Investigation of the sulfidation of Mo/TiO_2–Al_2O_3 catalysts by TPS and LRS

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A series of Mo/Al_2O_3 and Mo/TiO_2-Al_2O_3 catalysts were investigated by temperature programmed sulfiding (TPS) and laser Raman spectroscopy (LRS). The effect of TiO_2 on the sulfidability of molybdena was studied in detail. It is found that Mo/Al_2O_3 catalysts can be partially sulfided by O–S exchange at low temperature, forming molybdenum oxysulfide. The Mo–S bond subsequently ruptures in the presence of H_2 to produce H_2S. At 530–550 K deep sulfiding of molybdenum oxysulfide occurs forming crystalline MoS_2. When the surface of Al_2O_3 was covered by a monolayer of TiO_2, the sulfiding rate of molybdena at low temperature was not only greatly increased, but H_2S produced in the reduction of Mo–S species caused deep sulfiding of the catalyst which resulted in a decrease of the TPS peak temperature by 80–100 K. The results indicate that this promotion of the sulfiding of molybdena is enhanced with TiO_2 loading. The function of TiO_2 is explained by the weakened interaction between MoO_3 and Al_2O_3 due to the coverage of the Al_2O_3 surface by TiO_2.

Keywords: Temperature programmed sulfiding; laser Raman spectroscopy; Mo/Al_2O_3; Mo/TiO_2-Al_2O_3

1. Introduction

Due to the importance of supported MoO_3 catalysts in industry, Mo and Co or Ni promoted Mo catalysts supported on alumina or silica have been widely investigated. Recently we have reported results for Mo/Al_2O_3 from the angle of modification of the support [1–3]. It was found that the surface structure of MoO_3 was influenced by the coverage of TiO_2 on the Al_2O_3 surface. Molybdena existed mainly as octahedral species and the formation of an $Al_2(MoO_4)_3$ phase was inhibited on the TiO_2–Al_2O_3 carrier. The TPR results [4] showed that because the interaction between MoO_3 and Al_2O_3 was weakened, the reducibility of MoO_3 was enhanced. It is well known that the catalyst which has stronger reducibility at lower temperatures usually exhibits higher activity for some reactions [5–7]. We have observed recently that the activity of hydrodesulfurization of Mo/Al_2O_3 with TiO_2 modification increases. Moreover, it is interesting that Mo/TiO_2–Al_2O_3 catalysts without presulfiding or reducing treatment exhibited higher HDS activity when a monolayer TiO_2 covered the Al_2O_3 surface [8]. In order to reveal the nature of Mo catalysts supported on TiO_2–Al_2O_3 carrier, we have investigated the sulfidation behavior of Mo/TiO_2–Al_2O_3 catalyst by temperature programmed sulfidation (TPS) and in situ laser Raman spectroscopy (LRS). The TPS profile can give detailed information on the sulfidability and the sulfiding mechanism of the catalysts as a function of temperature. The LRS data can show the temperature of disappearance of molybdenum oxide species and the formation of molybdenum sulfide. These results are reported in this paper.

2. Experimental

2.1. SAMPLE PREPARATION

The preparation of Mo/TiO_2–Al_2O_3 catalyst has been reported in previous papers [1,2]. The TiO_2 content was 7.8, 11.2, 14.5 and 25.4 wt% respectively in the TiO_2–Al_2O_3 mixed carrier. MoO_3 loadings from 4 to 24 wt% were employed. Pure MoO_3 was obtained by decomposition of $(NH_4)_6MoO_7 \cdot 4H_2O$ at 773 K. These catalyst samples have been used in previous studies. In particular the structure of MoO_3 and its reducibility have been characterized by LRS and TPR [4,9].

2.2. TEMPERATURE PROGRAMMED SULFIDING (TPS)

The TPS measurements were carried out in a flow apparatus which consists of stainless steel and a quartz tube for holding the sample. A 13.0 vol% H_2S/H_2 mixture was used as the sulfiding gas. A thermal conductivity (TC) cell was used as the detector.

A 0.2 g sample was pretreated in Ar at 773 K for 2 h, then cooled to room temperature. H_2S/H_2 sulfiding gas flowed into the system at 40 ml/min. After the baseline TC signal was stable, heating of the sample was carried out at 10 K/min. A cool trap at 230 K was added to the system to remove water vapour produced in the sulfiding process.

2.3. LASER RAMAN SPECTROSCOPY (LRS)

Catalyst samples (0.2 g) were pressed into pellets and fixed in a quartz cell. 13.0 vol% H_2S/H_2 sulfiding gas flowed into the sample cell at the indicated temperature for 0.5 or 1 h. After cooling to room temperature the sulfiding gas was switched to a flow of Ar in order to purge the H_2S/H_2 mixture. The LRS measurements were then taken.

Laser Raman spectra were recorded by a Jobin–Yvon U-1000 Raman spectrometer with an Ar^+ laser, 488.0 nm and 300 mW were used.

3. Results

3.1. TPS

First it is determined that the TPS peaks measured by the thermal conductivity detector in the H_2S/H_2 sulfiding process include both H_2 and H_2S changes. Since the H_2 content in the mixture is very high (87 vol%), the change of the H_2 signal is relatively small compared with that of H_2S when the same amounts of H_2 or H_2S varied. It was examined that the ratio of the H_2 and H_2S signals is less than one tenth. Therefore, the peaks of TPS, especially these appearing at lower temperature, can be mainly attributed to the change of H_2S content. However, the reduction temperature of MoO_3 on Al_2O_3 or TiO_2–Al_2O_3 in 17 vol% H_2/Ar is higher than 673 K [4]. We found that the TPS profile of Mo/Al_2O_3 obtained in this experiment is consistent with the curve of H_2S detected by mass spectroscopy in ref. [10]. This means that the peaks of TPS recorded by TC reflect mainly the changes of the H_2S component.

3.1.1. MoO_3, Al_2O_3, TiO_2–Al_2O_3

The sulfiding behavior of MoO_3, Al_2O_3 and TiO_2–Al_2O_3 in TPS was first examined, and the results are shown in fig. 1. The positive peaks mean evolution of H_2S and negative peaks indicate H_2S consumption.

The MoO_3 TPS profile can be divided into three temperature regions: (1) From 400 to 575 K a peak of H_2S consumption appeared, which means that a part of the MoO_3 was sulfided. (2) In the range of 575–630 K there is a H_2S evolution peak, indicating some H_2S production in this temperature region. (3) Above 630 K a very broad H_2S consumption region can be discerned and the peak of maximum temperature is about 1125 K. When the temperature was raised to 1150 K the curve of TPS returned almost to the baseline.

The TPS profiles of the Al_2O_3 and TiO_2–Al_2O_3 carriers are similar. A sharp H_2S evolution peak is observed just above room temperature, but the tail of the peak for Al_2O_3 is longer. The H_2S evolution is considered to result from the desorption of H_2S adsorbed physically on the Al_2O_3 or TiO_2–Al_2O_3 carrier. No uptake of H_2S was detected, meaning the carrier cannot be sulfided to a detectable degree. After TPS to 1150 K, the TiO_2–Al_2O_3 sample was examined by LRS, and the results demonstrated that the characteristic bands of TiO_2 anatase greatly decrease. The black colour of the sample weakened the scattering signal, but no new peak was found.

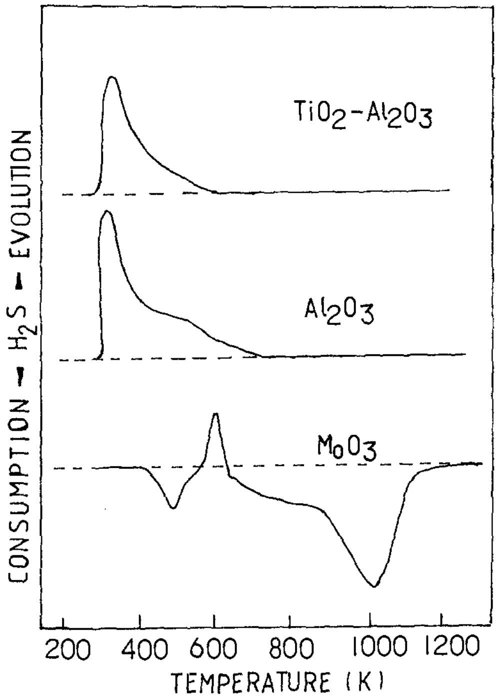


Fig. 1. TPS profiles of MoO_3, Al_2O_3 and TiO_2-Al_2O_3.

It was observed that the colour of MoO_3 changed gradually from greyish white to greyish black when the sample was contacted with a H_2/H_2S mixture at room temperature, which reveals that slight sulfiding of MoO_3 took place. No changes of colour for Al_2O_3 or TiO_2-Al_2O_3 carriers at room temperature can be seen.

3.1.2. Mo / Al_2O_3

Fig. 2 shows the TPS profiles of Mo/Al_2O_3 with various MoO_3 loadings. The profiles of MoO_3 supported on Al_2O_3 carrier are different from those of pure MoO_3. The TPS profile can be divided into four temperature regions:

(1) From 300 K, there is a sharp peak of H_2S evolution. The temperature of maximum and return to the baseline is dependent on Mo loading. The highest peak temperature is 325 K. The 4 wt% Mo/Al_2O_3 sample returned to the baseline at 400 K, the 8 and 12 wt% Mo/Al_2O_3 samples returned to the baseline at 375 and 350 K respectively.

(2) From 350–400 K to 450–485 K, there is a region of H_2S consumption. The peak area does not depend on Mo loading but the temperature of this region increases with a decrease in Mo loading. The 4 wt% Mo/Al_2O_3 sample was 400–485 K, that of the 8 wt% Mo/Al_2O_3 sample was 375–470 K and that of the 12 wt% Mo/Al_2O_3 sample was 350–450 K.

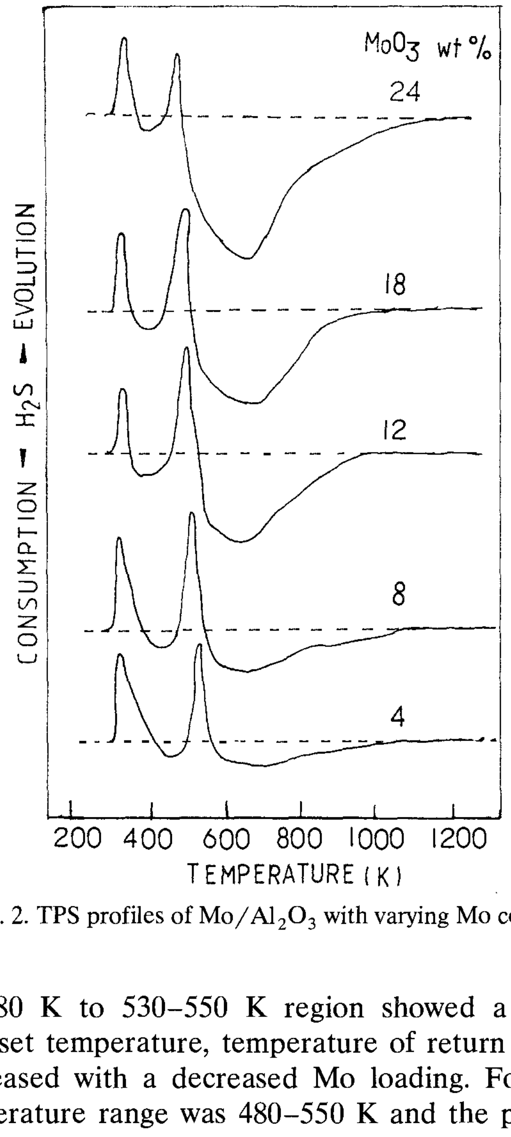


Fig. 2. TPS profiles of Mo/Al_2O_3 with varying Mo contents.

(3) The 450–480 K to 530–550 K region showed a sharp peak of H_2S evolution. The onset temperature, temperature of return to baseline and peak temperature increased with a decreased Mo loading. For 4 wt% Mo/Al_2O_3 sample, the temperature range was 480–550 K and the peak temperature was 530 K, for 8 wt% Mo/Al_2O_3 sample, the temperature range was 470–540 K and the peak temperature was 520 K, and for the 12 wt% Mo/Al_2O_3 sample, the temperature range was 450–530 K and the peak temperature was 500 K. The peak temperature decreased to 480 K for the 24 wt% Mo/Al_2O_3 sample.

(4) At temperature higher than 530 K there was a broad region of H_2S consumption and the peak area increased with Mo loading. At 1100 K, the TPS curves had essentially returned to the baseline.

The colour of the Mo/Al_2O_3 changed gradually from white to orange, brown and brown-black when the sample was contacted with the H_2S/H_2 mixture at room temperature. It reveals that a part of the MoO_3 was sulfided at lower temperature.

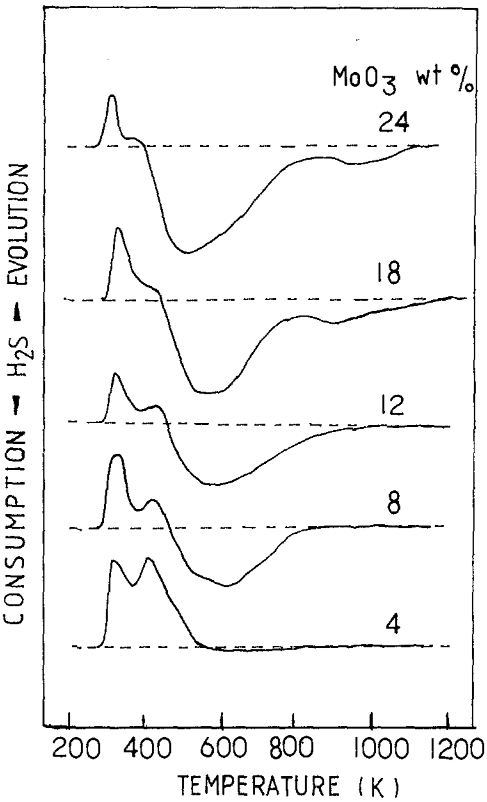


Fig. 3. TPS profiles of Mo/TiO_2–Al_2O_3 with varying Mo contents. TiO_2: 11.2 wt%.

The sulfiding profiles of Mo/Al_2O_3 samples with different Mo loadings showed that the sulfiding temperature region shifted forward with increasing Mo loading, but when the Mo loading was higher, the peak area in the high temperature region was larger. This means that most of the Mo species were sulfided fully at about 650 K.

3.1.3. Mo / TiO_2–Al_2O_3

Fig. 3 shows TPS profiles of Mo/TiO_2–Al_2O_3. When 11.2 wt% TiO_2 covered the Al_2O_3 surface, large changes in MoO_3 sulfiding behaviour took place. The profiles of Mo/TiO_2–Al_2O_3 can be divided into two temperature regions as follows:

(1) From 300 K to 450–550 K, there is a region of H_2S evolution. This region showed two H_2S evolution peaks with peak temperatures at 320 and 430 K and these temperatures were independent of Mo loading. However, the temperature of the return to the baseline decreased with an increase in Mo loading. For the 4 wt% Mo/Al_2O_3 sample, the profiles returned to the baseline at 550 K, with the 8 wt% Mo/Al_2O_3 this temperature was 465 K and with the 12 wt%

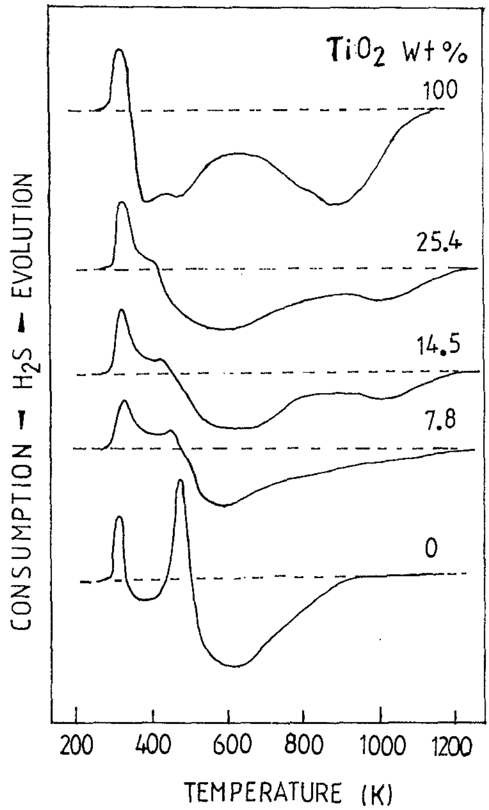


Fig. 4. TPS profiles of Mo/TiO_2-Al_2O_3 with varying TiO_2 contents. MoO_3: 12 wt%.

Mo/TiO_2-Al_2O_3 this temperature decreased to 450 K. The peak area of the second of the two peaks decreased with an increase in Mo loading. With a Mo loading of 18 wt%, the area of this second peak of H_2S evolution had decreased to appear only as a small plateau.

(2) At temperatures higher than 450 K (the 12 wt% Mo loading) or 550 K (the 4 wt% Mo loading), there is a broad region of H_2S consumption. The peak area increased with Mo loading as did the temperature of the return to the baseline.

The influence of TiO_2 content on the sulfiding of Mo species was also examined. The TPS profiles of Mo/TiO_2-Al_2O_3 with various TiO_2 contents are shown in fig. 4. When the TiO_2 content is higher than 14.5 wt%, i.e. one monolayer of TiO_2 on the Al_2O_3 surface, the second peak of H_2S evolution decreases to a small plateau or shoulder. On TiO_2 support a small peak of H_2S evolution and a broad region of H_2S consumption was seen.

3.2. LRS

The Mo/Al_2O_3 and Mo/TiO_2-Al_2O_3 samples with 15 wt% MoO_3 loading were examined at different sulfiding temperatures in situ by LRS and the results

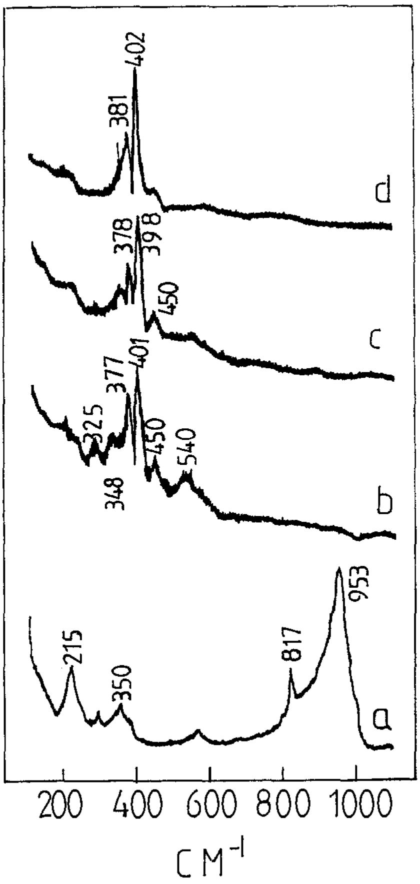


Fig. 5. In situ laser Raman spectra of 15 wt% MoO_3/Al_2O_3 sulfided at varying temperatures. (a) Oxide, (b) sulfided at room temperature, (c) sulfided at 473 K, (d) sulfided at 673 K.

are shown in figs. 5 and 6. Because the colour of both samples became brownish black when the H_2/H_2S mixture flowed into the sample cell for 0.5 h at room temperature, the scattering signal of the samples was very weak. Comparing figs. 5a and 5b, large changes in the spectra can be discerned. After sulfidation of Mo/Al_2O_3 samples at room temperature, the main bands of MoO_3 disappeared, and the bands at 377 and 401 cm^{-1}, attributed to the MoS_2 phase, appeared. Moreover, some broadened weak bands at 325, 348, 450 and 540 cm^{-1} can be seen. These bands reflect the presence of a complicated Mo–S–O structure [11–15]. When the sulfiding temperature was increased to 473 K, the intensity of the MoS_2 bands increased, while those bands attributed to the structure of Mo–S–O disappeared. After sulfiding at 673 K, only the bands of the MoS_2 phase exist at 381 and 402 cm^{-1}.

For Mo/TiO_2–Al_2O_3 the characteristic bands of MoO_3 and TiO_2 disappeared upon sulfiding of the sample at room temperature, and the broad bands

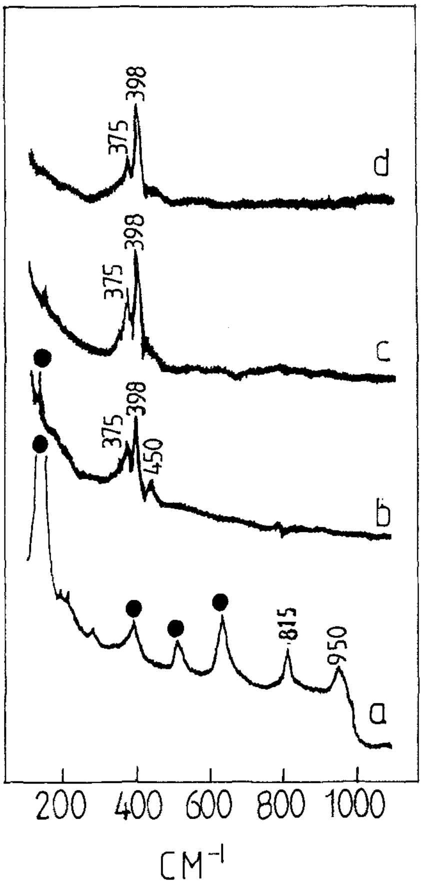


Fig. 6. In situ laser Raman spectra of 15 wt% MoO_3/TiO_2 (25.0 wt%)-Al_2O_3 sulfided at varying temperatures. (a) Oxide, (b) sulfided at room temperature, (c) sulfided at 473 K, (d) sulfided at 673 K. (●) TiO_2 (anatase).

of MoS_2 at 375 and 398 cm^{-1} emerged, but no bands of Mo-S-O structure were observed. No large change of the band intensity at 398 cm^{-1} took place with an increase in the sulfiding temperature.

The Mo/Al_2O_3 and Mo/TiO_2-Al_2O_3 samples after TPS to 1150 K were examined by LRS and the results showed that although the samples were exposed to air for a long time, only the MoS_2 phase existed on both samples. It means that the MoS_2 phase formed at high temperature is rather stable.

4. Discussion

The sulfidation of Mo/Al_2O_3 catalysts has been widely investigated. It is agreed [10,16–18] that the sulfidation mechanism at low temperature is dominated by O–S exchange reactions,

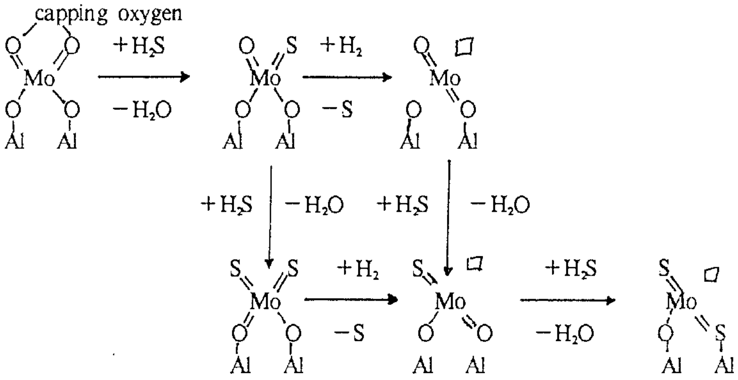
$$Mo^{6+}\text{-}O + H_2S \rightarrow Mo^{6+}\text{-}S + H_2O.$$

The heat of formation of MoO_3 (s) (180.33 kcal/mol) is much larger than that of MoS_3 (s) (61.2 kcal/mol) [19], which means the strength of the Mo–S bands is much less than that of the Mo–O bands, so the rupture of Mo–S bands takes place easily in the presence of H_2. When S is trapped by H_2 to form H_2S, the Mo^{6+} is reduced to lower valency. The results of Mo K-edge EXAFS indicated [20] that a Mo/Al_2O_3 sample sulfided at low temperatures exhibited a highly disordered structure with Mo–O and Mo–S bands. The structure rearrangement occurred upon an increase of the sulfiding temperature. When the rupture of Mo–O–Al linkages occurred, some small MoS_2 crystallites were formed. Moulijn and co-workers [10,17] carefully investigated Mo/Al_2O_3 and Co–Mo/Al_2O_3 samples using temperature programmed sulfiding and found that sulfiding of MoO_3 was carried out by many steps.

It is clearly seen that in our results the sulfidation behavior of MoO_3, Mo/Al_2O_3 and Mo/TiO_2–Al_2O_3 displayed large differences. The specific analysis of the TPS profiles of these samples follows.

For the MoO_3 sample three temperature regions exist in the TPS profile. The first peak of H_2S consumption is considered to be that a part of MoO_3 was sulfided through O–S exchange. The changes of the MoO_3 colour indicated the presence of this sulfiding at low temperature. The second positive peak centered at 600 K means a definite amount of H_2S was formed. It is due to the reduction of Mo–S species produced in the O–S exchange step by H_2. Over 630 K a broadened temperature region of H_2S consumption reflected that molybdenum oxysulfide continued sulfiding. The sulfidation of MoO_3 was completed at about 1100 K.

The TPS profiles of Mo/Al_2O_3 are different from those of pure MoO_3. First, when the sulfiding temperature was slightly above room temperature a sharp peak of H_2S evolution appeared. From the TPS profile of Al_2O_3 in fig. 1, this peak can be considered the desorption of H_2S physically adsorbed on the Al_2O_3 carrier. Secondly, the peak temperature of H_2S consumption at low temperature is relatively lower than that of pure MoO_3. It means that the dispersion of MoO_3 on Al_2O_3 favours its sulfidation. The peak areas show no change with MoO_3 loading, which revealed that the O–S exchange reaction only occurred in a part of the molybdenum species on the Al_2O_3 surface. Thirdly, the positive peak at 530 K is caused by the formation of H_2S. The Mo–S band was attacked by H_2 and ruptured. The S in the Mo–S species was reduced to H_2S sequentially. In this region some H_2 was consumed for the reduction of Mo^{6+}. Fourthly, above 630 K a widened peak of H_2S consumption is due to further sulfiding of molybdenum oxysufide and the peak areas increase with MoO_3 loading. The MoO_3 loading has a slight influence on the sulfidng temperature of the samples. When MoO_3 loading increased the sulfiding temperature shifted to



Scheme 1.

lower temperature. It is suggested that the increased loading of MoO_3 leads to a decrease of the M–O bond strength.

Acording to the result mentioned above, the sulfiding mechanism of Mo/Al_2O_3 can be suggested as in scheme 1. Monomeric tetrahedrally bonded Mo ions are taken as the model of Mo surface species.

That the capping oxygen ion in the tetrahedral MoO_4^{2-} species was reduced first by H_2 because of its higher activity has been suggested previously [21,22]. So it is imagined that in the sulfiding process this capping oxygen ion was also sulfided first. Under sulfiding conditions one or two capping oxygen ions can be replaced by S through O–S exchange to form complicated molybdenum oxysulfide. The LRS spectra show the bands for the Mo–O–S structure. The Mo–S bond ruptured readily in H_2. When the sulphur was reduced to H_2S, a vacancy appeared on the Mo^{6+} ion, and Mo^{6+} ion was reduced to Mo^{4+} ion. At high sulfiding temperatures a bridging oxygen in Mo–O–Al was replaced also by S, and crystalline MoS_2 formed.

The tetrahedral Mo monomers are present at low Mo surface coverage. At higher Mo contents the polymers of octahedral Mo species are the main forms [23]. The sulfiding of oxidic Mo polymers is similar to those presented in the tetrahedral Mo species. A series of O–S exchanges took place and disordered MoS_2 was formed [16,20]. The sulfidability of Mo species is supposed to be capping Mo=O > Mo–O–Mo > Mo–O–Al.

For Mo/TiO_2–Al_2O_3 catalysts the evolution of H_2S slightly above room temperature was caused by the desorption of H_2S physically adsorbed on TiO_2–Al_2O_3 support. TiO_2–Al_2O_3 has a peak of H_2S evolution similar to that of Al_2O_3. But the differences of Mo/TiO_2–Al_2O_3 and Mo/Al_2O_3 are: (1) No H_2S consumption peak at low temperature can be seen. (2) With respect to the Mo/TiO_2–Al_2O_3 sample, the second peak of H_2S evolution was at 430 K, while the corresponding temperatures for the Mo/Al_2O_3 samples were 480–530 K (which depended on Mo loading), and thus this temperature of the Mo/TiO_2–

Al_2O_3 sample was lower than those of the Mo/Al_2O_3 samples by 50–100 K. (3) In the high temperature H_2S consumption region, the peak area of the 4 wt% Mo/TiO_2–Al_2O_3 sample was very small. This indicated that even at 550 K, a large portion of the Mo had already been sulfided. When the Mo content was 8 wt%, deep sulfiding began at 450 K. However, with the Mo/Al_2O_3 samples, deep sulfiding only began at 530–550 K. Thus, in comparing Mo/TiO_2–Al_2O_3 with Mo/Al_2O_3, the sulfiding temperature can be seen to be lower by 80–100 K for the former. All these differences indicated that the MoO_3 on TiO_2–Al_2O_3 is easily sulfided. It is suggested that the interaction between MoO_3 and Al_2O_3 was weakened because of presence of TiO_2 on the Al_2O_3 surface: the O–S exchange reaction of surface molybdena species in the Mo/TiO_2–Al_2O_3 sample took place rapidly, and the most part of capping oxygen ions were replaced by S at low temperature. Furthermore, the bridging oxygen ion in Mo–O–Ti (Al) can be replaced by S at lower temperature. The H_2S produced in the stage of Mo–S bond rupture was almost used to carry out deep sulfiding. Thus the second H_2S evolution peak cannot be seen. It is not considered that the decrease of H_2S evolution peak is caused by the influence of H_2 signal. The reasons are that, on the one hand, the signal of H_2 is much smaller than that of H_2S. On the other hand, the peaks of H_2 consumption caused by reduction of the Mo^{6+} species are positive peaks. Therefore, the decrease of the H_2S evolution peak is only attributed to the fact that most of the H_2S produced was consumed in the deep sulfiding. The increment of TiO_2 content enhanced this function. This function of TiO_2 weakening the interaction of MoO_3 and Al_2O_3 has been reported in the previous papers [4,9].

Okamoto's [24] investigation by LRS and XPS indicated that sulfided Mo/Al_2O_3 consisted of MoS_2-like species and Mo^{5+} species, while Mo/TiO_2 sulfided fully to MoS_2-like species. Our LRS results indicated that the main bands of the Mo–S bond existed when Mo/TiO_2–Al_2O_3 was sulfided at low temperature. This reveals that modification of the Al_2O_3 surface by TiO_2 strongly influences the sulfiding of MoO_3 supported catalysts.

Mo/Al_2O_3 catalysts used in hydrodesulfurization reaction need to be pre-sulfided to be activated. When TiO_2 is used as the support for Mo and Co–Mo catalysts, pre-sulfiding is not necessary for activation [25–27]. In our investigation of Mo/TiO_2–Al_2O_3 catalysts, it was seen that pre-sulfiding is also not necessary for activity in thiophene hydrodesulfurization and cyclohexene hydrogenation [8]. The reason can be seen here to be the fact that these catalysts can be sulfided by sulfur containing reactant gases during reaction. Thus, these catalysts offer the advantage of avoiding pre-sulfiding.

References

[1] Z.B. Wei, Q. Xin, X.X. Guo, B.E. Shame, P. Grange and B. Delmon, Appl. Catal. 63 (1990) 305.

[2] Z.B. Wei, Q. Xin, X.X. Guo, P. Grange and B. Delmon, Appl. Catal. 75 (1991) 179.

[3] Z.B. Wei, Q. Xin, X.X. Guo, P. Grange and B. Delmon, in: *Proceedings on Catalytic Science and Technology*, Vol. 1 (Kodansha, Tokyo, 1991) p. 147.

[4] Z.B. Wei, S.C. Jiang, Q. Xin, S.S. Sheng and G.X. Xieng, Catal. Lett. 11 (1991) 365.

[5] R. Thomas, E.M. van Oers, V.H.J. de Beer, J. Medema and J.A. Moulijn, J. Catal. 76 (1982) 241.

[6] F.E. Massoth, Adv. Catal. 27 (1975) 266.

[7] B. Delmon et al., J. Chem. Soc. Faraday Trans. I 82 (1986) 2423.

[8] Z.B. Wei, S.C. Jiang and Q. Xin, to be published.

[9] Z.B. Wei, C.D. Wei and Q. Xin, Acta Phys. Chim. Sinica 82 (1992) 261.

[10] P. Arnoldy, J.A.M. van den Heijkant, G.D. Bok and J.A. Moulijn, J. Catal. 92 (1985) 35.

[11] G.L. Schrader and C.P. Cheng, J. Catal. 80 (1983) 369.

[12] E. Payen, M.C. Dhamelincourt, P. Dhamelincourt, J. Grimblot and J.P. Boonlle, Appl. Spectry. 36 (1982) 30.

[13] F.R. Brown and L.E. Makovsky, Appl. Spectry. 31 (1977) 44.

[14] A. Maezawa, M. Kitamura, Y. Okamoto and T. Imanaka, Bull. Chem. Soc. Japan 61 (1988) 2295.

[15] C.H. Chang and S.S. Chang, J. Catal. 72 (1981) 139.

[16] D. Arnoldy, J.A.M. van den Heijkant, G.D. de Bok and J.A. Moulijn, J. Catal. 92 (1985) 35.

[17] B. Scheffer, E.M. van Oers, P. Arnoldy, V.H.J. de Beer and J.A. Moulijn, Appl. Catal. 25 (1986) 303.

[18] H. Knozinger, *Proceedings on 9th ICC*, Canada 1988, p. 20.

[19] X.N. Zhang, *Chinese Handbook of Applied Chemistry*, 1st Ed. (NDI Press, 1986) p. 177.

[20] T.G. Parham and R.P. Merrill, J. Catal. 85 (1984) 295.

[21] T.K. Hall and F.E. Massoth, J. Catal. 34 (1974) 41.

[22] H.C. Yao, J. Catal. 70 (1981) 440.

[23] F.E. Massoth, *Advances in Catalysis*, Vol. 27 (Academic Press, New York, 1978) p. 265.

[24] Y. Okamoto, A. Moezawa and T. Imanaka, J. Catal. 120 (1989) 29.

[25] S. Matsuda and A. Koto, Appl. Catal. 8 (1983).

[26] M. Takenchi et al., US Patent 4,206,036 (1980).

[27] M. Takenchi, S. Matsuda, F. Nakajim and H. Okada, Hydrodesulfurization of thiophene in naphtha on titania-supported catalyst, presented at the National Meeting of American Chemical Society, Georgia 1981.