Catalytic properties of molybdena—alumina catalysts pretreated at high temperatures

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The dependence of the catalytic properties of molybdena—alumina catalysts reduced in hydrogen on the degree of reduction were followed in a model catalytic reaction of deuterium exchange in benzene. The reaction rate constant and the multiplicity factor decrease as the degree of reduction and the degree of dehydroxylation of the catalyst's surface increase.

Key words: molybdena—alumina catalysts; dehydroxylation of the catalyst surface; degree of reduction; deuterium exchange of benzene.

Molybdena—alumina catalysts are widely used in the chemical and petrochemical industry in hydrogenation and hydrodesulfurization processes. Research has been focused on the surface chemistry and catalytic properties of the molybdena—alumina system.[1] The reactions of benzene and alkylbenzene with deuterium has been studied over molybdena—alumina and alumina catalysts[3]. Benzene is not hydrogenated under atmospheric pressure over reduced and sulfidized molybdena—alumina, but the deuterium exchange reaction of benzene and was rapid at 70 °C over molybdena—alumina reduced at 500 °C. Multiple exchange was observed in the temperature range 70—250 °C. In the present work the catalytic activity of the molybdena—alumina system in deuterium exchange of benzene has been studied as a function of the reduction temperature.

Experimental

The catalyst was prepared by dry coating with $(NH_4)_6Mo_7O_{24}$ and Ketjen CK-300 alumina and had a surface area of 185 $m^2 \cdot g^{-1}$. Before each experiment, a portion of the catalyst ~200 mg) has been calcined overnight and then evacuated for 30 min at the same temperature. The catalyst was then reduced in a flow of ultrapure hydrogen (70 mL min^{-1}) for 2 h at 500 °C. In some experiments, higher reduction temperatures were used to increase the degree of reduction (*e*/Mo is an average number of electrons per Mo atom, the catalyst reduced below Mo^{6+} state). The catalyst was reactivated between experiments by employing the same procedure. The degree of reduction (*e*/Mo) was determined by measuring the consumption of O_2 necessary for complete reoxidation of the catalyst using the volumetric technique.[1]

The benzene used was the spectrophotometric grade sample, dried over sodium and degassed before use by a repeated freeze-pump-thaw technique.

Cylinder oxygen (99.5 %, Messer Griesheim GmbH) was passed through columns filled with anhydrous $CaCl_2$ and $Mg(ClO_4)_2$. The oxygen used in the volumetric reoxidation experiments had been condensed and distilled between liquid nitrogen traps.

Ultrapure D_2 was obtained by passing the gas through Pd—Ag filters.

A static reactor having a total volume of about 1000 mL with a stirrer was used for the experiments. A cylindrical well (inner diameter 15 mm; length 150 mm) with the catalyst was placed below the spherical part of the reactor. This section was heated to the required temperature, while the 1-L reactor remained at room temperature. The gas was pumped off from the sphere and delivered back over the catalyst. The catalyst was pretreated *in situ*. Following the pretreatment, known amounts of benzene and deuterium were introduced into the reactor and it was heated up to the reaction temperature.

Deuterated benzenes were analyzed for their deuterium distribution using a quadrupole mass spectrometer (Balzers QMC 421C-3) that was connected to the reactor system *via* a high-vacuum dosing valve. The product distribution was recorded at a low ionization potential (12 eV) to avoid fragmentation. Corrections were made for naturally occurring ^{13}C.

The experimental data were processed according to Kemball.[4] The initial rates were calculated from the first-order plots according to the following equations:

$$-\log(\Phi_\infty - \Phi) = k_\Phi t/2.303\Phi_\infty - \log\Phi_\infty,$$

where $\Phi = \Sigma i d_i$; i is the number of D atoms per molecule, and d_i is the mole fraction; Φ_∞ is the equilibrium value of Φ; k_Φ is the rate of incorporation of deuterium atoms into benzene expressed as the number of deuterium atoms per 100 benzene molecules per unit time; and

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

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

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percent per unit time. The ratio of these rate constants is the multiplicity factor $M = k_{\Phi}/k_0$, which gives an average number of deuterium atoms incorporated into each reacting benzene molecule during each residence on the catalyst's surface.

A Cahn RG2000 electrobalance was used to follow the dehydroxylation of the catalyst at elevated temperatures. The catalyst weight was 200 mg. The dehydroxylation studies were carried out in the temperature range of 500—900 °C. In each case, a freshly oxidized catalyst sample was used. On the basis of the weight change of the catalyst sample the amount of water removed was determined.

Results and Discussion

The degree of reduction of the molybdena—alumina catalyst was studied as a function of the reduction temperature, and was determined by following the amount of O_2 required for reoxidation (Fig. 1).

It should be noted that the reoxidation experiments gave only mean valence numbers. The mean valence state of Mo in the molybdena—alumina catalyst reduced at 500 °C was +4.3, while that in the catalyst reduced at 900 °C was +0.9. Evidently, a considerable amount of Mo^0 must be present at 800 °C and above. Hence, the mean valence state of the Mo ion in molybdena—alumina catalysts can significantly change with increasing the reduction temperature.

The deuterium exchange reaction of benzene was studied at 100 °C and at the molar ratio of benzene and deuterium ~1 : 8. The distribution of D atoms in benzene obtained at 100 °C on the catalysts prereduced at 500 °C for different times is shown in Fig. 2. The equilibrium composition was calculated according to the binomial distribution law and is given in Fig. 2 (curve *9*). It can be seen that the deuterium distribution approaches the equilibrium distribution after about 80 min.

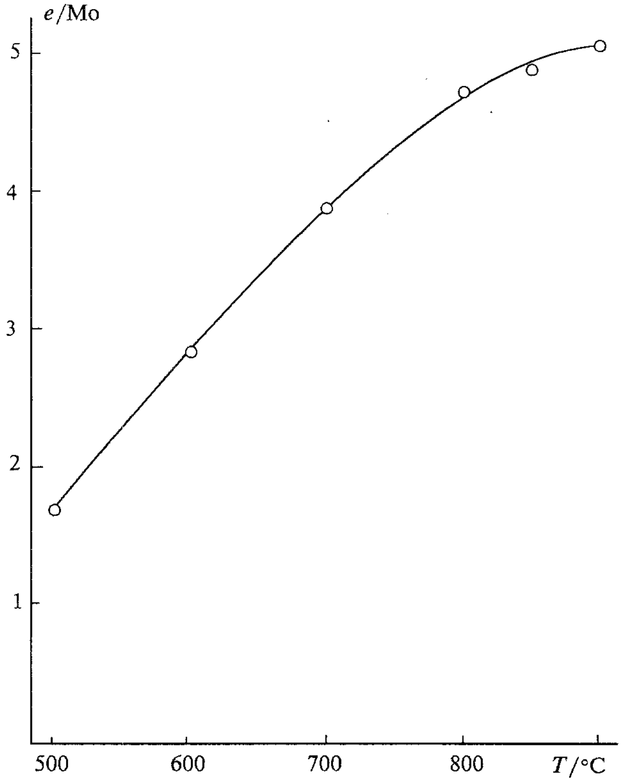

Fig. 1. Changes in the degree of reduction (*e*/Mo) as a function of the reduction temperature.

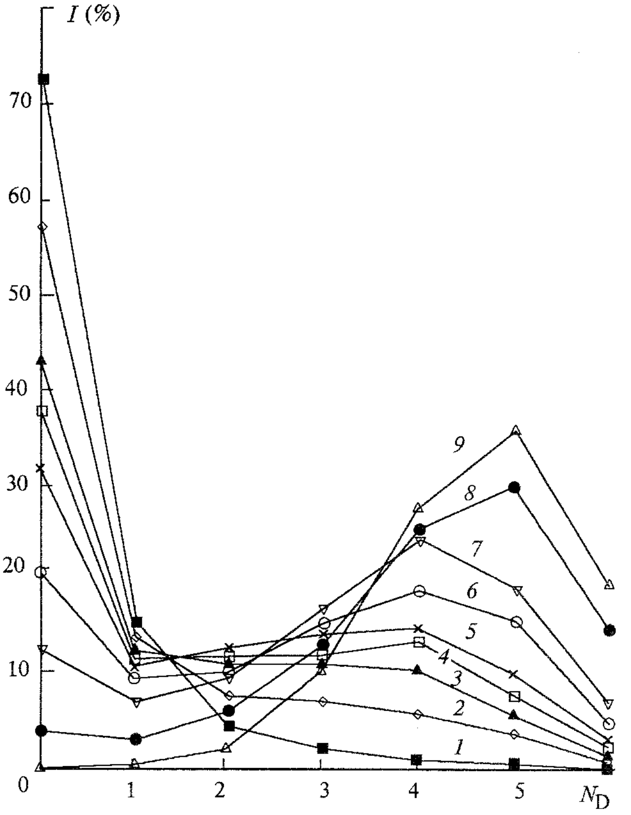

Fig. 2. Changes in the number of D atoms in C_6H_6 (N_D) and in the percentage (*I*) of isotopically labeled molecules during benzene—deuterium exchange over a reduced molybdena—alumina catalyst (*e*/Mo ≈ 1.7) as a function of the reduction time (*t*/min): 7 (*1*), 17 (*2*), 25 (*3*), 30 (*4*), 36 (*5*), 46 (*6*), 60 (*7*), 80 (*8*), and the calculated equilibrium distribution (*9*).

Experiments were carried out under similar conditions on molybdena—alumina catalysts reduced at successively higher temperatures (600, 700, 800, and 900 °C). The results obtained are summarized in Table 1 and in Fig. 3. These data show that high value of the multiplicity factor M ($M > 2$) can be achieved on catalysts reduced in this temperature range.

The rate constants (k_{Φ} and k_0) decrease as the reduction temperature increases. The value of k_{Φ} decreases from 13.3 to 1.5 min^{-1} when the reduction temperature on the catalyst is increases from 500 to 900 °C.

The variation in the multiplicity factor M points to multiple exchange ($M > 1$) over the reduction temperature range studied. The M value is close to 5 for the catalyst reduced at 500 °C, however, it decreases sharply

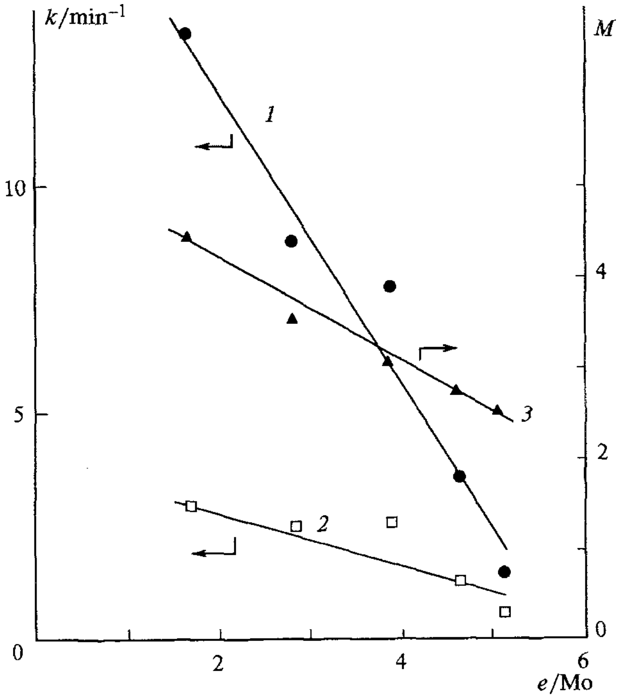

Fig. 3. Changes in the rate constants k_Φ (*1*) and k_0 (*2*) and the multiplicity factor M (*3*) in the exchange reaction benzene—D_2 as a function of the degree of reduction of the molybdena—alumina catalyst.

Table 1. Rate constants and multiplicity factors for the benzene—D_2 exchange reaction over a molybdena—alumina catalyst reduced at different temperatures

T/°C	k_Φ/min^{-1}	k_0/min^{-1}	M
500	13.3	2.9	4.6
600	8.8	2.5	3.6
700	7.9	2.6	3.1
800	3.6	1.3	2.7
900	1.5	0.6	2.5

Note. The reaction temperature is 100 °C, the amount of catalyst is 200 mg.

as the reduction temperature increases. The experimental results show that the high multiplicity factor value ($M \approx 5$), which is typical of a reduced catalyst by e/Mo $\approx$ 1.7 (*cf.* Ref. 3), can be significantly decreased if the catalyst is reduced at higher temperatures (800—900 °C).

It should be noted that the pattern of deuteration (hydrogenation) products obtained at 100 °C over a catalyst reduced at 900 °C corresponds to the literature data.[5]

The molybdena—alumina catalysts were reduced in a flow on microbalances and the amount of water formed during the reduction was determined, which corresponded to the degree of dehydroxylation of the catalyst. The degree of dehydroxylation, *i.e.*, the number of water molecules (Δ) removed with respect to the number of Mo atoms present in the catalyst ($5 \cdot 10^{20}$ atoms g^{-1}), increases as the reduction temperature increases (Fig. 4).

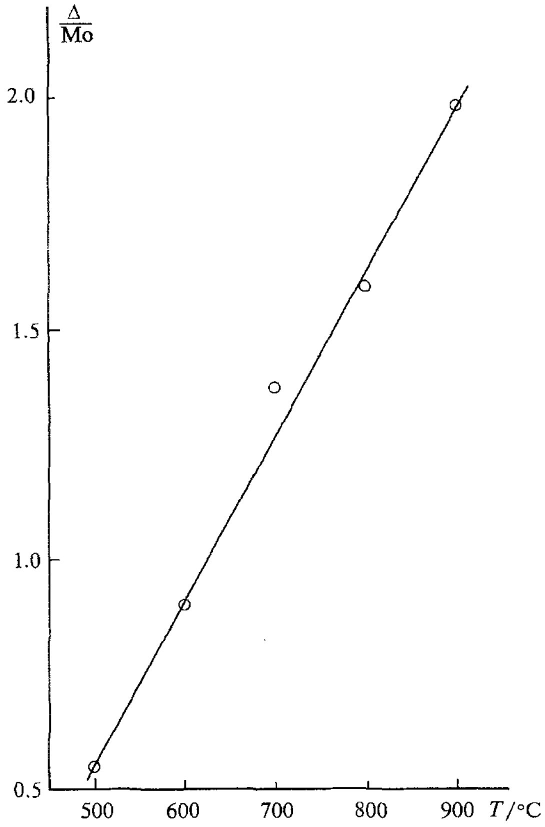

Fig. 4. Changes in the degree of dehydroxylation (Δ/Mo) of the molybdena—alumina catalyst as a function of the reduction temperature.

The literature data attest to the fact that the surface OH groups of the reduced molybdena—alumina catalyst play an important role in the deuterium exchange of benzene.[3] Selective poisoning of the surface with CO_2 and NO was carried out to confirm this statement. It was shown that CO_2 suppresses the deuterium exchange reaction by poisoning the alumina surface in a mixed catalyst.[3] Thus, obviously a rapid exchange reaction occurs between the OH groups on the surface of the catalyst and deuterium.[3] Hence, the OH groups affect the catalytic deuterium exchange in benzene. It has been suggested[3] that the coordinatively unsaturated sites of the molybdena—alumina system are much less reactive in the exchange reaction than those on the alumina surface. The coordinatively unsaturated molybdenum cations are the sites of dissociation adsorption of D_2 with subsequent spill-over of D atoms onto the alumina surface resulting in a multiple exchange process.

In light of the above, experiments were carried out to study the catalytic properties of molybdena—alumina catalysts reduced at elevated temperatures, which resulted in a higher degree of reduction. The catalytic activity of the reduced catalyst in the deuterium exchange reaction with benzene decreased as the reaction temperature increased (increase in *e*/Mo) (see Fig. 1); *M* decreased together with the catalytic activity. The degree of dehydroxylation of the catalyst increased as the reduction temperature increased (see Fig. 4); the catalytic activity and the multiplicity factor also decreased in this case (Fig. 5).

Thus, the experimental results obtained have furnished an additional evidence that the OH groups on the surface of the molybdena—alumina catalyst play an important role in the exchange reaction of benzene with D_2.

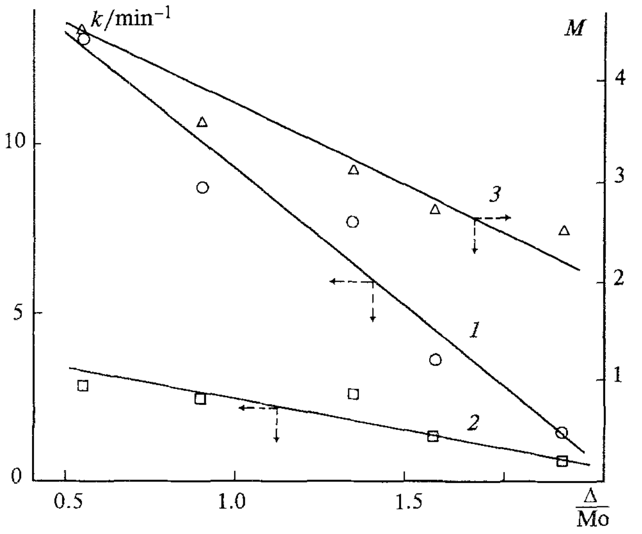

Fig. 5. Changes in the rate constants k_Φ (*1*) and k_0 (*2*) and the multiplicity factor (*3*) as a function of the degree of dehydroxylation of the catalyst.

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