

Reversible Hydrogen Adsorption on MoS₂ Studied by Temperature-Programmed Desorption and Temperature-Programmed Reduction

X. S. LI,* Q. XIN,* X. X. GUO,* P. GRANGE,† AND B. DELMON†,¹

**National Laboratory for Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China; and †Unité de Catalyse et Chimie des Matériaux Divisés, Université Catholique de Louvain, Place Croix du Sud 2, Boîte 17, B-1348 Louvain-La-Neuve, Belgium*

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The adsorption and desorption of hydrogen on MoS₂ were studied using a combination of temperature-programmed desorption (TPD) and temperature-programmed reduction (TPR) with a control of the maximum temperature. Reversible hydrogen adsorption was observed in the temperature range of 375–500 K. MoS₂ samples reduced in hydrogen at different temperatures behaved distinctively towards reversible hydrogen adsorption. The amount of the reversible hydrogen adsorption decreased when the sample was reduced in hydrogen at the medium temperature of 573–673 K, but its characteristics were not changed. For the sample reduced at high temperature, reversible hydrogen adsorption almost disappeared. In the TPR pattern, a reverse peak corresponding to hydrogen desorption was observed in the 500–673 K range. Based on these facts, the nature of the reversible hydrogen is discussed. The dependence of the reversible hydrogen adsorption on surface structure is also discussed. © 1992 Academic Press, Inc.

INTRODUCTION

In the hydrodesulfurization (HDS) process, at least three partners should be considered: the catalyst, the organic compound, and hydrogen. Much research has been done on the characterization of the active phases of HDS catalysts and the mechanism of ring opening of organic compounds (1–4), while relatively less attention has been focused on the hydrogen behaviour (5–15). The present study concerns hydrogen adsorbed on MoS₂, and is especially focused on its mobility on an unsupported MoS₂ sample from room temperature to 1173 K.

Polycrystalline molybdenum disulfide is frequently used as a model catalyst in studies related to hydrodesulfurization. The active sites of MoS₂ have been discussed by several authors (2, 3, 5, 6). It is generally accepted that the edge sites or corners are active centers in the HDS reaction (3, 4).

Recently, Kasztelan and Bonnelle and co-workers gave a detailed description of these sites, in which the special species containing H such as Mo-H and S-H were also considered (6–10). MoS₂ has long been recognized to have a high hydrogen capacity. The mechanism of hydrogen sorbed in MoS₂ and its mobility have been investigated both by experiment and by theoretical calculations (15–23). The formation of sulfhydryl groups in a linear form has been unequivocally detected by inelastic neutron scattering vibrational spectra (16–18) and silver titration (21–23). Through volumetric hydrogen uptake measurement, hydrogen adsorbed in MoS₂ was found to have a high capability for spillover onto the carrier Al₂O₃ (19). On the basis of quantum chemical calculations, the hydrogen atom in MoS₂ was found to be able to diffuse with a low energy barrier from the edge sites out over the basal planes, and hydrogen sorbed on the edge sites would be replenished by further heterolytic adsorption (20). These findings are very important to the basic study of HDS. For ex-

¹ To whom correspondence should be addressed.

ample, in the remote control model applied to cobalt molybdenum sulfide (4), hydrogen is regarded as having high mobility and can spill over from individual Co sites to molybdenum sites to create more active centers. In this case one would expect MoS₂ to be a good reservoir as hydrogen acceptor to supply enough active hydrogen for the HDS reaction (24). So far, there is unfortunately little experimental evidence to prove the hydrogen mobility on the HDS catalyst. A systematic study of hydrogen behaviour is required.

Temperature-programmed desorption (TPD) is very useful for characterizing the surface adsorbed species by its desorption pattern (11). Temperature-programmed reduction (TPR) is usually used to detect a reduction of the catalyst. A series of excellent studies have been made on HDS catalysts by TPR (25). In conventional TPR, it is difficult to obtain detailed information of hydrogen adsorption, because hydrogen consumption involves both adsorption and participation in reduction. It seems better to have a combination of TPD and TPR. In this way, the TPR technique is also available to study adsorption of hydrogen if a delicate procedure is designed, as presented in this paper. The advantage of cooperation of TPD and TPR is that it allows one to examine the hydrogen adsorption and its mobility on MoS₂, and to observe hydrogen adsorption in a reversible way below 573 K. This phenomenon is difficult to establish by individual TPD and TPR techniques.

EXPERIMENTAL

Materials

MoS₂ was prepared according to the homogeneous sulfide precipitation method (26–28). A reaction of (NH₄)₂S and (NH₄)₆Mo₇O₂₄ · 6H₂O solutions was carried out at 343 K for 1 h, then H₂SO₄ solution was added to the resulting solution, followed by filtering, washing and drying at 393 K to obtain a dark brown solid. This solid was sulfided in a gas mixture of 15% H₂S–85% H₂ (in volume) at 673 K for 4 h to form the MoS₂

sample examined by XRD. The surface area of the MoS₂ sample was 51.8 m² g^{−1} (28).

Commercial Ar, 5% H₂–Ar (Air Liquide products) were further purified by allowing the gases to flow over Oxyorb. H₂S/H₂ (Air Liquide product) was used without further purification.

TPD and TPR

A special experiment was designed by using TPD and TPR cycles and controlling the upper temperature on a multiple function gas system where a series of experiments are carried out; 0.5 g of catalyst sieved to the size range 0.3–0.8 mm was used in each experiment. Before TPD and TPR experiments, the MoS₂ sample was resulfided “*in situ*” at 573 K for 2 h. Ar and 5% H₂–Ar were chosen as carrier gases in TPD and TPR, respectively. The gas flow rate was always maintained at 30 cm³/min. Between the reactor and the thermal conductivity detector, a column filled with solid KOH powder was used to discard H₂S which is a product of hydrogenation of sulfur in MoS₂. A paper dipped in an AgNO₃ solution was placed on the gas vent to confirm that H₂S was completely adsorbed by the KOH. A mixture of ethanol and solid CO₂ was chosen as the cold trap. In the case of TPD, the TCD (thermal conductivity detection) signal observed is due to appearance of hydrogen in the Ar flow and attributed to hydrogen desorption. Hydrogen desorption and uptake were calculated by comparison of peak areas in TPD and TPR curves with that of pulse hydrogen in Ar for TPD and in 5% H₂–Ar for TPR. In TPR, a positive TCD signal will be attributed to a decrease of hydrogen content in the H₂–Ar gas flow and a negative TCD signal to an increase of H₂ content. The temperature program was controlled to a linear rate of 10 K/min for both TPD and TPR procedures.

RESULTS

After resulfidation, the MoS₂ sample was cooled from 573 K to room temperature in

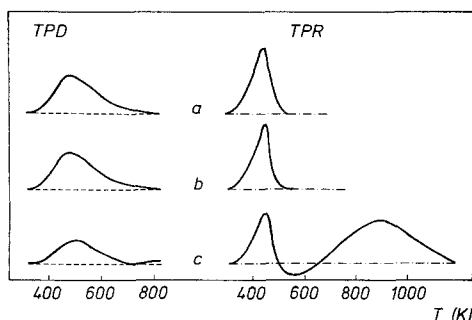


FIG. 1. TPD and TPR cycle patterns of the MoS_2 catalyst. After “*in situ*” sulfidation, the sample was cooled to room temperature in the sulfiding gas, and the first TPD was taken (a). When the sample was cooled in Ar to room temperature, the first TPR (a) was obtained. Afterwards, the sample was cooled in 5% H_2 -Ar to room temperature, and the second (b) and third (c) TPD and TPR cycles were measured subsequently.

the H_2S - H_2 gas mixture, then several TPD and TPR cycles were carried out as shown in Fig. 1. In the first TPD pattern, a broad hydrogen desorption peak appears in the 400–600 K range. The TPD was controlled to reach a maximum temperature at 873 K, then the sample was cooled to room temperature in argon. Argon was replaced by the H_2 -Ar reducing gas, and the first TPR run started. In the 350–573 K region, there is a sharp hydrogen consumption peak. In order to check the consumed hydrogen, the upper temperature of the first TPR run was controlled to 573 K, then the sample was cooled to room temperature in the reducing gas. Afterwards, a second TPD-TPR cycle was started in the same way (Fig. 1b). A similar phenomenon to that in the first TPD and TPR runs is observed. The hydrogen desorption peak in the second TPD pattern indicates that the consumed hydrogen in the first TPR run could desorb. The hydrogen consumption peak in the second TPR run indicates that the sample could adsorb hydrogen again. In the third TPD pattern of Fig. 1, a similar peak corresponding to desorption of the consumed hydrogen in the second TPR procedure appears. In the subsequent TPR, the temperature was raised

to 1173 K. In this case, another hydrogen consumption peak appears in the high temperature range. The high temperature peak covers a wide temperature range from 650 to 1173 K, while the low temperature peak is similar to those in the first and second TPR patterns. It is very surprising that a negative signal (reverse peak) occurred in the third TPR pattern in the temperature range 500–650 K. In addition, a dynamic equilibrium of the H_2 - MoS_2 system is discovered, as shown in Fig. 2: there is a new uptake of hydrogen on cooling from 573 K to room temperature, indicating that further hydrogen was adsorbed by the sample.

Influences of reducing at temperatures from 473 to 773 K on the TPD and TPR patterns of MoS_2 samples are depicted in Figs. 3 and 4. Fig. 3 shows a series of TPD and TPR patterns of MoS_2 reduced at 573 K for 1, 2, and 4 h, respectively, in separate experiments. It is seen that the hydrogen desorption peaks were shifted to lower temperature in the TPD patterns when the reduction time increased. In addition, a shoulder at about 380 K appears for all the samples reduced at 573 K. In the TPR patterns, both the lower temperature peak and the high temperature peak gradually decreased. Interestingly, the reverse peak in the TPR pattern became more intense with the increase in reduction time. The TPD and TPR pat-

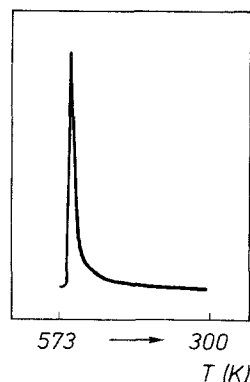


FIG. 2. Hydrogen consumption pattern of MoS_2 during cooling in 5% H_2 -Ar after a TPR to 573 K.

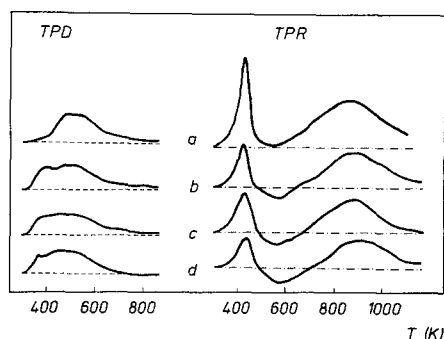


FIG. 3. TPD and TPR cycle patterns of the MoS_2 catalysts reduced at 573 K for (a) 0 h, (b) 1, (c) 2 h, and (d) 4 h, respectively.

terns of MoS_2 samples reduced at 473, 573, 673, and 773 K, respectively, are given in Fig. 4. For the samples reduced within 300–573 K, the TPD patterns show the same characteristics as in Fig. 1. Reduction at 673 K abruptly decreased the hydrogen desorption peak. Moreover, no evident peak of hydrogen desorption was observed for the sample reduced at 773 K. In the TPR patterns, the low-temperature peak clearly decreased while the high temperature peak showed little change for the sample reduced in the 300–573 K range (Figs. 4a–c). For the sample reduced at 673 K (Fig. 4d), the low-temperature peak remained nearly at the same level as in Fig. 4c, whereas the high-

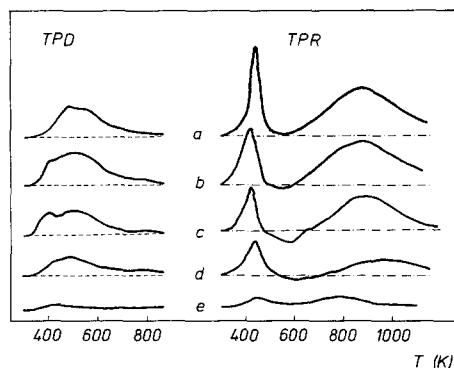


FIG. 4. TPD and TPR cycle patterns of the MoS_2 catalysts reduced at (a) 300 K, (b) 473 K, (c) 573 K, (d) 673 K, and (e) 773 K for 1 h, respectively.

TABLE I

Calculation of Hydrogen Desorption and Consumption in TPD and TPR Patterns of Reduced MoS_2

Reduction conditions		H/Mo			
		In TPD	In TPR		
			375–500 K	500–673 K	>673 K
Temp. (K)	Time (h)				
300	1	0.0120	0.0075	0	0.0258
473	1	0.0151	0.0061	0.0005	0.0232
573	1	0.0114	0.0040	0.0017	0.0148
673	1	0.0069	0.0040	0.0005	0.0072
773	1	0.0006	0.0021	0	0.0044
573	2	0.0097	0.0047	0.0018	0.0139
573	4	0.0104	0.0030	0.0027	0.0118

temperature peak largely decreased and the reverse peak became smaller than in Fig. 4c. After reduction at 773 K, the sample showed only two small peaks in the low and high temperature regions, and no reverse peak was observed.

Uptake of hydrogen on MoS_2 depends on the sample preparation and various values of H/Mo have been reported in the literature. In our case, the H/Mo ratio in TPD procedures for reduced MoS_2 at temperatures from 300 to 773 K were 0.012 to 0.006, which are within the range reported in the literature (16–19). The hydrogen uptake and desorption in TPR profiles were measured and are reported in Table I. Generally, the H/Mo ratio of TPD is larger than that of hydrogen consumed at temperatures from 375 to 500 K and less than the value of hydrogen consumed for the range 273 to 1173 K in the TPR pattern.

In order to recognize the effect of structure change on hydrogen adsorption and desorption, an additional TPD-TPR experiment was done on the sample reduced at 773 K, followed by resulfiding at 573 K for 2 h as seen in Fig. 5. The peaks of hydrogen desorption and hydrogen uptake observed in TPD and TPR patterns respectively are obviously larger than in its preceding state (Fig. 4e), but less than in Fig. 3a. It is inter-

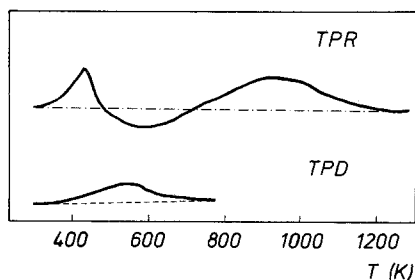


FIG. 5. TPD and TPR cycle patterns of the MoS₂ catalysts reduced at 773 K for 1 h, followed by resulfiding at 573 K for 2 h.

esting to note that the reverse peak appears in the TPR pattern again. This indicates that resulfidation partly restored the hydrogen capacity of MoS₂ nearly lost in the reduction at 773 K.

Figure 6a is a TPD and TPR cycle carried out on the MoS₂ sample preceded by a high-temperature TPR. There are no peaks evident in the TPD and TPR patterns. These phenomena demonstrate that reduction at high temperature almost completely eliminates the capability for hydrogen adsorption. In order to examine the effect of reduction at high temperature, a series of TPD-TPR cycles was carried out on the samples in which a high temperature TPR was followed by resulfiding at 573, 673, 773 and 873 K for 2 h separately, as displayed in Figs. 6b-e. The TPD and TPR patterns show much smaller peaks of hydrogen de-

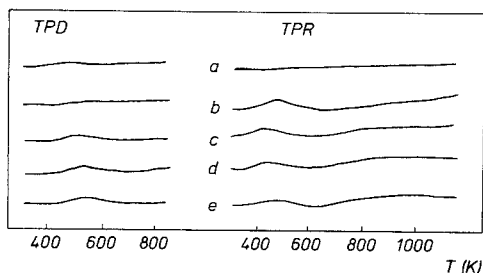


FIG. 6. TPD and TPR cycle patterns of the MoS₂ catalysts preceded by a TPR to 1173 K (a), then followed by resulfiding at 573 K (b), 673 (c), 773 K (d), and 873 K (e) for 2 h separately.

sorption and consumption. This shows that resulfidation does not restore the hydrogen capacity of MoS₂ disrupted by reduction at high temperature.

DISCUSSION

Assignment of Reversible Hydrogen

Scheffer *et al.* (25) had studied sulfided MoS₂ and Mo/Al₂O₃ samples by TPR. On MoS₂ they only found a hydrogen consumption peak in the high-temperature range. On the contrary, for the sulfided Mo/Al₂O₃ sample, the TPR pattern showed hydrogen consumption in three regions designated by these authors. In the low-temperature region of 300-550 K, a hydrogen-consumed peak was assigned to hydrogenation of a well-defined and highly reactive S species located on the edge sites of MoS₂ crystallites. In the medium-temperature region of 550-1000 K, a further hydrogen-consumption peak was regarded as being related to the hydrogenation of an S species which is more labile than stoichiometric sulfide sulfur. In the high-temperature region, a strong hydrogen consumption peak was attributed to the reduction of stoichiometric sulfide sulfur. In contrast to these findings, a low-temperature hydrogen consumption peak is seen on the MoS₂ sample in the present study. Furthermore, the consumed hydrogen at low temperature can desorb, as revealed by the subsequent TPD (see Fig. 1). The hydrogen consumption and desorption phenomena can be repeated several times, and the quantities of the consumed and desorbed hydrogen are not largely changed in each case. Hence, the hydrogen consumption peak at low temperature cannot be completely assigned to formation of H₂S. Instead, the low-temperature hydrogen consumed peak is proposed to arise mostly from hydrogen adsorption. This implication is supported by the fact that hydrogen can be sorbed by molybdenum sulfide, as reported by Wright and co-workers (16-18). The present TPD-TPR cycle experimental results convincingly prove that the sorbed hydrogen could be desorbed, and demon-

strate that a hydrogen adsorption-desorption phenomenon, via reversible hydrogen adsorption, exists on MoS_2 in the low-temperature range. This finding agrees well with the results reported by Polz *et al.* (19), who found using volumetric H_2 -uptake measurements that when an MoS_2 sample obtained after an H_2 uptake at 573 K was subsequently evacuated at 573 K, a second uptake was obtained with an identical hydrogen value. In fact, reversible hydrogen adsorption was recognized as early as 1949 by Badger *et al.* (15).

It is commonly accepted that the adsorbed hydrogen is bonded to S sulfur of MoS_2 to form sulfhydryl groups, but it seems that more than one kind of SH groups exist on the surface of MoS_2 . For example, Maternova (21, 22) had used silver titration to detect surface sulfhydryl groups which could not correspond to reversible hydrogen, because in the experiments the reversible hydrogen was desorbed by purging with nitrogen at 723 K. From comparison of the present results and Maternova's work, it is suggested that at least two kinds of sulfhydryl groups exist in MoS_2 , i.e., one consisting of the reversible hydrogen and another one associated with an irreversible hydrogen. The reversible hydrogen suggests that a kind of weak bonding, highly labile hydrogen, was produced in the hydrogen atmosphere. Since the H/Mo ratio is frequently found to be less than 1, as reported in the previous works (16–19), it is supposed that probably neither one nor two sulfur atoms but a MoS_2 cluster possesses the reversible hydrogen, which means that the reversible hydrogen could be transferred from one sulfur ion to its adjacent sulfur ions. In the movement, the reversible hydrogen could be desorbed and readsorbed, which can explain the hydrogen readsorption in the cooling procedure of Fig. 2 and the reverse peak in the TPR pattern. The hydrogen contained in the SH group detected by silver titration is probably related to an irreversible hydrogen adsorption (12, 19). Massoth (12) found that irreversible hydrogen was

formed even in the procedure of MoS_2 preparation.

Nature of Reversible Hydrogen

The TPD spectra of hydrogen give an indication of the energetics of hydrogen desorption from the surface. The TPD patterns indicate that hydrogen adsorption is in different sites, which may involve edge sites, basal plane, and sublayer or bulk. It is important to question whether this form of chemisorption is still a surface effect or a bulk effect. With regard to the fact that penetration usually requires higher energy than transfer on surface, we suggest that the hydrogen adsorption peak at temperature lower than 500 K is mostly due to surface hydrogen transfer, and that part of the hydrogen consumption peak around 800 K probably contains hydrogen penetration into the bulk and reduction of bulk MoS_2 (9). Since the desorption peak in TPD patterns is in good relation with the reversible hydrogen as revealed by TPD-TPR cycles (Fig. 1), the hydrogen desorption in TPD spectra is also assigned to surface hydrogen.

It is noteworthy that in the TPD patterns, the hydrogen usually desorbs in a wide temperature range, although the peak of reversible hydrogen adsorption is seen to be within the 350–500 K range. According to the quantum chemical calculations of Anderson *et al.* (20), hydrogen located on the edge sites is more mobile than on the basal planes, whereby a concept of hydrogen diffusion from the edge sites to the basal planes has been proposed by these authors. It is most probable that the reversible hydrogen adsorption corresponds to this procedure: hydrogen is first dissociated on the edge sites, then transferred to the basal planes and finally the edge sites are replenished by further adsorbing hydrogen. On the other hand, the TPD run shows a reverse process by the fact that hydrogen bonding to the edge sites first desorbs at low temperature, and hydrogen bonding to the basal plane transfers to the edge sites, then desorbs at a relatively high temperature. The possibility of hydro-

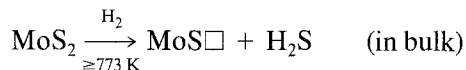
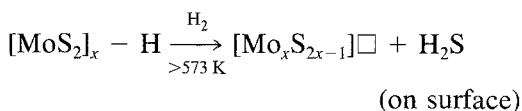
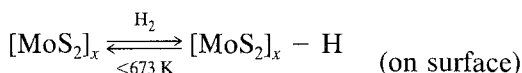
gen diffusion between the edge sites and the basal planes is also supported by the evidence that hydrogen uptake observed on the Al₂O₃-supported MoS₂ sample was always higher than on pure MoS₂ (15, 17, 19). Jalowiecki *et al.* (10) considered this phenomenon to be probably due to hydrogen spillover onto Al₂O₃. For hydrogen transfer, oxygen and hydroxyl groups are generally regarded to be good “bridges.” According to the present results, sulfur ions or sulfur groups are also capable of transferring hydrogen. Regarding the hydrogen transfer from the edge sites to the basal planes, the edge sites are regarded as a “port” for hydrogen adsorption-desorption on MoS₂.

In the present study, a specific characteristic of MoS₂ was obtained by a reverse peak appearing in the TPR run besides the reversible hydrogen adsorption under 500 K and the reduction peak at 800 K. This means that hydrogen desorptions occur in some TPR experiments. This phenomenon was not found in previous literature (25), but it is not accidental. For example, Menon and Froment (29) also observed a similar phenomenon for Pt/TiO₂ and Pt-black catalysts. Desorption and consumption of hydrogen occurred in different temperature ranges when Pt/TiO₂ was heated in 5% H₂-Ar. Furthermore, the phenomenon of hydrogen adsorption on the cooling MoS₂ sample (see Fig. 2) is very similar to platinum black and Al₂O₃- and SiO₂-supported platinum catalysts, on which there was a new uptake of hydrogen by platinum after cooling from 820 K in 5% H₂-Ar (29, 30). To explain these facts, it appears that an Mo-H bonding was formed which would be considered as hydrogen chemisorbed on Mo sites. From Table 1, it is shown that the amount of hydrogen desorbed in TPR is smaller than that of reversible hydrogen adsorbed. This suggests that the reversible hydrogen contains two different species. The intermediate Mo-H has been regarded by several authors (5, 6, 10, 11) as active sites in HDS and hydrogenation (HYD) reactions. However, the Mo-H species were not detected by in-

elastic neutron scattering vibrational spectra (16–18), and the hydrogen adsorbed on MoS₂ was observed not to react with oxygen at room temperature (13, 14). An in-depth study is required to improve the relation of hydrogen species and its features.

Effect of Temperature on Reversible Hydrogen

The influence of reduction of MoS₂ at different temperatures is discriminating towards the reversible hydrogen. Reduction is generally considered to change the surface structure of MoS₂ (24). The hydrogen consumption in the temperature range of 700–1000 K is evidently related to the reduction of MoS₂, since the hydrogen desorption peak did not appear on the sample heated at high temperature in the reducing gas. Even in the subsequent TPR run, no evident hydrogen consumption peak was found (see Fig. 6a). This fact indicates that the reversible hydrogen is closely related to the surface structure of MoS₂. The hydrogen behaviour is visualized as follows:



([MoS₂]_x: surface MoS₂ group, □: sulfur vacancy.)

In the reduction at low temperature, there exists a hydrogen adsorption-desorption equilibrium which plays a crucial role on the MoS₂ sample. Even after reduction at 573 K for a long time, the sample still showed an evident hydrogen adsorption and desorption phenomenon, although hydrogenation of the sulfur element could probably occur more or less in this process. In the medium temperature range of 573–773 K, from the

decrease of the hydrogen consumption peak at high temperature as seen in Fig. 4, an evident reduction of MoS_2 was proposed to produce sulfur vacancies on the surface. Disruption of surface structure could be partially restored by a resulfidation as seen in Fig. 5. In the high temperature range, there is a strong reduction of MoS_2 sample; probably some lattice sulfur was hydrogenated to produce a certain amount of bulk sulfur vacancies. Therefore, the surface structure of MoS_2 was completely disrupted, so that the sample lost its hydrogen capacity. Even a resulfidation could not restore the original adsorbability of hydrogen (see Fig. 6).

Usually, the HDS reaction is carried out at about 573 K (24). Dianis found that the weakly adsorbed hydrogen showed high activity in the hydrogenation of CO (11). Moreover, Okuhara *et al.* (5) and Jalowiecki *et al.* (9, 10) observed that the mobile hydrogen contributed to hydrogenation of ethylene and isoprene. It is reasonable to consider the reversible hydrogen as an important element in HDS and HYD reactions. Accordingly, if a promoter, i.e., cobalt or nickel which is more active to hydrogen dissociation, is associated with bulk MoS_2 or supported MoS_2 catalysts, it can be expected that the promoter will strengthen the hydrogen capacity of MoS_2 . In this regard, synergy between the active promoter and MoS_2 is natural to raise the activities in HDS and HYD (4). Further study designed to check the special role of the labile hydrogen is now under way.

CONCLUSIONS

Hydrogen on MoS_2 is found to behave differently in low-, medium-, or high-temperature regions. At temperature below 573 K, hydrogen shows a reversible adsorption. The hydrogen reversible adsorption is closely related to surface structure. In the medium temperature range of 573–773 K, surface sulfur is partially removed by hydrogenation to reduce the quantity of the labile hydrogen. Above 773 K, the surface structure is disrupted by a strong MoS_2 reduction

accompanied by a large number of sulfur vacancies produced in the bulk while the sample loses its adsorptivity towards hydrogen. Based on the experimental findings, the mobile hydrogen is regarded as corresponding to a fast hydrogen diffusion between the edge sites and the basal planes.

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REFERENCES

1. Grange, P., *Catal. Rev. Sci. Eng.* **21**, 135 (1980).
2. Ratnasamy, P., and Sivasanker, S., *Catal. Rev. Sci. Eng.* **22**, 401 (1980).
3. Prins, R., De Beer, V. H. J., and Somorjai, G. A., *Catal. Rev. Sci. Eng.* **31**, 1 (1989).
4. Delmon B., in "Catalysts in Petroleum Refining" (D. L. Trimm, S. Akashah, M. Absi-Halabi, and A. Bishara, Eds.), p. 1. 1989.
5. Okuhara, T., Tanaka, K. I., and Miyahara, K., *J. Catal.*, **48**, 229 (1977).
6. Kasztelan, S., *Langmuir* **6**, 590 (1990).
7. Drew, M. G. B., Mitchell, P. C. H., and Kasztelan, S., *J. Chem. Soc. Faraday Trans.* **84**, 697 (1990).
8. Wambeke, A., Jalowiecki, L., Kasztelan, S., Grimblot, J., and Bonnelle, J. P., *J. Catal.* **109**, 320 (1988).
9. Jalowiecki, L., Aboulaz, A., Kasztelan, S., Grimblot, J., and Bonnelle, J. P., *J. Catal.* **120**, 108 (1989).
10. Jalowiecki, L., Grimblot, J., and Bonnelle, J. P., *J. Catal.* **126**, 101 (1990).
11. Dianis, W. P., *Appl. Catal.* **30**, 99 (1987).
12. Massoth, F. E., *J. Catal.* **36**, 164 (1985).
13. Fu, Y. L., Tang, X. B., Huang, Z. G., Fan, C. Z., Ji, M. R., and Wu, J. X., *Appl. Catal.* **55**, 11 (1989).
14. Kalthod, D. G., and Weller, S. W., *J. Catal.* **95**, 455 (1985).
15. Badger, E. H. M., Griffiths, R. H., and Newling, *Proc. R. Soc., London, Ser. A* **197**, 184 (1949).
16. Wright, C. J., Sampson, C., Fraser, D., Moyes, R. B., Wells, P. B., and Riekel, C., *J. Chem. Soc. Faraday Trans. 1* **76**, 1585 (1980).
17. Sampson, C., Thomas, J. M., Vasudevan, S., and

- Wright, C. J., *Bull. Soc. Chim. Belg.* **96**, 1215 (1981).
18. Wright, C. J., Fraser, D., Moyes, R. B., and Wells, P. B., *Appl. Catal.* **1**, 49 (1981).
19. Polz, J., Zeilinger, H., Müller, B., and Knözinger, H., *J. Catal.* **120**, 22 (1989).
20. Anderson, A. B., Al-Saigh, Z. Y., and Hall, W. K., *J. Phys. Chem.* **92**, 803 (1988).
21. Maternova, J., *Appl. Catal.* **3**, 3 (1982).
22. Maternova, J., *Appl. Catal.* **6**, 61 (1983).
23. Miciukiewicz, J., Zmierzak, W., and Massoth, F. E., *Bull. Soc. Chim. Belg.* **96**, 915 (1987).
24. Lee, H. C., and Butt, J. B., *J. Catal.* **49**, 320 (1977).
25. Scheffer, B., Dekker, N. J. J., Mangnus, P. J., and Moulijn, J. A., *J. Catal.* **121**, 31 (1990).
26. Candia, R., Clausen, B. S., and Topsøe, H., *Bull. Soc. Chim. Belg.* **96**, 1225 (1981).
27. Göbölös, S., Wu, Q., and Delmon, B., *Appl. Catal.* **13**, 89 (1984).
28. Karroua, M., Ph.D. dissertation, Université Catholique de Louvain, Louvain-La-Neuve, Belgium 1991.
29. Menon, P. G., and Froment, G. F., *Appl. Catal.* **1**, 31 (1981).
30. Paál, Z., and Menon, P. G., *Catal. Rev. Sci. Eng.* **25**, 229 (1983).