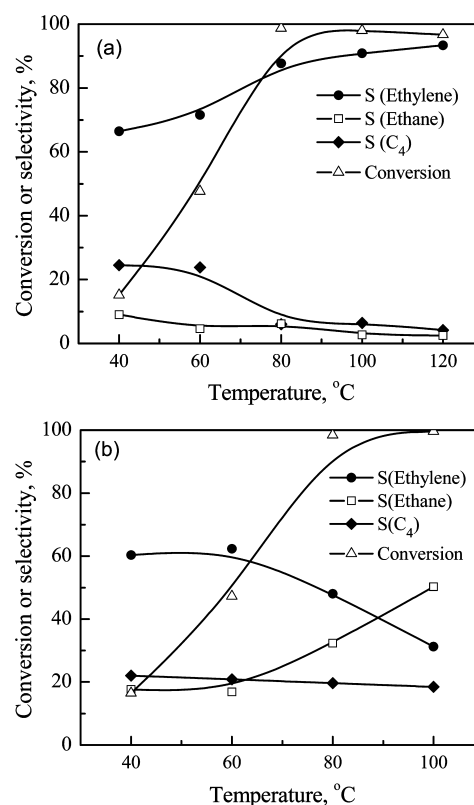

Figure 2. Effect of temperature on selectivities in (a) liquid phase (NMP) and (b) gas phase. H$_2$:C$_2$H$_2$ = 6, SV = 3600 mL·g$_{cat.}^{-1}$·h^{-1}.

The slight decrease in acetylene conversion with increasing temperature above 80 °C was due to the decreased solubility of acetylene in NMP, as discussed later in section 3.5. The selectivities to ethane, ethylene, and C$_4$ species were very different in the gas and liquid phases. The selectivity to ethane in the liquid phase decreased with increasing temperature, with a value of 9.1% at 40 °C which decreased to 2.7% at 100 °C and 2.5% at 120 °C, as shown in Figure 2a. In contrast, the selectivity to ethane in the gas phase was 18% at less than full conversion, which increased to 32% near full conversion at 80 °C, and it further increased to 50% at 100 °C, as shown in Figure 2b. The selectivity to C$_4$ species in the liquid phase was 24% below 80 °C, and it decreased to 4−6% above 80 °C. In the gas phase, the selectivity to C$_4$ species was 20% at all temperatures. Because the formation of both ethane and C$_4$ species were well-controlled in liquid-phase hydrogenation, the selectivity to ethylene was much higher than that in gas-phase hydrogenation. In addition, the selectivity to ethylene in the liquid phase increased with increasing temperature, and it exceeded 90% at 100−120 °C with an acetylene conversion above 96%.

The effect of temperature was also studied by Shitova et al. at 50−90 °C with a mixture of C$_2$H$_2$/CO/H$_2$/He (2:2:90:6) in NMP.[33] In that study, Sibunit (surface area, 320 m^2/g) was used as the support, and a CO stream was introduced to suppress ethane formation. For a better comparison, the reaction conditions used in the present work and in Shitaova's

work were compared in Table 1. The selectivities to ethane and oligomers decreased with increasing temperature. Without the

Table 1. Reaction Conditions Used in the Present and Shitova's Works

	present work	Shitova et al.
reactor type	semibatch stirred flask	shaker-type flow reactor
Pd loading	0.01 wt %	0.5 wt %
support and surface area	SiO_2, <1 m^2/g	Sibunit, 320 m^2/g
CO feed	none	2% in stream
$H_2:C_2H_2$ ratio	1:4–1:40	1:45

addition of CO, the selectivity to ethylene was only 11%. In the present study, with 0.01%Pd/LSA-SiO_2, ethane formation was controlled to a very low rate even in the absence of CO. One reason for this good result is that the low surface area SiO_2 was a better support that improved the selectivity to ethylene, because low surface area support favors ethylene desorption after the first step of hydrogenation.[22] Furthermore, the metal loading in Shitova's work is 50 times higher than that in the present work, which is another possible reason for the low ethylene selectivity without CO cofeed in their results.

3.3. Effect of Space Velocity. Comparative experiments on the effect of space velocity (GHSV) were carried out in the liquid phase and gas phase at 100 °C with 10:1 H_2/C_2H_2. The results are shown in Table 2 and Figure 3. In the liquid phase, the conversion of acetylene decreased with increasing GHSV, while, in the gas phase, the conversion remained at 100% for GHSVs below 12 000 mL·$g_{cat.}^{-1}$·h^{-1}, and it then decreased to 56% at 18 000 mL·$g_{cat.}^{-1}$·h^{-1} and to 34% at 24 000 mL·$g_{cat.}^{-1}$·h^{-1}. With increasing GHSV, the increase in selectivity to C_4 species is similar in both systems, but to a different extent. At low GHSVs, the selectivity to C_4 species was much higher in the gas phase than in the liquid phase. With increasing GHSV, the selectivity to C_4 slightly increased in the gas phase and became unchanged above 8000 mL·$g_{cat.}^{-1}$·h^{-1}. In the liquid phase, the selectivity to C_4 significantly increased with increasing GHSV to a value very similar to that in the gas phase at high GHSVs. With increasing GHSV, the selectivity to ethane significantly decreased from 41.5 to 9.1% in the gas phase, but it remained below 2.5% in the liquid phase. As a result, the selectivity to ethylene was significantly increased in the gas phase but slightly decreased in the liquid phase with increasing GHSV. Nevertheless, the lowest selectivity to ethylene in the liquid phase (81%) was still 10% higher than the highest selectivity to ethylene in the gas phase. A main feature of the liquid-phase hydrogenation was that the selectivity to ethane was always low at 1−2%, indicating that complete hydrogenation was effectively limited.

With increasing GHSV, the difference between the acetylene conversion in the gas and liquid phases increased. The faster decrease in conversion in the liquid phase indicated that the gas−liquid mass-transfer limitation existed at high GHSVs. At a higher space velocity, we believe that the decreased conversion of acetylene led to a higher acetylene coverage on the catalyst,
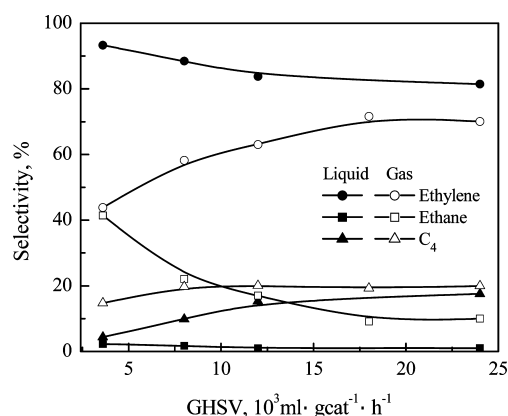

Figure 3. Effect of space velocity on selectivities in liquid- and gas-phase hydrogenation. T = 100 °C; $H_2:C_2H_2$ = 10.

which in turn led to more oligomerization reactions and C_4 species formation. Therefore, for the liquid-phase hydrogenation, a lower space velocity was better for a higher conversion and higher selectivity to ethylene.

To further compare the selectivity to ethylene in the gas-phase and liquid-phase hydrogenation, the selectivity to ethylene is plotted versus acetylene conversion in Figure 4.
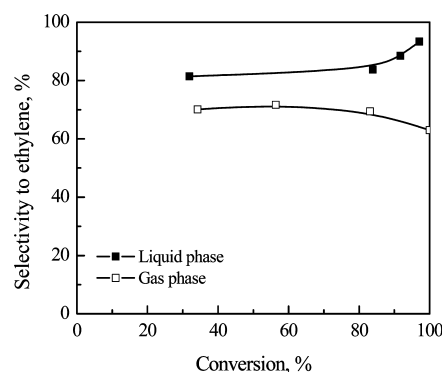

Figure 4. Effect of acetylene conversion on selectivity to ethylene.

At conversions below 80%, the selectivity to ethylene was about 70% in the gas phase and about 80% in the liquid phase, which was a difference of only 10%. However, at conversions near 100%, the selectivity to ethylene increased with increasing conversion in the liquid phase but it decreased in the gas phase. The liquid-phase hydrogenation had a high selectivity to ethylene at high acetylene conversions, which makes it very advantageous for the removal of trace acetylene from ethylene.

3.4. Effect of H_2:C_2H_2 Molar Ratio. The effect of H_2:C_2H_2 molar ratio was studied in both the gas and liquid phases at 100 °C and GHSV 3600 mL·$g_{cat.}^{-1}$·h^{-1}. The conversions were near 100% in both phases. The selectivities to ethylene, ethane, and C_4 species are shown in Figure 5. With increasing H_2:C_2H_2 ratio, the selectivity to C_4 species decreased in both the liquid and gas phases. The selectivity to C_4 species decreased from

Table 2. Effect of Space Velocity on Conversion of Acetylene

	GHSV = 3600 (ml·$g_{cat.}^{-1}$·h^{-1})	GHSV = 8000 (ml·$g_{cat.}^{-1}$·h^{-1})	GHSV = 12000 (ml·$g_{cat.}^{-1}$·h^{-1})	GHSV = 18000 (ml·gcat.$^{-1}$·h^{-1})	GHSV = 24000 (ml·$g_{cat.}^{-1}$·h^{-1})
liquid phase, %	97	92	84	–	32
gas phase, %	100	100	100	56	34

Figure 5. Effect of $H_2:C_2H_2$ ratio on selectivities in gas- and liquid-phase hydrogenation. $T = 100$ °C; GHSV = 3600 mL·$g_{cat.}^{-1}$·h^{-1}.

7.6% to 1.2% in the liquid phase and it decreased from 19.1% to 6.1% in the gas phase, indicating that a high $H_2:C_2H_2$ ratio can depress C_4 species formation. The selectivity to ethane was high in the gas phase, increasing from 34 to 64% with increasing $H_2:C_2H_2$ ratio, but it was always less than 3% in the liquid phase. As a result, the selectivity to ethylene increased from 92% to 95% with increasing $H_2:C_2H_2$ ratio in the liquid phase, but decreased from 47% to 30% in the gas phase.

Additional experiments were carried out in the liquid phase to study the effect of $H_2:C_2H_2$ ratio at different reaction temperatures. The results are shown in Figure 6. The selectivities to ethylene were the same at 80 and 100 °C, as shown in Figure 6b,c. The conversion of acetylene decreased with increasing $H_2:C_2H_2$ ratio at 80 and 100 °C, with a faster decrease at 100 °C. The conversion was close to 100% at 60 °C at all $H_2:C_2H_2$ ratios, but the selectivity to ethylene was much lower (79−85%) than those at 80 and 100 °C. The formation of C_4 species was the main side reaction at low $H_2:C_2H_2$ ratios, while the complete hydrogenation to ethane was the main side reaction at high $H_2:C_2H_2$ ratios. The selectivity to ethylene was usually higher than 90% at 80 and 100 °C. The highest selectivity to ethylene of 96% was obtained at 80 °C, $H_2:C_2H_2$ = 40, and GHSV = 3600 mL·$g_{cat.}^{-1}$·h^{-1}.

The conversion and selectivity in the liquid-phase hydrogenation was sensitive to the reaction temperature. At a low reaction temperature (60 °C), the acetylene conversion was high, but the selectivity to ethylene was much lower than those at 80 and 100 °C. The reason was that the solubility values of both acetylene and ethylene were relatively high at a low temperature. We believe that the high concentration of ethylene in the liquid resulted in an increased selectivity to ethane, and the high concentration of acetylene in the liquid led to a high acetylene coverage on the catalyst surface and an enhanced selectivity to C_4 species.

The effect of the $H_2:C_2H_2$ ratio was explained by the competing adsorption of H_2, C_2H_2 and C_2H_4 on the Pd surface and the formation of the carbide phase and hydride phase.[41,42] As the acetylene concentration decreased with increasing $H_2:C_2H_2$ ratio, the selectivity to C_4 species decreased and the selectivity to ethane increased. This was consistent with the results of García-Mota et al. who reported that the selectivity to alkane increased with increasing H_2:alkyne ratio.[42] In that study the authors proposed that at higher H_2:alkyne ratios, the formation of Pd−H changed the reaction selectivity toward the production of alkanes. This mechanism also explained the results of the present work about why a much lower selectivity
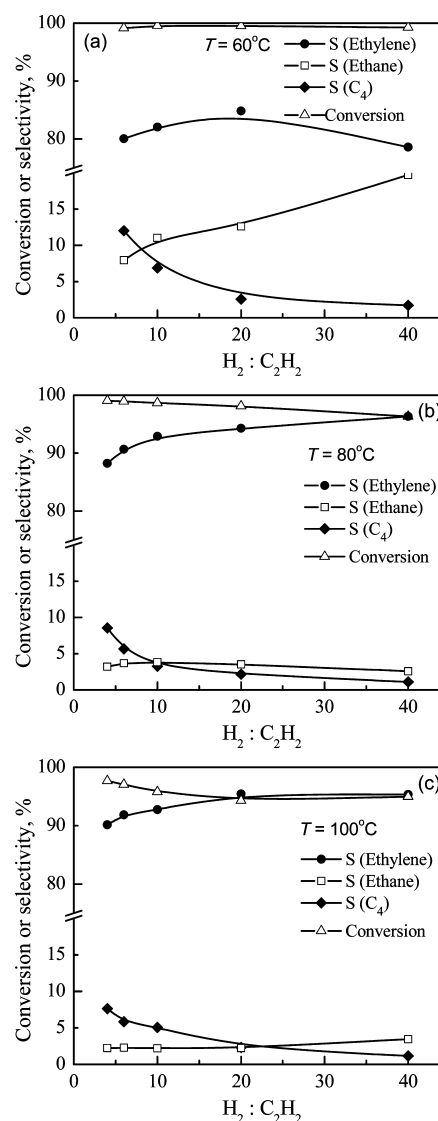

Figure 6. Effect of $H_2:C_2H_2$ on selectivity and conversion in NMP GHSV = 3600 mL·$g_{cat.}^{-1}$·h^{-1}: (a) 60, (b) 80, and (c) 100 °C.

to ethane was obtained in the liquid phase compared to that in the gas-phase hydrogenation. In the liquid phase, the formation of the hydride phase was significantly reduced due to the low solubility of hydrogen, and thus the formation of ethane was much less.

3.5. Solvent Effect. To examine the effect of the selective solubility of acetylene in the liquid phase, a comparative experiment was carried out using decane as a nonselective solvent. The solubilities of acetylene and ethylene in NMP and decane are shown in Figure 7. Acetylene has a much higher solubility than ethylene in NMP; whereas acetylene and ethylene had low and similar solubilities in decane. For a quantitative description, a selective solubility factor was defined as

$$\alpha = \frac{\text{dissolved acetylene (mol/kg)}}{\text{dissolved ethylene (mol/kg)}} \tag{6}$$

The selective solubility factor α of NMP was larger than 10, which indicated that NMP was a highly selective solvent for acetylene. With increasing temperature, the solubility of acetylene in NMP decreased much faster than that of ethylene.
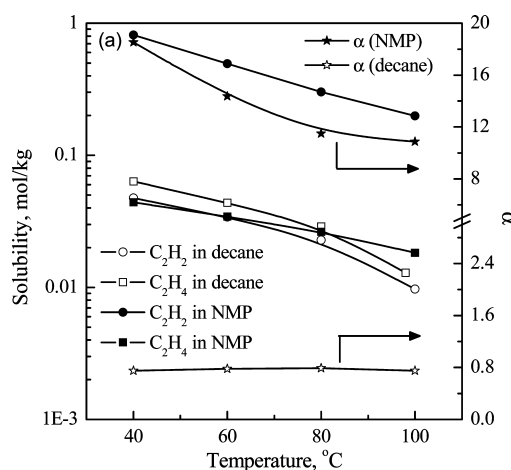
Figure 7. Solubility of acetylene and ethylene in NMP and decane. α = (dissolved acetylene (mol/kg))/(dissolved ethylene (mol/kg)).

As a result, the value of α in NMP decreased from 18.5 at 40 °C to 10.9 at 100 °C. In contrast, acetylene and ethylene have very similar solubilities in decane, with that of ethylene being a little higher. The value of α for decane was less than 1, and it was almost independent of temperature, indicating that decane is a nonselective solvent for acetylene.

The liquid-phase hydrogenation reactions using NMP and decane were studied at 10:1 H_2:C_2H_2 and GHSV of 3600 mL·$g_{cat.}^{-1}$·h^{-1}. The results are shown in Figure 8. At all temperatures, the conversion of acetylene was near 100% in NMP and was 90−94% in decane. This was due to the much lower solubility of acetylene in decane. The selectivity to ethane was much higher in decane than in NMP. Accordingly, the selectivity to ethylene in decane was about 70%, which was similar to that in the gas phase. In contrast, in NMP, the
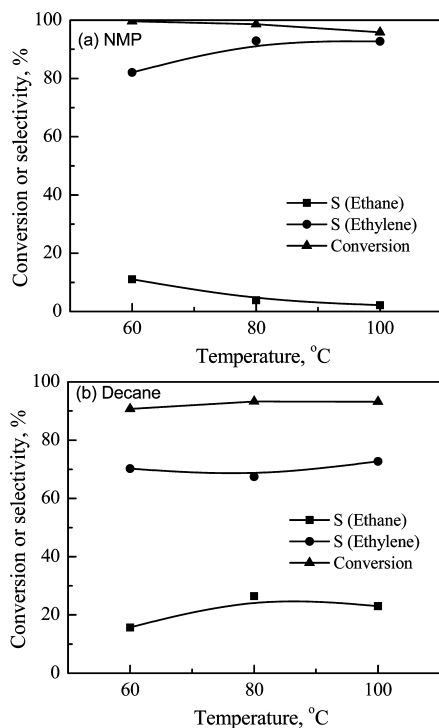
selectivity to ethylene was about 90%. These results indicated that a selective solvent effectively suppresses the production of ethane and C_4 species. Besides the selective solubility factor, the absolute values of the acetylene and ethylene solubilities were also important. A high acetylene solubility tended to give more C_4 byproduct, while a high ethylene solubility gives more ethane from complete hydrogenation. This explained the lower selectivity in NMP at 60 °C where the solubilities of both acetylene and ethylene were higher than those at 80 and 100 °C.

3.6. Catalyst Stability. The catalyst in the liquid-phase hydrogenation showed good stability, but only under certain conditions, namely, a relatively high temperature, high H_2:C_2H_2 ratio, and low space velocity. At such conditions, no green oil was observed under these conditions after 12 h of reaction. However, severe deactivation occurred at low reaction temperatures, low hydrogen ratios, and high space velocities. Under these latter conditions, some dark brown flecks were formed on and around the catalyst and in the solvent within the first 2 h. Figure 9 shows the catalyst stability at 60 and 100 °C
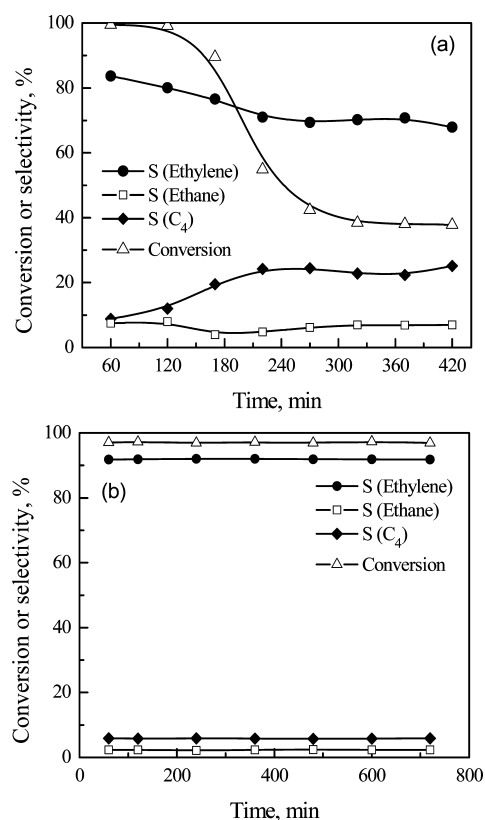

Figure 9. Catalyst stability in NMP at H_2:C_2H_2 = 6 and GHSV = 3600 mL·$g^{cat.-1}$·h^{-1}: (a) T = 60 °C; (b) T = 100 °C.

with 6:1 H_2:C_2H_2 and GHSV = 3600 mL·$g_{cat.}^{-1}$·h^{-1}. At a low temperature (60 °C), the catalyst suffered severe deactivation in the first 2 h, with the acetylene conversion decreasing from 100 to 40%, and the selectivity to ethylene decreasing from 83% to 70%. In contrast, the catalyst at a higher temperature (100 °C) showed much better stability, with no detectable deactivation in 12 h. The main cause of deactivation was the high coverage of acetylene and C_4 species on the Pd particles. Both acetylene and C_4 species have high solubilities in NMP, as shown in Table 3.[1] It is commonly accepted that the C_4 species are the precursors of green oil.[43] At the conditions where catalyst

Figure 8. Liquid-phase hydrogenation in (a) NMP and (b) decane. H_2:C_2H_2 = 10; GHSV = 3600 mL·$g_{cat.}^{-1}$·h^{-1}.

Table 3. Solubility of C$_4$ Species in NMP, m^3/m^3 (in Standard State)

	T = 20 °C	T = 40 °C	T = 60 °C
C$_2$H$_4$	1.9	1.17	–
C$_2$H$_2$	38.7	24.0	14.75
i-C$_4$H$_8$	32	16	8.5
C$_4$H$_6$	94	43	24
C$_4$H$_4$	–	292	95

stability was poor, the acetylene and C$_4$ species concentrations in the liquid were high, which in turn led to high coverages of these species on the catalyst surface and catalyst deactivation.

4. CONCLUSIONS

The selective hydrogenation of acetylene was studied using 0.01 wt % Pd/LSA-SiO$_2$ in both the gas and liquid phases. In the liquid-phase hydrogenation, NMP and decane were used as selective and nonselective solvents, respectively. The results led to the following conclusions:

(1) The introduction of a selective solvent significantly enhanced the selectivity to ethylene. The selectivity to ethylene was 80−96% in NMP, while it was less than 70% in the gas phase.

(2) In the liquid-phase hydrogenation, the selectivity to ethylene strongly depended on the selective solubility of the solvent. A selective solvent (NMP) significantly enhanced the selectivity to ethylene, while a nonselective solvent (decane) did not affect the selectivity to ethylene.

(3) A high reaction temperature, low space velocity, and high H$_2$:C$_2$H$_2$ ratio gave increased selectivity to ethylene in NMP. At T = 80 °C, GHSV = 3600 mL·g$_{cat.}$$^{-1}$·h^{-1}, H$_2$:C$_2H_2$ = 40, a high selectivity to ethylene of 96% was obtained.

(4) The catalyst had a good stability at a high temperature, high hydrogen ratio, and low space velocity. Catalyst deactivation under conditions different from these was caused by the high concentrations of acetylene and C$_4$ species in NMP.

ASSOCIATED CONTENT

Ⓢ Supporting Information
Schematic graph of gas-phase hydrogenation of acetylene with catalyst packed in a fixed bed reactor, a diagram of the apparatus of solubility measurement, and text discussing the different conversions in Figures 2a and 6a. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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