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Reactions of Benzene and Alkylbenzenes with Deuterium over Molybdena–Alumina and Alumina Catalysts

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The reactions of D_2 with aromatic systems were studied. Benzene did not hydrogenate at atmospheric pressure. On the other hand, exchange between benzene-d_0 and D_2 was facile at 70° and 1 atm over reduced (e/Mo $\approx$ 1.7) and at 200° over sulfided (e/Mo $\approx$ 3.0) catalysts. The exchange reaction also occurred over the alumina support at an intermediate rate. Over alumina the exchange at 70° was stepwise ($M = k_\phi/k_0 \approx 1.0$), but as the temperature and hence k_0 increased, multiple exchange ($M \geq 2.0$) set in. The usual tests showed that this was not a result of a pore diffusion limitation. The rate of exchange of C_6D_6 with the alumina hydroxyl groups increased sharply as the temperature was increased to near 200° in a way which mimicked the increase in M. Thus, the increase in multiplicity may be ascribed to the opening of new pathways for exchange. The much faster rates and higher values of M obtained over the reduced catalysts than over the sulfided ones, coupled with the results of poisoning experiments using NO and CO_2 (both of which drastically reduced the rates and returned the exchange process to $M \approx 1.0$), demonstrated that with the reduced catalyst both portions of the surface act synergistically. The results may be rationalized by the supposition that exchange occurs on the alumina support and that hydrogen may spill-over on reduced catalysts, but not on sulfided ones. In the exchange reactions, alkylaromatics were found to have higher rates for ring than for side chain hydrogens. © 1987 Academic Press, Inc.

INTRODUCTION

Molybdena–alumina catalysts are of great importance because of their use in hydrodesulfurization processes as well as for coal liquefaction. Research in our laboratories has been summarized in review articles (*1–3*) where it has been integrated with a vast amount of other literature. This research has been focused on defining the surface chemistry of these catalysts and relating it to catalytic functions. The reactions of cyclopropane (*4*), the hydrogenation of olefins (*4, 5*) and diolefins (*2, 3*), the mode of chemisorption of hydrogen (*6*), and the isomerization and metathesis of *n*-butenes (*7*) have been studied as diagnostic tools to obtain information on the nature of the catalytic sites and the kinds of intermediates which form thereon. The present work is a natural extension of this program to include aromatic hydrocarbon systems. Benzene was the first molecule selected for study. Besides hydrogenation, exchange between deuterium and unreacted substrate was anticipated (*8–10*). However, it was found that benzene could not be hydrogenated over any of these catalysts (including reduced cobalt molybdena–alumina) at hydrogen pressures up to 1 atm under thermodynamically favorable conditions. Hence, the present paper is concerned mainly with the exchange reactions of benzene and alkylbenzenes with D_2.

Kemball (*8*) has published extensively on the reactions between benzene and deuterium over platinum and palladium films (*11*). The exchange reaction as well as the deuteration occurred simultaneously on these metals. The results suggested that multiple exchange occurred by a process of "repeated second-point adsorption."

The ratio of the rates of exchange and deuteration varied with the different

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metals. The rates were high, but comparable over nickel films (*12*), but the reverse was true over tungsten. The exchange of alkylbenzenes with D_2 was studied over nickel films (*12, 13*) and over titanium dioxide (*14*). On nickel films the exchange in the alkyl group was generally as fast as in the ring positions. Similar results were obtained over homogeneous platinum catalysts (*15*).

Alumina has also been previously studied as a catalyst for the exchange of benzene, toluene and *m*-xylene with deuterium (*16, 17*). These results suggested a stepwise exchange over the alumina with the replacement of a single hydrogen atom at a time. However, the exchange rates of the side groups of the alkylaromatic hydrocarbons were slower than those of the ring positions whereas the rates of exchange of the rings of the different aromatic hydrocarbons were fairly constant (*16*). The exchange of benzene has also been studied over nickel ion-exchanged zeolites of *X*-type (*18, 19*) where again stepwise reaction was observed.

Different mechanisms have been suggested for the exchange of benzene with deuterium (*20*), viz., the dissociative chemisorption of the benzene, the abstraction-addition mechanism, the reaction between dissociatively chemisorbed deuterium and physisorbed benzene, and the reactions of associative sorption of benzene with H (D). Kemball (*11*) described the multiple exchange of benzene on metals as involving the dissociative chemisorption of benzene and the formation of di-σ-adsorbed-C_6H_4 which reacted with chemisorbed deuterium.

The present work extends these studies to reduced and sulfided molybdena-alumina catalysts and to MoS_2. With the former, clearly two parts of the surface exist (*3*), the coordinatively unsaturated molybdena centers which dissociate hydrogen (*2, 6*) and are effective in hydrogenation (*2, 4*), and the exposed alumina portion which is developed on reduction or sulfiding (*3*). Since alumina is a well-known catalyst for exchanging or mixing H and D into hydrocarbons, both portions may be expected to participate in these reactions to a greater or lesser extent. MoS_2 was included to evaluate the effectiveness of the unsupported catalyst.

EXPERIMENTAL

Catalysts and pretreatment procedures. The γ-alumina support used in the preparation of the molybdena catalysts was Ketjen CK-300. It had a surface area of 192 m^2/g and a pore volume of 0.5 cm^3/g. It was studied so that comparisons could be made with the molybdena preparations. The standard pretreatment of the alumina included calcining in flowing dry O_2 at 500°C for 1 hr, and evacuation for 2 hr at the same temperature. In a few experiments, after the standard pretreatment it was further evacuated at successively higher temperatures (600, 700, and 800°C) to effect further surface dehydroxylation of the alumina (*21–23*). In each case a freshly pretreated sample was used.

The molybdena–alumina catalyst (8% Mo) was the same as used in most of our earlier work (loc. cit.). It was prepared by the incipient wetness technique using the alumina described above. It had a surface area of 185 m^2/g. Before each experiment an aliquot (usually ~200 mg) was calcined overnight at 500°C in flowing dry oxygen and then evacuated for 30 min at the same temperature. The catalyst was reduced in flowing ultrapure hydrogen (~70 cm^3/min) for 2 hr at 500°C and evacuated for 1 hr at 500°C before cooling *in vacuo* to room temperature to start the experiments. The catalyst was reactivated between experiments by employing the same *standard procedures* which resulted in an extent of reduction of $e/\text{Mo} = 1.7 \pm 0.1$.[3]

Sulfided molybdena–alumina was also studied. To provide reliable data on extents

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[3] Average number of electrons per Mo the catalyst has been reduced below Mo^{6+}.

of reduction, the sulfiding was carried out with the procedure given by Valyon and Hall (*25*) which leads to e/Mo ≈ 3.0 and greatly enhances hydrogenation activity (*3*). After an overnight calcination, the catalyst (~200 mg) was flushed with He (100 cm^3/min) at 500°C for 20 min and cooled to 350°C. The sulfiding was carried out at 350°C for 4 hr in a gas flow containing 10% H_2S in H_2 (77 cm^3/min) followed by flushing with He (100 cm^3/min) at 500°C for 1 hr. The catalyst could be regenerated by calcining in flowing oxygen followed by reduction in H_2 for 2 hr before a final oxidation, all at 500°C. This procedure removed essentially all the sulfur (*25*).

Hydrocarbon reactants. The benzene, toluene and *m*-xylene were Aldrich 99 + % spectrophotometric grade reagents which were dried over sodium and outgassed before use by a repeated freeze–pump–thaw technique. Perdeuteriobenzene (Cambridge Isotope Laboratories) was given the same pretreatment; it had an isotopic purity of 99.6%.

Gases. Cylinder oxygen (99.6%) obtained from Linde was dried by passing through columns filled with anhydrous $CaCl_2$ and $MgClO_4$. The O_2 used in the volumetric reoxidation experiments had been condensed and distilled between liquid nitrogen traps.

The helium gas (Linde, nominal purity 99.995) was passed over anhydrous $CaCl_2$, $MgClO_4$, and activated charcoal at −195°C. The maximum impurity content at this stage was estimated to be ~1 ppm.

Ultrapure H_2 and D_2 were made as needed by passing these gases through Pd–Ag thimbles. The 10% H_2S–H_2 mixture (Matheson Gas Products) had a nominal purity of 99.5% and was used as received. NO was distilled between dry ice and liquid nitrogen traps to eliminate N_2O, NO_2, and H_2O. CO_2 was Matheson research grade (purity 99.995) and was frozen and outgassed before use.

Procedures. A static stirred reactor having a total volume of about 1100 cm^3 was used for the experiments. A cylindrical well (17 mm i.d. × 180 mm deep) in which the catalyst was placed extended below the spherical reactor. This section was heated to the desired temperature while the one-liter sphere remained at room temperature. Mixing was both by convection and by circulation with an all glass pump (~200 ml/min). The gas was pumped from the center of the sphere and delivered back over the catalyst. When required, condensible gases could be separated from the noncondensible hydrogen mixture by cooling a trap in the recirculation loop with liquid nitrogen. Kovar joints and Cajon ultratorr unions were used to connect the reactor to a BET-type vacuum system. The catalyst was pretreated *in situ*. ACE Teflon stopcocks were used in the system to avoid contact of the benzene with the stopcock grease. A known pressure of benzene (usually 25 Torr) was introduced into the reactor and then frozen (−195°C) while a given pressure of D_2 (usually ~200 Torr) was added. The system was then quickly heated to the reaction temperature. The mixing of the reactants was enhanced by the recirculation pump; the mixed exiting gas was continually sampled by the mass spectrometer. It was confirmed that the reaction rate was not limited by the pumping speed.

Analysis of the deuterated benzenes for their deuterium distributions was accomplished using a quadrupole mass spectrometer (ULTEK QUAD 250 A). It was connected to the reactor system via a leak valve so that the change in the product distribution could be monitored continuously with the time. The time lag was ~1 min. Less than 1% of the total gas volume per hour was removed for the analysis which was carried out at low ionization potential (~12 eV) to avoid the fragmentation. Corrections were made for the presence of naturally occurring ^{13}C.

The treatment of the experimental data followed that given by Kemball (*8*, *11*). The initial rates were calculated from first-order plots according to his equations, viz.,

$$-\log(\phi_\infty - \phi) = k_\phi t/2.303\phi_\infty - \log \phi_\infty, \quad (1)$$

where $\phi = \Sigma i d_i$, i is the number of D per molecule and d_i is the mole fraction i; ϕ_∞ is the equilibrium value of ϕ; k_ϕ is the rate of entry of deuterium atoms into the benzene calculated as deuterium atoms per 100 molecules per unit time; and

$$-\log(x - x_\infty) = k_0 t/2.303(100 - x_\infty) - \log(100 - x_\infty), \quad (2)$$

where x is the percentage of benzene-d_0; x_∞ is the equilibrium value of x; and k_0 is the rate of disappearance of benzene-d_0 in percent per unit time. The ratio of these rate constants, $M = k_\phi/k_0$ gave the mean number of deuterium atoms entering each reacting benzene molecule during each residence on the catalyst.

Adsorption measurements. A Cahn electrobalance Model RG2000 was used to test the reversibility of the benzene adsorption on the reduced catalyst before and after the chemisorption of oxygen. The experimental techniques were adopted from Deeba and Hall (*26*). The catalyst weight was ~200 mg. The temperature of the benzene saturator was maintained constant at 26 ± 0.3°C, thus providing a vapor pressure of 100 ± 0.3 Torr in the flowing He stream (65 cm^3 (NTP)/min). A standard BET system was used to measure N_2 surface areas and CO_2 and NO chemisorptions. These chemisorptions were determined at room temperature as described earlier (*3, 25, 27, 28*).

RESULTS

Exchange of benzene with D_2 over reduced molybdena–alumina was studied at temperatures where the hydrogenation of the benzene is favored thermodynamically, viz., between 70 and 250°C. The isotopic distributions in the benzenes obtained at 70°C at various times are shown in Fig. 1. These data clearly show maxima for benzenes-d_1, -d_2, and -d_3 while the sigmoidal shapes of the -d_4, -d_5, and -d_6 curves indicate that major amounts of these products were formed by secondary reactions, but see later. The equilibrium composition was calculated according to the binomial distribution law. Equilibrium was approached in about 90 min at 70°. Experiments were also carried out at higher temperatures (200 and 250°C). The data obtained were similar to those of Fig. 1, but in each case equilibrium was approached more rapidly. The first products formed (after 2 min) contained all species up to and including benzene-d_6.

Figure 2 shows two examples of plots made to obtain the rate constants, k_ϕ and k_0, for alumina. One set (solid lines) yielded $M = k_\phi/k_0 = 1.1$, while the other (dashed lines) produced $M = 4.6$. Over the reduced catalysts high values of M were obtained, but no hydrogenation products were formed (Table 1).

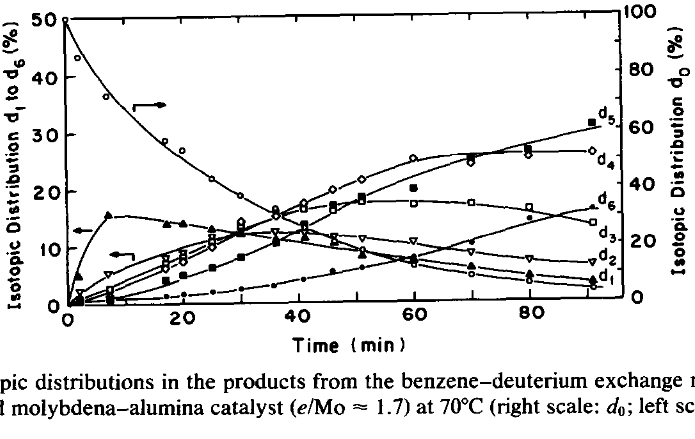

FIG. 1. Isotopic distributions in the products from the benzene–deuterium exchange reaction over 200 mg reduced molybdena–alumina catalyst (e/Mo ≈ 1.7) at 70°C (right scale: d_0; left scale: d_1 to d_6).

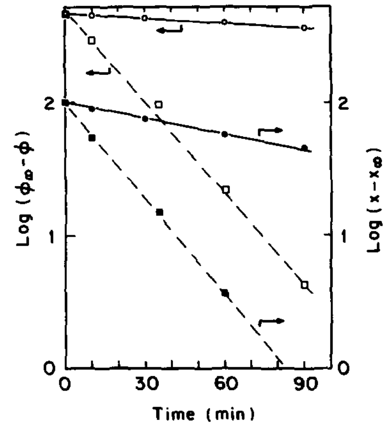

FIG. 2. Rate plots for the exchange of benzene with deuterium over γ-alumina according to Kemball (*8*). For 70°C: ○, ● ($M = 1.1$); for 400°C: □, ■ $M = 4.6$. Solid points yield k_0, open points k_ϕ.

Exchange over the sulfided catalyst was studied in the same way. In contrast with data for the hydrogenation and exchange of olefins and cyclopropanes (*3–5*), the benzene rates were considerably slower than those over the reduced catalyst under comparable conditions. To confirm this point, check runs with $C_3H_6 + D_2$ were made in the present system. The benzene data are listed in Table 1. At 70°C, over the sulfided catalyst the reaction was too slow to conveniently measure. Hence, results are reported for higher temperatures (200 to 450°C). Again, there was no indication of the hydrogenation reaction at 250°C, even when long reaction times (up to 18 hr) were used. Below 300°C, the data conformed fairly well to stepwise exchange by succes-

TABLE 1

Rate Constants and Multiplicity Factors for the Benzene–Deuterium Exchange Reaction over Molybdena–Alumina and Unsupported MoS_2

Reaction temperature (°C)	Reduced Mo/Al_2O_3 ($e/Mo \simeq 1.7$)			Sulfided Mo/Al_2O_3 ($e/Mo \simeq 3.0$)			γ-Alumina[a]			Unsupported MoS_2[b]		
	k_ϕ (min^{-1})	k_0 (min^{-1})	M	k_ϕ (min^{-1})	k_0 (min^{-1})	M	k_ϕ (min^{-1})	k_0 (min^{-1})	M	k_ϕ (min^{-1})	k_0 (min^{-1})	M
70	15.12	3.04	4.97				0.52	0.48	1.08	0.01	0.01	1.00
	1.55^c	1.25^c	1.24^c				0^d	0^d	—			
	0.06^e	0.05^e	1.20^e				0.63^f	0.61^f	1.03^f			
							2.16^g	1.61^g	1.34^g			
							0.61^h	0.48^h	1.27^h			
200	24.26	4.78	5.07	0.82^i	0.65^i	1.26^i	4.01	3.18	1.26			
							15.87^f	4.70^f	3.38^f			
250	33.97	6.50	5.22	1.44^i	0.98^i	1.47^i	9.74	3.91	2.49	0.60	0.41	1.46
				6.43^j	1.93^j	3.33^j						
300				$3.0^{k,2}$	$2.1^{k,2}$	$1.5^{k,2}$	11.7	4.4	2.7			
							11.6^l	3.9^l	3.0^l			
350				$12.2^{k,3}$	$4.7^{k,3}$	$2.6^{k,3}$				0.71	0.62	1.15
400							24.2	5.2	4.6			
							27.9^f	5.6^f	5.0^f			
450				$23.9^{i,1}$	$5.3^{i,1}$	$4.5^{i,1}$						
				$22.4^{k,4}$	$5.0^{k,4}$	$4.4^{k,4}$						

[a] Parent alumina oxidized and evacuated at 500°C unless otherwise noted.

[b] Supplied by Dr. R. R. Chiannelli; surface area was 40 m^2/g; before the experiments it was freshly sulfided.

[c] Molybdena–alumina was poisoned by NO (3.90 cm^3 NTP/g) after the reduction.

[d] Taken from Ref. (*17*), poisoning the alumina with 1.5×10^{13} CO_2 molecules/cm^2.

[e] Molybdena–alumina was poisoned by CO_2 (0.76 cm^3 NTP/g) after the reduction.

[f] γ-alumina oxidized at 500°C and evacuated at 600°C.

[g] γ-alumina oxidized at 500°C and evacuated at 700°C.

[h] γ-alumina oxidized at 500°C and evacuated at 800°C.

[i] Standard sulfiding pretreatment.

[j] Sulfiding at 350°C with H_2S/H_2 and flushing with H_2 at 500°C.

[k] Evacuated for 30 min at 200°C; numbers from 1 through 4 refer to the experimental sequence run on the same sulfided catalysts (i, l).

[l] γ-alumina received a standard sulfiding pretreatment.

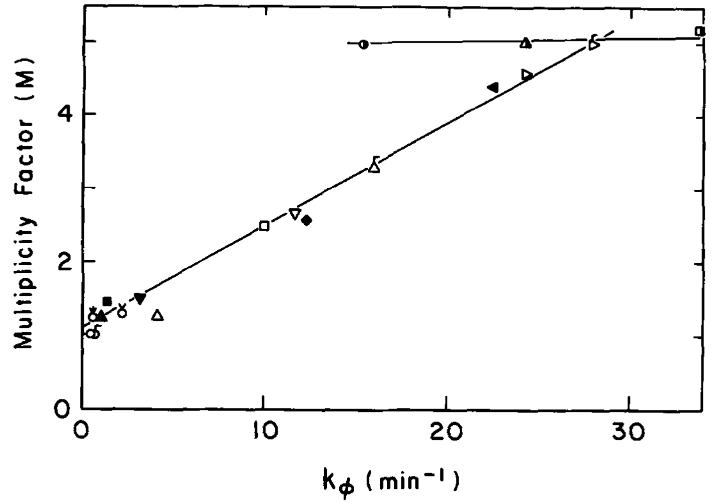

FIG. 3. The change of the multiplicity factor as a function of the rate constant (k_ϕ). Empty symbols: γ-Al_2O_3 oxidized at 500°C, evacuated at 500°C; empty symbols with flag: γ-Al_2O_3 evacuated at 600°C; empty symbol with double flag: γ-Al_2O_3 evacuated at 700°C; empty symbol with triple flag: γ-Al_2O_3 evacuated at 800°C; half-filled symbols: reduced Mo/Al_2O_3 (e/Mo $\approx$ 1.7); filled symbols: sulfided Mo/Al_2O_3 (e/Mo $\approx$ 3.0). The shape of the symbols represents the reaction temperature. (○: 70°C; △: 200°C; □: 250°C; ▽: 300°C; ◇: 350°C; ▷: 400°C; ◁: 450°C.)

sive reaction. The multiplicity factor (M) calculated was much lower than those obtained over the unpoisoned reduced catalysts, i.e., 1.5 vs 5.2, respectively. When, however, the reaction was studied at higher temperatures, product distributions and M values typical of multiple exchange could be obtained, just as with the parent alumina, *vide infra*.

Following an experimental run where freshly sulfided molybdena–alumina was tested at 450°C, the reactants were evacuated for 30 min at 200°C. Then the same catalyst was used for an experiment at 300°C; the same procedure was repeated at 350° and finally at 450°C (to check the reproducibility). These results are indicated by footnotes k in Table 1.

Experiments were made in which hydrogen treatment (at 500°) was used instead of a helium flushing. The results (Table 1, footnote j) showed substantial increases in k_ϕ, k_0, and M as S was removed from the surface and the coordinatively unsaturated sites (CUS) became more accessible. Multiple exchange (M = 3.33) now occurred at 250° as was typical for the reduced catalyst at much lower reaction temperatures. A similar increase in the oxygen chemisorption values measured at −78°C occurred concomitantly. The oxygen chemisorption was about 0.3 cm^3 (NTP)/g on freshly sulfided molybdena–alumina after a helium treatment at 500°C. After hydrogen flushing, the oxygen chemisorption increased to 3.8 cm^3 (NTP)/g.

Exchange over the parent alumina was studied as a reference blank. Saunders and Hightower (*17*) reported that the C_6H_6/D_2 exchange was facile over a similar alumina, yielding M = 1.14 at 67°C, the highest temperature they studied. We have extended their data in several ways. Two procedures were used to vary the two rates; first the reaction temperatures were changed (70, 200, 300, 400°C) and second, following the standard pretreatment, the dehydroxylation temperature of the γ-alumina was increased from 500 to 600 to 700 and to 800°C. The experimental results are presented in Table 1 and are collected in Figs. 3 and 4. In agreement with Saunders and Hightower

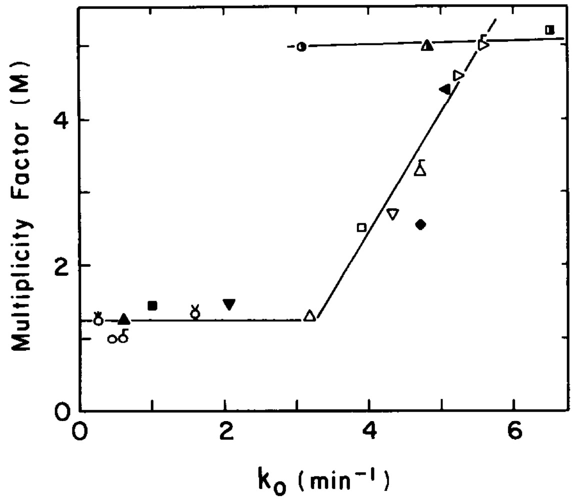

FIG. 4. The change of the multiplicity factor as a function of the rate constant (k_0). Symbols are the same as in Fig. 3.

(*17*), the value of M following the standard pretreatment was around 1.1 at 70°C. When the reaction temperature was increased, however, a new phenomenon was observed: at 200°, $M \approx 1.3$; at 300° $M \approx 2.7$, and finally at 400°, $4.2 < M < 4.9$. Interestingly, M increased about linearly with k_ϕ (Fig. 3), but at first remained relatively constant (near 1.2) with k_0 and then increased abruptly above 200°C to near 5.0 (Fig. 4). Still more interesting, data for all reaction temperatures and all pretreatment temperatures fell on the same curves, as did the data for the sulfided catalysts. The reduced catalysts behaved differently; with these (Figs. 3 and 4) the values of M always fell near 5.0, except when the catalyst was poisoned with NO or CO_2.

It was confirmed that the sulfiding had no significant effect on the alumina. In these experiments the γ-alumina received the standard sulfiding pretreatment. The data are listed as footnote l in Table 1 for 300°C. These results are very close to those measured on oxidized and evacuated γ-alumina.

Exchange of C_6D_6 with the hydroxyl groups of γ-alumina was investigated to check for the possible involvement of these groups in the C_6H_6/D_2 reaction. The experiments were made at different reaction temperatures (70, 120, 200, 300, and 400°C) in the presence of 250 Torr of helium using the alumina pretreated at 500°C. Between each experiment the catalyst was treated with hydrogen overnight to remove deuterium from the catalyst. The same experiment was also carried out over reduced molybdena catalysts at 70 and 300°C.

It is known from previous work (*23*) that the number of the hydroxyl groups available on γ-Al_2O_3 pretreated at 500°C is about 4×10^{14} OH/cm^2, while on the reduced catalyst the value is about 2×10^{14} OH/cm^2. Thus, 200 mg of these catalysts should contain about 1.4×10^{20} and 7×10^{19} OH, respectively. Therefore, about 40 cm^3 (NTP) C_6D_6 (10.7×10^{20} molecules or 64×10^{20} D atoms) were introduced into the system. The exchange reaction took place and approached the equilibrium distribution both on γ-alumina and on reduced Mo/Al_2O_3 although the concentrations of d_0, d_1, d_2 species were too small to be observed. Rate constants for these exchange reactions were calculated from the slopes of plots of $\log(x_6 - x_{6,\infty})$ vs t, where x_6 is the mole fraction benzene-d_6 in the distribution and t is

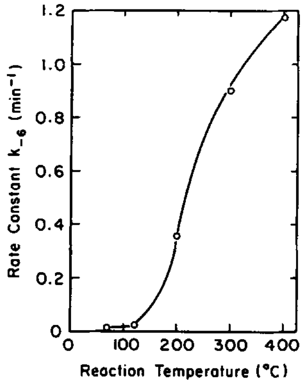

FIG. 5. The rates of exchange of C_6D_6 with the surface OH groups of γ-alumina pretreated at 500° as a function of temperature.

the time. The values of k_{-6} obtained for γ-alumina showed a sharp increase near 200°C (Fig. 5) similar to that for M vs k_0 (Fig. 4). Increasing the evacuation temperature of the γ-alumina from 500 to 600°C, but retaining the same reaction temperature (200°C), increased the rate constant (k_{-6}) from 0.35 to 0.5 min^{-1}.

Benzene hexadeuterobenzene exchange was studied over the reduced catalyst and over γ-alumina evacuated at 500°C. A total of 40 cm^3 (NTP) of a 50 : 50 mixture of C_6H_6 and C_6D_6 was used over 200 mg of catalyst. Helium was added to bring the total pressure to 300 Torr and the reaction was carried out at 70 and 300°C. In each case, stepwise exchange distributions were obtained as shown in Fig. 6 for 70°C corresponding to $M = 0.98$. The more rapid apparent decrease in benzene-d_6 than benzene-d_0 undoubtedly reflects the mixing-in of hydrogen from the surface OH groups. Interestingly, the mixing reaction was much faster over the reduced molybdena catalyst than over the parent alumina. Equilibrium was approached in about 60 min over the reduced catalyst at 70°C, whereas with γ-alumina 210 min was required.

Exchange of benzene over reduced catalysts poisoned with NO was investigated. It has been shown previously (*2, 21, 27, 28*) that NO adsorbs on reduced molybdena–alumina as a dinitrosyl species (or as an NO dimer) bound to the molybdena portion of the surface. It was also found that this NO acts as a selective poison for the hydrogenation of olefins (*2, 4*) and for the dissociative chemisorption of hydrogen (*6, 22*). In the present work, our objective was to test its effect on the exchange reaction. Therefore, an excess of the lethal dose, 0.77 cm^3 (NTP), or about 1.03×10^{20} NO/g catalyst was chemisorbed on 200 mg of the reduced catalyst. This corresponded to 5×10^{19} dimer pairs bound to about 10% of the Mo on the catalyst (5×10^{20} Mo atom/g).

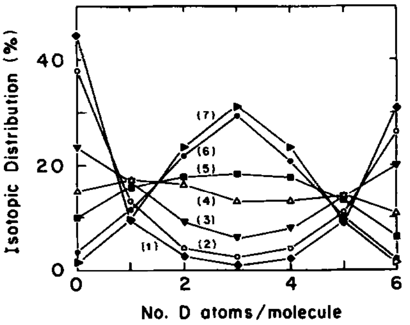

FIG. 6. Deuterium distribution from C_6H_6/C_6D_6 exchange reaction over 200 mg γ-alumina at 70°C after 7 min (1); 15 min (2); 30 min (3); 60 min (4); 90 min (5); 210 min (6); calculated equilibrium distribution (7).

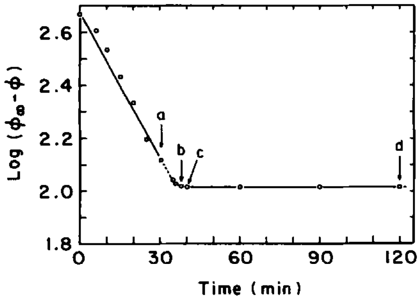

FIG. 7. Rate plot for C_6H_6/D_2 exchange reaction over the reduced molybdena–alumina catalyst (e/Mo ≈ 1.7). After 30 min 4.57 cm^3 (NTP) CO_2 was introduced to 200 mg of catalyst providing an apparent coverage of $\sim 3 \times 10^{14}$ CO_2/cm^2 in excess of the lethal dose. At point a, $\phi = 334.7$; at point b, $\phi = 365.0$; at point c, $\phi = 365.7$; and at point d, $\phi = 365.7$; $\phi_\infty = 469.17$ (calc.).

TABLE 2

Product Compositions from the Toluene–Deuterium Exchange Reaction over 200 mg Reduced Molybdena–Alumina (e/Mo ≈ 1.7)

Time (min)	Product composition		
	Overall	Ring	Methyl
15	$C_7H_{4.7}D_{3.3}$	$C_6H_{2.27}D_{2.73}$	$CH_{2.43}D_{0.57}$
45	$C_7H_{2.5}D_{5.5}$	$C_6H_{0.80}D_{4.20}$	$CH_{1.70}D_{1.30}$
120	$C_7H_{1.7}D_{6.3}$	$C_6H_{0.55}D_{4.45}$	$CH_{1.15}D_{1.85}$

The C_6H_6/D_2 exchange reaction was carried out at 70°C because at this temperature a significant difference exists in the M values obtained from the reduced catalyst (M ≈ 5) and from the γ-alumina support (M ≈ 1). The results obtained (Table 1, footnote c) were characteristic of a stepwise exchange and support the notion that on the poisoned catalyst the reaction took place over the free alumina portion of the surface only, and that the NO molecules effectively poisoned the contribution made by the molybdena sites. Note that the rate constant, k_ϕ, was lowered by nearly a factor of 10 by site poisoning and that the value of k_0 became comparable with those for alumina pretreated at the higher temperatures.

The effect of CO_2 poisoning was also tested. The reduced catalyst was exposed to excess CO_2 for a few minutes and the gas phase removed. The residual adsorption amounted to about 0.76 cm^3 (NTP)/g. Rather to our surprise, CO_2 [which chemisorbs selectively on the alumina portion of the surface (*3*, *21*)] was found to be a much more effective posion than NO [which chemisorbs selectively on the molybdena portion] (Table 1, footnote e). Moreover, it is evident that a synergism exists which leads to the high values of M only when both kinds of sites are available.

The effectiveness of CO_2 as a poison is further illustrated in Fig. 7 where the course of the exchange reaction was being followed in the usual way. On the introduction of CO_2 into the system, the exchange rate (and k_ϕ) fell abruptly to zero.

Exchange of toluene and m-xylene with D_2 over reduced molybdena–alumina was carried out over 200 mg of catalyst at 350°C. A C_7H_8/D_2 molar ratio of 1 : 12.5 was used. Samples of the reacted gas were taken at different reaction times (15, 45, and 120 min) for NMR analysis to assay separately the exchange of the ring and methyl hydrogens. The average sample composition was calculated on the basis of combined MS and ^{1}H-NMR data and these results are shown in Table 2. The product distribution data from the exchange reaction resembled that of Fig. 1; the fraction of the original hydrogen remaining in the two portions of the toluene molecule as a function of reaction time is shown in Fig. 8. It is clear that exchange in the ring positions occurred faster than in the side chain.

The ratio of the initial rates of disappearance of toluene-d_0 by exchange into the aromatic ring to that into the methyl group position was estimated from these data as about 3.2. A similar conclusion was deduced using the modified procedure described by Crawford and Kemball (*12*). The rate constants (k_ϕ, k_0, k_A, k_B) were deduced. The definitions of k_ϕ and k_0 are un-

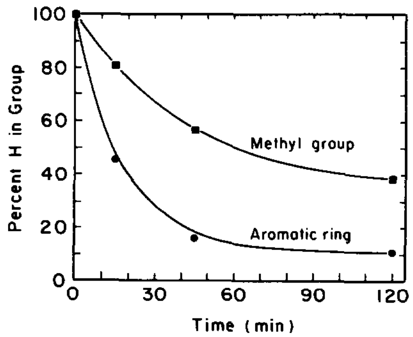

FIG. 8. The change of the hydrogen content of the toluene molecule during the toluene–deuterium exchange over the reduced molybdena catalyst at 350°C. The ordinate is the average atom percentage of H in each group, i.e., the percentage of the original three hydrogens in the methyl group and the percentage of the original five ring hydrogens remaining at various times.

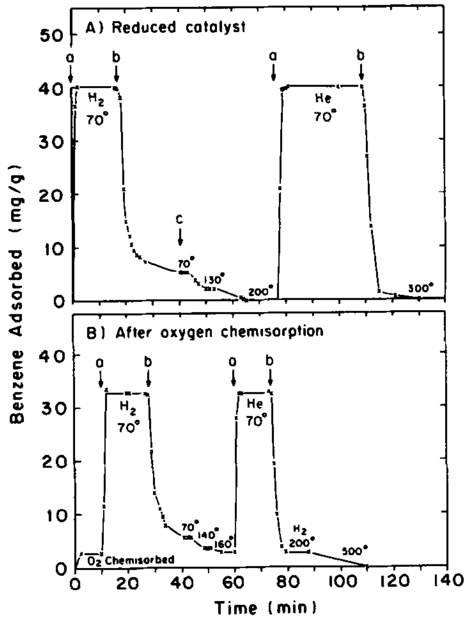

FIG. 9. Benzene isobars at 100 Torr and desorption kinetics determined in a flow microbalance over (A) 200 mg of reduced molybdena–alumina (*e*/Mo ≈ 1.7) and (B) the same catalyst after oxygen chemisorption on the molybdena sites.

On curve A, the benzene was admitted to the catalyst at $t = 0$ (point a) and flushed from the catalyst starting at point b. Note that it was necessary to raise the temperature from 70° to above 130° to effect complete desorption. Results obtained in flowing He were essentially identical to those in flowing H_2.

On curve B, the catalyst was first contacted with O_2 at −78°C and then flushed with He before raising the temperature to 70°C. The initial weight gain was due to oxygen chemisorption. Benzene was admitted to the catalyst at point a. Again, results in H_2 and He carrying gas were essentially identical.

changed; k_A and k_B were defined (*12*) by $k_\phi = k_A + k_B$, where k_A is the initial rate of entry of deuterium atoms into aromatic positions and k_B is the initial rate of entry of deuterium atoms into methyl groups. The calculated rate constants ($k_\phi = 27.48\ \text{min}^{-1}$, $k_A = 20.46\ \text{min}^{-1}$, $k_B = 7.02\ \text{min}^{-1}$, $k_0 = 7.01\ \text{min}^{-1}$) lead to $M = 3.9$ and a ratio of the rate constants for the exchange (k_A/k_B) is 2.9. Thus, the hydrogen atoms in the ring exchanged with deuterium approximately three times as fast as those in the methyl group. Hydrogenation of the toluene was not observed. Moreover, the dealkylation or disproportionation of toluene to form benzene at 350°C was very small (less than 1%).

The exchange of *m*-xylene with deuterium was studied using a reactant molar ratio of 1 : 13.8. The isotopic distributions from the exhange reaction were similar to those obtained for toluene. The formation of higher deuterated species (d_5–d_{10}) could be observed in small quantities from the very beginning of the reaction (5 min) indicating multiple exchange. The calculated rate constants $k_\phi = 18.62\ \text{min}^{-1}$, $k_A = 13.74\ \text{min}^{-1}$, $k_B = 4.88\ \text{min}^{-1}$, $k_0 = 3.80\ \text{min}^{-1}$) also indicated a multiple exchange ($M = 4.9$) and the ratio of the rate constants $k_A/k_B = 2.8$ was derived in agreement with the data for toluene (2.9).

Adsorption studies. The adsorption of H_2 on reduced molybdena–alumina has been thoroughly investigated previously (*6*) and it is known that the room temperature chemisorption is very small (~0.1 cm^3 (NTP)/g). The adsorption of benzene was studied briefly to assess the possibility that a strong chemisorption might be responsible for the high values of M found for the reduced catalyst. Equilibrium isobars were determined by passing a constant vapor pressure of benzene (~100 Torr) in flowing H_2 or He over ~200 mg of the reduced catalyst in a flow microbalance. The data are shown in Fig. 9. The initial uptake of the benzene at 70° was fast (Fig. 9, point a), the adsorption reaching its equilibrium value within 2–3 min. At point b, the saturator was bypassed and the benzene desorbed rapidly at first, then became very slow as point c was approached. Here, the temperature was raised to 130° and then to 200°. The data showed that, within experimental error, the adsorption was completely reversible, but that there was a fraction (~15%) which was more strongly held than the rest. Blank runs with the parent alumina yielded nearly the same results, thus negating the idea that this more strongly held fraction might be associated with molybdena sites. The strong chemisorption retained at 70° was 1.14 and 1.18 mg per 200 mg of alumina in the two preparations, respectively. It may be supposed that this chemisorption has a relatively long residence time and this could lead to multiple exchange. The equilibrium adsorption at point b was sufficient to cover about 70% of the total surface area and the large facile portion may be supposed to exchange rapidly with the more strongly held benzene.

To test whether the strongly adsorbed benzene was held exclusively by alumina sites, another experiment was made. Before the adsorption of the benzene, oxygen was chemisorbed at −78°C on ~200 mg of freshly reduced catalyst (Fig. 9B). The oxygen chemisorption amounted to 0.55 mg corresponding to O/Mo = 0.2. The amount of benzene adsorbed (point b) at 70°C was now somewhat lower (30.0 vs 40.0 mg/g), as was the strong chemisorption at point c. Therefore, although the isobars determined on the poisoned (B) and unpoisoned catalyst (A) were qualitatively similar, the oxygen chemisorption appeared to reduce both the total adsorption at 70°C and the strongly held chemisorption. This is not the result expected were the strong centers located on the molybdena portion of the surface.

DISCUSSION

Reduced and sulfided molybdena–alumina catalysts are notably effective for hydrogenation of simple olefins (*4*) and diolefins (*3*). Ethene reacts rapidly with D_2 at temperatures as low as that of dry ice. The principal product is ethane-d_2; only minimal exchange into the unreacted ethene is observed (*5*). Thus, hydrogenation is much faster than exchange and the exchange which is observed can be readily accounted for as part of the hydrogenation mechanism.

With propene, exchange into the unreacted olefin became more important, but propane-d_2 was still the chief initial product (*4*). With these olefins, the hydrogenation rate increased rapidly with extent of reduction (*3*) and was accordingly faster on sulfided catalysts ($e/\mathrm{Mo} \sim 3$) than on reduced ones ($e/\mathrm{Mo} \approx 1.8$). The hydrogenation of propene was not affected by CO_2 chemisorption, but was completely poisoned by a lethal dose of NO, a result (*4*) which distinctly contrasts with those of the present work.

With butadiene (*2*), exchange occurred at a rate comparable with hydrogenation; the terminal vinyl hydrogen atoms exchanged much faster than the internal ones in a manner reminiscent of exchange of terminal olefins with D_2 over alumina (*10, 29*). The hydrogenation rate was inhibited by adsorbed butadiene and appeared to be limited by access of H_2 or D_2 to the catalytic sites. Sulfided catalysts were less active for this reaction than reduced ones and MoS_2 was essentially inactive under similar conditions, as in the present work. With this background, it was supposed that *exchange* as well as *hydrogenation* was centered on coordinatively unsaturated sites on molybdena centers, but clearly this need not always be so.

In the present work benzene was not hydrogenated at atmospheric pressure over any of these catalysts unless the reduction temperature was raised to 800°C or above (where values of $e/\mathrm{Mo} > 4$ were obtained), suggesting that metallic Mo may have been responsible. By contrast, the C_6H_6/D_6 exchange, as well as the C_6H_6/C_6D_6 exchange, was facile at 70°C. Therefore, it could be concluded that the absence of hydrogenation could not be attributed to the inability of the reduced or sulfided catalyst to activate hydrogen. Indeed, with the standard reduced catalyst, multiple exchange ($M \approx 5$) was the rule, indicating that the rate of exchange was faster than the desorption rate from the exchange sites. The question of hydrogenation will be the subject of a later paper.

When the first alumina experiment was run at 70°C, stepwise exchange characterized by $M = 1.1$ was obtained, confirming the results of Saunders and Hightower (*17*).

On increasing the temperature, however, M increased into the range observed for the reduced molybdena–alumina catalyst. Moreover, these higher values could also be obtained by further dehydroxylating the alumina surface. The experimental results showed that regardless of how the rate constants were increased, the multiplicity factor also increased and all of these data, as well as those for the sulfided catalysts fell on the same curves (Figs. 3 and 4). The relationship between M and k_ϕ (Fig. 3) was linear in the range $0 < k_\phi < 30\ \text{min}^{-1}$. The plot of the multiplicity factor as a function of k_0 (Fig. 4) showed a sudden increase in M at about $k_0 \approx 3\ \text{min}^{-1}$. Stepwise exchange occurred below this point while above it the multiple exchange became the rule. This unusual behavior suggested that some physical process was controlling the value of M, e.g., pore diffusion. The constant, k_0, characterizes the rate at which reactant molecules can exchange with deuterium at least once; k_ϕ characterizes the rate of flow of deuterium into these same molecules. Multiple exchange occurs when the molecules can react several times before they escape the catalyst.

Multiple exchange which occurred over reduced molybdena–alumina corresponded to $k_0 \geq 3.0\ \text{min}^{-1}$, i.e., the break point on Fig. 4. The sulfided molybdena–alumina exchanged more slowly than the pure alumina, other things being equal, but otherwise behaved quite similarly suggesting that the reaction is occurring mainly on the uncovered alumina portion of the surface. In agreement with this, unsupported MoS_2 showed no exchange activity at 70°C, although rates became easily measurable at 250°C. This suggests that CUS molybdena sites are much less active for the exchange reaction than those on the alumina surface.

TABLE 3

Reaction Rate Constant for Benzene–Deuterium Exchange over 250 mg γ-Al_2O_3[a] Using Different Catalyst Particle Sizes

Particle size		Reaction temperature (°C)	Rate constant, k_0[b] (min^{-1})
Mesh	mm		
18–20	1.000–0.841	300	4.40 ± 0.35
Parent alumina (From Table 1)			
50–60	0.297–0.250	300	4.60 ± 0.35
120–140	0.125–0.105	300	4.33 ± 0.30

[a] Oxidized and evacuated at 500°C.

[b] Average rate constant values.

The high M values obtained in the exchange reaction over the reduced catalyst can be attributed to one of at least two possibilities. As mentioned above, M would be expected to increase with temperature as a natural consequence of a pore diffusion limitation. The other likely possibility is that the residence time of chemisorbed benzene is long relative to the rate of exchange. If this were the case it would be necessary to assume that on raising the temperature the rate of exchange increases faster than the rate of desorption of benzene molecules from the surface so that the benzene molecule may react many times per residence on a site. The relatively weak chemisorption of benzene (Fig. 9) and the low activation energy for exchange obtained from our data for alumina (4.5 kcal/mol) argue against this possibility. Our value is in good agreement with that of Saunders and Hightower (*17*) (4.3 kcal/mol). Let us consider the possibility of a diffusion limitation first.

Standard engineering calculations were carried out following the method outlined by Satterfield (*30*) and a similar calculation was made by Butt (*31*). Effectiveness factors close to unity were obtained in both cases. In the worst case (highest temperature) the calculation for alumina yielded $\eta = 0.98$. Calculations for reduced molybdena–alumina yielded similar results. These results were checked experimentally by separating out two very different particle sizes, performing duplicate experiments, and comparing these data with the value for the same conditions reported in Table 1. All of these results (Table 3) were identical within experimental error. Therefore, pore diffusion effects cannot be the explanation. Nevertheless, the low value of the activation energy (4.5 kcal/mol) and the still lower value obtained for the reduced catalyst (2.1 kcal/mol) are indicative of some sort of a diffusion process. By contrast, the higher value obtained for the sulfided catalyst (10.9 kcal/mol) suggests that in this case the reaction was not diffusion controlled, *vide infra*.

The results of the poisoning experiments were quite informative. NO, which is a poison for the CUS, reduced k_0 to about half its unpoisoned value and lowered k_ϕ by about an order of magnitude. CO_2, which is a poison for the exchange sites on alumina (*17*, *29*), was much more effective; it virtually eliminated the exchange reaction (Fig. 7 and Table 1) over the reduced catalyst. It is thus clear that both portions of the surface function synergistically to produce the high values of k_ϕ and M. A hint as to the manner in which this is accomplished is furnished by the data of Fig. 5. The parameter k_{-6} is a measure of the self-diffusion rate of transport of H(D) across the surface to the reaction centers. On the alumina surface this process is poisoned by CO_2. Figure 5 shows that the rate constant increases by two orders of magnitude between $125° < T < 400°$. Indeed these data together with those of Fig. 6 suggest that the surface hydroxyl groups participate in the exchange process in this temperature range and act in concert with the exchange centers to effect the catalysis by a stepewise process even at 70°C (Fig. 6).

What then is the role of the molybdena CUS? Evidently these dissociate D_2; atoms spill-over onto the alumina surface and thus provide a much higher flux of D toward the exchange centers and this in turn leads to multiple exchange. With the sulfided catalyst the exchange process is obviously different as suggested by its much higher activation energy. Either spill-over does not occur, or else the alumina portion is already poisoned. Thus, possibly the observed exchange at $T \geq 200°$ was that actually occurring at the molybdena CUS. The sketchy data for MoS_2 supports this view, but further investigation is needed.

Several further matters deserve comment. The microbalance measurements were made to assess the possibility that strong adsorption of benzene was responsible for multiple exchange. It was found that within experimental error complete desorption occurred at 200° and above. Moreover, a major fraction (85%) of the equilibrium adsorption at 70°C was readily reversible at this temperature and must have been physically adsorbed over the entire surface (as expected for a liquid near its boiling point). A small portion of this was, however, more strongly bound, and it is possible that it was this portion which was active in the exchange. The prior chemisorption of oxygen at 78°C reduced both the total adsorption at 70°, and the more strongly adsorbed portion. Interestingly, and perhaps significantly, the irreversible chemisorption was almost exactly the same on the reduced catalyst (1.14 mg), and on the parent alumina (1.18 mg).[4] Thus, the data are not inconsistent with the picture presented above. A more detailed study is needed to clarify these issues.

The supplementary experiments with the alkylbenzenes showed exchange in the side chains was slower, but only by a factor of about 3, than with the ring hydrogens. These results are in general agreement with those of Saunders and Hightower on alumina. The fact that both the molybdena–alumina catalyst and alumina behave in the same way supports the hypothesis that free alumina surface catalyzes the exchange reaction in both cases. The exchange in the methyl groups may be related to the facile exchange of CH_4 with CD_4 and with D_2 reported by Larson and Hall (*32*).

The C_6D_6/OH exchange experiments confirmed that the alumina portion of the surface must play an important role in these

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[4] Normalized for the same amount of alumina support (200 mg).

processes, especially at higher temperatures. This illustrates a limitation which is put on what may be deduced from deuterium tracer experiments carried out over alumina-supported transition metal oxide catalysts, where the mechanistic information may be disguised by extraneous exchange.

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