The Effects of Pressure on the Hydrogenation of Benzene and Naphthalene over Reduced and Sulfided Molybdena–Alumina Catalysts

In earlier work (1, 2) it was shown that benzene could not be hydrogenated under 1 atm total pressure over the same reduced or sulfided molybdena–alumina catalyst which was hyperactive for olefin hydrogenation after similar pretreatment. Hydrogenation became detectable, however, after reduction at 800°C where the *average* oxidation number was 1.3 (e/Mo = 4.7) and the reaction became facile after reduction at 900°C where metallic molybdenum was evidently present (O.N. = 0.9); others (3, 4) have also reached this latter conclusion. Catalysts reduced below 600°C, as is the customary procedure, have O.N. ≈ 4; they contain mainly Mo^{4+} together with small amounts of Mo^{5+}, balanced by some lower valence states, but no evidence of Mo^0 or metallic molybdenum has been expected or reported. Indeed the finding of Brenner, Burwell, and their co-workers (3, 5, 6) that the Mo^0 produced by decarbonylation of $Mo(CO)_6$ is spontaneously oxidized by reducing alumina hydroxyl groups makes it highly unlikely that Mo^0 could exist until or unless the preparation is heated into the range where complete dehydroxylation of the alumina is approached, i.e., to temperatures in excess of 850°C in accordance with the cited literature. It was suggested (2), therefore, that the hydrogenation of benzene carried out with $P_{H_2} \sim 1$ atm might be used as a sensitive diagnostic test for the presence of this metal or conceivably some other low-valence state. In the present work these results have been extended to much higher hydrogen pressures.

In spite of the fact that benzene could not be hydrogenated on conventionally prepared catalysts (reduced at $T < 600°C$), ex-change between D_2 and the benzene hydrogens occurred at 70°C. It was shown, however, that this process took place largely on the alumina portion of the surface although it was synergistically influenced by the dissociation of D_2 on the molybdena sites. The exchange reaction could be effectively quenched by the chemisorption of CO_2 prior to reaction. CO_2 has been shown to chemisorb selectively on the alumina portion of the surface (7).

The same molybdena–alumina catalyst (8% Mo) studied previously (1, 2) was used in the present work. It had been prepared by impregnation of γ-alumina (Ketjen CK300) with ammonium paramolybdate using the incipient wetness technique. Its surface area was ~185 m²/g and it was reduced or sulfided *in situ* under atmospheric pressure in the reactor using previously described procedures (2). The extent of reduction, e/Mo, was controlled by varying the final reduction temperature. The standard sulfiding procedure using 10% H_2S in H_2 at 350°C produced an average oxidation state (8) of $\sim e/Mo \approx 3.0$. The benzene and naphthalene were Aldrich 99.9+% spectrophotometric-grade reagents which were dried over sodium and outgassed using repeated freeze–pump–thaw cycles before use. Naphthalene was hydrogenated in benzene solution (10.9 wt% naphthalene). Linde H_2 (nominal purity 99.95%) was used after passing through a commercial molecular sieve drying attachment.

The fixed-bed high-pressure flow reactor consisted of a stainless-steel tube (12.5-mm o.d., 9.5-mm i.d.) fitted with a stainless-steel fritted disk which supported ~1 g of catalyst. The reactor was maintained at the

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desired temperature within ±1°C with a thermostated furnace. The catalyst temperature was taken as that at the outer reactor wall at the position of the catalyst bed. Total reactor pressure was read upstream from the inlet from a calibrated gauge. Pretreatment was *in situ*. Hydrogen and liquid benzene or naphthalene in benzene were introduced at the top of the reactor into a 100-mm-long preheater section filled with inert quartz (2- to 3-mm-diameter chips). The liquid feed was added to the stream of H_2 using a 254-0300 Series Perkin–Elmer metering pump; mixing occurred in the preheater before reaching the catalyst bed. A high-pressure mass flow controller (Brooks Instrument Division, Model 5850E) and a pressure regulator (Automatic Switch Company, No. 8262C79) were used to maintain the desired pressure and flow rate (usually ~30 liter/hr). The effluent from the reactor was cooled in a water condenser where it was separated into gas and liquid. The latter product was removed from the reactor via a drain valve for analysis. Blank runs were made by substituting the alumina support for the catalyst, but no hydrogenation of benzene could be detected under the most severe conditions.

The liquid products were separated using a Gow-Mac Series 750 apparatus equipped with a FID detector. A stainless-steel column (⅛-in. o.d. × 9 ft) packed with 3% P-1500 on 80/120 Carbopack B was used at 110°C with He carrier gas (35 cm³/min). Only C_6H_6 and C_6H_{12} appeared in the products. No trace of C_6H_8 or C_6H_{10} was ever observed. The reaction products from naphthalene hydrogenation (tetralin and decalin) were analyzed using a column (⅛-in. o.d. × 6 ft) of 10% SP2100 on 80/100 Supelcoport at 150°C and a He flow rate of ~15 cm³/min.

In preliminary experiments carried out in glass, it was found that cyclohexene and cyclohexadiene could be hydrogenated over the reduced (e/Mo = ~1.7) catalyst at room temperature and subatmospheric pressures at rates comparable to those for
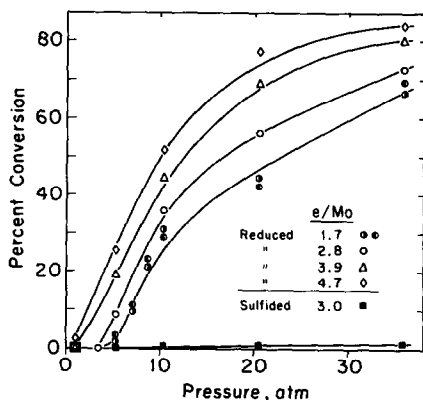

FIG. 1. Effect of hydrogen pressure on conversion of benzene to cyclohexane over ~1 g of a reduced and/or sulfided conventional molybdena–alumina catalyst (8% Mo) at 250°C. The flow rate of H_2 was maintained constant at about 30 liters/hr. The benzene feed rate was ~12 ml (liq)/hr providing a mole ratio of C_6H_6 : H_2 ≈ 1 : 10. The open circles correspond to the catalyst reduced in H_2 to various extents; the solid squares are for the sulfided catalyst. The half-filled circles are points taken as the pressure was increased, ◑, or decreased, ◐, respectively.

cis-2-butene and butadiene, respectively. With the sulfided catalyst the rates for simple olefins were much faster than those for the reduced catalyst, but the reverse was true for butadiene. In all cases the rates increased with P_{H_2} and were inhibited by increasing concentrations of olefins. As shown in Fig. 1 the behavior was strikingly different with benzene. Benzene hydrogenation could not be detected under 1 atm unless the catalyst had been reduced to e/Mo > 4.7. Above a certain critical pressure, however, hydrogenation began and the rate at first increased rapidly with H_2 pressure, but then leveled off above about 50% conversion (presumably as back reaction became increasingly important). The temperature selected for these tests was 250°C where the equilibrium constant is 17.0, i.e., about as high as could be conveniently used and still avoid thermodynamic limitations. An interesting feature was that the only product obtained was cyclohexane. The chromatograms showed no evidence of cyclohexene. As indicated in Fig.
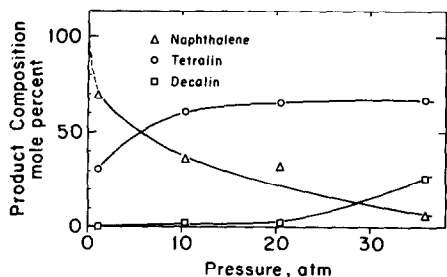
FIG. 2. Effect of hydrogen pressure on the reactions of naphthalene with H_2. In this work a 10.9 wt% solution was substituted for the pure benzene used in Fig. 1. Otherwise, the experiments were identical. Only naphthalene was hydrogenated below ~20 atm. At higher pressures, products of benzene hydrogenation were observed.

1, data were fairly reproducible on increasing or decreasing the pressure. Note that the critical pressure needed for the onset of hydrogenation decreased with increasing extent of reduction.

It was most interesting that the sulfided catalyst was virtually inactive. Only trace amounts of hydrogenation products were observed even under 36 atm. This is in contrast with simple olefins which hydrogenate much faster over the sulfided than over the reduced catalyst (7). To confirm this point, propene was hydrogenated under 1 atm at room temperature immediately following the benzene hydrogenation experiments. As reported previously (7), essentially complete conversion of propene to propane occurred over the sulfided catalysts under these conditions.

The hydrogenation of naphthalene (10.9 wt% in benzene) was studied at 250°C over 1 g of reduced molybdena–alumina (e/Mo = 1.7). The liquid feed rate of the solution was 12 ml/hr and a hydrocarbon to hydrogen mole ratio of 1 : 8 was maintained. The results are presented in Fig. 2. At 1 atm, approximately 30% conversion of naphthalene to tetralin was obtained, but no decalin was detected; i.e., one ring could be hydrogenated but not the other under conditions where benzene could not be hydrogenated. Under 30 atm, about 90% of the naphtha-

lene was reacted to 75% tetralin and 15% decalin. Now the benzene solvent was hydrogenated simultaneously and competitively, but its conversion was approximately fourfold lower than in the absence of naphthalene.

It is curious that catalysts which are so active for the hydrogenation of simple olefins and diolefins will not hydrogenate benzene under even much more severe conditions. Moreover, it is strange that naphthalene can be hydrogenated to tetralin but not to decalin under atmospheric pressure and that these reactions appear to go either to completion or not at all; i.e., products other than cyclohexane, tetralin, and decalin were not observed.

Some similarity might be expected between the characteristics of the hydrogenation of the first ring of naphthalene and those for the hydrogenation of butadiene. Indeed, the sulfided catalyst was relatively ineffective for both these hydrogenations; the exact opposite was found for simple olefins. On the other hand, much higher temperatures were required for naphthalene hydrogenation than for butadiene.

It may be supposed that benzene hydrogenation over catalysts with e/Mo < 2 must take place in a stepwise manner adding hydrogen one molecule at a time. This is because sites on supported metal oxide catalysts, unlike those on metals, must be regarded as isolated so that multiple hydrogenation to cyclohexane cannot occur during one residence on the surface. The first step, the hydrogenation of benzene to cyclohexadiene, is thermodynamically uphill due to loss of the benzene resonance energy. The standard state free-energy change, $\Delta G^0_{298} = +13.7$ kcal/mol, corresponds to an equilibrium constant of 1×10^{-10} at this temperature. At 250°C the value is 3.8×10^{-9} and the equilibrium ratio of cyclohexadiene to benzene under 1 atm is $\sim 10^{-10}$; under 100 atm it is $\sim 10^{-8}$. Moreover, under the higher pressure the surface concentration of adsorbed hydrogen is probably $\sim 10^2$ times higher than that under

1 atm (Henry's Law). Evidently these circumstances are sufficient to allow the second and third steps to proceed at measurable rates to the thermodynamically favored products ($\Delta G^0_{298} = -5.5$ and -23.4 kcal/mol for hydrogenation to cyclohexene and cyclohexane, respectively). On a metal surface this problem does not exist; the benzene molecule can lie flat on the surface and multiple hydrogenation can occur. Hence, when the catalyst is deeply reduced ($e/Mo > 4$) Mo metal begins to form and this limitation is relaxed.

Recently Shabtai et al. (9) studied the stereochemistry of naphthalene hydrogenation over sulfided Co- and Ni-promoted molybdena–alumina and tungsta–alumina catalysts. All of these, in contrast with transition metal catalysts, preferentially formed the trans-decalin isomer rather than the cis-isomer favored by all the metals. The latter behavior resulted from addition of hydrogen from the same side across the double bond common to the two rings, i.e., from the metal to the molecule flat on the surface. By the same token, the favored formation of the trans-decalin over the molybdena catalysts was attributed (9) to addition to opposite sites of the molecule, possibly because the hydrogen chemisorption is heterolytic. The picture evolved from these and the present results suggests that hydrogenation is stepwise on the catalyst. Tetralin is formed first, relatively easily. Hydrogenation of the common double bond is slow and critical, and is followed by rapid saturation to decalin. A more complete and satisfying explanation of the results cannot be given at the present time.

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