JOURNAL OF CATALYSIS **131**, 127–132 (1991)

Exfoliated MoS_2 for Stabilization and Activation of Pt Oxidation Catalysts

BIJAN K. MIREMADI AND S. ROY MORRISON

Energy Research Institute, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

Received May 2, 1990; revised December 4, 1990

The use of a monolayer of Mo ions to stabilize and help activate Pt/Al_2O_3 catalysts is investigated. The monolayer of Mo is deposited using exfoliated MoS_2 single molecular layers, which deposit on the alumina support as a single-layer coating. It is found that the presence of the resulting monolayer of molybdenum stabilizes the Pt against sintering to at least 800°C. It is also found that the initial activity for oxidation is enhanced substantially. It is concluded that the Mo monolayer also induces dispersion of the Pt.

INTRODUCTION

In several earlier articles and patents (*1–7*) we have discussed the exfoliation of MoS_2 and other disulfides (*8, 9*) into single layers (*2–6*) and the use of these layers to provide catalyst/promoter/support configurations (*3–5, 9*). As MoS_2 itself is an important catalyst for hydrodesulfurization, and has been shown sulfur-resistant in methanation catalysis, our first efforts (*3*) were on studies of how to use the exfoliated MoS_2 as the catalyst. However, another use for the single layers is as a "glue" to attach other catalysts to a support, as was earlier suggested by Yermakov *et al.* (*10*) and later by other researchers (*11, 12*). They found that a pretreatment of an oxide support by molybdenum improved the sintering resistance of a Pt catalyst, suggesting that the Mo bonded well to the support because of its ionic character when an oxide, and bonded well also to the Pt because of *d*-orbital interactions.

Using single-layer MoS_2 we have a much improved deposition method for the molybdenum. Specifically, we show below that the single layers of MoS_2 tend to deposit from suspension onto Al_2O_3 as a single-layer coating. This is expected to provide a better substrate than one where the Mo is deposited in crystallites (using impregnation). The interpretation is as follows: The point of zero charge (pzc) of MoS_2 is between 2 and 3. At about pH 7 we observe an attraction between the MoS_2 single layers that are negatively charged with adsorbed OH^- present on their surfaces (*1*), and are strongly attracted to the alumina which, with its pzc of 7 or 8, has a net positive charge on its surface (*13*). But as illustrated in Fig. 1 and discussed briefly in Ref. (*3*), it only requires one layer of the MoS_2 deposited on the surface of the alumina to give the suspended powder a negative charge repelling further coating by layers of MoS_2. Thus quite accurately (although undoubtedly there will be overlap of layers) we can expect an even monolayer on the powder. By permitting the alumina to settle through a suspension of single layers of MoS_2 or simply by having one monolayer of MoS_2 available to coat the alumina, we can separate and dry the monolayer-covered alumina. This was expected to be a much improved technique over the Yerkamov technique because it will provide a homogeneous "glue" to connect the catalyst to the alumina.

This report presents the results comparing the activity and stability of catalysts with such a "glue" with catalysts prepared otherwise identically but without the exfoliated MoS_2 single layers.

To show the strong interaction between Pt

0021-9517/91 $3.00

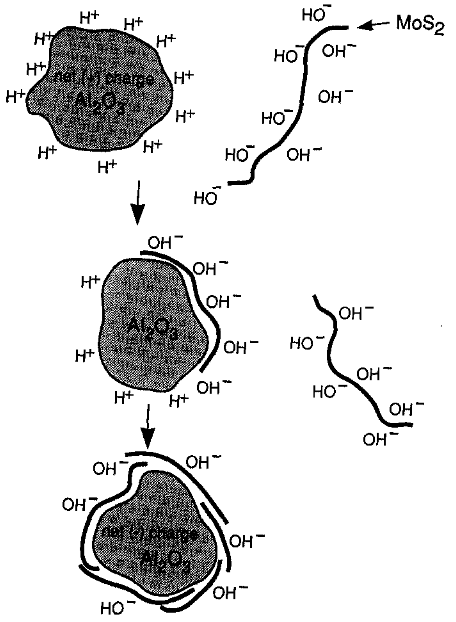

FIG. 1. Coating of a monolayer of MoS_2 on alumina. The positive charge on the alumina at pH 6.8 attracts one monolayer, but the surface charge is then negative, attracting no further MoS_2.

and single-layer MoS_2 which, as discussed below, apparently leads to a high and stable dispersion of the Pt, we have made an "inclusion compound" of Pt in MoS_2. These are compounds where a cation adsorbs on the single layers, causes the restacking of the single layers, and is trapped between the layers (*2*). In the present study the cation is positively charged platinum. The inclusions are monitored by the strong but uniform expansion or contraction of the MoS_2 particles with up to a monolayer of inclusions between the MoS_2 layers.

2. EXPERIMENTAL

2.1 Preparation of Exfoliated MoS_2

As discussed in detail elsewhere (*1, 2*) powdered MoS_2 (source: 98% powder from Johnson Matthey) is intercalated with lithium by exposure for up to 48 hours to *n*-butyllithium dissolved in hexane. Although the technique is relatively expensive, for research quantities this procedure provides a convenient method of intercalation. After several washes with hexane under an inert atmosphere the powder is collected and dried. The material, which has been shown to have about one Li atom per Mo atom, is then immersed in water with suitable agitation, whereupon the reaction

$$2\ Li + 2\ H_2O \rightarrow 2\ LiOH + H_2$$

generates the gaseous hydrogen that forces the layers apart. They remain apart because at pH greater than about 2 (the pzc for the MoS_2) the surface double layer prevents flocculation. We have made measurements (*14*) similar to electrophoresis measurements on the layers which confirm the negative surface charge. We have also published a series of studies (*2*) showing that the addition of positive charges to the MoS_2 single-layer surfaces induces flocculation, further indication that the negative surface charge (and the resulting double layer) maintains the single layers in suspension.

2.2 Deposition of Monolayer MoS_2 on Al_2O_3

It is easily calculated that about 0.3 g single-layer MoS_2 should coat 90 m^2 (1 g) of the Alon γ-alumina. To test the estimate, 1 g γ-alumina was added to aqueous suspensions containing an estimated 0.1, 0.2, 0.4, and 0.5 g (±30%) of single-layer MoS_2 at pH 7. When the alumina settled, the MoS_2 suspension was cleared for the first two samples, while residual MoS_2 remained suspended in the second two cases. This simple experiment provided both the evidence that our model, that only one layer should adsorb, is followed, and an empirical value for the amount of MoS_2 we should add to form the monolayer.

For the catalytic study we have deposited exfoliated MoS_2 onto the Alon γ-alumina of surface area 90 m^2/g and onto a "fractured" alumina obtained by lithiating a porous alumina (Alcan type AA-101) and fracturing it in water (*15*). This treatment of porous alumina leads to platelets the order of 0.1 μm in width and less than 100 Å in thickness (as estimated from surface area measurements and SEM observations).

In the Alon alumina case the procedure was as follows: The pH of the MoS_2 suspension was adjusted to pH 6.8 by addition of HNO_3. A value for the total area of the MoS_2 was estimated (some is lost during decanting). Enough Al_2O_3 to provide approximately the same surface area (0.2 g MoS_2/g Al_2O_3) is prepared in a suspension also at pH 6.8 and mixed with the MoS_2 suspension. As MoS_2 single layers are attracted to the alumina parrticles they settle and the MoS_2 suspension clears. The liquor was decanted and the sample washed several times to remove the LiOH.

After coating with the exfoliated molybdenum sulfide, the coated alumina support was dried and heated to about 200°C in air. It was hoped that this treatment would improve the adhesion of the MoS_2 single layers to the Al_2O_3 so there would be little tendency to float off during the subsequent slurry preparation.

In the preparation of the fractured alumina catalyst the porous alumina powder is mixed with powdered MoS_2 and both are immersed in the hexane solution of *n*-butyllithium. The weight ratio of alumina/MoS_2 is 5 : 1. In this case the final aqueous suspension of MoS_2/Al_2O_3 is highly basic. The suspension clears (the particles flocculate) when the pH is lowered to 7. In this case the reactions can be very complex (*15*) during the lithiation step and during the immersion in water. The reactions are still under investigation. The reason for reporting results using this material is that the platelet particle shape is considered the best for obtaining a high area support for catalysts based on exfoliated MoS_2. Thus we study the relatively low area Alon alumina to elucidate mechanisms, and we offer results with the fractured alumina to indicate one technique to increase the area of Mo-coated alumina. It has been shown (*15*) that simple porous alumina with a large particle size is not useful as a support for exfoliated MoS_2. We observed that the methanation activity of exfoliated MoS_2 on porous alumina is extremely low, suggesting the reasonable conclusion that the single-layer sheets of MoS_2 simply cover the pores, rather than entering the pores.

The deposition of Pt was carried out using two different methods, precipitation and impregnation. In the precipitation method, as is described in detail in Refs. (*2*, *3*), we have included Pt between the MoS_2 layers in the form of $Pt(OH)^+$ simply by raising the pH of a $PtCl_2$ solution to about 7 and mixing simultaneously the MoS_2 and Al_2O_3 suspensions with pH 7 $PtCl_2$ solution. The resulting mixture clears and MoS_2–Pt–Al_2O_3 flocculates, in a few minutes time. Since the $Pt(OH)_2$ tends to precipitate at about pH 10, we found the final pH, 9.6, was effective in flocculating the MoS_2–alumina platelet suspension.

For Pt impregnation, the support powder was slurried in a 0.2 *M* solution of $PtCl_2$ (2 cc/g of Al_2O_3) attempting again to coat the γ-alumina to 1 monolayer. The powder was dried in air to room temperature. Some blank samples were also prepared for the purpose of comparison.

Oxidation of methane at 350°C was used as the test reaction. The composition of the gas stream was 4% CH_4, 84% Ar, and 12% oxygen, and the flow rate was 20 cc/min. One hundred milligrams of the catalyst in powder form was tested. The yield of CO_2 and of methane was monitored by GC.

2.3 Results

Both the Pt-impregnated and Pt-precipitated catalysts were tested for activity and stability, relative to suitable blanks. For the results of Fig. 2 the catalyst was heat treated ("annealed") in methane at various "sintering" temperatures for 5–10 h, followed by tests of the oxidation activity at 350°C. Each line represents a single catalyst, annealed to successively higher temperatures.

Between anneals, the activity was measured typically at $\frac{1}{2}$–1 h after turning on the oxygen, and then at 2 h and up to 5 h of reaction time. The results showed a constant activity with time (slowly increasing generally by up to 5%) unlike recent results

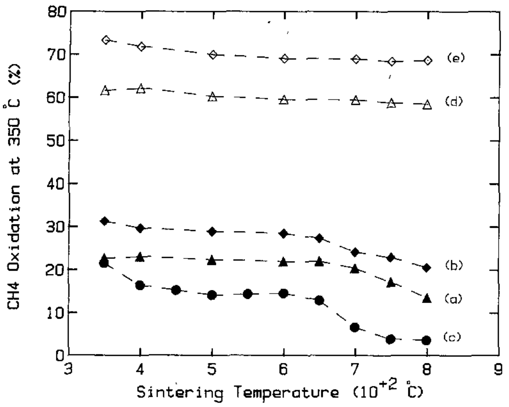

FIG. 2. Oxidation of methane at 350°C by impregnated Pt. Curves a to c are Pt on Al_2O_3. Curves d and e are Pt on Mo-coated Al_2O_3. One hundred milligrams catalyst is used, containing 5% Pt by weight. Curve c shows the results on a commercial catalyst.

(*16, 17*). We conclude there is negligible change in catalyst dispersion at 350°C.

The results in Fig. 2, where the Pt was deposited by impregnation, include measurements on blanks: (a) Pt/γ-alumina (b) Pt/alumina platelets, and (c) a commercial catalyst. A fourth blank, not shown because the activity at 350°C was negligible, was MoS_2 on γ-alumina. The Pt/alumina blanks are to be compared to the Pt/MoS_2/alumina combinations, viz: (d) Pt/MoS_2/γ-alumina, (e) Pt/MoS_2/alumina platelets, and (f) Pt/MoS_2 with no alumina (not shown because of its very poor oxidation activity). The case of Pt/MoS_2/γ-alumina where the MoS_2 was deposited after Pt impregnation of the alumina was studied but the results are not shown because it is almost identical to (d). In Fig. 3 an analogous comparison is made, in this case using precipitated Pt. Among all the above catalysts (d) and (e) showed the highest activity with no decay of activity to 800°C, while the others showed a lower activity per gram of Pt and a lower sintering temperature. Degradation, presumably from sintering, begins at about 650°C, in agreement with the results of others (*18, 19*). Unfortunately with the Mo present, sintering of the Pt could not be followed by gas adsorption because Mo adsorbs CO. A measurement of CO adsorption on a Pt/alumina platelets catalyst (no Mo) was made, before and after heating the catalyst to 800°C for 16 h. The CO adsorption was in the ratio Pt/CO = 1/1 initially, but dropped to Pt/CO = 8/1 after 16 h in methane at 800°C. The Pt/Mo/Al atomic ratios are measured by SEM–EDX before their use as a catalyst.

Figure 4 shows the X-ray powder diffraction pattern (XRD) of samples of inclusion compounds at various Mo/Pt ratios. Figure 4(a) represents the XRD of restacked MoS_2 with no Pt. Figure 4(b) represents the XRD for a sample with a Mo/Pt ratio of 44. Here the two phases of restacked single-layer MoS_2 and Pt-included MoS_2 are both present, the latter showing a 56% expansion in *c*-spacing. Figure 4(c) shows that a single expanded-lattice phase is present with a Mo/Pt ratio of 3.4.

3. DISCUSSION

It should be noted that we use the term MoS_2 when we are discussing the single layers and a single-layer coating before heating. After heating the catalyst there is no reason to believe there is still a coherent MoS_2 film on the surface, and suggest interaction with the alumina will break up the film and a

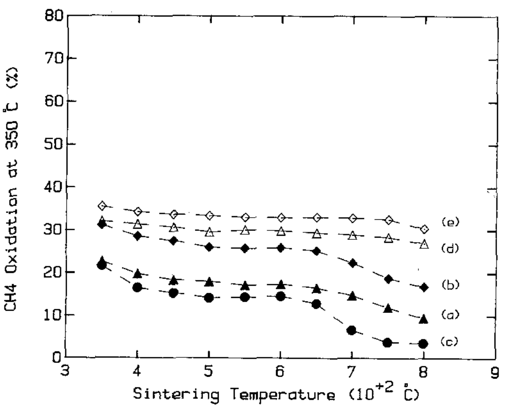

FIG. 3. Oxidation of methane at 350°C by precipitated Pt. Curves a to c are Pt on Al_2O_3, curves d and e are Pt on Mo-coated alumina. Pt content 5% by weight.

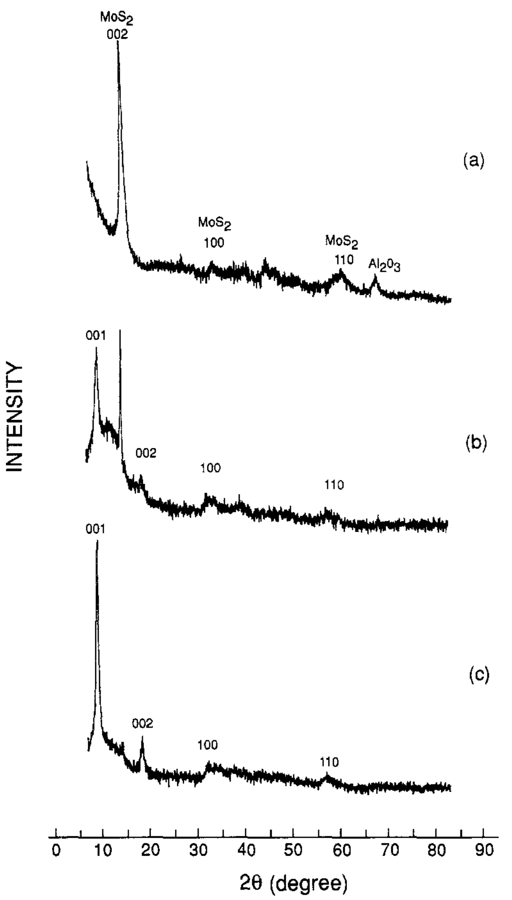

FIG. 4. X-ray diffraction pattern of Pt on Mo-coated alumina prepared by Pt precipitation. (a) No Pt. The (002 line is at $2\theta = 14.35°$). (b) Little Pt (Mo/Pt = 44 in at.%). There is enough Pt to expand some of the MoS_2 crystallites in the c-direction, giving a (001) line of the expanded lattice at $2\theta = 9.25°$. (c) Mo/Pt = 3.4. All MoS_2 particles are totally expanded by about 56%.

better term for the coating is a "monolayer of Mo" without specifying the anion associated with the Mo.

The results (Figs. 2 and 3) show clearly the expected degradation of activity starting at about 650°C reported by others (*19, 20*) to be typical of Pt on Al_2O_3 in various gases. The figures also show the substantially improved stability for the oxidation catalyst with the monolayer of Mo "glue" added. The stability with MoS_2 present is an observation independent of the cause of degradation in the case of Pt on Al_2O_3. However, as mentioned, the temperature range is as expected for sintering, so we assume that dominates the degradation. The much higher activity with the Mo present, as seen for example comparing curb (a) to curve (d) in Fig. 2, was unexpected. Unfortunately, the methane oxidation in this series is too complex to compare activity of the various samples on a linear scale. The conditions were picked to study stability, not activity. Further studies are needed to quantify the observed increase in activity.

The observation that the higher activity per gram Pt is found whether the MoS_2 layer is deposited before or after the impregnation of the Pt, or whether the Pt is introduced by precipitation, suggests that the presence of the Mo induces dispersion of the Pt. That is, the higher oxidation activity of the Pt (presumably due to better dispersion) could arise (a) because during impregnation one obtains a higher dispersion with the MoS_2-covered alumina, or (b) because the presence of the Mo induces dispersion at high temperature. In the latter case the dispersion would be associated with a strong Mo–Pt bond that favors the dispersion of the Pt over the surface. The high activity found even when the MoS_2 layer is deposited on γ-alumina after the Pt impregnation (where presumably the Pt is initially in the form of clusters), suggests the latter is the case, suggesting a very active role of the Mo.

The effect in XRD measurements of included Pt on the MoS_2 is so strong as to be baffling. A 56% expansion of the lattice, with apparently a very small fraction of a monolayer of Pt present, is difficult to explain. It seems clear, however, judging from the shift of the X-ray line, that the Pt is strongly bonded to the Mo on the "basal plane" of the MoS_2. We suspect from this and other measurements that the single-layer MoS_2 becomes kinked, enabling a much stronger bonding than would be possible on the basal plane of single-crystal MoS_2.

We assume that the higher activity with the fractured alumina as the support is simply due to the increased surface area which, because of the mixing of the powders before immersing in water, is again evenly coated with Mo.

4. CONCLUSIONS

We have been able to coat an Al_2O_3 support with Mo ions, providing evidence that they form a coherent monolayer. Used as a Pt oxidation catalyst, we find a high stability against sintering, which we attribute to strong bonding between the Mo ions and the alumina on the one side, and the Pt and the Mo on the other. There is evidence that the Pt becomes highly dispersed when heated with a Mo monolayer, the evidence arising because a high activity is found independent of whether the Pt is deposited before or after the Mo monolayer. From experiments with the Pt forming an "inclusion compound" we conclude there is a very strong Pt–Mo interaction.

ACKNOWLEDGMENTS

We acknowledge the assistance of T. Cowan in some of the above measurements.

REFERENCES

1. Joensen, P., Frindt, R. F., and Morrison, S. R., *Mater Res. Bull.* **21,** 457 (1986).
2. Gee, M. A., Frindt, R. F., Joensen, P., and Morrison, S. R., *Mater. Res. Bull.* **21,** 543 (1986).
3. Miremadi, B. K., and Morrison, S. R., *J. Catal.* **103,** 334 (1987).
4. Miremadi, B. K., and Morrison, S. R., *Surf. Sci.* **173,** 605 (1986).
5. Miremadi, B. K., and Morrison, S. R., *J. Catal.* **112,** 419 (1988).
6. Morrison, S. R., Frindt, R. F., Joensen, P., and Gee, M. A., U.S. Patent 4,822,590 (1989).
7. Morrison, S. R., Frindt, R. F., Joensen, P., and Gee, M. A., and Miremadi, B. K., U.S. Patent 4,853,359 (1989).
8. Miremadi, B. K., and Morrison, S. R., *J. Appl. Phys.* **63,** 4970 (1988).
9. Miremadi, B. K., and Morrison, S. R., *J. Appl. Phys.* **67,** 1515 (1990).
10. Yermakov, Yu. I., Kuznetsov, B. N., and Rynden, Yu. A., *React. Kinet. Catal. Lett.* **2,** 151 (1975).
11. Gandhi, H. S., and Shelef, M., *Catal Auto. Poll. Control,* 199 (1987).
12. Gandhi, H. S., Yao, H. C., and Stepien, H. K., *ACS Symp. Ser.* **178,** 143 (1982).
13. Parks, G. A., *Chem. Rev.* **65,** 177 (1965).
14. Unpublished data.
15. Miremadi, B. K., and Morrison, S. R., *Mater. Res. Bull.* **25,** 1139 (1990); patent application S168DV-15P.
16. Hicks, R. F., Ori, H., Young, M. L., and Lee, R. G., *J. Catal.* **122,** 280 (1990).
17. Otto, K., *Langmuir* **5,** 1364 (1989).
18. Taylor, K. C., *in* "Catalysis" (J. R. Anderson and M. Boudart, Eds.). Springer, Berlin, 1984.
19. Wanke, S. E., and Flynn, P. C., *Catal. Rev.-Sci. Eng.* **12,** 93 (1975); *Catalysis* **109,** 407 (1988).