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The Mechanism of Pyridine Hydrogenolysis on Molybdenum-Containing Catalysts

I. The Monolayer MoO_3–Al_2O_3 Catalyst: Preparation and Catalytic Properties

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Preparation of a MoO_3–Al_2O_3 catalyst with a monolayer of molybdenum oxide on the alumina was possible by adsorbing $MoO_2(OH)_2$ at 600°C from the gas phase. From the amounts of molybdenum adsorbed and the surface areas of the catalysts a characteristic value of 17 Å^2 was calculated for the area occupied by one MoO_3 molecule. Longer times of preparation and high partial pressures of $MoO_2(OH)_2$ yielded an aluminum molybdate ($Al_2O_3 \cdot 3MoO_3$) as evidenced by X-ray analysis. High coverage of the alumina with molybdenum oxide was also possible by adsorbing polymolybdate ions from acid solutions.

The dehydrogenation of cyclohexane on the prepared catalysts was studied using a pulse reactor. For the different catalysts the rate of dehydrogenation, expressed per unit weight of MoO_3, was found to be constant.

Hydrogenolysis of pyridine at high hydrogen pressures on a monolayer MoO_3–Al_2O_3 catalyst and a cobalt promoted MoO_3–Al_2O_3 catalyst showed that both catalysts have the same activity and selectivity pattern.

INTRODUCTION

In a series of papers we intend to present the results of investigations into the mechanism of pyridine hydrogenolysis on molybdenum-containing catalysts. This paper deals with the preparation of a monolayer MoO_3–Al_2O_3 catalyst. In following papers the kinetics of pyridine hydrogenation and piperidine hydrogenolysis at low and high hydrogen pressures and the conversion of amines will be reported. The results of adsorption studies of hydrogen and nitrogen bases on Al_2O_3 and MoO_3–Al_2O_3 using various techniques will also be presented.

Especially for the adsorption studies we tried to prepare a catalyst with a monolayer of molybdenum oxide and a small free alumina surface. Two different methods were examined, one in which the molybdenum oxide was adsorbed on the γ-Al_2O_3 from the gas phase and one in which the adsorption took place from the liquid phase.

Buiten (*1*) showed that a MoO_3–SnO_2 catalyst with a monolayer of molybdenum oxide on the tin oxide could be prepared by adsorption of molybdenum hydroxide from the gas phase. At high temperatures and high partial pressures of water vapor molybdenum oxide is converted into the volatile $MoO_2(OH)_2$ (*2*). This compound was transported to the tin oxide surface by flowing a mixture of air and water vapor successively through a bed of MoO_3 and SnO_2 particles. The $MoO_2(OH)$ or MoO_3 was very strongly adsorbed on the SnO_2 surface. From more or less constant weight percentages of MoO_3 and the agreement between the theoretical monolayer MoO_3 percentage and the one experimentally found, he concluded that a monolayer was formed.

Besides this technique we tried to prepare a monolayer MoO_3–Al_2O_3 catalyst by adsorption of molybdate ions from acid solutions on the alumina. The formation of polymolybdate ions in acid solutions is well known (*3*, *4*) and can be formulated as:

$$n MoO_4^{2-} + (2n - 2)H^+ \rightleftarrows [Mo_nO_{2n+2}(OH)_{2n-2}]^{2-}.$$

The polymerization can be observed at pH < 7 and with concentrations of molybdenum > 0.001 M. An increase of the molybdenum concentration increases the polymerization factor n. A decrease of the pH also increases n. Values of $n > 7$ were found at a pH between 1 and 2 and a molybdenum concentration above 0.05 M. If these large polymolybdate ions adsorb very strongly on an alumina surface the preparation of a monolayer molybdena–alumina catalyst may also be possible in the liquid phase.

The formation of a MoO_3–Al_2O_3 catalyst with the molybdenum oxide well spread out over the alumina surface has been mentioned by different authors. Russell and Stokes (*5*) measured the dehydrogenation activity of MoO_3–Al_2O_3 catalysts. The activity was linearly related with the molybdenum content; however, the activity became constant when the amount of molybdenum was raised above 0.052 at. %. Assuming 15 Å^2 as the surface area for one molybdenum trioxide molecule, Russell and Stokes showed that the maximum activity was due to the attainment of complete coverage of the alumina surface with a monolayer of molybdenum oxide. [The value of 15 Å^2 was calculated from the density of molybdenum trioxide; Buiten (*1*) experimentally found a value of 20–25 Å^2 for the adsorption of MoO_3 on SnO_2.]

The spreading of molybdenum oxide over alumina was also shown by Lipsch and Schuit (*6*) from reflectance measurements on a mixture of MoO_3 and Al_2O_3 particles. Accepting a thickness of the MoO_3 monolayer of 5 Å (i.e., 10.8 Å^2 for the area of one MoO_3 molecule) they calculated that in the commercial dehydrosulfurization catalyst CoO–MoO_3–Al_2O_3 the molybdenum oxide covers about 20% of the alumina surface.

The coordination of molybdenum in molybdena–alumina catalysts has been investigated by various authors (*5–8*). Some of this research was done on the cobalt-promoted catalyst; however, no evidence was found for the formation of a cobalt molybdate on the alumina. Thus, the incorporation of molybdenum into the promoted and the nonpromoted catalyst is expected to be identical (*6*). Lipsch and Schuit (*6*) concluded from infrared transmission measurements that there was an octahedral coordination of the molybdenum in the oxide lattice. However, for the same catalyst Ashley and Mitchell (*7*) observed by reflection measurements that the molybdenum was tetrahedrally coordinated. Only a small part of the molybdenum was present in an octahedral coordination. They explained the results of Lipsch and Schuit (*6*) by assuming octahedral molybdenum more inside the alumina structure. Asmolov and Krylov (*8*) reported tetrahedral molybdenum at a low molybdenum content and octahedral molybdenum at higher molybdenum contents.

The formation of an aluminum molybdate has been discussed by several authors. Doyle and Forbes (*9*) reported a slow reaction of Al_2O_3 and MoO_3 at 700°C. The compound $Al_2O_3 \cdot 3MoO_3$ was formed. Ishii and Matsuura (*10*) and Asmolov and Krylov (*8*) mentioned the existence of a "combined form" of molybdenum oxide on alumina. This combined form did not dissolve in ammonia. It was suggested that this combined form may be aluminum molybdate.

In this paper two methods for the preparation of a monolayer MoO_3–Al_2O_3 catalyst, the formation of an aluminum molybdate and a first activity test of the prepared catalyst, are discussed. The activity of a commercial CoO–MoO_3–Al_2O_3 desulfurization catalyst has also been measured.

METHODS

Catalyst Preparation from the Gas Phase

In the preparation from the gas phase a flow of air of 15 liters/hr was saturated with water vapor to a pressure of 0.5×10^5 N/m^2 (the amount of water was determined after condensation). The mixture first flowed through a bed of MoO_3 particles (1.2–2.0

mm, 15 cm high, $d_i = 6$ mm, $T = 595°C$, $P_{MoO_2(OH)_2} = 20\ N/m^2$) and then through a bed of alumina particles (0.3–0.6 mm, 10 cm high, $d_i = 12$ mm, $T = 600°C$). The pressure drop over the two beds was about $0.1 \times 10^5\ N/m^2$. The somewhat lower temperature of the MoO_3 bed was chosen to prevent condensation of the MoO_3 between the molybdena and the alumina bed. The temperature of the alumina was constant within 2°C. Under these circumstances about 5 days were needed before the molybdenum oxide front broke through and formed MoO_3 particles at the reactor outlet. At the end of the experiment the catalyst bed was divided into 10 fractions. The molybdenum contents of these fractions, and in some cases also their surface area, were determined.

Catalyst Preparation from the Liquid Phase

In the preparation from the liquid phase a fresh solution of 1% ammonium molybdate (pH 1–9) flowed through a bed of alumina particles (0.3–0.6 mm, 2–50 g, $\phi = 50$–300 ml/hr). At the outlet of the reactor the pH was measured and the molybdate concentration and the alumina concentration were determined. During the preparation samples were taken from the top of the alumina bed and analyzed for their molybdenum content. The time of preparation was mostly 4 hr (sometimes about 1 wk). After the preparation alumina samples were taken at different heights of the bed, dried and calcined for at least 1 hr at 500°C.

Some of the catalysts were extracted in an ammonia–ammonium nitrate buffer. After four extractions with this buffer (24 hr each time) the molybdenum content of the catalyst was constant.

Materials

Al-K: γ-Al_2O_3 (kindly supplied by Ketjen, Amsterdam, BET surface area 213 m^2/g, $\bar{r}_{pore} \approx 30$ Å);

Al-D: $(\gamma + \delta)$-Al_2O_3 (aerogel, Degussa, 78 m^2/g, $\bar{r}_{pore} \approx 125$ Å); and 4% CoO–12% MoO_3–Al_2O_3 (Ketjenfine, 235 m^2/g).

Analysis

The molybdenum content of the MoO_3–Al_2O_3 catalysts was analyzed by X-ray fluorescence (*11*). The molybdenum concentration in solutions was determined complexometrically with EDTA and eriochromium-black-T at pH 10 after precipitation of the molybdate (as calcium molybdate) in a boiling $CaCl_2$ solution (*12*).

The aluminum concentrations were determined with EDTA and eriochromium-black-T. The normal complexometric analyses at pH 7 and xylenol orange was impossible due to an interfering effect of the molybdate ions.

The surface areas of the catalysts were determined by argon adsorption at −196°C (13.8 Å², $P_0 = 230$ mm Hg).

X-Ray analyses were made with Cu–$K\alpha$ radiation. The Guinier-de Wolff and the Guinier-Lenné techniques and a diffractometer were used.

Catalytic Activity

The catalysts were reduced for at least 16 hr at 450°C at the hydrogen pressure of the following experiment.

The conversion of cyclohexane was measured in a pulse reactor (0.5μl pulse, 1g catalyst, $P_{H_2} = 1.6 \times 10^5\ N/m^2$, $T = 350°C$). The height of the catalyst bed was about 2 cm. The gas flow rate was 3.6 liter (NTP)/hr. A 3 m didecyl phthalate column at 80°C was used for the gas chromatographic analyses.

The conversion of pyridine was carried out in high pressure equipment. A stainless steel U-type reactor with an internal diameter of 6 mm was used. The amount of catalyst was 3.5 g. The gas flow rate was 28 liter (NPT)/hr. The total pressure was $60 \times 10^5\ N/m^2$. The linear gas speed in the reactor (empty tube) 1.0 cm/sec. The partial pressure of pyridine was $0.78 \times 10^5\ N/m^2$.

The reaction time was defined as: $t = mP/\phi_t$ in which

m = mass of catalyst (kg);
P = total pressure (N/m^2);
ϕ_t = total moles fed to the reactor (moles/sec).

This definition of the reaction time was used to take into account the influence of the total pressure on the reaction time. The reaction time was 6.1×10^7 kg N sec/m² moles. The products were analyzed by gas chromatography (*13*). More information about the equipment is given elsewhere (*14*).

At the end of an experiment (after 50 hr) the reproducibility of the pyridine hydrogenolysis was tested at several temperatures. The CoO–MoO–Al_2O_3 catalyst gave reproducible results. An activity decline of about 25% was found for the MoO_3–Al_2O_3 catalyst at 250 and 300°C.

RESULTS

Catalyst Preparation in the Gas Phase

The effect of water vapor partial pressure, $MoO_2(OH)_2$ partial pressure, temperature and surface area of the alumina on the preparation was investigated. A characteristic plot of the weight amount of molybdenum oxide in the catalyst as a function of the bed length is given in Fig. 1. High amounts of molybdenum in the first samples followed by a rather sharp decrease to a constant level was found in all experiments. When the experiment was stopped before the molybdenum oxide reached the last alumina particles, a sharp front of MoO_3 could be observed. This indicates that the adsorption of the oxide or hydroxide on the alumina is very strong. The results of a number of experiments are given in Table 1. For each experiment the level of the constant MoO_3 content and the total weight of molybdenum oxide adsorbed above this level ("excess MoO_3") are given. Accepting a monomolecular layer of the molybdenum oxide, the surface area occupied by one molecule of MoO_3 can be calculated from the surface area and the weight of molybdenum oxide at the constant level. For experiments at different conditions a value of about 17 Å^2 was found.

X-Ray diffraction of all our samples showed no molybdenum oxide. The samples with a MoO_3 content above 30% showed a characteristic diffraction pattern, which did not belong to the alumina or to one of the molybdenum oxides. Very good correlation was found between the diffraction pattern of our samples and that of $Al_2O_3 \cdot 3MoO_3$ (*15*). The spectrum was very distinct when the temperature of a mixture of alumina and molybdenum oxide particles was slowly raised from 500 to 600°C (2°C/min). We observed the appearance of the $Al_2O_3 \cdot 3MoO_3$ spectrum at 535°C and the disappearance of the MoO_3 spectrum at 585°C. Remarkable was the disappearance of the $Al_2O_3 \cdot 3MoO_3$ spectrum on prolonged heating (50 hr) at 600°C.

A decrease of the surface area during the preparation process was found for the Al-K material. This was not the case for the Al-D material. The areas for alumina and those obtained several times for the MoO_3–Al_2O_3 catalysts are given in Table 2. The areas are expressed per gram of Al_2O_3.

Several catalyst samples were extracted with an ammonia/ammonium nitrate solution. A part of the molybdenum oxide

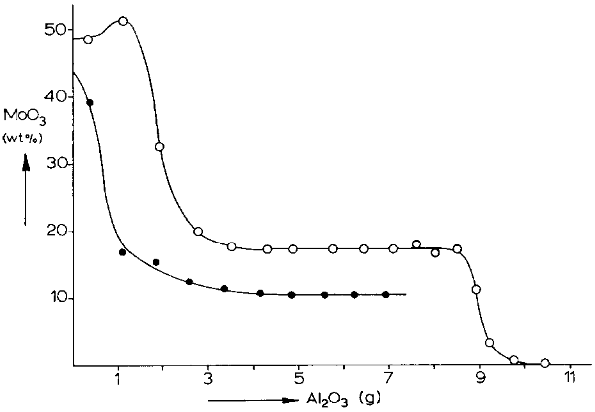

FIG. 1. Molybdenum oxide content as a function of the bed length or the weight of alumina downstream for the preparation from the gas phase at 600°C; (●) Al-D, (○) Al-K.

TABLE 1
RESULTS OF THE CATALYST PREPARATION FROM THE GAS PHASE

Expt	Type of alumina	T (°C)	P_{H_2O} 10^5 N/m²	ϕ_{air} (l/hr)	Time of Expt (hr)	Amount of water transported (liters)	Excess MoO_3 (g)	MoO_3 (wt%) at constant level	Surface area at constant level of molybdenum content (m²/g cat.)	Area for one MoO_3 molecule (Å²)
1	Al-D	615	0.7	8	94	0.69	0.56	10.3	72	16.5
2	Al-K	600	0.2	27	300	1.52	1.5	17.5	117	16.1
3	Al-K	600	0.4	15	200	1.55	1.8	17.4	121	16.7
4[a]	Al-K	600	0.6	26	195	4.48	5.6			
5[b]	Al-K	600	0.5	15	150	1.36	1.5			
6[c]	Al-K	600	0.5	16	165	1.31[c]	0.8	15.2	108	17.1
7	Al-K	520	0.7	18	620	12.2	1.4	18.0	130	17.3

[a] In Expt 4, 26 g alumina were used instead of 10 g.

[b] In Expt 5, the alumina was a presintered Al-K with a surface area of 155 m²/g.

[c] In Expt 6, the gas stream from the MoO_3 bed was diluted with a stream of water vapor and air. (ϕ_{air} = 16 liters/hr, $P_{H_2O} = 0.5 \times 10^5$ N/m².) The partial pressure of $MoO_2(OH)_2$ was lowered by a factor of two in this case. The ϕ_{air} and the amount of water given in the table are based only on the stream through the MoO_3 bed.

remains on the catalyst, namely 7 wt % for a catalyst prepared in the liquid phase and 3–5 wt % for those prepared in the gas phase. This amount was independent of the original amount of molybdenum oxide in the sample. The X-ray pattern of aluminum molybdate disappeared after extraction.

Catalyst Preparation in the Liquid Phase

The effect of the ammonium molybdate concentration, liquid feed rate, pH and adsorption time on the weight of molybdenum oxide adsorbed on the alumina were studied. In Fig. 2 a typical plot is given of the concentration of ammonium molybdate in the effluent and the weight of molybdenum oxide adsorbed as a function of the time. The pH of the effluent was about 8 in the first 2 hr, then decreased rather fast to a value of 5, followed by a slow decrease to the pH value of the feed. This change in pH is caused by the formation of poly-ions. These ions adsorbed on the alumina or are formed on the alumina surface.

TABLE 2
SURFACE AREAS OF Al_2O_3 AND MoO_3/Al_2O_3 PREPARED FROM THE GAS PHASE AND FROM THE LIQUID PHASE

Sample	Treatment	Surface area (m²/g Al_2O_3)	Remarks
Al_2O_3	—	213	
Al_2O_3	600°C, $P_{H_2O} = 0.5 \times 10^5$ N/m²	190 155	After 11 hr Constant, after 80 hr
MoO_3/Al_2O_3	600°C, $P_{H_2O} = 0.5 \times 10^5$ N/m²	140 90	Constant level of wt% MoO_3 45 wt% MoO_3
Al_2O_3	20°C, [AM] = 0, pH 1	230	
MoO_3/Al_2O_3	20°C, 1% AM solution, pH 1	240	

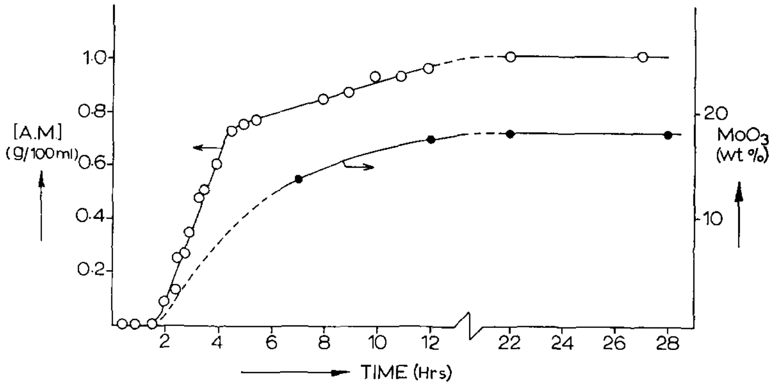

FIG. 2. The ammonium molybdate [AM] concentration in the effluent and the molybdenum oxide content of the catalyst at reactor outlet as a function of the time of preparation (pH 2; 45 g Al_2O_3; ϕ = 300 ml/hr).

The liquid feed rate has little effect on the amount of molybdenum adsorbed. The profile for ammonium molybdate, expressed as the ammonium molybdate concentration [AM] in the effluent as a function of total volume of solution fed to the reactor, was somewhat sharper in the case of the low liquid feed rate.

The weight of molybdenum adsorbed was determined as a function of the time at different pH values (10 g Al_2O_3; ϕ = 100 ml/hr). At low pH (<3) a "constant" molybdenum content was obtained within 20 hr; at higher pH (>5) it took about 70 hr to reach a constant wt % MoO_3. At pH < 2 and high [AM] a small linear increase of the molybdenum content as a function of the time was observed. For the experiment at pH 1 this increase was about 1 wt % MoO_3/24 hr for alumina at the end of the bed and about twice as much for alumina in the first part of the bed. This increase is due to the formation of molybdenum oxide particles already in the solution. To determine the effect of the pH on the weight of molybdenum oxide adsorbed on the alumina a correction for this effect has to be made. The "constant level" of wt % MoO_3 at longer times of adsorption were extrapolated to $t = 0$. The influence of the pH on the weight of molybdenum oxide in the samples is given in Fig. 3.

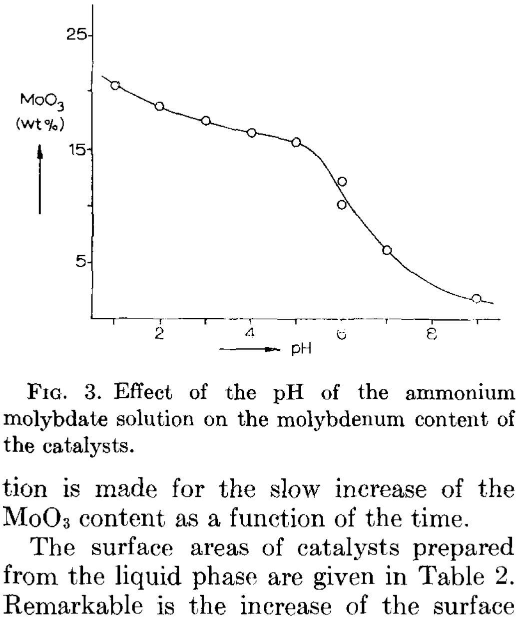

FIG. 3. Effect of the pH of the ammonium molybdate solution on the molybdenum content of the catalysts.

The [AM] has little effect on the amount of molybdenum oxide adsorbed (Table 3). The difference will be even less if a correction is made for the slow increase of the MoO_3 content as a function of the time.

The surface areas of catalysts prepared from the liquid phase are given in Table 2. Remarkable is the increase of the surface area of alumina by treatment with a nitric acid solution.

TABLE 3
EFFECT OF THE AMMONIUM MOLYBDATE [AM] CONCENTRATION ON THE WEIGHT OF MoO_3 ADSORBED[a]

[AM] (%)	MoO_3 (wt%)
1.0	17.8
0.5	17.4
0.2	16.8

[a] pH 2; 10 g Al_2O_3; ϕ = 100 ml/hr; t = 50 hr.

Measurements of Catalytic Activity

The catalytic activity of the $CoO-MoO_3-Al_2O_3$ catalyst and the homemade $MoO_3-Al_2O_3$ catalysts were investigated by studying the conversion of cyclohexane at low hydrogen pressure and the conversion of pyridine at high hydrogen pressure.

The *conversion of cyclohexane* was investigated by the pulse technique. Benzene was always the most important product. Methylcyclopentane and cracking products were also formed, especially on the $MoO_3-Al_2O_3$ catalysts.

On $CoO-MoO_3-Al_2O_3$ the conversion of cyclohexane into benzene appeared to be insensitive to the amounts of cyclohexane injected. This indicates that the reaction is of the first order in cyclohexane. Hence, it is possible to compare reaction rate constants studying the conversion of cyclohexane on the different catalysts. When other products than benzene were found it was assumed that they were formed by a first order parallel reaction. The results are given in Table 4.

Alumina appears to be inactive. The cobalt-promoted $MoO_3-Al_2O_3$ catalyst showed a selective formation of benzene. Methylcyclo-pentane and cracking products were formed on the $MoO_3-Al_2O_3$ catalyst. In the case of alumina and the extracted catalyst, the conversion of cyclohexane into cracking products was small; next to benzene methylcyclopentane was the most important product. The low conversion into methylcyclopentane on the molybdena–alumina is due to the high cracking rate of methylcyclopentane on these catalysts, as was experimentally found in a separate experiment.

The *conversion of pyridine* was studied as a function of the temperature at a hydrogen partial pressure of 60×10^5 N/m². The results obtained on the $CoO-MoO_3-Al_2O_3$ and the 22% $MoO_3-Al_2O_3$ catalyst are given in Fig. 4a and b. The reaction time in both cases was 6.1×10^7 kg N sec/m² moles.

The organic reaction path is discussed elsewhere (*14*). It was shown that the compound *N*-pentylpiperidine was formed from pentylamine and piperidine or directly from two piperidine molecules.

DISCUSSION

Catalyst Preparation from the Gas Phase

The constant level of the MoO_3 content (Fig. 1) and the same value (17 Å²) obtained for the area of one MoO_3 molecule under different experimental conditions (Table 1) strongly suggest the presence of a monolayer of molybdenum trioxide on the alumina.

TABLE 4

ACTIVITY OF DIFFERENT CATALYSTS FOR THE CONVERSION OF CYCLOHEXANE (CH)

Catalyst	(wt%) MoO_3	Surface area (m²/g cat.)	Conversion of CH	Arbitrary units		k_1/wt MoO_3 (arbitrary units)
				k_1[a]	k_2[a]	
Al_2O_3	0	213	0.006	0.002	0.0005	
$CoO-MoO_3-Al_2O_3$	12.0	235	0.58	0.42	<0.001	3.5
$MoO_3-Al_2O_3$[b]	15.2	128	0.86	0.63	0.23	4.1
$MoO_3-Al_2O_3$[c]	22.0	195	0.91	0.95	0.13	4.3
$MoO_3-Al_2O_3$[d]	6.7	225	0.29	0.11	0.05	1.7

[a] The reaction scheme was taken to be:

$$\begin{array}{l} \text{cyclohexane} \xrightarrow{k_1} \text{benzene} \\ \qquad\qquad\quad \big|\xrightarrow{k_2} \text{methylcyclopentane} + \text{cracking products} \end{array}$$

Assumption of zero order of the second reaction does not change the values of k_1 more than 10%.

[b] Catalyst prepared from the gas phase.

[c] Catalyst prepared from the liquid phase.

[d] 22% $MoO_3-Al_2O_3$ catalyst extracted in a buffer of ammonia and ammonium nitrate.

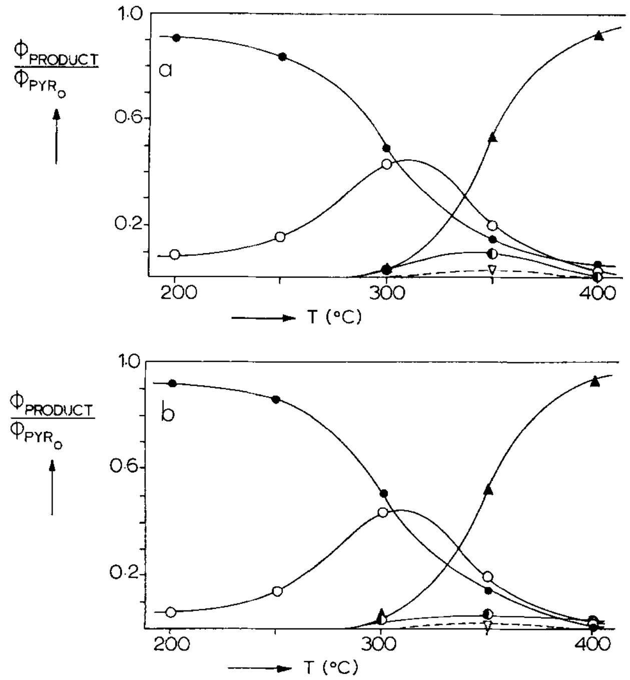

FIG. 4. Conversion of pyridine as a function of reaction temperature on the 4% CoO–12% MoO_3–Al_2O_3 catalyst (a) and the 22% MoO_3–Al_2O_3 catalyst (b) under the same experimental conditions; (●) pyridine, (○) piperidine, (◐) *N*-*n*-pentylpiperidine, (▽) *n*-pentylamine, (▲) ammonia.

Evidence for the high coverage of the original alumina surface with MoO_3 was also found by infrared spectroscopic measurements (*16*). The spectrum of the OH groups of alumina was far less intense on the MoO_3–Al_2O_3 catalyst. The band positions were also changed. In a separate paper more detailed information about the MoO_3–Al_2O_3 catalyst (before and after the reduction of the catalyst) will be presented.

From models of the different planes of alumina we tried to calculate a theoretical value of the area for one MoO_3 molecule. However, models of the alumina surface are not well known. Peri (*17*) reported a model for the 100 plane of alumina; his model was idealized and did not take into account the presence of tetrahedral aluminum between two 100 planes. We designed models of the different planes by cleaving an alumina crystal in different directions. The following assumptions were made in our model of the monolayer catalyst.

1. The Al ions in between the split layers were counted as 50%.
2. The vacancies in the Al_2O_3 structure were taken into account by diminishing, if present, the Al ions above the first oxygen layer; the Al ions left above this first layer were transformed into H ions ($3H^+/Al^{3+}$).
3. The molybdenum ions are incorporated in such a way that the new structure forms a continuation of the alumina crystal. Figure 5 demonstrates incorporation of tetrahedral and octahedral molybdenum.

The results of the calculations of the theoretical area occupied by one MoO_3

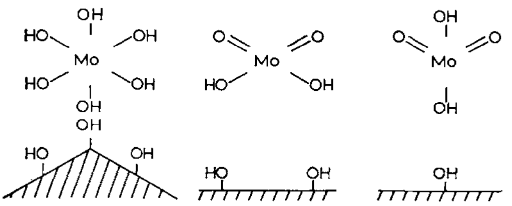

FIG. 5. Models of the incorporation on alumina of octahedral Mo (a), tetrahedral Mo on the 100 plane (b) and tetrahedral Mo on the 111 plane (c); in cases (a) and (c) three oxygen ions are needed per molybdenum ion, in case (b) only two oxygen ions.

molecule are given in Table 5. These data show that our experimental value of 17 Å^2 is well within the range. It also indicates that there is a preference for tetrahedral coordination, if the 100 plane is predominantly exposed. The model of the MoO_3–Al_2O_3 catalyst, based on Peri's model of the alumina surface, was less satisfying. The Mo–Mo distance for molybdenum on the 100 plane of Al_2O_3 was 3.95 Å in the structure based on Peri's model and 4.6 and 5.6 Å in those based on our model.

An estimate of the molybdena surface of the CoO–MoO_3–Al_2O_3 catalyst may be given. Using 17 Å^2 as the surface area for one MoO_3 molecule we calculated a coverage of 35–40% of the alumina surface with the molybdenum oxide. Lipsch and Schuit (*6*) reported a value of 20% based on the assumption that the thickness of a monolayer is 5 Å. However, if a monolayer of MoO_3 is considered to have the thickness of one layer of oxygen ions a value of 3 Å is more acceptable.

The lower surface areas of the MoO_3–Al_2O_3 catalysts compared to the value of the sintered alumina (Table 2) will certainly be due to the decrease of the mean pore diameter from 60 to 54 Å. A decrease in surface area of about 15 m^2/g may be expected.

The adsorption of excess molybdenum oxide in the first part of the alumina bed is due to the formation of an aluminum molybdate as could be shown by X-ray analysis. The position of the lines of the spectrum were identical with those reported for $Al_2O_3 \cdot 3MoO_3$ (*15*).

TABLE 5
SURFACE AREAS FOR ONE MoO_3 MOLECULE ON THE DIFFERENT PLANES OF ALUMINA (Å^2) CALCULATED FROM OUR MODEL AND THAT USED BY PERI (*17*)

	No. of oxygen atoms/100 Å^2	Mo	
		Octahedral	Tetrahedral
100 plane (Peri)	12.8	Not possible	15.6
100 plane	12.8	Not possible	15.6
110 plane (α)	9.1	22.0	Not possible
110 plane (β)	9.1	22.0	22.0
111 plane (α)	14.8	26.6	Not possible
111 plane (β)	14.8	26.6	26.6

The total weight of excess MoO_3 given in Table 1 was found to be related with the reaction conditions:

$$\text{excess } MoO_3 = \text{const.} \times P_{MoO_2(OH)_2} \times MoO_3 \text{ monolayer present} \times t,$$

where t = time of preparation. This correlation could be derived because dividing the weight of excess MoO_3 by the time, $P_{MoO_2(OH)_2}$ and the weight of water transported, yielded constant values (within 15%) for Expts 2, 3, 5 and 6. The amount of water transported is proportional to the total area of MoO_3 monolayer formed as far as experiments at the same temperature are concerned. The value for Expt 4 was 25% lower, possible due to insufficient saturation of air with molybdenum oxide. No information can be given yet about the influence of the rate of diffusion of aluminum ions into the MoO_3 monolayer on the rate of formation of the aluminum molybdate.

Catalyst Preparation from the Liquid Phase

The ammonium molybdate concentration was found to have little effect on the amount of molybdenum adsorbed on the alumina (Table 3). Figure 2 still shows an increase of the weight of molybdenum oxide adsorbed, when ammonium molybdate was already found in rather high concentration in the effluent. This indicates that the adsorption process is slow. We cannot discriminate whether this is due to the slow transport of poly-ions to the alumina surface or the slow formation or rearrangement of the poly-ions on the alumina surface.

The only variable which had an important effect on the molybdenum content was the pH, as shown in Fig. 3. This may be expected because the mean size of polymolybdate ions is a function of the pH.

Calculations of the surface area occupied by one MoO_3 molecule yielded values higher than 20 Å^2, compared with 17 Å^2 obtained with the preparation from the gas phase. This indicates that the molybdenum content per square meter of Al_2O_3 is less for the preparation in the liquid phase. The same conclusion applies to both Al_2O_3-K and

Al_2O_3-D. This difference may be due to the higher amount of oxygen ions or hydroxyl ions per molybdenum ion for the molybdenum adsorbed from the liquid phase. (The same reason was suggested for the effect of the pH shown in Fig. 3.)

Catalytic Activity of the Catalysts

From the reaction rate constants of the cyclohexane dehydrogenation (Table 4) it can be concluded that the catalyst with the highest amount of molybdenum oxide was most active. The dehydrogenation activity per gram molybdenum oxide is practically constant. The somewhat lower value for the commercial desulfurization catalyst can be due to the better spreading out of the molybdenum oxide in the MoO_3–Al_2O_3 catalysts. We have no explanation of the high isomerization and cracking activity of the cobalt-free catalysts. It is important that the monolayer catalysts prepared according to the two different methods showed the same catalytic behavior. The catalyst prepared from the gas phase showed a higher cracking activity but the same dehydrogenation activity. An indication of equal properties of the MoO_3–Al_2O_3 catalyst prepared from the gas phase and from the liquid phase was also found in the adsorption of benzene at 200°C. [The method used is described in paper II of this series (*18*).] The number of moles per square meter of catalyst was about the same for both catalysts and more than 10 times the value obtained for the alumina.

An interesting point is the low dehydrogenation activity and rather high isomerization activity of the molybdenum in the 6.7% MoO_3–Al_2O_3 catalyst. This indicates that the molybdenum left after extraction will have other catalytic properties.

The conversion of pyridine was studied on the molybdena–alumina catalyst to find out whether the catalyst has the same activity as the cobalt promoted molybdena–alumina catalyst. Figure 4a and b show that the activity and selectivity pattern for both catalysts are the same. In fact the catalytic activity per unit weight of molybdenum oxide is lower for the catalyst without cobalt (nearly a factor of 2). This is in contrast to the results of the cyclohexane experiments. The difference may be due to a higher activity decline of the molybdena–alumina catalyst especially during the first hours of the high pressure experiments. It is important that both catalysts have the same general behavior and that the results obtained for both catalysts can be compared.

Structure of the MoO_3–Al_2O_3 Catalyst

The fact that the molybdenum only partly dissolves during the extraction of the catalyst indicates that the *monolayer* MoO_3 is present in two forms; one of the two is strongly bonded to the alumina.

If the catalyst contains a high amount of molybdenum oxide, the molybdenum may also be present as molybdenum trioxide and as an aluminum molybdate. This could be concluded from the X-ray spectra of the catalysts of Ishii and Matsuura (*10*) and from spectra we obtained of catalysts prepared according to the normal impregnation method. In contrast with these authors we observed that both types of molybdenum dissolved in ammonia (Ishii and Matsuura prepared their catalysts by coprecipitation); hence, the "combined" form of molybdenum (*8, 10*) may not be the aluminum molybdate.

From these results, our activity tests (Table 4) and the linear relation between catalytic activity and molybdenum content of the MoO_3–Al_2O_3 (*5*) a model of the catalysts prepared according to the normal impregnation method may be suggested. This catalyst may contain molybdenum present as MoO_3, an aluminum molybdate and molybdenum well spread out over the surface. The amount of MoO_3 and aluminum molybdate may be low; it depends on the method of impregnation and the amount impregnated. The molybdenum, well spread out over the surface, will have a heterogeneous character in respect to chemisorption and catalytic properties.

CONCLUSIONS

1. A MoO_3–Al_2O_3 catalyst with a monolayer of molybdenum oxide on the alumina was prepared by adsorption of molybdenum oxide from the gas phase on the alumina. The surface occupied by one molecule of molybdenum trioxide for this catalyst was 17 Å².

At high temperatures and relative high pressures of $MoO_2(OH)_2$ an aluminum molybdate ($Al_2O_3 \cdot 3MoO_3$) was formed.

2. Preparation of a monolayer catalyst was also possible by adsorption of molybdate poly-ions from aqueous solutions. The pH has an important effect on the adsorption equilibrium. The surface occupied by one molybdenum trioxide molecule was 20–25 Å² in this case.

3. Pulse experiments with cyclohexane showed a correlation between dehydrogenation activity of the molybdenum-containing catalyst and their molybdenum content. The cobalt-free catalysts showed a relatively high cracking activity.

4. The conversion of pyridine at high pressures of hydrogen showed that the $CoO-MoO_3-Al_2O_3$ and the $MoO_3-Al_2O_3$ catalyst have the same activity and selectivity pattern.

5. The $MoO_3-Al_2O_3$ catalyst prepared according to the normal impregnation method may contain molybdenum present for a small part as MoO_3 and an aluminum molybdate, besides molybdenum present as a monolayer on the surface. The molybdenum present as a monolayer will have a heterogeneous character.

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