Monolayer- and Crystal-Type MoO_3 Catalysts: Their Catalytic Properties in Relation to Their Surface Structures

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Various MoO_3 catalysts have been prepared by means of adsorption of molybdenum on supports from molybdate solutions or from the gas phase. Complete monomolecular layers of Mo^{6+} oxide can be prepared on the carriers Al_2O_3, Cr_2O_3, TiO_2, CeO_2, and ZrO_2, whereas on SiO_2 crystallites of MoO_3 are formed. Reduction experiments show that the higher valencies of Mo are stabilized in the case of a monomolecular layer. Alcohol dehydration, pentene hydrogenation, and poisoning of these reactions with pyridine reveal that MoO_2 present as a monolayer is less acidic than crystalline MoO_2. On the complete monolayer catalysts investigated, mostly more than 70% of the dehydration and hydrogenation activities can be correlated with sites showing a relatively high acidity which are equivalent to 10–20% of the Mo content. The CO oxidation rates on the oxidized catalysts are antiparallel to those of the reactions on the reduced ones mentioned above; relatively basic sites preferentially chemisorb CO. The conclusion is that the activity pattern of the catalysts is a function of the acidity of the supports. It is suggested that Mo^{5+} ions contribute to the formation of the active acid sites after reduction with hydrogen.

INTRODUCTION

In addition to the experimental results of Russell and Stokes (1), many other facts recently reported point to the existence of a monomolecular layer of (reduced) molybdenum oxide on alumina (2–8). Sonnemans and Mars (5) showed that complete monolayers of MoO_3 on alumina may be prepared by adsorption either of $MoO_2(OH)_2$ from the gas phase or of polymolybdate ions from aqueous solutions. This completeness was proved by means of infrared transmission spectroscopy (7).

Several chemical and catalytic properties of the (complete) monolayer MoO_3–Al_2O_3 catalyst have been examined. It was found that MoO_3 on alumina is reduced much less easily than pure (i.e., "bulk") MoO_3 (4, 9–11). The support "stabilizes" the higher Mo valencies so that reduction with hydrogen for 16 hr at 450°C yields a mean valence not lower than 4.1 (11), provided a complete MoO_3 monolayer was present originally.

Also some experiments have been reported regarding the number and the nature of the sites active for (de)hydrogenation of aromatic and olefinic molecules (12, 13). Only a small fraction of the reduced molybdenum ions on alumina were found to show (Lewis) acidity and to be active (11, 12). These and other phenomena induced us to suggest that Mo^{5+} ions are taking part in the sites active for (de)hydrogenation reactions (11).

Recently, the preparation of approximately complete Mo^{6+} oxide monolayers was described on supports other than alumina, i.e., on Cr_2O_3, TiO_2, CeO_2, and ZrO_2 (8). The proof of the presence of a monolayer was based on several criteria. A model derived from simple electrostatics was used to describe the thermal stabilities of the monolayer catalysts and the affinities for salt formation. It was found that MoO_3 on SiO_2 behaves chemically like pure MoO_3

so that this does not form a real monolayer (or a two-dimensional salt), but rather separate crystallites on the SiO_2, or perhaps a monolayer interacting only very slightly with the support (8, 10). It was also concluded that the monolayers did not seem to be destroyed by reduction.

In this paper, the influence of several supports on the catalytic and chemical properties of the molybdenum oxide is reviewed for some reactions. Especially the properties of the complete monolayer (two-dimensional salt) type have been studied because here the active site is liganded not only by neighboring Mo oxide units but also by carrier cations. The catalytic reactions used are: the dehydration of 2-propanol, the hydrogenation of cis-2-pentene, and the oxidation of carbon monoxide. For comparison, the same reactions have been studied on molybdenum oxide itself, both pure and on SiO_2, and on some of the pure supports.

The nature of the active sites is discussed in terms of acidities and Mo valencies on the basis of the results of the catalytic and poisoning experiments.

MATERIALS AND METHODS

Preparation of the catalysts. The preparation of the catalysts took place as described previously (5, 8, 10).

Catalytic activities. The activities of the catalysts were measured either by means of continuous flow experiments or by the pulse method (5, 8). The former method was used for the oxidation of CO. There, the total surface area of the catalysts used varied between 10 and 60 m^2. The gas flow rate was 3.5 liter hr^{-1} (STP), and the partial pressures of CO and O_2 were 0.16–0.50 atm, whereas He was used as an inert gas. CO_2 was determined by means of a semicontinuous titration technique in a nonaqueous solution (14). The determination of CO_2 was accurate within ±5%.

The conversion of 2-propanol and of pentene was carried out in a pulse reactor (8).

Hydrogen was used as the carrier gas (3.5 liter hr^{-1}, STP). The amount of catalyst was such that its surface area was 12 m^2; the quantity of reagent injected varied from 5 to 15 μl. Gas chromatographic analysis completed the experiments. For the analysis of products from the decomposition of 2-propanol a 20% Carbowax 600 Chromosorb W, acid-washed, 60- to 80-mesh column with a length of 1.5 m and a 0.25-in. diameter was used. The column temperature was 80°C. In the case of pentene hydrogenation the column had a length of 4 m and was filled with 20% didecylphthalate in Chromosorb W.A.W. of 60–80 mesh. The temperature was 55°C.

Reduction and valence measurements. The reduction and valence measurements were performed as described in detail previously (8, 10, 11).

During the reduction the temperature was raised from 20°C to 330–450°C in at least 4 hr because otherwise local overheating of the catalyst particles may take place, especially when pure MoO_3 is reduced (see later).

The titration method used for determining the Mo valence is based on the reoxidation *in situ* of the Mo ions by means of $NaIO_4$ in solution. The IO_3^- ions formed are determined by titration with thiosulfate.

RESULTS

1. Valence Measurements

It turns out that monolayer MoO_3 is far less easily reducible than pure MoO_3 and MoO_3 on SiO_2 as shown in Table I. These results mean that the higher Mo valencies are stabilized not only by alumina, but also by the other supports (except for SiO_2). This also means that the support must interact very intimately with the molybdenum ions. For further details, see (10).

2. Catalytic Activities

After reduction with hydrogen to an average valence of 4 (Table I) the catalytic activi-

TABLE I

Temperatures Needed for Reaching an Average Mo
Valence of 4 after Reduction for 16 hr with Hydrogen
($P = 1$ atm)

Catalyst	Temperature of reduction (°C)
MoO_3-TiO_2	450
MoO_3-CeO_2	400
$MoO_3-Al_2O_3$	450
MoO_3-ZrO_2	430
MoO_3-SiO_2	330
MoO_3	330

ties for the dehydration of 2-propanol and
the hydrogenation of cis-2-pentene were
studied by pulse experiments. A more de-
tailed description of the decomposition of
2-propanol is found elsewhere (8). The re-
sults on the dehydration (following half-
order kinetics) are shown in Figs. 1 and 2. It
is apparent that the activities of the reduced
monolayer catalysts are higher than those of
the (reduced) carriers and are much lower
than that of MoO_2. The activity of ZrO_2 is

FIG. 2. The activities for the dehydration of 2-
propanol at 250°C vs those for the oxidation of carbon
monoxide at 350°C. Dimensions of $k_{CO\ ox}$: liters hr^{-1}
(m^{-2} of catalyst).

about zero, because this catalyst adsorbs
water very strongly; thus the alcohol chemi-
sorption is presumably hindered. Also SiO_2
shows no activity, whereas the activities of
MoO_2 and of MoO_2-SiO_2 are not constant.

For the hydrogenation of cis-2-pentene,
pulse experiments have also been performed
at 250°C. The catalysts and the carriers were
prereduced in the same manner as in the
case of the 2-propanol dehydration. The ex-
periments show that the reaction at a hydro-
gen pressure of 1 atm is best described by
first-order kinetics with respect to the pen-
tene pressure, ln $(P^0_{pentene}/P_{pentene})$ being
practically constant for every $P^0_{pentene}$. It
was found that on reduced monolayer mo-
lybdena–carrier catalysts pentane is the
only product. If, however, bulk MoO_2 or
MoO_2 on SiO_2 is the catalyst, isomeriza-
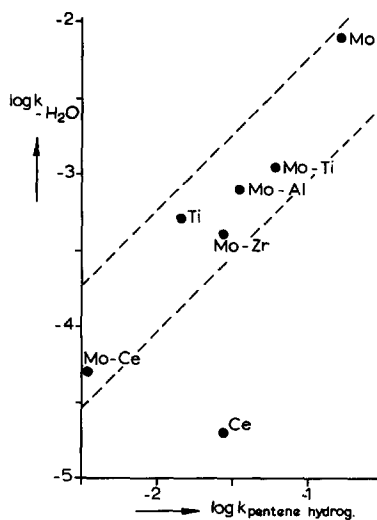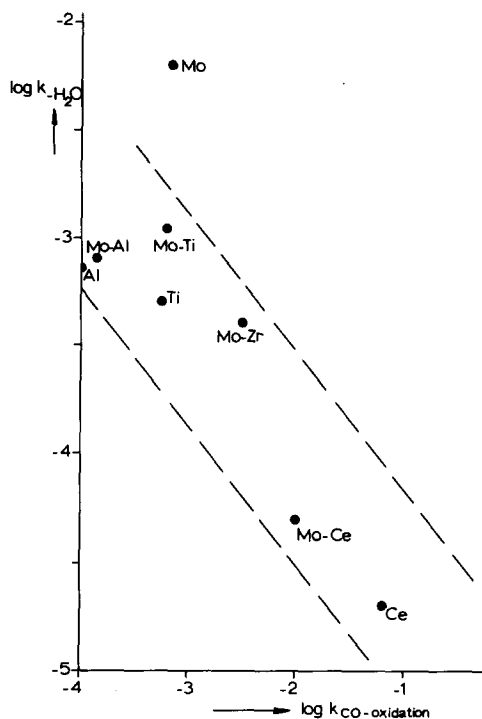tion, polymerization, and cracking prod-

FIG. 1. The activities, found by pulse experiments,
for the dehydration of 2-propanol (k_{-H_2O}) vs those for
the hydrogenation of cis-2-pentene (both at 250°C).
k_{-H_2O} is given in mole$^{1/2}$ time^{-1} m^{-2} (8), $k_{pentene\ hydrog.}$ in
liters hr^{-1} (m^{-2} of catalyst).

ucts, as well as pentene, are formed. These products indicate the presence of very strongly acidic sites. Moreover, a decreasing activity is noted in the case of both MoO_2 and MoO_2-SiO_2, possibly due to fouling.

The hydrogenation activities of the supports themselves are found to be lower than those of the corresponding monolayer catalysts (except for CeO_2), or even undetectable (in the case of Al_2O_3, SiO_2, and ZrO_2). The reaction rate constants of the hydrogenation of pentene are plotted in Fig. 1 against those of the dehydration of 2-propanol.

As the *oxidation of carbon monoxide* is very exothermic, the following measure was taken to avoid any adverse thermal effect during the oxidation process. A gas mixture, containing about 33% of CO, was passed through the system during the warming up of the reactor until a temperature was reached at which a conversion of not more than 5% was achieved. By varying the P_{CO}, the P_{O_2}, and the temperature, the reaction order, the rate constants, and the energies of activation were determined. In Fig. 2 the activities at 350°C, found either directly or by using the Arrhenius plots, are shown against those for the dehydration of 2-propanol of the corresponding reduced catalysts at 250°C. They are all characterized by a zero order with respect to the oxygen partial pressure and a first order in P_{CO}.

3. Poisoning Experiments

In order to obtain information about the number and the nature (i.e., the acid strength; see later) of the sites active for the hydrogenation of pentene and the dehydration of 2-propanol, the following experiments were carried out. Small quantities of pyridine (corresponding to about 2% of the Mo oxide molecules on the catalyst surface) were successively injected in a pulse reactor, containing a catalyst loading corresponding to a surface area of 12–24 m², at 250°C. Each pyridine pulse was followed after a short
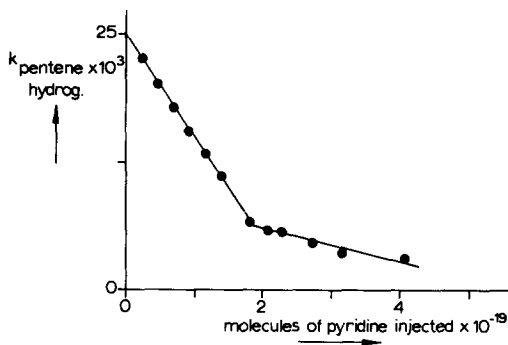

FIG. 3. The specific rate constant of the hydrogenation of *cis*-2-pentene at 250°C, as a function of the number of pyridine molecules injected. Catalyst, Mo^{4+}–oxide–ZrO_2; surface area, 24 m².

time by a pulse of 8 μl of pentene. The first-order rate constant was plotted against the total amount of pyridine injected. In Fig. 3 a typical example of the results is given. For about half an hour after each pyridine pulse it was checked whether the activity decrease was constant or not, i.e., if all pyridine molecules were irreversibly adsorbed. This proved to be about the case until a "break" in the titration curve was obtained. It took a day before the activity was about half restored. Raising the temperature to 350°C, however, resulted in a complete restoration after 16 hr.

After the "break" the activity could largely be restored by purging with the carrier gas at the reaction temperature for a short period of time.

DISCUSSION

On the Possibilities of Explaining the Relative Activities of Monolayer Catalysts

The results of the dehydration of 2-propanol and the hydrogenation of *cis*-2-pentene may be discussed in the light of the following facts. Many investigators in this field consider acidic sites to be responsible for the dehydration of alcohols (15–18) as is also substantiated by our poisoning experiments. Dehydration is also correlated with the *z/r* values of the cations of various

oxides, acting as the catalysts, where z and r are their charge and radius (in Å), respectively (19–21). Moreover, other authors connect the acidity of oxides with these z/r values (22, 23) in such a way that a higher value of z/r corresponds to a higher acidity of the oxide. For the catalysts we used, the activity for the dehydration of 2-propanol tends to increase with an increasing z/r value of the cations if pure MoO_2 and the carriers alone are the catalysts (see Fig. 4). If it is taken into account that under the reducing circumstances Ti^{4+} may partially be converted into Ti^{3+} (24), Mo^{6+} into Mo^{5+} (11), and Ce^{4+} into Ce^{3+} (as has been found in our laboratory), it may be assumed that the differences between the z/r values of the carrier cations on the one hand and that of the Mo ions on the other are large. This means that the possible differences between their acidities are large too.

On inspection of the activities for dehydration of the molybdenum oxide monolayer catalysts it is striking that these can also be correlated with the z/r value of the *carrier cations* (Fig. 4): If z/r of the carrier cations increases, the activity for dehydration tends to increase also. A comparison of the activities of pure and supported MoO_2 shows that the support lowers the MoO_2 acidity. The

activity of Mo^{4+} oxide on ceria, for example, is less than that of Mo^{4+} oxide on alumina, or on Mo^{4+} oxide itself, the latter being the best catalyst.

It could be thought that the "effective" z/r values, i.e., the effective charge of the Mo ions, their effective radius, or both, are affected by the carrier cations owing to polarizing influences. However, in the case of molybdena–ceria, for example, the difference between the z/r values is too large for a satisfactory explanation in the above-mentioned terms. Other features, not quite understood as yet, must in addition play an important role.

The hydrogenation of alkenes can be discussed in the same manner, by assuming that, here also, acidic sites are involved in the catalytic activity (12, 25, 26) as is supported by our poisoning experiments. In Fig. 1, a parallelism is shown between the activity trend of monolayer catalysts for dehydration of 2-propanol and that for hydrogenation of alkenes, the slope of the dashed lines being about unity. Thus, perhaps acidic sites having the same origin are responsible for *both* reactions, as is also suggested by the results of the poisoning experiments (see later). During dehydration reactions these sites may be covered by H_2O. Poisoning with pyridine reveals indeed that the latter reagent is more readily desorbed when water or alcohol are present in the system.

In contrast with the experiments on the dehydration of 2-propanol and the hydrogenation of pentene, the experiments on the oxidation of CO reveal that the sequence of the catalysts with increasing activities is about the reverse of that for the two foregoing reactions (Fig. 2). The oxidation of CO on oxidic catalysts in the presence of gaseous oxygen is enhanced if (weak) basic sites are available (26–29). It is concluded that carbon monoxide is adsorbed on O^- or O^{2-} species or at least on sites, such as metal ion vacancies, in which those species are involved (26, 29). In the case of our catalysts
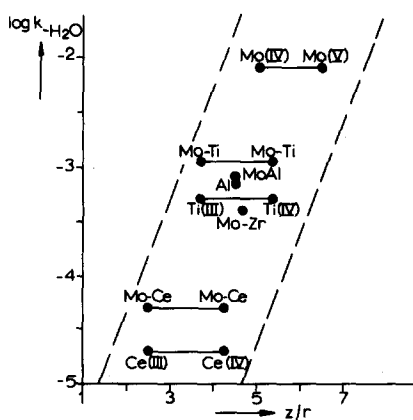

FIG. 4. The activities for the dehydration of 2-propanol on the various catalysts vs the ratio z/r of the cations of the carriers and of Mo^{4+} and Mo^{5+}, respectively.

consisting of more or less basic carriers and of MoO_3, the basic properties of MoO_3 are apparently influenced by the carriers. The increasing trend in the CO oxidation activity of the monolayer catalysts shows a parallelism with the decreasing z/r values of the supports. Therefore, the antiparallelism in Fig. 2 reflects the involvement of different types of sites, acidic ones (Lewis and/or Brønsted) with the hydrogenation and dehydration reactions and basic ones with the oxidation of carbon monoxide.

Poisoning Experiments

The following interesting facts emerge on inspection of Fig. 3. Firstly, the portion of the curve depicting a strongly decreasing activity can be assigned to strongly acidic sites which adsorb pyridine irreversibly. Secondly, the break of the curve implies the presence of weakly acidic sites which adsorb (part of the) pyridine reversibly. It is not yet possible to determine the amount of pyridine needed for a complete suppression of the activity because of a lack of experimental data. Perhaps adsorption measurements by a gravimetric method combined with the results from poisoning experiments could give information on how to extrapolate the first line to the horizontal axis. It is very interesting, however, to have information on that

TABLE II

The Fraction of Strongly Acidic Mo Ions on the Surface of Various Catalysts, Found by Poisoning[a]

Catalyst	Molecules irreversibly adsorbed pyridine/atoms Mo (%)	k_{strong} (%)	k_{weak} (%)
Mo^{4+} oxide–TiO_2	~15	70	30
Mo^{4+} oxide–Al_2O_3	~20	100	—[b]
Mo^{4+} oxide–ZrO_2	~20	76	24
Mo^{4+} oxide–Cr_2O_3	~8	54	46
MoO_2	—	90	10

[a] The fractions of activities, belonging to strong and weak acids, are indicated by k_{strong} and k_{weak}, respectively.

[b] From Refs. (11) and (12).

part of the activities in which strongly acidic sites are involved. This is given in Table II.

It has to be noted that the fraction of sites of strong acidity in connection with the dehydration of 2-propanol has only been measured for Mo^{4+} oxide–Al_2O_3 and for Mo^{4+} oxide–TiO_2. This fraction proved to be of the same order of magnitude as those for the hydrogenation of cis-2-pentene.

For all monolayer catalysts investigated the average surface area available for one pyridine molecule at the break in the curve is larger than that reported in the literature (30–32). Moreover, ammonia (having a smaller diameter than pyridine) and pyridine have been found to be adsorbed in equal amounts (33). These facts, coupled with our observation that the pyridine surface area on bulk MoO_2 is about 30 Å^2, i.e., lower than in the case of the other catalysts, indicate that the determination of the strongly acidic sites by the pyridine adsorption method is not affected by steric hindrance.

It turns out that on the monolayer catalysts investigated more than half of the activities for alkene hydrogenation can be correlated with sites with strong acidity. These strong acidities can be ascribed to 10–20% of the total molybdenum content.

The question arises whether the nature of the sites, responsible for hydrogenation, and perhaps also for dehydration activities, can be described in a more specific manner. Previously, it was suggested that Mo^{5+} ions are involved in the sites active for (de)hydrogenation on molybdena–alumina with an average Mo valence of about 4. Their concentration was up to about 20% of the Mo content, as found both from our valence measurements and from the literature (11). This figure has also been established recently by Hall and Lo Jacono, when the average valence of the Mo ions is about 4 (34) and is approximately equal to that found for the strongly acid sites (Table II). From Table I it is seen that reduction to Mo^{4+} with hydrogen seems to proceed with about equal difficulty when Al_2O_3, ZrO_2, CeO_2, and TiO_2

are the supports [see also (10)]. These facts, along with the parallelism found for hydrogenation and dehydration activities on the monolayer catalysts, lead us to suggest that after reduction at 400–450°C on the monolayer molybdenum oxide–carrier catalysts about 10–20% of the molybdenum ions have a valence of 5, and that these ions may play a role in the formation of the sites active for hydrogenation as well as for dehydration.

The Stability of the Monolayer upon Reduction

Finally, some attention has to be paid to the conservation of the monolayer character of the molybdenum oxide after reduction. Recently, it was reported by Parekh and Weller (35) that reduction of a 15% MoO_3–Al_2O_3 catalyst with a surface area of about 170 m^2/g yielded a specific surface area of the MoO_2 fraction which was not more than 30% of the total surface area available. Their method was based upon the chemisorption of oxygen both on monolayer MoO_2 and on pure molybdenum oxide which was also thought to be MoO_2 after reduction with hydrogen at 350°C. They assumed that the chemisorption capacities of both catalysts are equal. From this they concluded that reduction of MoO_3 on Al_2O_3 causes a conversion of monolayer MoO_3 to microcrystals of MoO_2.

Some remarks may be made regarding this conclusion. In the first place higher reduction temperatures cause a lower final average valence of molybdenum as shown also by our own experiments (10) at 350°C, giving an average Mo valence of about 3.5, i.e., lower than 4, when starting from pure (bulk) MoO_3.

In the second place the reduction of pure MoO_3 must be performed very carefully (10) because otherwise local overheating may lead to an even lower Mo valence. This was also shown by Cimino and De Angelis (36). They observed that reduction of bulk MoO_3 at 400°C in a stream of pure hydrogen provides a surface Mo valence near zero.

In the third place Parekh and Weller started with ammonium molybdate, which, as was shown previously (10), leads to a lower final molybdenum valence than when bulk MoO_3 is reduced under the same circumstances.

On this basis we conclude that the oxygen adsorption capacity of their bulk "MoO_2" will probably be higher than that of the monolayer MoO_2, due to its higher degree of reduction. Furthermore they did not start with a complete MoO_3 monolayer, but with about half the maximum coverage (i.e., Θ_{MoO_3} ≈ 0.5) (1, 5, 7, 8), taking into account also that the impregnation technique they used does not only yield monolayer MoO_3, but also microcrystals (4, 37). Thus, Θ_{MoO_2} from this point of view alone could never be larger than about 0.5.

Taking into account both factors (higher degree of reduction and incomplete MoO_3 monolayer) leads us to the conclusion that the monolayer character is conserved during reduction, in accordance with our results, mentioned in Ref. (7). The results presented here also support this view, not only for MoO_3 on alumina, but also on the other supports (except for SiO_2). The differences between monolayer MoO_2–support catalysts, "bulk" MoO_2, and the supports themselves for the various chemical and catalytic properties mentioned in this paper cannot be explained properly if monolayer MoO_3 is converted into crystals of MoO_2.

SUMMARY

1. Monomolecular layers of MoO_3 are not converted into MoO_2 crystals upon careful reduction with hydrogen, but into monolayers of MoO_2.

2. Reduced monomolecular layers of molybdenum oxide on various carriers contain acidic sites active for hydrogenation and dehydration reactions. The activities for these reactions can roughly be correlated with the z/r value of the carrier cations.

3. The basicity of the Mo^{6+} oxide monolayers is also influenced by the carriers. A

higher activity for the oxidation of carbon monoxide is accompanied by lower activities for dehydration and hydrogenation reactions and lower z/r values of the carriers.

4. More than half of the activity for dehydration and for hydrogenation is due to active sites with strong acidity.

5. From analogous behavior in various respects between Mo^{4+} oxide–alumina and other monolayer catalysts it is possible to attribute the strongly acidic sites to the presence of Mo^{5+} ions.

ACKNOWLEDGMENTS

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