REDUCED MOLYBDENUM OXIDE CATALYSTS WITH HIGH SURFACE AREAS. PREPARATION AND ACTIVITES

T. Fransen, P. C. van Berge* and P. Mars

Twente University of Technology, Department of Chemistry,
P.O. Box 217, Enschede, The Netherlands

From solutions of ammonium molybdate this salt was precipitated with acetone. Decomposition in air at 330° C yields MoO_3 with a specific surface area of 17 m^2/g, by means of reduction with hydrogen 4.5, 4 and 3.5 valent oxides may be formed with 30, 50 and 80 m^2/g, respectively. Molybdenum (VI) oxide present as a monomolecular layer on supports is much less readily reduced than unsupported MoO_3. This difference reflects the interaction of Mo ions with ions of the support. The reducibilities of the various catalysts show that Mo(VI) oxides interact far less with SiO_2 than with Al_2O_3, CeO_2 and ZrO_2. This is also reflected in the rates of 2-propanol decomposition on these catalysts, the activities on MoO_x and on MoO_x-$SiO2$ being much higher than on the other catalysts.

Соль молибдата аммония была высаждена из ацетона. Разложение на воздухе при 330°С приводит к образованию MoO_3 с удельной поверхностью 17 м²/г; при восстановлении водородом образуются окислы с валентностью 4, 5, 4 и 3,5, удельная поверзность которых равна 30, 50 и 80 м²/г, соответственно. Окись молибдена (VI), присутствующая в виде мономолекулярного слоя на носителе, восстанавливается гораздо труднее, чем MoO_3 без носителя. Это различие отражает взаимодействие ионов Мо с ионами носителя. Способность к восстановлению различных катализаторов указывает на то, что окислы Мо(VI) взаимодействуют гораздо слабее с SiO_2, чем с Al_2O_3, CeO_2 n ZrO_2. Это отражается на скоростях разложения 2-пропанола в присутствии этих катализаторов. Активность на MoO_x и на MoO_x – SiO_2, намного выше, чем в случае других катализаторов.

*Present address: Rands Afrikaans University, P. O. Box 524, Johannesburg, South Africa

INTRODUCTION

Many investigations have been made concerning the reduction of pure (i. e. unsupported) MoO_3 with hydrogen under various conditions /1-8/. Recently, also the reduction of Mo(VI) oxide on alumina and on silica has been studied. It was concluded that the reduction of Mo(VI) oxide on Al_2O_3 is more difficult because the Mo oxide shows a strong interaction with the support ions /5,8,9,10/.

To achieve a better understanding of the influence of supports on the reduction rates and catalytic activities, we have studied these properties and those of unsupported Mo oxides with known Mo valences and with specific surface areas.

EXPERIMENTAL

1. Preparation of MoO_2

15 g ammonium molybdate was dissolved in 1 l demineralized water at room temperature. Addition of 2 l acetone yields a precipitate, which, after drying at 100^oC for 8 hrs, was found to be dehydrated ammonium molybdate. The compound was pressed into tablets at 0.5 ton/cm^2 and crushed to particles with diameters between 0.3 and 0.6 mm. Finally, decomposition in air at 330° for 24 hrs yielded MoO_3 particles with a specific surface area of about 17 m^2/g. The reason for pressing the molybdate instead of the final product is the difficulty of pressing MoO_3 into tablets.

2. Reduction and measurement of valences and surface areas

Reduced Mo oxides were prepared from MoO_3 and also directly from ammonium molybdate by heating it in a stream of hydrogen (50 cm^3 NTP min^{-1}). To avoid overheating of the particles the temperature was raised from 20 to 320-450°C in at least 4 hours.

The reactor had an internal diameter of about 10 mm and contained about 50 mg MoO_3. Reduction was continued for a period of 16 hrs after attainment of the desired temperature. No change in product properties was observed when starting with 10% hydrogen in nitrogen and raising the hydrogen content up to 100% over 4 hrs at the desired temperature.

The average Mo valence was determined by means of the titration method of Bourret et al. /11/. Basically, the reduced molybdenum oxides are dissolved upon stirring with a solution of $NaIO_4$, providing the following oxidation:

$$Mo^{(6-x)+} + xH^+ + \frac{x}{2} IO_4^- \longrightarrow Mo^{6+} + \frac{x}{2} H_2O + \frac{x}{2} IO_3^-$$
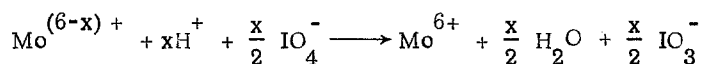
Stirring took place till the color due to reduced Mo ions vanished. The IO_3^- ions formed were determined by the thiosulfate titration method.

The titration vessel was already connected with the reactor during the reduction, because the reduced samples are highly oxidizable, sometimes even pyrophoric. The equiment could be handled in such a way that after reduction and evacuation the catalyst could be brought into the titration vessel quantitatively by washing with the oxidizing reagent solution, which had been introduced via a stopcock.

Blank runs as well as determinations of the Mo valence in MoO_2 with a surface area lower than 1 m^2/g were carried out. The valence measured in the latter case was between 3.99 and 4.08.

Argon adsorption measurements were performed at $-196\,^{\circ}C$ in the reduction vessel itself. Prior to this, evacuation was carried out at about $300\,^{\circ}C$ for 3 hrs to remove adsorbed gases. The surface areas were calculated applying the BET equation.

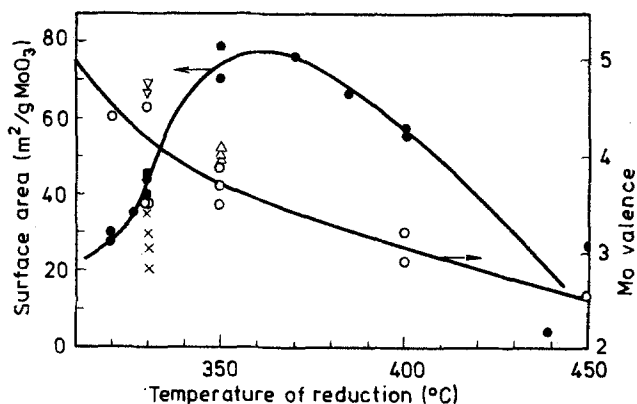Bulk MoO_2 was supplied by K. & K. Laboratories Inc.; the ammonium molybdate was a Merck product.

5

Fig. 1. Molybdenum valence and specific surface area after reduction with hydrogen for 16 hrs at different temperatures. o and ●: starting from MoO_3; × and ▽ : starting from ammonium molybdate; △ : starting from MoO_3 with water (10 Torr) in the hydrogen feed

RESULTS AND DISCUSSION

Reduction of unsupported Mo oxide

Figure 1 shows the surface area and the valence of Mo after reduction of MoO_3 at various temperatures. Results obtained from direct reduction of ammonium molybdate are also included. An increase of reduction in the low temperature region is accompanied by an increase of surface area due to pore creation by removal of oxygen. Reduction to a valence lower that 3.5 diminishes the surface area strongly. This is in contrast with the findings by Hillis, Kemball and Roberts /12/ for the reduction of MoO_2 (~1 m^2/g).

The combined decomposition and reduction of ammonium molybdate at 330° C lead to a lower valence and a somewhat larger surface area than reduction of pure MoC_3 at the same temperature. This must be due to stronger reduction by ammonia and not to extra pore creation by the ammonia molecules themselves: pure MoO_3 yields about the same surface area and valence upon reduction at 390° C.

448

Other investigators reported somewhat higher /1/ or lower /2/ valences after reduction than we observed. This fact may be due to the use of non-porous, i.e. "bulk" MoO_3 and to the influence of diffusion and heat transfer limitations. Cimino, using the ESCA technique, has found that the Mo valence at the surface is considerably lower than in the bulk /5/. If this difference is present in our case, it will be much smaller because of the high specific surface areas (small crystallite sizes) of our materials and because of the long reduction time used (16 hrs).

Reduction of supported catalysts

As already described elsewhere /8-10/, the reducibility of Mo(VI) oxide on Al_2O_3 is far less pronounced than that of pure MoO_3 (Table 1). This applies also when CeO_2 and ZrO_2 are used as support. These catalysts have been prepared by means of adsorption of $MoO_2 (OH)_2$ from the gas phase or of molybdate ions from solution (pH = 1) /13/. The Mo(VI) oxide on these supports consists of a complete monomolecular layer of Mo oxide units, forming a two-dimensional salt /14/. The results show that the higher valences are stabilized.

Some authors /9,15/ suggest that in case of Mo(VI) ox-Al_2O_3 water (e.g. produced during reduction and being desorbed slowly from the alumina) may poison the reduction reaction. Treatment with dry hydrogen at 450^oC for two weeks, causing water removal, still yields Mo with a valence not lower than four /10/.

Moreover, we found that the presence of water vapor (p_{H_2O} = 10 Torr) during reduction does not influence the final result drastically, neither for the Mo(VI)ox-Al_2O_3 catalyst at 450^oC, nor for pure MoO_3 at 350^oC (see Fig. 1). We may therefore conclude that it is the strong interaction of Mo ions with the support that causes stabilization of the higher valences.

The behavior of silica is quite different from that of the other supports. In this case adsorption of molybdate ions from acid solutions is not effective for the

Table 1
Temperatures needed for reaching a Mo valence of 4 in 16 hrs,
rate constants per surface area for 2-propanol dehydration at $250^{\circ}C$

Catalyst	Reduction temperature ($^{\circ}C$)	Surface area (m^2/g)		k^*
		support	catalyst	
$Mo^{4+}ox-Al_2O_3$	450	72	72	0.8
$Mo^{4+}ox-ZrO_2$	450	130	120	0.7
$Mo^{4+}ox-CeO_2$	400	70	58	0.05
MoO_2	330	-	50	7.0^{**}
$Mo^{4+}ox-SiO_2$ (gas phase prepared)	330	300	24-31	2.2^{**}

*Half-order reaction constant in arbitrary units
**The activity is not constant

formation of a complete Mo(VI) oxide monolayer. The silica surface is also
incompletely covered with Mo(VI) oxide via adsorption from the gas phase. During
sintering, caused by the preparation conditions, the covered part retains its
surface area and a complete monolayer is formed. Valence measurements reveal
that this complete monolayer is reduced as easily as if it were pure MoO_3 (Table
1). This points to a weaker interaction of the Mo(VI) oxide with SiO_2 than with
other supports. This anomalous behavior of MoO_3-SiO_2 has also been established
by other authors on the basis of rather qualitative investigations /5/. An explanation
for the differences in the degree of interaction between monolayer and carrier
has been given in terms of electrostatics /14/.

Catalytic activities

The catalytic activities of the various catalysts for 2-propanol dehydration
(Table 1) reflect the differences in interaction between Mo oxide and the supports.

450

The activities of MoO_2 and of MoO_2-SiO_2 are comparable but much larger than those of the other catalysts. Moreover, they are not stable, possibly owing to poisoning of strongly acidic sites. Obviously the Mo(VI) oxide on silica is reduced to MoO_2 crystallites. This again shows the relatively weak interaction of Mo oxide with silica.

ACKNOWLEDGEMENT

REFERENCES

1. J. von Destinon-Forstmann: Can. Metallurgical Quart., 4, 1 (1965).

2. D. T. Hawkins, W. L. Worrell: Metall. Trans., 1, 271 (1970).

3. C. Vassilev, T. Nikolov and M. Chimbulev: Trans. Inst. Mining and Metallurgy, 77, C 36 (1968).

4. H. Kay, B. G. Langston: J. Metals, 877 (1964).

5. A. Cimino, B. A. De Angelis: J. Catal., 36, 11 (1975).

6. O. Bertrand, L. C. Dufour: Compt. Rend., C., 278, 315 (1974).

7. A. Sárdi: Acta Chim. (Budapest), 39, 145 (1963).

8. F. E. Massoth: J. Catal., 30, 204 (1973).

9. P. Sondag, Do Quang Kim, F. Marion: Compt. Rend., C, 259, 4704 (1964).

10. T. Fransen, O. van der Meer, P. Mars: J. Phys. Chem. (In press).

11. P. Bourret, J. Lecuire, C. Weis: Chim. Anal., 52, 48 (1970).

12. M. R. Hillis, C. Kemball, M. W. Roberts: Trans. Faraday Soc., 62, 3570 (1966).

13. J. Sonnemans, P. Mars: J. Catal., <u>31</u>, 209 (1973).

14. T. Fransen, P. C. van Berge, P. Mars in: "Preparation of Catalysts", Proc. Int. Symp., Brussels, 1975, p. 405. Elsevier, Amsterdam 1976.

15. P. Ratnasamy, A. V. Ramaswamy, K. Banerjee, D. K. Sharma, N. Ray: J. Catal., <u>38</u>, 19 (1975).