The reduction behavior of Mo/TiO_2-Al_2O_3 catalyst

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The effect of TiO_2 modified Al_2O_3 surface on the reducibility of MoO_3 has been studied by TPR and XPS. The results show that Mo^{6+} in Mo/TiO_2-Al_2O_3 can be reduced to much lower valency, especially at low Mo loading. The influence of the calcination temperature on the reduction of Mo^{6+} on Al_2O_3 and TiO_2-Al_2O_3 carriers is different. The data reveals that the reducibility of Mo^{6+} on Al_2O_3 slightly decreased, while that on TiO_2-Al_2O_3 increased when the calcination temperature was raised. It is suggested that the stronger tetrahedral site of the Al_2O_3 surface was first occupied by TiO_2 and main octahedral Mo^{6+} in polymeric species-; and a small crystalline MoO_3 formed on TiO_2-Al_2O_3, whereas the formation of tetrahedral Mo^{6+} species and $Al_2(MoO_4)_3$ phase was inhibited.

Keywords: TiO_2-Al_2O_3; Mo/Al_2O_3; Mo/TiO_2-Al_2O_3; temperature programmed reduction (TPR); X-ray photoelectron spectroscopy (XPS)

1. Introduction

The effect of the nature of the carrier on the surface structure and the chemical behavior of supported active components have been widely inverstigated. It is well known that there is a definite degree of interaction between the active component and the support which may play an important role. The dispersion of supported metal or metal oxides, adsorption properties of the catalyst and their catalytic activity are influenced by the nature of the carrier. Recently some interesting results were obtained for TiO_2 which is used as a promoter on high surface area supports, such as Al_2O_3 or SiO_2 [1–4]. Due to the presence of TiO_2 on the Al_2O_3 surface, modifing effectively the interaction between active component and support, the dispersion and chemical properties of the catalyst were improved.

The distribution of TiO_2 supported on Al_2O_3 or SiO_2 and surface acidity of TiO_2-Al_2O_3 binary oxide were systematically investigated. We have reported studies on the effect of preparation techniques on the morphology and properties of TiO_2-Al_2O_3 mixed oxide using BET, XRD, XPS, TEM, AEM and TPD of ammonia adsorption [5]. It was found that a homogeneous dispersion of TiO_2 could be obtained by grafting and impregnating methods. The influence of TiO_2 on Mo/Al_2O_3 catalyst was also studied [6]. The conclusion was that TiO_2 covered on Al_2O_3 surface can effectively improve the dispersion of MoO_3 on Al_2O_3 and the hydrodesulfurization (HDS) activity of thiophene. An interesting phenemenon was found that [7] the modification of the Al_2O_3 surface by TiO_2 made MoO_3 exhibit octahedral or polymeric surface species which are considered the precursor of the active phase of MoO_3. Furthermore, the formation of $Al_2(MoO_4)_3$ of spinel structure and tetrahedral Mo species which are hardly reduced was inhibited.

The present work describes the effect of TiO_2 on the reducibility of MoO_3 supported on TiO_2-Al_2O_3 carrier using TPR and XPS. The influence of calcination temperature and MoO_3 content for a series of Mo/TiO_2-Al_2O_3 catalysts was examined.

2. Experimental

1. CATALYST PREPARATION

Preparation of the TiO_2-Al_2O_3 carrier and Mo/TiO_2-Al_2O_3 catalysts has been described in detail previously [5]. The TiO_2-modified Al_2O_3 was prepared by non-aqueous impregnation of γ-Al_2O_3 using a solution of titanium isopropoxide Ti $(O\text{-}iPr)_4$ dissolved in isopropanol. Supports having TiO_2 loading from 7.8 to 25.4 wt% were prepared. Molybdena was deposited on the TiO_2-Al_2O_3 (TA) using ammonium heptamolybdena. MoO_3 loadings from 4 to 24 wt% were employed. The samples were usually calcined at 773 K for 6 hr. In order to examine the effect of the calcination temperature, the sample with 18 wt% MoO_3 was calcined at 873 or 973 K, respectively.

2. CATALYST CHARACTERIZATION

TPR measurements were made in a flow apparatus with mixed Ar-H_2 (17 vol%) as the reducing gas and a thermal conductivity detector. The mixed gas flow was 40 ml/min. The heating rate of the samples was 10 K/min. The quantities of the samples were 0.1 g. Before TPR the samples were pretreated in Ar at 773 K for 2 hr.

X-ray photoelectron spectra of reduced Mo/TA catalysts were obtained with a VG ESCALAB MKII spectrometer. The catalyst pellets, pressed at 2000 kg/cm^{-2}, were treated in a reaction chamber at 773 K in a 40 ml/min flow ultrahigh purity hydrogen for 2 hr. The treated catalysts were then transferred directly to the analysis chamber without contact with air. The residual pressure inside the analysis chamber was below 10^{-9} Torr. Al Kα radiation (1486.0 eV) operated at 14 kV and 20 mA was used. All binding energies were referenced to the Al 2p line (74.7 eV).

3. Results

1. THE EFFECT OF TiO$_2$

The TPR profiles of Mo/TA samples with various contents of TiO$_2$ are shown in fig. 1. The background experiment of TiO$_2$-Al$_2$O (14.5 wt% TiO$_2$) without MoO$_3$ has been carried out. The results showed that the TPR profile was a base line and no reduction peaks appeared. Nevertheless, it is not sure that the reduction of a small part of TiO$_2$ in the TPR process did not happen because TiO$_2$ is a reducible oxide. The results of electroconductivity measurement revealed that [8] a low valency Ti^{3+} ions produced when TiO$_2$ was heated over 400 K in H$_2$. The binding energy of Ti 3p^{4+} in Mo/TiO$_2$-Al$_2$O$_3$ samples reduced at 773 K in H$_2$ shifted slightly to higher energy direction. But the amount of H$_2$ consumption of TiO$_2$ reduction can be neglected by thermal conductivity detector. Therefore, the TPR peaks observed can mainly be contributed to the reduction of MoO$_3$.

Two peaks are observed for all samples in fig. 1 indicating the presence of two species of molybdenum. The first peak temperature decreases from 693 K to

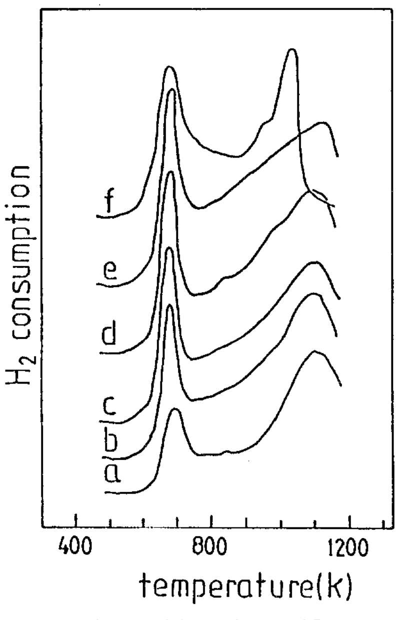

Fig. 1. TPR profiles of Mo/TA catalysts with various TiO$_2$ content MoO$_3$ 12 wt%, TiO$_2$ wt%: a, 0; b, 7.8; c, 11.2; d, 14.5; e, 25.4.

Table 1
The change of peak temperature and amounts of H_2 consumption in TPR MoO_3: 12 wt%

Catalysts	TiO_2 (wt%)	Temp. of 1st peak (K)	Temp. of 2nd peak (K)	Amount of H_2 consumption up to 773 K (ml/mmol)	H/Mo up to 773 K
Mo/A	0	693	1100	9.39	0.96
Mo/TA-3	7.8	681	1098	13.86	1.41
Mo/TA-4	11.2	679	1093	15.93	1.62
Mo/TA-5	14.5	684	1098	16.89	1.72
Mo/TA-6	25.4	685	1134	17.83	1.82
Mo/T	100	683	1037	28.60	2.96

679–685. K. The peak intensities increased with TiO_2 content. The second peak maximum is almost at 1100 K. The amount of H_2 consumption up to 773 K can be estimated by the integral of the peak area of the TPR profile. The H/Mo atomic ratios were also calculated. The results and the peak maximum temperatures are summarized in table 1.

It is seen from table 1 that the atomic ratios of H to Mo gradually increase with TiO_2 content. An H/Mo ratio near 1 for the Mo/Al_2O_3 sample suggests that Mo^{6+} was reduced to Mo^{5+}. An increase of H/Mo ratio to 1.41–1.82 for the Mo/TA samples implied that more Mo^{6+} ions were reduced to Mo^{4+} which revealed that the presence of TiO_2 can promote the reduction of Mo species. For Mo/TiO_2 samples Mo^{6+} can be reduced to a much lower valency at the same reduction temperature. When the reduction temperature was over 1150 K, the H/Mo atomic ratio was close to 6, indicating that Mo^{6+} was reduced to a metallic state.

The TPR profiles of various MoO_3 loadings supported on Al_2O_3 and TiO_2-Al_2O_3 with 11.2 wt% TiO_2 are shown in fig. 2. For the Mo/A samples the intensity of the first peak is relatively small at low Mo loading, but it is increased

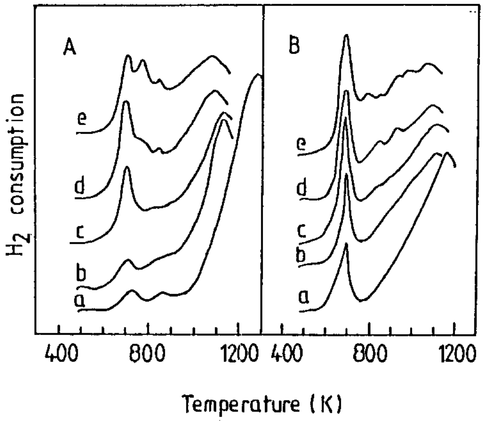

Fig. 2. TPR profiles of Mo/A(A) and Mo/TA(B) (TiO_2 11.2 wt%) catalysts with various MoO_3 loadings MoO_3 wt%: a, 4; b, 8; c, 12; d, 18; e, 24.

Table 2
The change of peak temperature and amount of H_2 consumption in TPR

Catalyst	TiO_2 (wt%)	MoO_3 (wt%)	Temp. of first peak (K)	Amount of H_2 consumption up to 773 K (ml/mmol)	H/Mo up to 773 K
Mo(1)/A		4	712	3.84	0.40
Mo(2)/A		8	707	5.05	0.52
Mo(3)/A		12	693	9.37	0.96
Mo(4)/A		18	691	14.63	1.51
Mo(5)/A		24	689	13.38	1.38
Mo(1)/TA	11.2	4	674	10.02	1.02
Mo(2)/TA	11.2	8	674	11.17	1.14
Mo(3)/TA	11.2	12	679	15.93	1.62
Mo(4)/TA	11.2	18	679	13.82	1.41
Mo(5)/TA	11.2	24	685	16.04	1.64

with the raising of the Mo loading. When the Mo loading is higher than 18 wt%, more peaks can be seen, indicating that several Mo species exist on the samples at high Mo loading.

For the Mo/TA samples the intensity of the first peak is larger compared with that of Mo/A without TiO_2 at low Mo loading. No obvious changes of the peak intensity was seen with Mo loading. The maximum temperature of the first peak was relatively lower.

The data in table 2 show clearly the changes in the H/Mo ratio and the maximum temperature of the first peak for the Mo/A and Mo/TA samples with different Mo loadings.

The H/Mo atomic ratio is only 0.4–0.52 for the Mo/A samples at 4–8 wt% Mo loading, meaning less Mo^{6+} can be reduced to lower valency, while the H/Mo ratio increased to 1.02–1.14 for the Mo/TA samples at the same low Mo loading. Furthermore, the maximum temperature of the first peak for Mo/TA is lower by 30–40 K than for the Mo/A samples. These differences diminished at higher Mo loadings.

The Mo 3d XPS spectra of Mo/A and Mo/TA showed that the binding energies of the Mo $3d_{5/2}$ and Mo $3d_{3/2}$ levels are 233.0 ± 0.2 and 235.7 ± 0.3 eV, respectively, indicating the presence of Mo^{6+} in these samples. No influence of TiO_2 on the valence state of molybdenum was observed, however, the molybdenum atomic concentration on Mo/TA is higher than that of Mo/A [6,7]. When the samples were reduced at 773 K in H_2, a shoulder peak of low valency of $Mo^{(6-\delta)+}$ appeared. The proportion of Mo^{4+}, Mo^{5+} and Mo^{6+} states can be estimated by deconvolution of the Mo 3d doublet [8]. Fig. 3 shows the deconvolution of the Mo 3d doublet of reduced Mo/Al_2O_3 and Mo/TiO_2-Al_2O_3 catalysts. The results are shown in fig. 4. For the Mo/A samples the proportion Mo^{4+} ions increased with raising the Mo loading. The Mo^{5+} ions reached

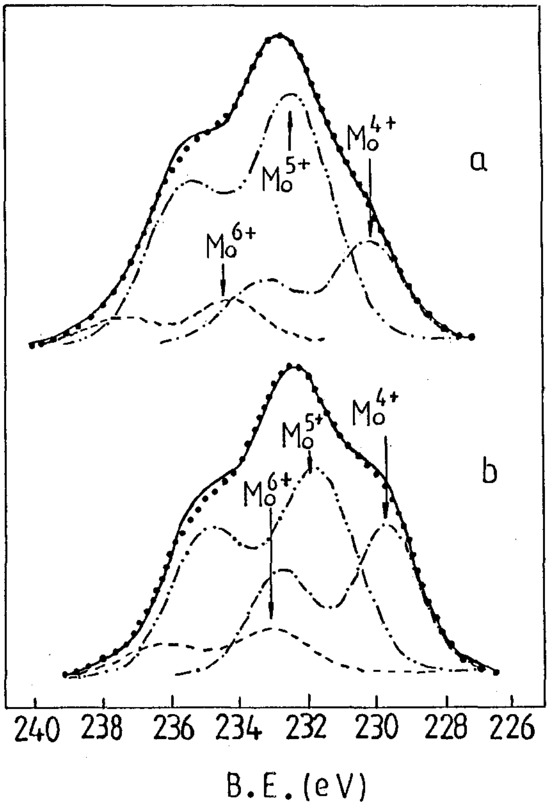

Fig. 3. The deconvolution of Mo 3d doublet of Mo/A (a) and Mo/TA (b) (TiO_2 11.2 wt%) catalysts reduced at 773 K in H_2 for 2 h. MoO_3 18 wt% ——— experimental curve, · · · computer fitting curve.

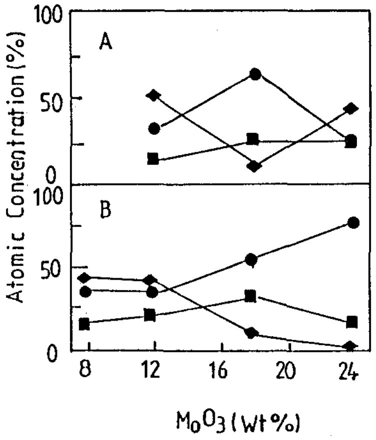

Fig. 4. The valence state distribution of Mo/A (A) and Mo/TA (B) (TiO_2 11.2 wt%) catalysts reduced at 773 K in H_2 for 2 h. ■ Mo^{4+}, ● Mo^{5+}, ◆ Mo^{6+}

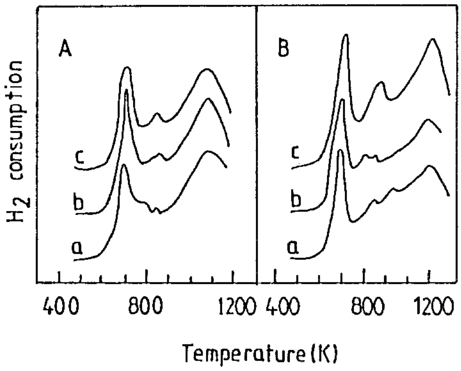

Fig. 5. TPR profiles of Mo/A (A) and Mo/TA (B) (TiO_2 11.2 wt%) calcined at (a) 773, (b) 873, (c) 973 K, MoO_3 18wt%.

maximum value, while the intensity of Mo^{6+} ions was lower at 18 wt% Mo sample. For Mo/TA samples, the maximum intensity of Mo^{4+} is higher than that of Mo/A. The Mo^{5+} ions increased when Mo loading is higher than 12 wt%, while the intensity of Mo^{6+} decreased gradually with Mo loadings. It is clearly seen that the intensity of Mo^{5+} is usually higher than that of Mo^{4+} in all Mo/A and Mo/TA. However, the presence of TiO_2 favored the reduction of more Mo^{+6} ions to Mo^{+4} ions at the same MoO_3 loading.

2. THE INFLUENCE OF CALCINATION TEMPERATURE

Fig. 5A, B show respectively the TPR profiles of Mo/A and Mo/TA catalysts which have been calcined at different temperatures. Table 3 shows the amounts of H_2 consumed for samples reduced up to 773 K. No remarkable change of the maximum temperature of the first peak for Mo/A was observed when the calcination temperature was raised from 773 to 973 K. However, the H/Mo atomic ratio slightly decreased after calcination at 973 K. For the Mo/TA samples the maximum temperature of the first peak increased with calcination

Table 3
The change of peak temperature and amount of H_2 consumption in TPR. MoO_3: 18 wt%

Catalyst	TiO_2 (wt%)	Calcination temp. (K)	Temp. of first peak (K)	Amount of H_2 consumption up to 773 K (ml/mmol)	H/MO up to 773 K
Mo/A		773	691	14.63	1.51
Mo/A		873	704	14.64	1.51
Mo/A		973	694	13.34	1.36
Mo/TA	11.2	773	679	13.82	1.41
Mo/TA	11.2	873	685	15.85	1.61
Mo/TA	11.2	973	695	17.04	1.77

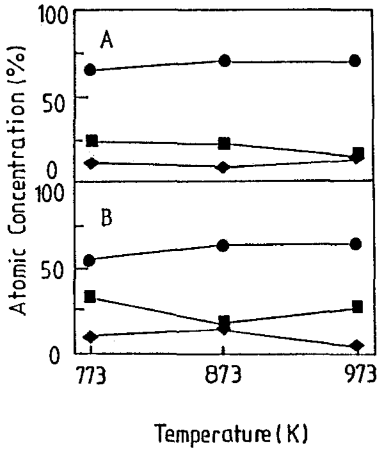

Fig. 6. Influence of calcination temperature on the valence state distribution of Mo/A (A) and Mo/TA (B) (TiO_2 11.2 wt%) catalysts reduced at 773 K in H_2 for 2 h. MoO_3 18 wt%. ■ Mo^{4+}, ● Mo^{5+}, ◆ Mo^{6+}

temperature. The peak at 850 K became larger and an increase of the H/Mo ratio was also seen.

Fig. 6 shows the proportion of Mo^{4+}, Mo^{5+} and Mo^{6+} ions in Mo/A and Mo/TA samples calcined at different temperatures. The decrease of Mo^{4+} ions and increase of Mo^{6+} ions can be obviously seen for Mo/A catalysts after calcination at 973 K. But no great change in intensity of Mo^{5+} occurred. For Mo/TA catalysts the minimum intensity of Mo^{+4} can be observed at 873 K calcination. The intensity of the Mo^{+4} ion is higher than that of Mo/A at 773 and 973 K calcination.

4. Discussion

It is well known that [9–12] Mo^{6+} ions in Mo/A of low Mo loading are distributed to two different alumina sites: a tetrahedral site M(t) and an octahedral site Mo(o). The M(t) is a predominant species at low levels of Mo and is not reducible because of its strong interaction with Al_2O_3, while the Mo(o) concentration increases with Mo loading and is reducible or partially reducible.

The structure of MoO_3 supported on Al_2O_3 has been examined by RLS [7,13]. The results show that several kinds of Mo species existed with the variation of Mo loadings. The tetrahedral MoO_4^{2-} is the main species at 4% Mo loading. The octahedral MoO_6^{6-} and polymeric $Mo_6O_{24}^{6-}$ were observed at middle levels of MoO_3. When MoO_3 loading is over 18%, crystalline MoO_3 and $Al_2(MoO_4)_3$ phase were formed.

When Mo is below the amount of a monolayer dispersion of MoO_3 on the carrier, the TPR profile can be divided into two temperature regions: a low temperature region of 600–800 K and a high temperature region of 800–1200 K. The former is assigned to the reduction of M(o), whereas the latter is related to the reduction of M(t). The situation when the Mo^{4+} or Mo^{5+} ions were further reduced to metallic state also occurred in the high temperature region. At high Mo loading TPR profiles were complicated because of the formation of crystalline MoO_3 and the $Al_2(MoO_4)_3$ phase. Multiple peaks in the TPR profiles at high levels of Mo can be considered as the reflection of different reduction temperature required for various Mo^{6+} species. However, it is possible to assume that an increase of Mo^{6+} reducibility with Mo loading is due to the increment of Mo(o) species concentration on the weaker sites of Al_2O_3. The maximum intensity of Mo^{5+} was obtained for the 18% Mo sample, which corresponds to the amount for a monolayer. Fig. 4 indicated also that most part of Mo^{6+} was reduced to Mo^{5+} and Mo^{4+} at 773 K in H_2. It can be explained that MoO_3 existed mainly in octahedral polymeric species or small crystalline MoO_3 by RLS results [13]. When MoO_3 loading is over a monolayer, due to the formation of larger crystalline MoO_3 and $Al_2(MoO_4)_3$ phase, the H/Mo ratio and Mo^{4+} ions decreased. In the $Al_2(MoO_4)_3$ phase the Mo^{6+} is known to be tetrahedrally surrounded and is hardly reducible.

When the surface of Al_2O_3 was covered homogeneously by TiO_2, the reducibility of Mo^{6+} was obviously enhanced, especially at lower Mo loadings. The LRS results of M/TA indicated that [7] only Mo(o) in polymeric species at lower Mo loadings and additional smaller crystalline MoO_3 were present at higher Mo loadings. No MO(t) or $Al_2(MoO_4)_3$ phase was found. We imagined that the stronger tetrahedral sites on Al_2O_3 surface were first occupied by TiO_2, so that the interaction between MoO_3 and Al_2O_3 was weakened and reducible Mo species were increased. MoO_3 supported on TiO_2 can be reduced to a much lower valency. The reason is that, on the one hand, Mo^{6+} existed only as octahedral species which is reducible on a TiO_2 carrier [14]. On the other hand, the reducibility of TiO_2 itself can play the role of a relay for promoting reducibility of Mo [16,17]. We suggest that a layer of TiO_2 on Al_2O_3 can also play the similar role as the TiO_2 carrier. Therefore, the reducibility of Mo^{6+} is increased with the TiO_2 content because of the effect of more TiO_2. This interesting result can be used to improve the activities of Mo catalyst, because in some reactions the lower valency Mo was considered having the active sites. We have observed an obvious increment of HDS activity of thiophere for Mo/TA [7].

The different influence of calcination temperature on the reducibility of M/A and M/TA can also be seen. For Mo/A an increase of the calcination temperature made the reducibility of Mo^{6+} slightly less due to more Al_2 $(MoO_4)_3$ phase formation, especially at 973 K. For M/TA the H/Mo ratio increased with calcination temperature, but Mo^{4+} ions are less at 873 K. LRS results indicated that [13] the crystalline MoO_3 disappeared and TiO_2 aggregated to a larger particle at 873 K. It is assumed that a part of the MoO_3 moved to the Al_2O_3 surface originally occupied by TiO_2. When the calcination temperature was raised to 973 K, most part of the anatase TiO_2 transformed to rutile structure, but the $Al_2(MoO_4)_3$ phase was hardly formed.

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