JOURNAL OF CATALYSIS **101**, 314–322 (1986)

Silica and Alumina Catalysts, Activated by Hydrogen Spillover, for the Conversion of *n*-Heptane at 270°C

M. LACROIX,[1] G. M. PAJONK, AND S. J. TEICHNER

Laboratoire de Thermodynamique et Cinétique Chimiques, UA 231 du CNRS,
Université Claude Bernard Lyon I, 43 Bd. du 11 Novembre 1918, 69622 Villeurbanne Cedex, France

Received June 25, 1985; revised December 20, 1985

On a silica aerogel activated at 430°C by hydrogen spillover, *n*-heptane is dehydrogenated at 270°C into heptene and heptadienes by stoichiometric interaction with spilled-over hydrogen and is dehydrocyclized catalytically into toluene which in turn is hydrocracked into benzene, methane, and ethane. On activated δ-alumina, *n*-heptane is catalytically dehydrogenated at 270°C into heptene and heptadienes by spilled-over hydrogen which is easily reformed from molecular hydrogen. © 1986 Academic Press, Inc.

INTRODUCTION

A series of recent papers from this laboratory (*1*, *2*) has drawn attention to the catalytic properties of cracking and hydrocracking of aromatic hydrocarbons at 170°C acquired by silica which has been activated by hydrogen spillover. These entirely new catalytic activities of silica seem to be related to the acidic active centers developed on the silica surface by the spillover activation procedure. A second type of catalytic centers with hydrogenating properties at 170°C, at least for ethylene and acetylene, coexists with the first type. The sites of the second type are not acidic as they are not poisoned by ammonia (or by oxygen). The simultaneous presence of these two types of sites pertains to bifunctional catalysts and until now had never been reported for inorganic oxides usually employed as catalyst carriers, such as silica.

Similarly, but not identically, alumina in the form of δ-alumina aerosol (Degussa), activated by hydrogen spillover, develops efficient sites for hydrogenation at 170°C of ethylene, benzene, cyclohexadienes, and cyclohexene (to cyclohexane) (*2*). No acidic sites are involved during catalysis of these hydrocarbons as poisoning by ammonia (or by oxygen) is not recorded. The behavior of a very pure amorphous alumina aerogel (overall impurity content smaller than 1 ppm) is practically identical to that of δ-alumina with respect to the activation by hydrogen spillover and the resulting catalytic activity in the hydrogenation of ethylene (*3*). A reactant such as *n*-heptane seems to be a suitable test molecule because it may either dehydrogenate or also isomerize and dehydrocyclize depending on the nature of catalytic sites which are operating on spillover-activated oxides.

Moreover, the spilled-over species which are present on the oxide surface (or which may be evacuated) may play a role in a reaction with a paraffin. They were not required for the catalytic hydrogenation by molecular hydrogen of ethylene, acetylene, and benzene on alumina or silica or for cracking and hydrocracking of benzene, cyclohexene, and cyclohexadienes on silica (*2*).

EXPERIMENTAL

All activation procedures and sequences using a new type of "elevator" batch reactor with greaseless joints and valves have

---

[1] Permanent address: Institut de Recherches sur la Catalyse, 2, avenue A. Einstein, 69626 Villeurbanne Cedex, France.

0021-9517/86 $3.00

been fully described in the previous publications (*1*, *3*). Pure grade normal heptane was introduced into the reactor through a temperature-controlled saturator. Pure grade He, C_2H_4, H_2, NO, and NH_3 were supplied from gas cylinders. High surface area (900 m^2/g) silica, in the aerogel form, was prepared as reported by Teichner *et al.* (*4*). δ-Alumina (from Degussa) is a nonporous alumina aerosol with a surface area of 90 m^2/g. Usually 1 g of each oxide was used in the experiments. The impurity content of silica aerogel in elements like Al, Mn, Mg is smaller than 1 ppm and the limit of the detection of Fe and other transition elements (<0.2 ppm) was not attained in the arc spectrography analysis. The δ-alumina contained 1 ppm of Mn and a few ppm of Mg and Fe but other transition elements were not detectable. The neutron activation analysis of silica and alumina samples after their activation by hydrogen spillover disclosed that the Pt content of activated SiO_2 and Al_2O_3 was below the sensitivity limit (<6 ppb) of the method.

The source of the spilled-over hydrogen consisted of a small amount (20–40 mg) of a Pt/Al_2O_3 catalyst containing 0.6% Pt with a 44% dispersion. This catalyst was removed from the reactor (by the "elevator" device) after the activation at 430°C of silica or alumina by the spilled-over hydrogen under 1 atm pressure of molecular hydrogen. Reaction partners were analyzed by gas chromatography with a flame ionization detector and a 1.5-m column (at 100°C) filled with 20% Carbowax 20 *M* on 80 to 100-mesh Chromosorb. The vector gas (nitrogen) pressure was 0.7 atm.

For all conversion tests in the batch reactor of 1-liter volume the partial pressure of *n*-heptane was 7.5 Torr and that of H_2 (or He) complemented the total pressure to 1 atm.

RESULTS

In this work a standard run means (i) activation of either silica or alumina by hydrogen spilled-over from Pt/Al_2O_3 catalyst at 430°C (ii) elimination of this catalyst by the "elevator" device, and (iii) reaction at 270°C of 7.5 Torr of *n*-heptane with 752 Torr of H_2 referred to as a standard mixture. Thus a standard run proceeds in the presence of the spilled-over hydrogen species, still adsorbed on the surface of silica or alumina after activation, but in the absence of Pt/Al_2O_3 catalyst. Blank tests were performed with the standard mixture on silica and alumina samples, simply heated in H_2 at 430°C in the absence of Pt/Al_2O_3 catalyst (molecular hydrogen "activation"). No activity at 270°C toward the conversion of *n*-heptane was recorded for these samples. Similarly, the Pt/Al_2O_3 catalyst was inactive at 270°C for the conversion of *n*-heptane.

1. Conversion over Spillover-Activated Silica

Figure 1 shows the products of conversion against time on stream in a standard run at 270°C. A limited conversion of *n*-heptane (20%) is recorded within 48 h of contact. In decreasing order the yields are methane and ethane 6% (each), heptene and heptadienes 2.5%, benzene 1.5%, and toluene 0.6%. These data are interpreted with the help of the previous results (*1*, *2*, *5*) concerning the reaction of benzene over spillover-activated silica under similar conditions. It has indeed been shown that benzene at 170°C is transformed into (i) ethane in the presence of H_2 or (ii) acetylene in the presence of He. These reactions are catalytic on the surface of silica and they do not require the spilled-over hydrogen species. Heptene and heptadienes (Fig. 1B) can only result from the dehydrogenation of *n*-heptane over activated silica. Heptatriene is not detected, but toluene (Fig. 1D) may result from the dehydrocyclization of this olefin. The properties of activated silica in hydrogenolysis [benzene giving ethane (*5*)] account for the transformation of toluene into benzene and methane (Figs. 1A and C) and also for the fraction of benzene or toluene into ethane (Fig. 1A).

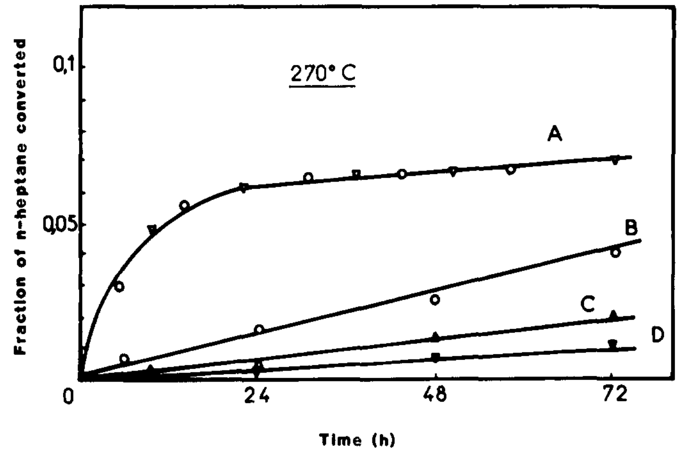

FIG. 1. *n*-Heptane conversion with time on stream in a standard run on silica. (A) Fractions converted into methane (○) and ethane (▽), (B) fractions converted into heptene + heptadiene, (C) fraction converted into benzene, (D) fraction converted into toluene.

It has been shown previously that the spilled-over hydrogen (*2*) which remains on silica or alumina after spillover activation may be easily desorbed by evacuation or exhausted by the reactants in the first run (*5*). Also, a second run was carried out after evacuation at 270°C of the first mixture of Fig. 1. No reaction was observed when a new standard mixture was introduced into the reactor (even after 72 h of contact). It therefore follows that the spilled-over hydrogen which is present during the first run is required to start the conversion of *n*-heptane in the presence of molecular hydrogen.

No reaction was recorded on a freshly activated silica which, previous to the run with *n*-heptane and molecular hydrogen, was evacuated at 270°C in order to desorb the spilled-over hydrogen. This behavior shows the inability of the catalyst to activate the paraffin in the presence of molecular hydrogen without the help of adsorbed spilled-over hydrogen species.

The situation is different if neither spilled-over hydrogen nor molecular hydrogen is present. If the freshly activated silica is first evacuated at 270°C and then a mixture of *n*-heptane and helium is introduced the reaction proceeds easily with the results shown in Fig. 2. Under these conditions 60% of the *n*-heptane is converted after 48 h into methane, heptene, and heptadienes, ethane, acetylene, toluene, and benzene (in decreasing order of yields). Acetylene is now detected because of an insufficient hydrogen amount, released in the mixture, to convert acetylene into ethane. As the molecular hydrogen is not initially present (it is in a great excess, 752 Torr, in a standard mixture) in this experiment, being substituted by helium, any hydrogen released from *n*-heptane (or other intermediates) is scavenged by acetylene (giving ethane). As mentioned previously, cracking of toluene formed by dehydrocyclization of intermediate olefins gives methane and benzene and cracking of the aromatic ring in helium produces acetylene (*2*, *5*). A second run conducted after evacuation of the first mixture gives exactly the same results and demonstrates the catalytic behavior of the activated silica.

According to the nature of the products formed (Fig. 2) strong acidic sites seem to be required to convert the paraffin. These sites must have been created by the spillover activation process because nonactivated silica (heated at 430°C in molecular hydrogen) is inert toward the *n*-heptane–helium mixture at 270°C. Poisoning experiments carried out with either NH_3 or the pretreatment of activated silica

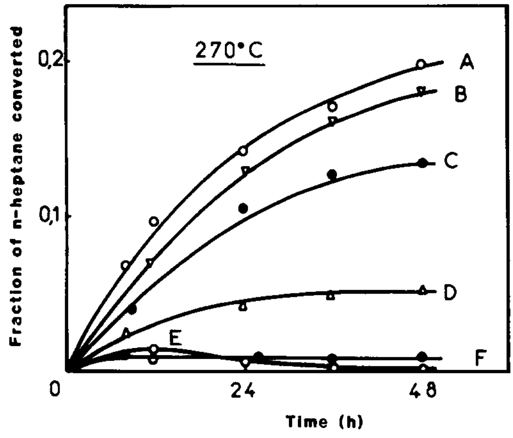

FIG. 2. Conversion of *n*-heptane in helium with time on stream on silica. (A) CH_4, (B) heptene + heptadienes, (C) ethane, (D) acetylene, (E) toluene, (F) benzene.

by O_2 at 270°C result in a total suppression of the activity towards *n*-heptane in helium. They confirm the acidic nature of at least a fraction of active centers (*2*) involved in the conversion of *n*-heptane.

To cast some light on the influence of molecular hydrogen, runs were performed with various partial pressures of hydrogen in *n*-heptane–helium mixtures. Figure 3 shows that increasing the initial partial pressure of hydrogen results in a very sharp decrease in the initial rate of the conversion. The same reaction products as in Fig. 2 are observed with the exception of acetylene which is converted to ethane by scavenging hydrogen. The decelerating effect of molecular hydrogen on the conversion of *n*-heptane can be easily understood if it is recalled that spilled-over hydrogen activation of silica creates also hydrogenation centers active in the hydrogenation of ethylene or acetylene at 170°C (*6*). If the first step in the conversion of *n*-heptane is its dehydrogenation into heptene and heptadiene onto these centers this step will be decelerated in the presence of molecular hydrogen (Fig. 3).

Summing up, silica activated by hydrogen spillover is a dehydrogenating and cracking catalyst toward *n*-heptane in the absence of molecular and spilled-over hydrogen (in helium, Fig. 2). In the presence of an excess of molecular hydrogen the reaction is limited (Fig. 1) and is observed only if the spilled-over hydrogen is present. Under these conditions the reaction is probably not catalytic but results from the interaction of this hydrogen with *n*-heptane. Previous results (*2, 5*) disclosed that the amount of the spilled-over hydrogen on 1 g of activated silica is of the order of 1.5 cm^3. The total amount of *n*-heptane in the standard mixture is 10 cm^3 (7.5 Torr in 1-liter volume of reactor). The reaction (Fig. 1) is limited to 20% conversion, or about 2 cm^3 of *n*-heptane. The stoichiometry of the interaction between the spilled-over hydrogen and *n*-heptane is not known. Assuming that one spilled-over hydrogen atom reacts with one molecule of *n*-heptane, 1.5 cm^3 of spilled-over hydrogen would convert 3 cm^3 of *n*-heptane. Once the spilled-over hydrogen is exhausted by the first run with the standard mixture a second run (*n*-heptane + H_2) shows no conversion.

In the absence of molecular hydrogen and of spilled-over hydrogen (in He) the re-

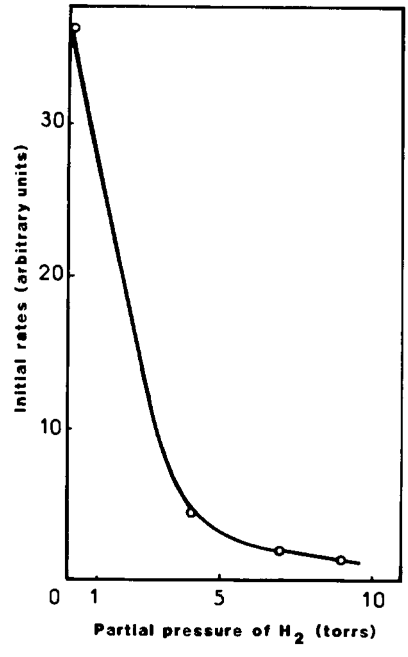

FIG. 3. Influence of the partial pressure of H_2 on the rate of conversion of *n*-heptane in helium at 270°C on silica.

action is catalytic and proceeds through a mechanism which implies dehydrogenating and acid centers. As long as acetylene is present as a reaction product, hydrogen pressure cannot build up as hydrogen is scavenged by acetylene (giving ethane). The reaction rate decreases when the hydrogen pressure increases (Fig. 3).

2. *Conversion over Activated Alumina*

When alumina activated by hydrogen spillover is contacted at 270°C with a standard mixture under the conditions of the standard run (spilled-over hydrogen species still present) a 95% conversion of *n*-heptane is recorded within a few hours (~7 h) as shown in Fig. 4A. A notable difference from the behavior of activated silica is observed as *n*-heptane is almost specifically transformed into heptene and heptadienes (selectivity 89%) with low percentages of dehydrocyclization products and those resulting from their hydrocracking (ethane and methane 4% each, benzene and toluene 2 and 0.5%, respectively). Thus, activated alumina is mainly a selective dehydrogenation catalyst of *n*-heptane into mono- and di-olefins but barely into dehydrocyclization and hydrocracking products. A second dose of *n*-heptane introduced at the end of the first run is still more readily converted (95% in 2 h) selectively to heptene and heptadienes, as shown in Fig. 4B, with no products of dehydrocyclization and hydrocracking reactions. The conversion of two doses (20 cm^3) of *n*-heptane cannot result from the stoichiometric reaction of *n*-heptane with the initial spilled-over hydrogen (1.5 cm^3 per gram of alumina) (*2*, *6*) which would be in an insufficient amount with respect to *n*-heptane (see the above comments for silica). If this type of hydrogen is reformed, from molecular hydrogen, on activated alumina the reaction would be typically catalytic and any amount of *n*-heptane would be converted by this interaction. The evacuation at 270°C of the standard mixture of reacted *n*-heptane must also remove the spilled-over hydrogen. As, however, after the introduction at 270°C of a new dose of a standard mixture of hydrogen and *n*-heptane the reaction proceeds easily (kinetics similar to that of Fig. 4B), it can be concluded that if the spilled-over type hydrogen is required for the dehydrogenation of *n*-heptane (in the presence of molecular H_2) at 270°C, it should be reformed on activated alumina from H_2 of the mixture. It was indeed shown previously that on activated alumina, in contrast to silica, the spilled-over type of hydrogen species can be reformed from molecular hydrogen, at least at 430°C, without the need of Pt/Al_2O_3 activator (*7*). A test for the presence of the spilled-over hydrogen on the surface of alu-

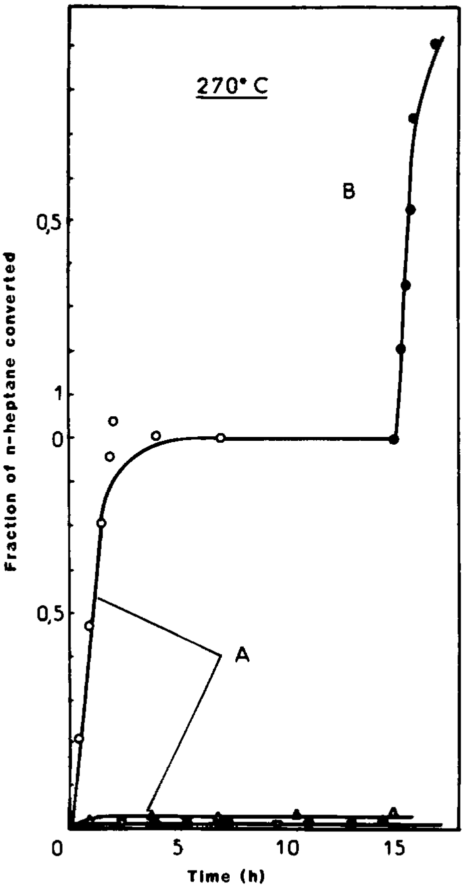

FIG. 4. Dehydrogenation reaction of *n*-heptane with time on stream on alumina. (A) Standard run; (○) heptene and heptadienes, (▲, △) methane and ethane, (▽) toluene, (●) benzene. (B) Second dose of *n*-heptane: (●) heptene and heptadienes.

mina or silica (after the activation procedure at 430°C in H_2 in the presence of Pt/Al_2O_3 catalyst and its removal) consists in the catalytic hydrogenation of ethylene (50 cm^3) by an excess of molecular hydrogen, at 145–170°C. An induction period in this run (Fig. 5A) has been correlated with the presence of the spilled-over hydrogen species ($\sim$1.5 cm^3 per gram of solid). These species are exhausted by the first run with ethylene or by a previous evacuation of the solid. In the absence of the spilled-over hydrogen the hydrogenation of ethylene exhibits kinetics with a continuously decreasing rate (in a batch reactor) and the mechanism of this catalytic hydrogenation has been given in detail (*2, 6, 7*).

Catalytic hydrogenation of ethylene was performed at 145°C on a sample of activated alumina previously evacuated at 270°C and as the induction period was absent it was concluded that spilled-over hydrogen species are removed by evacuation at 270°C (*3, 6, 8*) and are not reformed at 145°C from H_2 in the (C_2H_4 + H_2) mixture. A second test of hydrogenation of ethylene was carried out on an activated alumina sample, first evacuated at 270°C as before but then contacted with molecular hydrogen (700 Torr) for 13 h at 270°C only. The hydrogenation of ethylene at 145°C now proceeded with an induction period (as in Fig. 5A), indicating that spilled-over hydrogen had been reformed on evacuated activated alumina, contacted at 270°C with molecular hydrogen. On activated silica evacuated and again contacted with H_2, even at 430°C, the spilled-over type of hydrogen is not reformed (*2, 6*). Also a limited conversion of *n*-heptane in H_2 is recorded at 270°C in the first run on silica (Fig. 1), due to the stoichiometric (noncatalytic) interaction with the spilled-over hydrogen existing on the surface and no conversion in the presence of H_2 is recorded on evacuated silica, without the spilled-over hydrogen (see above).

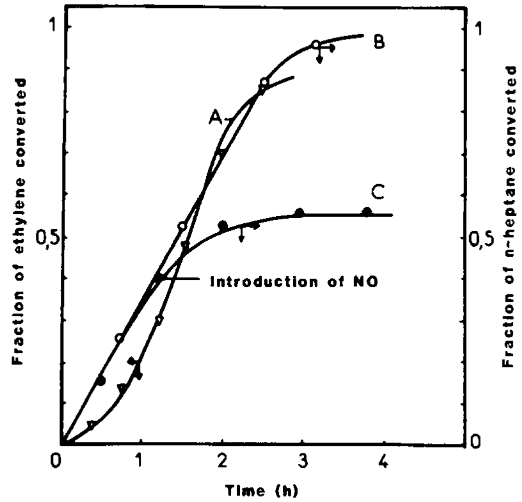

FIG. 5. Conversion of *n*-heptane at 270°C and hydrogenation of ethylene at 145°C on alumina. (A) hydrogenation of ethylene at 145°C, (B) dehydrogenation of *n*-heptane at 270°C, (C) influence of NO in the reaction of dehydrogenation of *n*-heptane.

A similar conversion of *n*-heptane (into heptene and heptadienes) is obtained in a run where an activated alumina sample is first evacuated at 270°C, then contacted with 700 Torr of H_2 for 14 h and finally mixed with 7 Torr of *n*-heptane. The results are similar to those shown in Fig. 5B where a complete conversion of *n*-heptane into heptene and heptadienes is registered. The presence of spilled-over type hydrogen species seems therefore to be required for the conversion of *n*-heptane on alumina in the presence of molecular hydrogen. In this reaction the spilled-over hydrogen plays two roles: first, it activates (at 430°C in H_2) the sample of alumina, and second, it allows the reaction of *n*-heptane (dehydrogenation) in the presence of molecular hydrogen.

The conversion at 270°C of *n*-heptane in helium on activated and then evacuated alumina is very small (less than 12% in 24 h) and the products of the reaction are methane, ethane, and toluene, with no traces of heptene and heptadienes. The reaction seems therefore of the type found previously with heptane in helium on silica (dehydrocyclization and hydrocracking) but with much smaller activity on alumina.

Poisoning experiments performed with

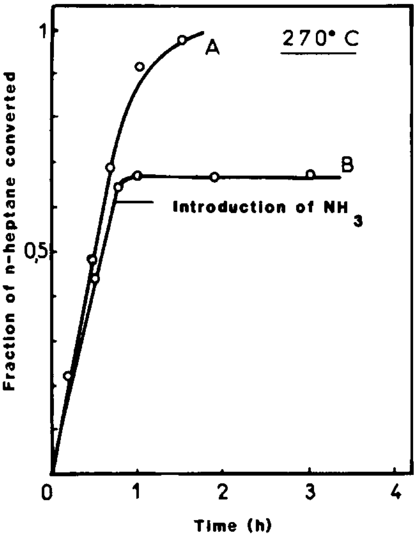

FIG. 6. Conversion of *n*-heptane with time on stream on alumina. (A) standard run, (B) introduction of a dose of NH_3.

NO (Fig. 5C) or with NH_3 (Fig. 6B) during *n*-heptane conversion at 270°C demonstrated the blocking of the reaction. Also, activated alumina was found to be inactive in the conversion of *n*-heptane in hydrogen if previous to the run the solid is reoxidized (in O_2 or in air) at 430°C or even at 270°C. This oxidation pretreatment, or the introduction of NH_3 during the run are, however, without any effect on the hydrogenation of ethylene on alumina (or on silica) (*6*, *7*), which proceeds without the induction period, showing that the spilled-over type of hydrogen is not reformed on the preoxidized surface of alumina.

The poisoning effect of NH_3 and also of NO may be explained by the reaction of these molecules with the spilled-over hydrogen species, required on alumina for the conversion of *n*-heptane in molecular H_2. NO is known as a radical scavenger and ammonia may combine with hydrogen adsorbed species if these species are of protonic type (H^+ or H_3^+) (*9*).

DISCUSSION

The interaction of spilled-over hydrogen at 430°C with oxides usually considered as simple catalyst carriers, namely silica and alumina, creates in these oxides catalytic centers for reactions with olefins, aromatics, and paraffins (*2*) which have never been observed on these supports. The success in unravelling these properties in this work stems from the experimental procedure allowing the removal of the metallic catalyst (Pt/Al_2O_3) which is the activator of molecular hydrogen and provides hydrogen spilling over on the oxide to be activated. The conventional catalytic properties of Pt would screen the new properties of the oxide if the Pt activator was not removed from the reactor.

It has been shown previously (*1*, *2*) that silica and alumina activated by hydrogen spillover behave differently in the reaction with aromatics (benzene, cyclohexadienes) at 170°C, whereas their hydrogenating activity toward ethylene or acetylene is very similar. These catalytic properties, created by hydrogen spillover activation, are independent of the presence or absence of the spilled-over hydrogen on the surface of the oxide during the catalytic run despite the fact that activated silica is not able to reform the spilled-over type of hydrogen from molecular hydrogen (in the absence of Pt/Al_2O_3 catalyst) at 430°C, whereas activated alumina exhibits this property at 430°C (*3*) or even at a lower temperature (270°C).

The catalytic behavior of activated silica in the hydrocracking at 170°C of benzene (or 1–3 cyclohexadiene) into ethane, which is not found on alumina, was correlated with the development of acidic sites by hydrogen spillover activation (*5*). Weaker acidic sites (or in a much smaller number) are created on alumina, as only hydrogenation of benzene or cyclohexadienes at 170°C into cyclohexane is registered (*5*). Moreover, for both oxides similar very active hydrogenating sites are created allowing the hydrogenation of ethylene and acetylene into ethane at fairly low temperatures (145°–170°C) (*3*, *6*, *7*). The spillover activation implies the formation of dissociated hydrogen species (such as $H^{\cdot}$ or H^+) and their migration on the surface of the oxide (*10*). These species probably remove (at 430°C) some coordinatively unsaturated (c.u.s.) surface oxygen ions and unscreen the cations like Si^{4+} which are the potential acid sites. This is in agreement with the poisoning properties of NH_3 or with the deactivation of silica by oxygen pretreatment prior to the reaction with *n*-heptane in He (see above). However, another type of sites, presenting the hydrogenation activity toward ethylene or acetylene, is simultaneously created by hydrogen spillover activation. These sites are not sensitive to NH_3 nor to the oxygen pretreatment (*6*). Their nature is, for the moment, difficult to establish. They may be formed by some particular O^{2-} c.u.s. surface species whose c.u.s. character is increased by the removal of other O^{2-} ions by the spilled-over hydrogen (*3*). These ions are basic in nature and would be not poisoned by NH_3. The oxygen pretreatment may even increase their amount (the activity in the hydrogenation of ethylene or acetylene is increased), whereas it screens the acid sites (the activity in cracking of benzene is suppressed). The same consideration applies to alumina activated by hydrogen spillover with the difference being that the unscreened Al^{3+} ions either are present in much smaller amounts or are much weaker in acidity.

The behavior of the two oxides in the interaction with paraffins such as *n*-heptane is different. On silica, in the absence of molecular hydrogen (in He), dehydrogenating and acidic centers are probably involved in the dehydrocyclization and hydrocracking of *n*-heptane at 270°C into methane, heptene, and heptadienes, ethane, acetylene, toluene, and benzene (Fig. 2), the reaction being catalytic and requiring only the surface sites on silica. In the presence of molecular hydrogen the rate of the reaction is reduced (Fig. 3), but the same type of reaction with *n*-heptane is still possible (Fig. 1) (except for the formation of acetylene) provided that the spilled-over hydrogen, adsorbed on silica after its activation, is still present. However, the conversion is now not catalytic and stops once the amount of the spilled-over hydrogen is exhausted by the reaction. It is known that activated silica is not able to reform the spilled-over type of hydrogen from molecular hydrogen, even at 430°C (*7*). One is tempted to consider an abstraction of two or more hydrogen atoms from the paraffin by a radical process, where $H_{(sp)}$ stands for the spilled-over hydrogen, initially (after activation) present on the surface of silica:

$$H_{2(g)} \rightarrow 2\ H_{(sp)}$$

$$H_{(sp)} + C_7H_{16} \rightarrow C_7H_{15} + H_{2(g)}$$

$$C_5H_{15} + H_{(sp)} \rightarrow C_7H_{14} + H_{2(g)},\ \text{etc.}$$

Activated alumina behaves differently in the reaction with *n*-heptane. The spillover activation does not seem to develop strong acidic sites and the dehydrocyclization and hydrocracking of *n*-heptane are observed only to a very limited extent (Fig. 4A), whereas heptene and heptadienes are major products. Moreover, this reaction, in contrast to silica, proceeds easily in the presence of molecular hydrogen and is of catalytic nature as many doses of *n*-heptane can be converted. Now it is known (*2, 3, 6*) that the spilled-over type of hydrogen can be reformed from molecular hydrogen on activated alumina at 270°C (temperature of the conversion of *n*-heptane), but not at 145°C (temperature of the hydrogenation of ethylene). One is therefore again tempted to consider that this type of hydrogen is required for the conversion of *n*-heptane on alumina in the presence of molecular hydrogen according to the radical process described above. Because the spilled-over type of hydrogen is continuously reformed on alumina from molecular hydrogen at 270°C the reaction is of a catalytic nature, in contrast to silica where the initial spilled-over hydrogen is exhausted in the first run with *n*-heptane and is not reformed from molecular hydrogen. In the absence of H_2 (in He) the rate of conversion of *n*-heptane on silica is not reduced (Fig. 3) and the catalytic reaction of conversion by dehydrocyclization and hydrocracking is well observed (Fig. 2) without the need for the spilled-over type of hydrogen species. In the absence of molecular hydrogen and the spilled-over type of hydrogen (in He) alumina exhibits only very limited catalytic activity in dehydrocyclization and hydrocracking, which can be linked with the acidic type of sites, in a much smaller amount (or much weaker) on activated alumina than on activated silica.

CONCLUSIONS

The difference in the behavior toward *n*-heptane of activated silica and activated alumina may be summed up by concluding that hydrogen spillover activation of silica creates a bifunctional catalyst with hydrogenating–dehydrogenating and acidic centers which can function in dehydrocyclization and hydrocracking only in the absence of molecular hydrogen, or in a noncatalytic way in the presence of molecular hydrogen if some spilled-over type of hydrogen is present on the silica surface. The activation of alumina gives mainly a monofunctional catalyst where acidic centers are weak or present in small amounts. Its dehydrogenation activity in the presence of molecular hydrogen is of a catalytic nature because the spilled-over type of hydrogen which is required for this reaction is continuously reformed on the alumina surface from molecular hydrogen.

REFERENCES

1. Lacroix, M., Pajonk, G. M., and Teichner, S. J., *in* "Proceedings, International Congress on Catalysis, 7th (Tokyo, 1980)," p. 279. Kodansha/Elsevier, Tokyo/Amsterdam, 1981.
2. Teichner, S. J., Pajonk, G. M., and Lacroix, M., *in* "Surface Properties and Catalysis by Non-Metals," p. 457. Reidel, Dordrecht, 1983.
3. Maret, D., Pajonk, G. M., and Teichner, S. J., *in* "Spillover of Adsorbed Species," p. 215. Elsevier, Amsterdam, 1983.
4. Teichner, S. J., Nicolaon, G. A., Vicarini, M. A., and Gardes, G. E. E., *Adv. Colloid Interface Sci.* **5,** 245 (1976).
5. Lacroix, M., Pajonk, G. M., and Teichner, S. J., *Bull. Soc. Chim. Fr.* 258, 265 (1981).
6. Lacroix, M., Pajonk, G. M., and Teichner, S. J., *Bull. Soc. Chim. Fr.* 87, 94 (1981).
7. Lacroix, M., Pajonk, G. M., and Teichner, S. J., *Bull. Soc. Chim. Fr.* 101 (1981).
8. Teichner, S. J., Mazabrard, A. R., Pajonk, G., Gardes, G. E. E., and Hoang-Van, C., *J. Colloid Interface Sci.*, **58,** 88 (1977).
9. Bianchi, D., Lacroix, M., Pajonk, G. M., and Teichner, S. J., *J. Catal.* **68,** 411 (1981).
10. Conner, W. C., Pajonk, G. M., and Teichner, S. J., *in* "Spillover of Sorbed Species," Advances in Catalysis, Vol. 34. Academic Press, 1986.