

# Synthesis of higher alcohols from syngas over ultrafine Mo–Co–K catalysts

Ye Zhang\*, Yuhan Sun and Bing Zhong

State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, PO Box 165, Shanxi 030001, PR China  
E-mail: zhangye1999@hotmail.com

Received 31 January 2001; accepted 3 July 2001

Ultrafine Mo–Co–K catalysts were prepared and tested for higher alcohol synthesis. The catalysts exhibited high catalytic activity. The effect of the mole ratio of cobalt and molybdenum in the catalysts upon the catalytic performance of higher alcohol synthesis was investigated. Among the ultrafine Mo–Co–K catalysts, the best one corresponded to the Co/Mo mole ratio of 1:7. The XPS spectra revealed that molybdenum was present in two species:  $\text{Mo}^{6+}$  and  $\text{Mo}^{4+}$  on the surface of reduced catalysts, and the  $\text{Mo}^{4+}$  species content depended strongly on the Co/Mo mole ratio. The selectivity towards higher alcohols was found to be related to the  $\text{Mo}^{4+}$  species content. A linear relation between the selectivity and  $\text{Mo}^{4+}$  species content led to the conclusion that the  $\text{Mo}^{4+}$  species was the main active species for higher alcohol synthesis over the ultrafine Mo–Co–K catalysts.

**KEY WORDS:** Mo–Co–K catalyst; ultrafine particle; higher alcohol synthesis

## 1. Introduction

The catalytic conversion of syngas to higher alcohols is generally recognized as a promising route for providing clean fuels and feed stocks of chemical industry in view of both environmental protection and resources utilization. Although there have been various catalyst systems for higher alcohol synthesis from syngas [1–17], a great effort is being made to improve both activity and selectivity of catalysts. Much attention has recently been paid to alkali-promoted supported Mo catalysts doped with Group VIII metals due to their high activity and sulfur resistance [13–15,18–25]. Among them, the Mo–Co–K catalyst system showed an excellent catalytic performance for higher alcohol synthesis [13–15,21,25]. Fujimoto [21] found that supported Co–Mo–K catalyst was active towards the syngas conversion to aliphatic alcohols containing 1–7 or more carbon atoms at temperatures from 200 to 300 °C and under pressures from 1.0 to 7.0 MPa. Murchison [14] claimed that the addition of CoS to  $\text{K}_2\text{CO}_3$ -promoted  $\text{MoS}_2$  on carbon gave better conversion and alcohol selectivity than NiS or FeS. Santiesteban [13] and Bian [25] reported that both activity and the selectivity to  $\text{C}_{2+}$  alcohols were strongly enhanced by the additions of Co and K into supported Mo catalyst. On the other hand, some investigators found that supports in supported Mo catalysts were unfavourable to the formation of alcohols arising from the dehydration of alcohols on the acidic sites of supports [26–31]. Lowenthal [27] and Bian [28] reported that supported Mo catalysts were sensitive to the surface acidity which resulted from either the supports themselves or the interaction between supports and metals, and low surface acidity was in favour of enhancing the se-

lectivity to higher alcohols in such a catalytic system. Furthermore, Saito and Anderson [32] found that the specific activity to higher alcohols of unsupported Mo catalysts was comparable to that of the best metallic catalysts. For these reasons, unsupported Mo–Co–K catalyst system was chosen for the synthesis of higher alcohols in this work. Moreover, it has been known that ultrafine catalysts had high activity due to large surface area and active surface atoms. Thus, unsupported Mo–Co–K catalysts were prepared in the form of ultrafine particles.

In this paper, higher alcohol synthesis over ultrafine Mo–Co–K catalysts was studied. The effect of the Co/Mo mole ratio upon the catalytic performance was investigated.

## 2. Experimental

### 2.1. Preparation and characterization of catalyst

Ultrafine Mo–Co–K catalysts were prepared by the sol-gel method followed by supercritical fluid drying (SCFD) technique. Firstly, a molybdenum sol was prepared by dissolving 16.5 g of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  in a  $\text{H}_2\text{O}_2$  (as a complex-agent) aqueous solution (1 ml  $\text{H}_2\text{O}_2$  (30%) + 5 ml  $\text{H}_2\text{O}$ ) under stirring at room temperature, and then  $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  (the amount was determined by different Co/Mo mole ratios) and KCl (the amount maintained 1 wt% in all catalysts) were directly added to the above solution, which led to a hydrogel of Mo–Co–K 3–5 min later. Finally, 400 ml of ethanol was added to the hydrogel, and a supercritical fluid drying operation was carried out in a high pressure caldron: temperature and pressure were raised to 260 °C and 7.5 MPa, the ethanol was released slowly after equilibrating for 30 min under the above conditions.

\* To whom correspondence should be addressed.

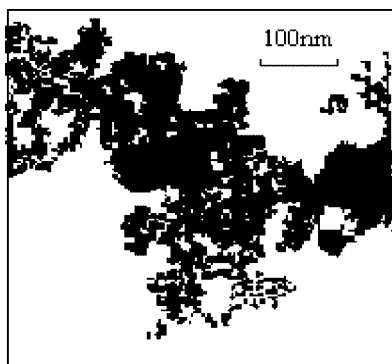


Figure 1. TEM micrograph of the ultrafine Mo-Co-K (Co/Mo = 1:7, K wt1%) catalyst ( $\times 100\,000$ ).

Table 1

Effect of Co/ Mo molar ratio on the texture of ultrafine Mo-Co-K catalysts.

Catalyst		$S_{\text{BET}}$	$V_{\text{PN}}$	Average pore	Physical phase
Co/Mo	K (wt%)	( $\text{m}^2/\text{g}$ )	( $\text{cm}^3/\text{g}$ )	diameter (nm)	
0	1%	17.5	0.088	11.5	$\text{MoO}_3$
1:10	1%	19.8	0.114	10.1	$\text{MoO}_3$
1:7	1%	22.1	0.099	8.9	$\text{MoO}_3, \text{CoMoO}_4$
1:2	1%	20.8	0.113	10.9	$\text{MoO}_3, \text{CoMoO}_4, \text{K}_2\text{Mo}_4\text{O}_{13}$

The ultrafine powder was then calcined at  $350^\circ\text{C}$  for 3 h in air. As a result, ultrafine Mo-Co-K catalysts were obtained.

Transmission electron microscopy (TEM) of the catalysts was carried out by a Hitachi H-600 and the TEM micrograph of a typical sample is shown in figure 1.  $\text{N}_2$  adsorption at 77 K was performed (on a Micromeritics Sorptmatic1900 instrument) to obtain the BET surface area, pore volume and average pore size of the catalysts. Prior to the measurement, the samples were degassed at  $300^\circ\text{C}$  for 3 h ( $10^{-2}$  Torr). Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Dmax- $\gamma$  C X-ray diffractometer with Cu  $\text{K}\alpha$  radiation at a scanning rate of  $6^\circ/\text{min}$ . The textural and structural properties of the ultrafine Mo-Co-K catalysts were characterized as listed in table 1.

X-ray photoelectron spectroscopy (XPS) was detected on an ESCALAB MKII electron spectroscopy instrument with the Mg  $\text{K}\alpha$  radiation at 1256.6 eV. Before detection, the catalysts were reduced in flowing  $\text{H}_2$  (30 ml/min) at  $350^\circ\text{C}$  for 10 h and then cooled to the ambient temperature in  $\text{H}_2$  flow. The samples were transferred in highly pure  $\text{N}_2$  for the XPS test. The analyzer energy was 50 eV, the base pressure  $10^{-9}$  Pa and the step 0.1 eV. The contamination C was used as the internal reference and the binding energy of C(1s) was 284.7 eV. The peak deconvolution was carried out from Gaussian components defined by the position, height and width.

## 2.2. Apparatus and method for activity test

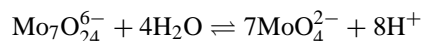
The catalytic test for higher alcohol synthesis was conducted at 6.0 MPa,  $300^\circ\text{C}$  and  $10000\text{ h}^{-1}$  in a fixed-bed

stainless-steel reactor with ID of 10 mm. The catalyst in ultrafine powder form was tabletted, and then cracked into 40–60 mesh. 0.5 g of the catalyst was loaded and reduced in flowing  $\text{H}_2$  (30 ml/min) at  $350^\circ\text{C}$  for 10 h before the activity test. After that, the reactor was cooled to below  $100^\circ\text{C}$ . Following the introduction of syngas ( $\text{H}_2/\text{CO} = 2$ ), temperature and pressure were raised to the reaction conditions. All products were *in situ* analyzed by gas chromatographs after the reaction became steady.

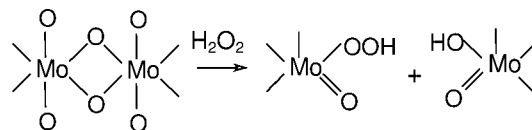
## 3. Results and discussion

### 3.1. Preparation chemistry of molybdenum sol

Ultrafine molybdenum-based catalysts have not been studied often, probably mainly because molybdenum compounds have some particular properties, such as the low solubility, high crystallizability [33] and so on, which led to the difficulty to form sol and further to form gel and ultrafine particles. The preparation of the ultrafine particles of conventional metal oxides, such as  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$  and  $\text{ZrO}_2$ , was intensively investigated in literature. Alkaline was the common precipitation agent. However, this method seemed to be improper for the preparation of ultrafine molybdenum-based catalysts, because for the pure molybdenum source, *i.e.*, ammonium heptamolybdate (AHM), there is a dissolving equilibrium in water:



It was found that the above equilibrium moved to the right side when alkaline was added to this system. In other words, AHM existed in dissolved ion form  $\text{MoO}_4^{2-}$  in alkaline aqueous solution, which was unfavourable for the formation of the precursor, *i.e.*, sol of ultrafine particles. Therefore, it is necessary to explore other ways to form molybdenum sol. It was reported that the polymolybdate structure could be decomposed by the scission of  $\text{H}_2\text{O}_2$  as follows [34]:



The present new method of preparation of AHM sol is based on this reaction. According to the above reaction, the function of  $\text{H}_2\text{O}_2$  can be explained to increase the solubility of AHM in water in two ways: (i) The larger  $\text{Mo}_7\text{O}_{24}^{6-}$  group was cut to smaller  $\text{Mo}_x\text{O}_y\text{H}_z^{\delta-}$  groups ( $x < 7$ ,  $y < 24$ ) by  $\text{H}_2\text{O}_2$ . Generally speaking, a smaller group is dissolved easier than a larger group for the same category. (ii) The smaller  $\text{Mo}_x\text{O}_y\text{H}_z^{\delta-}$  group has a more hydrophilic group  $-\text{OH}$ . The dissolved smaller  $\text{Mo}_x\text{O}_y\text{H}_z^{\delta-}$  group constituted a molybdenum sol particle or its precursor, which combined with  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and KCl to form Mo-Co-K gel and further ultrafine particles in the following steps.

### 3.2. Effect of the Co/Mo mole ratio on the catalytic performance

Figure 2 and table 2 show the higher alcohol synthesis results over the ultrafine Mo–Co–K catalysts with different Co/Mo mole ratios. It can be found that the performance of higher alcohol synthesis over the ultrafine Mo–Co–K catalysts changes greatly with the Co/Mo mole ratio. The activity and selectivity towards higher alcohols increase with increasing Co/Mo mole ratio up to Co/Mo = 1 : 7 and then decrease above Co/Mo = 1 : 7. The activity and selectivity of the ultrafine Mo–Co–K catalysts reach maxima at the Co/Mo mole ratio of 1 : 7. It could be considered that there is a synergistic interaction between the Co and Mo which is responsible for the high activity of higher alcohol synthesis.

### 3.3. Correlation between alcohol selectivity and surface Mo<sup>4+</sup> species content

In order to get insight into the effect of Co/Mo mole ratio on the higher alcohol synthesis performance, XPS of reduced and unreduced catalysts were carried out. For the Co(2p) XPS spectra, unreduced and reduced samples were almost the same. But for the Mo(3d) XPS spectra, a significant change was found (see figure 3). Compared with unreduced samples, reduced samples showed obvious shoulder peaks near 229.6 eV (see figure 3), which were assigned to

the spectra of Mo(3d<sub>5/2</sub>) in MoO<sub>2</sub> [35]. This indicated that MoO<sub>2</sub> appeared on the surface of reduced samples. In addition, the content of MoO<sub>2</sub> in the reduced catalysts varied with the Co/Mo mole ratio (as shown in figure 3). Peak deconvolution was carried out (see figure 4) and then the Mo<sup>4+</sup> species content could be obtained. It was found that the Mo<sup>4+</sup> species content changed in the same trend as the selec-

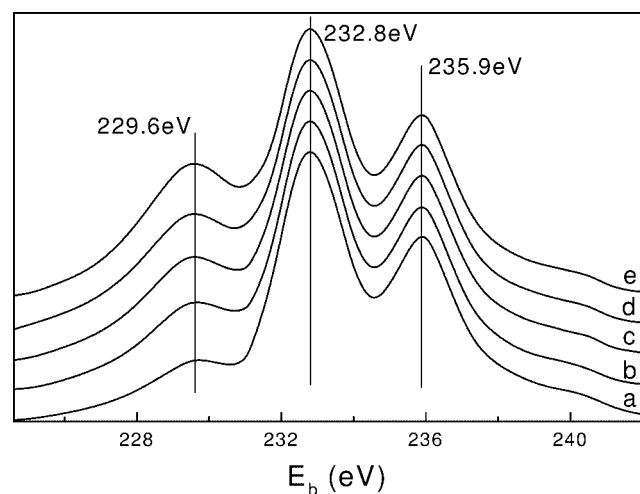


Figure 3. Mo(3d) XPS spectra of the ultrafine Mo–Co–K catalysts with the Co/Mo mole ratio of 0 (a), 1 : 10 (b), 1 : 2 (c), 1 : 4 (d) and 1 : 7 (e) after reduction.

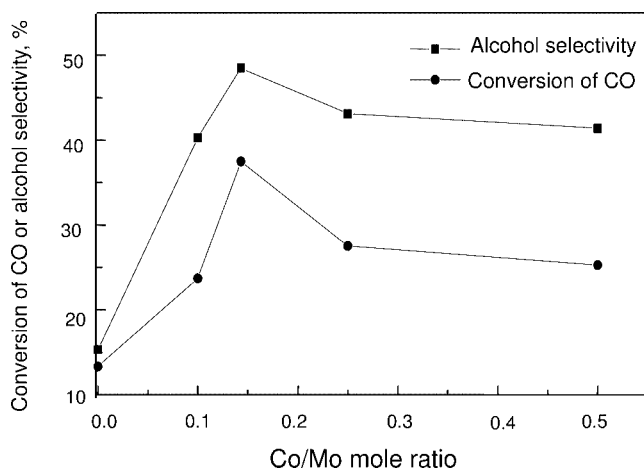


Figure 2. The effect of Co/Mo mole ratio on the higher alcohol synthesis of catalysts.

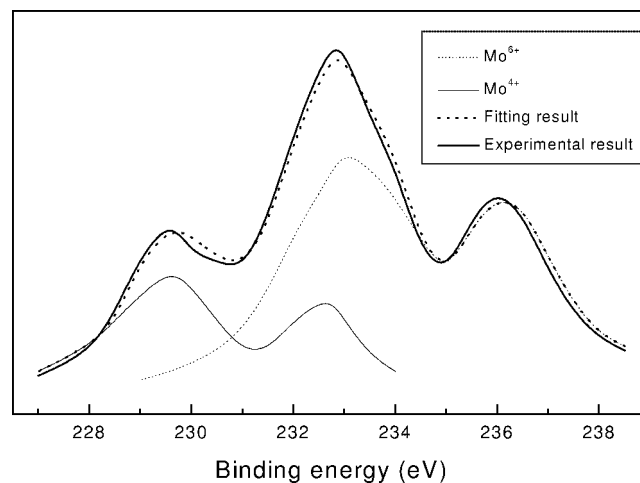


Figure 4. Deconvolution of Mo(3d) XPS spectra for reduced ultrafine Mo–Co–K catalysts.

Table 2  
The catalytic performance of the ultrafine Mo–Co–K catalysts.<sup>a</sup>

Catalyst		CO conv. (mol%)	Alc. sel. (mol%)	C <sub>n</sub> OH sel. (mol%)				C <sub>2+</sub> OH/ C <sub>1</sub> OH	Alc. STY (g/kg h)
Co/Mo	K (wt%)			MeOH	EtOH	PrOH	BuOH		
0	1%	13.3	15.3	72.5	24.2	2.6	0.7	0.38	67.1
1 : 10	1%	23.7	40.3	51.4	31.5	11.7	5.5	0.94	267.0
1 : 7	1%	37.5	48.5	48.2	25.2	17.9	8.9	1.08	624.4
1 : 4	1%	27.5	43.1	50.1	30.4	13.2	6.3	0.99	390.5
1 : 2	1%	25.3	41.4	56.5	30.9	8.5	4.1	0.77	364.9

<sup>a</sup> Reaction conditions: 300 °C, 6.0 MPa and 10000 h<sup>−1</sup>.

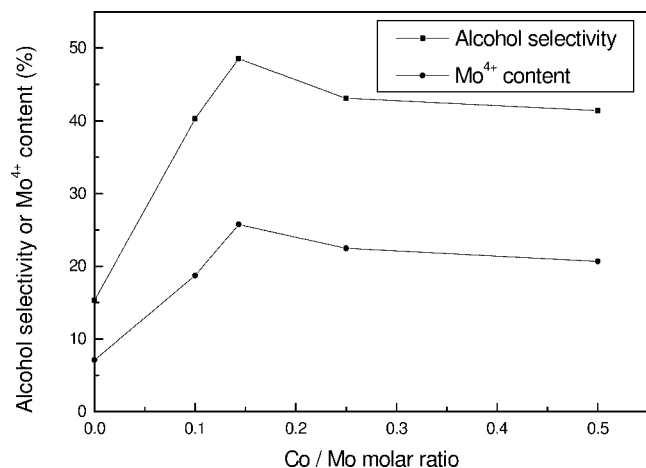


Figure 5. The correlation between the selectivity to higher alcohols and the Mo<sup>4+</sup> content on the surface of the ultrafine Mo–Co–K catalysts.

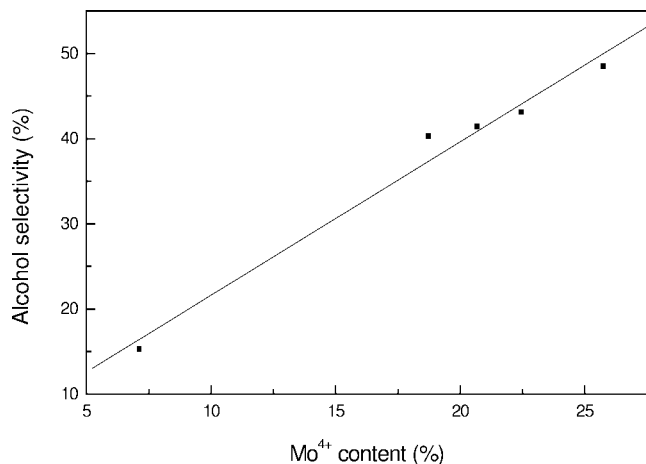


Figure 6. The selectivity to higher alcohols plotted as a function of the Mo<sup>4+</sup> content on the surface of the ultrafine Mo–Co–K catalysts.

tivity to higher alcohols with the Co/Mo mole ratio (see figure 5). The maximum Mo<sup>4+</sup> species content corresponded to the maximum selectivity to higher alcohols. Furthermore, the selectivity to higher alcohols changed linearly with the Mo<sup>4+</sup> species content in the reduced catalysts (see figure 6), *i.e.*, the synthesis of higher alcohols was closely related to the existence of Mo<sup>4+</sup> species. This indicated that Mo<sup>4+</sup> species might be the main active phase for the synthesis of higher alcohols. This conclusion was in accordance with that of Muramatsu *et al.* [36]. It was also notable that the C<sub>2</sub>+OH/C<sub>1</sub>OH ratio changed greatly with the Co/Mo mole ratio (see table 2) and with the Mo<sup>4+</sup> species content. This implied that more Mo<sup>4+</sup> species on the surface of the catalysts were also favourable to the formation of C<sub>2</sub>+OH.

#### 4. Conclusions

The ultrafine Mo–Co–K catalyst showed high activity for higher alcohols synthesis from syngas. The catalytic activity and selectivity over the ultrafine Mo–Co–K catalysts were significantly influenced by the Co/Mo mole ratio of the cat-

alysts, which showed the maxima at 1 : 7 of the Co/Mo mole ratio. The formation of higher alcohols was closely associated with the presence of Mo<sup>4+</sup> species on the surface of the catalysts. A linear relation between the Mo<sup>4+</sup> species content and the selectivity towards higher alcohols led to the conclusion that the Mo<sup>4+</sup> species on the catalysts acted as the active phase for higher alcohols synthesis.

#### Acknowledgement

This work was supported by National Natural Science Foundation of China. We greatly thank the State Key Laboratory for Physical Chemistry of Solid Surfaces (in Xiamen University) for supplying the XPS spectrometer and the deconvolution program for XPS analysis. We would like to thank Professor Hongwei Xiang and Professor Jianguo Wang for helpful discussions.

#### References

- [1] G.J. Quarderer and G.A. Cochran, PCT Int. Appl. WO 8403696 (Cl.C07C27/06) (1984); US Appl. 476674 (1983).
- [2] G.J. Quarderer, G.A. Cochran, R.R. Stevens and C.B. Murchison, Eur. Pat. Appl. EP 180719 (Cl.C07C29/32) (1986); US Appl. 668598 (1984).
- [3] N.E. Kinkade, PCT Int. Appl. WO 8503074 (Cl.C07C29/16) (1985); US Appl. 567244 (1983).
- [4] Y.C. Xie, B.M. Naasz and G.A. Somorjai, Appl. Catal. 27 (1986) 233.
- [5] K. Klier, Chem. Ind. (Dekker) (1981) 5 (Catal. Org. React.) 195.
- [6] K. Klier, in: *Heterog. Catal. Proc. Symp. Ind. – Univ. Coop. Chem. Program Dep. Chem.*, Texas A & M Univ., 1984, p. 252.
- [7] K.J. Smith and R.B. Anderson, Can. J. Chem. Eng. 61 (1983) 40.
- [8] K.J. Smith and K. Klier, Prepr. Am. Chem. Soc. Div. Petr. Chem. 37 (1992) 214.
- [9] E. Tronconi, C. Cristiani, N. Ferlazzo, P. Forzatti, P.L. Villa and I. Pasquon, Appl. Catal. 32 (1987) 285.
- [10] E. Tronconi, L. Lietti, P. Forzatti and I. Pasquon, Appl. Catal. 47 (1989) 317.
- [11] P. Forzatti, C. Cristiani, N. Ferlazzo, L. Lietti, E. Tronconi, P.L. Villa and I. Pasquon, J. Catal. 111 (1988) 120.
- [12] P. Forzatti, E. Tronconi and I. Pasquon, Catal. Rev. Sci. Eng. 33 (1991) 109.
- [13] J.G. Santiesteban, C.E. Bogdan, R.G. Herman and K. Klier, in: *Proc. 9th Int. Congr. on Catalysis*, Vol. 2 (1988) p. 561.
- [14] C.B. Murchison, M.M. Conway, R.R. Stevens and G.J. Quarderer, *Proc. 9th Int. Congr. on Catalysis*, Vol. 2 (1988) p. 626.
- [15] G.J. Quarderer, in: *AIChE Spring National Meeting*, New Orleans, USA, 1986, p. 25.
- [16] A. Kiennemann, C. Diagne and J.P. Hindermann, Appl. Catal. 53 (1989) 197.
- [17] T.Y. Park, I.-S. Nam and Y.G. Kim, Ind. Eng. Chem. Res. 36 (1997) 5246.
- [18] M. Inoue, K. Nakajima, A. Kurusu, T. Miyake and T. Inui, Appl. Catal. 49 (1989) 213.
- [19] M. Inoue, A. Kurusu, H. Wakamatsu, K. Nakajima and T. Inui, Appl. Catal. 29 (1987) 361.
- [20] Z.R. Li, M. Jiang and Y.L. Fu, J. Fuel Chem. Technol. 25 (1997) 266.
- [21] K. Fujimoto and T. Oba, Appl. Catal. 13 (1985) 289.
- [22] G. Lu, C.F. Zhang and Y.Q. Cang, Appl. Catal. 150 (1997) 243.
- [23] E.C. Alyea, D. He and J. Wang, Appl. Catal. 104 (1993) 77.
- [24] L.J. Feng, X.G. Li, E. Kugler and D. Dadyburjor, Chin. J. Catal. 20 (1999) 63.

- [25] G.Z. Bian, Y.S. Ma and Y.L. Fu, *Acta Phys. Chim. Sin.* 12 (1996) 406.
- [26] T. Tatsumi, A. Muramatsu and H. Tominaga, *Appl. Catal.* 34 (1987) 77.
- [27] E.E. Lowenthal, S. Schwarz and H.C. Foley, *J. Catal.* 156 (1995) 96.
- [28] G.Z. Bian, Y.L. Fu, L. Fan and K. Fujimoto, *Chin. J. Catal.* 19 (1998) 260.
- [29] T. Tatsumi, A. Muramatsu, K. Yokota and H. Tominaga, *Shokubai (Catalysts)* 28 (1986) 481.
- [30] G.Z. Bian, L. Fan, Y.L. Fu and K. Fujimoto, *Acta Phys. Chim. Sin.* 14 (1998) 401.
- [31] J.Y. Zhang, Y.J. Wang and L. Chang, *Appl. Catal.* 126 (1995) 205.
- [32] M. Saito and R.B. Anderson, *J. Catal.* 63 (1980) 438.
- [33] J.Z. Zhang and H.D. Li, *Mater. Sci. Progr.* 6 (1992) 332.
- [34] H.F. Barry, in: *Chemistry and Uses in Molybdenum*, Proc. 4th Int. Conf., Golden, CO, 1982.
- [35] C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder and G.E. Muilenberg, *Handbook of X-ray Photoelectron Spectroscopy* (Perkin-Elmer, Eden Prairie, MN, 1979).
- [36] A. Muramatsu, T. Tatsumi and H. Tominaga, *J. Phys. Chem.* 96 (1992) 1334.