The Role of the Reactor Wall in the Thermal Hydrocracking of Polyaromatic Compounds

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The Role of the Reactor Wall in the Thermal Hydrocracking of Polyaromatic Compounds

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The thermal hydrocracking of hydrindene (500°C, 80 atm) was found to be affected profoundly by the nature of the reactor wall. In a stainless steel (SS) reactor the conversion dropped and the selectivity changed while passing through the primary aging stage; aging of a gold-plated reactor resulted in an increasing conversion, starting from almost zero. In both reactors a steady state was established at essentially the same conversion and selectivity, which was not dependent on the S/V ratio of the reactor nor static or flow conditions. It is concluded that the α ring-opening reactions of indan, resulting in toluene and n-propylbenzene, are initiated and terminated at the aged reactor wall; the β ring-opening of indan leading to o-ethyltoluene is predominantly homogeneous and is not affected by the aged reactor wall.

Introduction

It is well known that in many gas-phase reactions which are considered to be essentially homogeneous, interference of the reactor wall cannot be disregarded. Perhaps the most important industrial example is the thermal cracking of hydrocarbons. Several techniques are reported in the literature aimed at elucidation and/or eliminating the specific effects of the reactor wall, such as change of the surface-to-volume ratio of the reactor, pretreatment of the reactor wall by oxygen, acids, and sulfur compounds, or change of the wall material (Crynes and Albright, 1969). More recently, gold reactors, which are expected to have no or a very low activity on thermal cracking, have been used (Blakemore, et al., 1973; Cramers, 1967; Johnson, et

al., 1972), together with the development of a completely wall-less reactor, allowing the study of reactions under conditions absolutely free from any interfering surface (Taylor, et al., 1972). Notwithstanding the extensive experimental work, no picture of the mechanism has been obtained as yet; in fact, with more sophisticated techniques the complexity of the surface reactions became more extended.

During investigations on the thermal hydrocracking of polyaromatic compounds which was reported recently (Oltay, et al., 1973a,b; Penninger and Slotboom, 1973a,b), several effects, such as the effect of the reactor age on conversion and selectivity, temperature history, etc., came to light which had to be attributed to a participation of the reactor wall. In an attempt to differentiate between the various wall effects experienced in our thermal hydrocracking experiments, a special experimental study was undertaken with hydrindene (indan), which is one of the

model substances we used in the hydrocracking study on polyaromatics.

Experimental Section

Most of the experiments were carried out under continuous flow conditions in a high-pressure reaction system as described before (Penninger and Slotboom, 1973a). The wall effects were examined in two reactors of identical dimensions (117 mm inside length, 13 mm i.d.) but of different construction material. One was made of AISI 316 SS, the other of plain C-steel and electroplated inside with a gold layer so that all parts of the surface coming into contact with either hot hydrogen or indan were covered. The thickness of the gold layer was 15 μm, corresponding with approximately 2500 monoatomic gold layers. Some experiments were also done under static conditions in an AISI 316 SS autoclave (85 cm³) with arrangements for injection of indan and for withdrawal of samples of the reactor contents after the autoclave had reached the required temperature and pressure.

All reaction products were analyzed by glc (Penninger and Slotboom, 1973a). Hydrogen, (Hoek N.V., Rotterdam) with impurities (ppm) such as N_2 (100), O_2 (5), hydrocarbons (5), CO (5), and CO_2 (5) (according to the manufacturers' specifications) was used without further pretreatment.

Indan was obtained by hydrogenation (20°C, 200 atm of H_2, 5% Pd/activated carbon) from indene (Fluka purum) in a glc purity of 99.5%. Main impurities were unconverted indene and polymethylbenzenes; the indan was dried over silica gel. Usually the reactions were carried out at a temperature of 500°C, a total pressure of 80 atm, and with a molar ratio of hydrogen-to-indan of 10.

Reaction times for the flow reactor, defined as the ratio of reactor volume to the total volume of reactants at reactor inlet conditions, were 100 sec; in the batch autoclave reaction times went up to several hours.

Results

Primary and Secondary Aging Effects of the Stainless Steel Reactor. Previous experiments revealed considerable changes in conversion and product distribution during the first period of operation of a reactor, whereafter a steady-state situation was established. In order to obtain a more detailed picture about these reactor aging effects, especially at low conversion levels of indan, experiments were repeated in the aged reactor after it was filled with fresh stainless steel turnings.

Under a continuous flow of hydrogen at 80 atm the reactor was heated to the required temperature whereafter the supply of indan was started. Taking this as the zero time, the composition of the reaction products was determined at increasing aging time and as Figure 1 shows, the most prominent change in the cracking pattern took place during the first hour of operation. Parallel to an overall decrease in conversion, changes occur in the selectivity of the cracking reactions.

Compounds such as styrene, cumene, and other polymethylbenzenes disappeared almost completely after 1 hr, while the main reaction products, toluene, indene, and n-propylbenzene, fell to a steady level. This effect is called "primary aging." In long-term operation a "secondary aging" effect came to light; it showed itself in a further decline of the formation rate of toluene, n-propylbenzene, and indene, but with a much smaller slope than in the primary aging phase. After a total operation time of approximately 300 hr, during which no wall reactivation was attempted, the rate constants of the reactions had
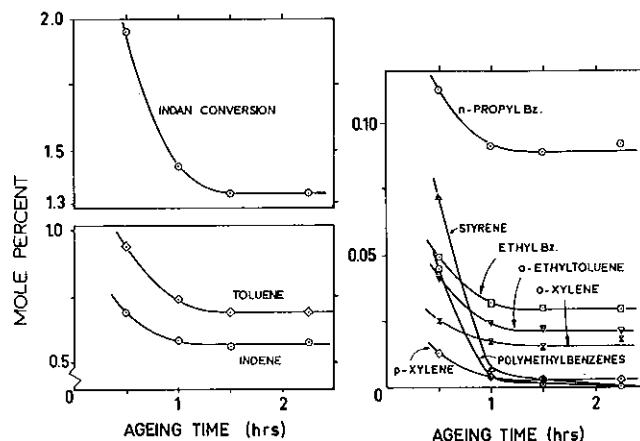

Figure 1. Effects of primary aging of the SS flow reactor. Temperature, 500°C; total pressure, 80 atm; molar ratio $H_2/I = 10$; reaction time, 100 sec; S/V ratio 13.3 cm⁻¹.

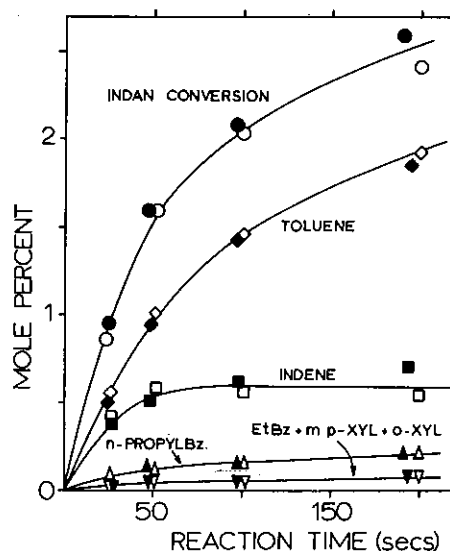**Figure 2.** Effect of the S/V ratio of the flow reactor. Temperature, 500°C; total pressure, 80 atm; molar ratio $H_2/I = 10$; filled symbols, S/V ratio = 13.3 cm⁻¹; open symbols, S/V ratio = 3.1 cm⁻¹.

dropped to approximately 50% of the original values, while changes in the cracking selectivity were not observed. This observation suggests that after the steady state in conversion and selectivity had been established after the primary aging phase, there still remained the problem of a possible participation of the reactor wall in the hydrocracking reactions.

As a first attempt to obtain an answer to that problem, the effect of an increased surface-to-volume (S/V) ratio of the reactor was studied. Product distributions obtained in an empty reactor and in a reactor filled with SS turnings, both after primary aging, were compared. At low indan conversions of up to 2.5 mol % at 500°C in the SS flow reactor, no change was observed in the conversion rate and product selectivity by increasing the S/V ratio from 3.1 to 13.3 cm⁻¹ (Figure 2). This was also found under static conditions in the autoclave at 520°C and conversion levels of up to 60% (Figure 3), when the S/V ratio was increased from 1.5 to 6.5 cm⁻¹. At higher indan conversion the toluene formation and consequently the demethylation to benzene was retarded by the increased S/V ratio. One may conclude that the S/V ratio of the reactor did not show any influence on the hydrocracking pattern over a wide range of conversions under both flow and static conditions. Thus it appears that the thermal hydrocracking
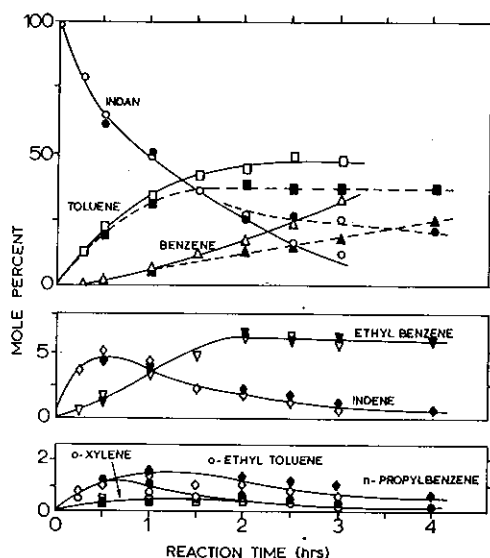
Figure 3. Effect of the S/V ratio of the batch reactor. Temperature, 520°C; total pressure, 80 atm; molar ratio $H_2/I = 4$; dotted line, filled symbols, S/V ratio 6.5 cm^{-1}; solid line, open symbols, S/V ratio 1.5 cm^{-1}.
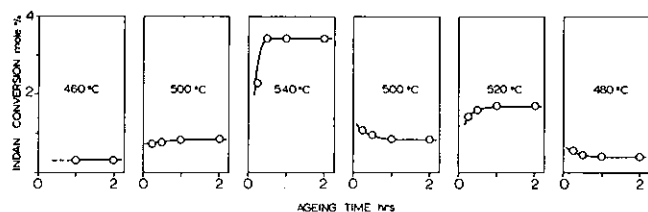

Figure 4. Temperature history effects of the SS flow reactor. Total pressure, 80 atm; molar ratio $H_2/I = 10$; reaction time, 100 sec; S/V ratio, 3.1 cm^{-1}.

in a SS reactor is only a homogeneous reaction once the reactor surface has aged. However, after further experimental work, which is reported in the following section, this statement had to be revised.

Temperature History Effects. It was found that there exists a reactor "temperature history" effect, which is illustrated in Figure 4. There the conversion obtained at different temperature levels is plotted *vs.* the operation time at that temperature; furthermore, the data are presented from left to right in the same consecutive order as the experiments were carried out. Between each set of measurements at a particular temperature the indan flow was stopped and the reactor thoroughly flushed by repeated pressure release in order to remove any concentration of hydrocarbon. Then the temperature was adjusted to a new value, meanwhile continuing the hydrogen flow, whereafter the indan supply was restarted. The data show clearly that a steady conversion level at a new temperature is only established after a certain operation time at that temperature. There is a conversion increase if the previous temperature was lower than the new temperature, while the conversion decreases if the previous temperature was higher. These observations form conclusive proof that the reactor wall remains an active partner in the thermal hydrocracking, also after the primary aging stage of the wall has passed. In fact, the data indicate that the surface conditions of the aged reactor wall is temperature dependent and adapts itself to the new temperature only slowly. An important aspect of this process is that the steady conversion at a particular temperature is independent of the previous temperature cycle, so that the adaptation of the surface condition is apparently a re-
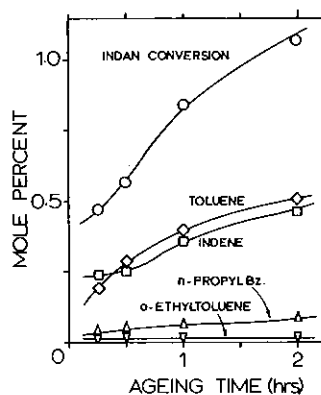

Figure 5. Effects of aging of the gold-lined flow reactor. Temperature, 500°C; total pressure, 80 atm; molar ratio $H_2/I = 10$; reaction time, 100 sec; S/V ratio 3.1 cm^{-1}.

versible process. For this the presence of a hydrocarbon is essential; hydrogen alone was not able to accomplish surface adaptation.

Aging Effects of the Gold-Plated Reactor. Another important observation which stresses the continuous participation of the reactor wall in thermal hydrocracking was the aging effects of the gold-plated reactor. Here the tendency plotted in Figure 5 was observed which is completely different from that of the SS reactor. With an increase in aging time a strong increase in conversion occurred, due to the increasing formation rate of toluene, indene, and n-propylbenzene and even after a 2-hr aging time a steady level was not reached. Of interest is that compounds such as o-ethyltoluene, ethylbenzene, and o-xylene are not affected by the aging and exhibit the same formation rate independent of aging time. Thus the gold reactor undergoes a slow process of activation which affects only part of the cracking products. The curves in Figure 5 tend to the steady-state concentrations obtained in the SS reactor (see Figure 1). Thus it is expected that the conversion and product selectivity are essentially the same in the aged gold reactor and in the aged SS reactor. The main conclusion, however, is that the thermal hydrocracking proceeds only in the presence of an active reactor wall; absence thereof results in zero or very low reaction rate.

Discussion

The experimental data show clearly that the reactor wall continues its participation in the cracking reactions also in the aged SS reactor and is in fact essential for those reactions to proceed at a measurable rate. Further explanation of these effects can now be given, especially those observed in the gold-plated reactor. Here it was found that n-propylbenzene, indene, and toluene were highly sensitive to the aging conditions while o-ethyltoluene and other products were independent thereof. From these facts one may conclude that the β ring-opening of indan, which results in the latter compounds, is predominantly homogeneous. Also in the aged SS reactor this reaction must be homogeneous since the values in the Arrhenius parameters previously measured in the reactor are $A = 2.5 \times 10^{13}$ sec-1 and $E^* = 68–69$ kcal/mol (Penninger and Slotboom, 1973a). The latter is equal to the energy of dissociation of the appropriate C–C bond.

On the other hand, the α ring-opening of indan, resulting in toluene and n-propylbenzene and which is evidentally a chain reaction (Penninger and Slotboom, 1973a), is highly sensitive to the aging conditions of the gold reactor. In fact this reaction does not proceed at all or only at a very low rate in the unaged gold reactor, as an extrapola-

tion to zero time of the curves in Figure 5 indicates. The chain reactions are thus developed only in the presence of an "active" reactor wall, which may be either unaged or aged SS or aged gold and the surface area of which is not critical in the range of S/V ratios examined. Hence the initiation and termination reactions, that is the formation and removal of H atoms (Penninger and Slotboom, 1973a), are heterogeneous and are both dependent on the size of the surface to the same extent. Thus the surface of the reactor has no effect on the steady-state concentration of the H atoms but remains essential for their formation.

The experimental fact that the dehydrogenation of indan to indene also increases parallel to toluene and n-propylbenzene is a strong indication that the H atoms are formed and controlled by this reaction in the manner proposed previously (Penninger and Slotboom, 1973a); further experimental work on this matter is currently in progress.

A tentative explanation for the wall effects can be found in the formation of coke deposits on the reactor wall. Although coke formation has been a common phenomenon in hydrocarbon cracking for a long time, further details have only recently been reported in literature. Cramers (1967) found that in the thermal cracking of hydrocarbons in SS reactors excessive coke formation occurred, which resulted in a strong decrease of both the conversion rate and the product selectivity; in a gold reactor coke formation was much slower but actually occurred and resulted in an increase of the conversion rate which parallelled the amount of coke present on the gold surface. This was determined by burning out and measuring the carbon oxides formed. The pyrolytic coke thus activated hydrocarbon cracking reactions and this can be attributed to the presence of free radicals which were actually detected by esr (Holbrook, et al., 1968). Also in our hydrocracking experiments coke deposition was observed. After 2 hr of primary aging at 500°C coke deposits with approximately 0.3 mg of C/cm² of reactor wall were formed. Assuming the coke to be pure carbon this coke layer had a thickness of approximately 1 μ.

The primary aging effects of the SS reactor in our thermal hydrocracking experiments on indan could thus be understood as being a deactivation of highly active "steel" sites such as nickel and chromium atoms by deposition of coke. The coke deposit formed has a much lower activity and catalyzes only the chain reaction of the α ring-opening. Coke formation in the gold-plated reactor causes an increase of activity, especially with respect to the α ring-opening and indan dehydrogenation. Apparently in both the SS reactor and the gold-plated reactor the coke sites prevail after the primary aging stage. Various aspects of this tentative picture of the wall effects in thermal hydrocracking reactions call for further clarification, and current work is directed toward obtaining relevant experimental evidence.

Acknowledgment

Literature Cited

Blakemore, J. E., Barker, J. R., Corcoran, W. H., *Ind. Eng. Chem., Fundam.,* **12,** 147 (1973).

Cramers, C. A., Dissertation, Eindhoven University of Technology, Eindhoven, The Netherlands, 1967.

Crynes, B. L., Albright, L. F., *Ind. Eng. Chem., Process Des. Develop.,* **8,** 25 (1969).

Holbrook, K. A., Walker, R. W., Watson, W. R., *J. Chem. Soc. B,* 1089 (1968).

Johnson, D. W., Pipkin, O. A., Sliepcevich, C. M., *Ind. Eng. Chem., Fundam.,* **11,** 244 (1972).

Oltay, E., Penninger, J. M. L., Konter, W. A. N., *J. Appl. Chem. Biotechnol.,* **23,** 573 (1973a).

Oltay, E., Penninger, J. M. L., Koopman, P. G., *Chimia,* **27,** 318 (1973b).

Penninger, J. M. L., Slotboom, H. W., *Recl. Trav. Chim. Pays Bas,* **92,** 513 (1973a).

Penninger, J. M. L., Slotboom, H. W., *Erdoel. Kohle,* **26,** 445 (1973b).

Taylor, J. E., Kulich, D. M., Hutchings, D. A., Frech, K. J., Kenneth, J. F., Abstracts, 163rd National Meeting of the American Chemical Society, Boston, Mass., No. Petr 033, April 1972.