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Structure and reactivity of ultrafine Ce–Mo oxide particles

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Abstract

Two series of the Ce–Mo oxide catalysts for the partial oxidation of toluene to benzaldehyde have been prepared, respectively, by the sol–gel and coprecipitation methods and characterized by using various techniques. The results have shown that the catalytic reactivity is strongly composition related; and ultrafine Ce–Mo oxide particles prepared by the sol–gel process are apparently a better catalyst than large Ce–Mo oxide particles with a same composition but prepared by the coprecipitation method. The highest yield of benzaldehyde is obtained when the composition of the ultrafine particles reaches the vicinity of $Ce/(Ce + Mo) = 0.50$, corresponding to a catalyst consists of both CeO_2 and $Ce_2(MoO_4)_3$. The reaction mechanism and the promotion effect of the excess CeO_2 in the ultrafine Ce–Mo oxide are discussed to explain why ultrafine Ce–Mo oxide particles prepared by the sol–gel method are good for the partial oxidation of toluene.

Keywords: Ultrafine particles; Ce–Mo oxides; Structure; Reactivity

1. Introduction

Partial oxidation of toluene to benzaldehyde via gas phase process is one of the current challenges in the field of catalysis. In the 1960s, Rhône-Poulenc used direct oxidation of toluene to produce benzaldehyde on a commercial scale [1–3]; and another one-step process for the oxidation of toluene by air under moderate pressure to produce aromatic aldehydes or alcohols was reported from Japan [4]. However, both these processes had very poor economic profit. Due to the significance of this reaction in chemical industry, it has been extensively investigated, and great efforts have been made in searching more effective catalysts with better economic profits [1–20]. As expected, metal oxide catalysts have been widely explored for this purpose. Although, a great variety of unpromoted and promoted oxide catalysts have been claimed to be effective for the partial oxidation of toluene, it is generally recognized that mixed Mo-based and V-based oxides exhibit the best performance in catalyzing the formation of the partial oxidation products. In short, the research works were mainly focused on Bi–Mo–O and Fe–Mo–O systems in the 1970s [5–7]; on supported MoO_3 and V_2O_5 in the 1980s [8–13] and on supported or unsupported Mo- and V-based oxides in the 1990s [14–20]. The reaction mechanism is often described by the redox model suggested by Mars and van Krevelen [21], i.e. the hydrocarbon reacts with the surface lattice oxygen ions on the catalyst to form oxidized products, and the reduced-oxide is reoxidized to its initial state through the implantation of oxygen from the gas phase.

Although, the direct gas phase oxidation of toluene to benzaldehyde has been studied for long, successful results are scarce, as so far none of these catalysts is found to produce benzaldehyde in a yield good enough for commercial application. In the current industrial practice, a conventional three-step process including side-chain chlorination and subsequent hydrolysis, which is obviously not environmental friendly, is still

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used mainly for the production of benzaldehyde from toluene. Thus, to explore new effective catalysts for this reaction is still a project of great interest.

In the past decade, research on ultrafine metal oxide particles has received considerable attentions [22,23], and these kinds of materials are expected to have unique catalytic properties because of their nano-scale particle size. Among the methods used for the preparation of ultrafine oxide particles, sol–gel technique is unique in producing samples mixed on a molecular scale, which provides an opportunity for tailoring the properties of oxide catalysts [24,25]. In this work, the structure and reactivity of ultrafine Ce–Mo oxide particles prepared by the sol–gel technique are studied and compared with those of corresponding oxide particles prepared by the coprecipitation method.

2. Experimental

2.1. Sample preparation

Ultrafine Ce–Mo oxide particles with different Ce/(Ce + Mo) atomic ratios were prepared by the sol–gel method using citric acid as a complexing polyfunctional hydroxyacid reported previously [26]. Cerium nitrate, ammonium molybdate and citric acid aqueous solutions were prepared separately and then mixed with a molar ratio of citric acid to metallic ions of 1:3. The pH value of the mixture was adjusted to be 0.5 by adding an appropriate amount of nitric acid solution. The mixtures thus obtained were first kept in a water bath for gelation, and then the gels were dried at 393 K and calcined at 673 K. For comparison, the conventional coprecipitation method was also used to prepare the complex Ce–Mo oxide sample by mixing aqueous solutions of cerium nitrate and ammonium molybdate at required ratio, and the precipitates formed were dried at 393 K and calcined at 823 K. It was proved [26] that to form the required compound, i.e. $Ce_2(MoO_4)_3$ from the mixed oxides, 823 K was needed for samples prepared from coprecipitation method, while 673 K was good enough for the precursors obtained from sol–gel process.

2.2. Partial oxidation of toluene

Partial oxidation of toluene was carried out in a quartz U-type fixed bed microreactor with 250 mg catalyst under the reaction conditions of 0.1 MPa and 673 K with feeding gas either at a helium flowing rate of 20 ml/min with a volume ratio of He/O_2/toluene = 50/5/1 (for samples of Table 1) or at a flowing rate of 8 ml/min with a volume ratio of air/toluene = 9 (for samples listed in Tables 2 and 3). All the samples were pretreated at 673 K for 0.5 h in flowing air or helium–oxygen mixture before reaction; and the reaction usually takes 4–7 h on stream to reach a steady state for data collection. The reaction products mainly consisting of CO, CO_2, H_2O and benzaldehyde were analyzed by an on-line GC. The conversion of toluene and the selectivity of benzaldehyde were evaluated by the following equations, respectively:

$$\text{conversion of toluene}(\%) = \frac{(C_{T0} - C_{TR}) \times 100}{C_{T0}};$$

$$\text{selectivity of benzeldehyde}(\%) = \frac{C_{BA} \times 100}{C_{T0} - C_{TR}},$$

where C_{T0} is the original amount of toluene; C_{TR} the amount of toluene remained after reaction; and C_{BA} the amount of benzaldehyde produced.

Table 1
Structure and catalytic properties of various samples[a]

Sample	CeO_2	MoO_3	$Ce_2(MoO_4)_3$	$Ce_2(MoO_4)_3$
Preparation method	Sol–gel	Sol–gel	Coprecipitation	Sol–gel
Particle size (nm)	10–20	>100	>100	20–40
BET surface area (m^2/g)	41.0	5.1	4.2	20.3
Conversion of toluene (%)	63.4	36.3	58.2	60.3
Benzaldehyde selectivity (%)	0	17.9	19.1	52.3
Benzaldehyde yield (%)	0	6.5	11.1	31.5

[a] Reaction conditions: 250 mg of sample at 0.1 MPa, 673 K, and with feeding gas at a helium flowing rate of 20 ml/min with a volume ratio of He/O_2/toluene = 50/5/1.

Table 2
Partial oxidation of toluene on the ultrafine Ce–Mo oxides[a]

Ce/(Ce + Mo) atomic ratio	Conversion of toluene (%)	Benzaldehyde selectivity (%)	Benzaldehyde yield (%)
0	24.0	6.0	1.4
0.33	37.0	13.0	4.8
0.44	33.0	32.0	10.6
0.50	34.0	37.0	12.6
0.56	41.0	30.0	12.3
0.67	54.0	15.0	8.1
1.00	54.8	0	0

[a] Reaction conditions: 250 mg of sample at 0.1 MPa, 673 K, and with feeding gas at a flowing rate of 8 ml/min with a volume ratio of air/toluene = 9.

Table 3
Partial oxidation of toluene on the Ce–Mo oxides with a Ce/(Ce + Mo) atomic ratio of 0.5[a]

Preparation method	Coprecipitation	Sol–gel
Conversion of toluene (%)	35.5	34.0
Benzaldehyde selectivity (%)	16.0	37.0
Benzaldehyde yield (%)	5.7	12.6
Surface Ce/Mo atomic ratio	2.2	1.4

[a] Reaction conditions: 250 mg of sample at 0.1 MPa, 673 K, and with feeding gas at a flowing rate of 8 ml/min with a volume ratio of air/toluene = 9.

2.3. Characterization

X-ray diffraction patterns were obtained with a Shimadzu-3A diffractometer with Cu Kα radiation (0.15418 nm). The BET surface area measurements were performed on a micromeritics ASAP-2000 instrument (N_2 adsorption at 77 K). The shape and size of the oxide particles were elucidated by TEM using a JEM-100S transmission electron microscopy. FT–Raman spectra were taken on a Bruker RSF 100 spectrometer fitted with an InGaAs detector cooled by liquid nitrogen. XPS measurements were performed in a V.G. ESCALAB MKII spectrometer, and the binding energies were referenced to the C_{1s} peak at 284.6 eV.

3. Results and discussion

The particle size and BET surface area of $Ce_2(MoO_4)_3$ samples prepared by different methods are shown in Table 1. TEM results reveal that the sol–gel method provides $Ce_2(MoO_4)_3$ particles in the range of 20–40 nm and the Ce–Mo oxide particles with different Ce/(Ce + Mo) atomic ratios thus prepared are also ultrafine ranging from ca. 15 to 80 nm; in contrast, the particles obtained by the coprecipitation method are >100 nm. The results are consistent with the BET surface area measurements, which have shown that the surface area of ultrafine $Ce_2(MoO_4)_3$ particles is about 20.3 m^2/g, while that of sample prepared by the coprecipitation is as low as 4.2 m^2/g.

As shown in Table 1, it is interesting to note that the $Ce_2(MoO_4)_3$ samples prepared by the two different methods have a similar conversion, but apparently different benzaldehyde selectivity. Ultrafine $Ce_2(MoO_4)_3$ particles have a much higher selectivity than large oxide particles prepared by the coprecipitation method. This implies that ultrafine oxide particles have rather unique catalytic properties for the partial oxidation of toluene, and by decreasing the size of the complex Ce–Mo oxide particles to nanometric scale, the selectivity to benzaldehyde could be remarkably improved.

To explore the influence of composition on the structure and catalytic properties of the ultrafine Ce–Mo oxide catalysts, samples with different Ce/(Ce + Mo) atomic ratios were prepared by the sol–gel method and characterized. The catalytic properties of samples with different Ce/(Ce + Mo) atomic ratios ranging from 0 to 1.0 is shown in Table 2. The results point to the fact that the composition of the ultrafine Ce–Mo oxides has a strong impact on their catalytic properties. As with the increase of Ce/(Ce + Mo) atomic ratio, the yield of benzaldehyde increases slowly to a maximum value in the vicinity of Ce/(Ce + Mo) = 0.5, and finally drops to zero for pure CeO_2. Complementary XRD results have revealed the co-existence of MoO_3 and $Ce_2(MoO_4)_3$ in samples with a Ce/(Ce + Mo) atomic ratio <2/5, and on the contrary, there are CeO_2 and $Ce_2(MoO_4)_3$ in samples, when the atomic ratio is higher than this value. Together with the reactivity data listed in Table 2, the above results suggest that an appropriate amount of excess CeO_2 in the ultrafine Ce–Mo oxide is a good promoter for the partial oxidation of toluene to benzaldehyde, although CeO_2 alone is a catalyst for the complete oxidation of toluene.

For comparison, the catalytic reactivity and surface composition of samples with a Ce/(Ce + Mo) atomic ratio of 0.5 prepared, respectively by the sol–gel and coprecipitation methods are listed in Table 3. The results further confirm the fact that ultrafine Ce–Mo oxide particles have an obviously higher selectivity to benzaldehyde than those corresponding large oxide particles prepared by the coprecipitation method. To figure out the reasons for these differences, the structure and reactivity of the Ce–Mo oxide samples are further explored.

XRD patterns of the ultrafine Ce–Mo oxide with a Ce/(Ce + Mo) atomic ratio of 0.5 before and after reaction are shown in Fig. 1. Noticeably, besides the

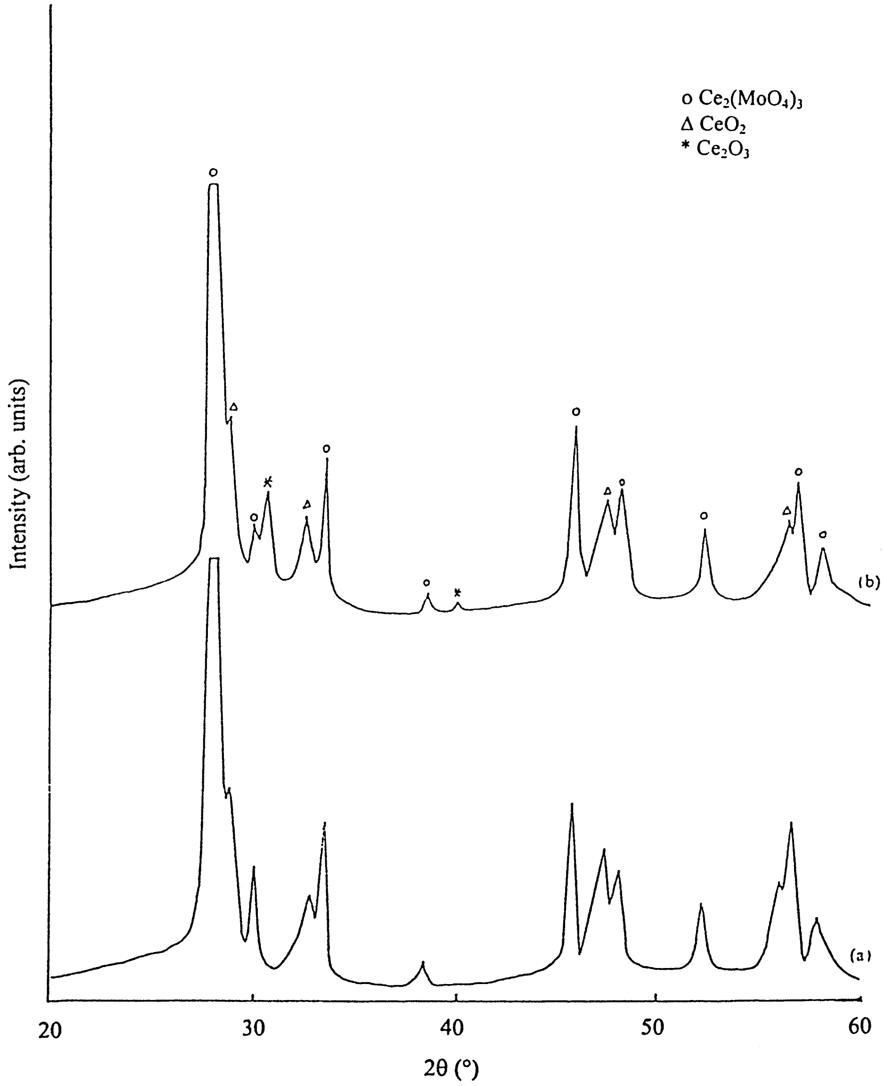


Fig. 1. XRD patterns of the ultrafine Ce–Mo oxide with a Ce/(Ce + Mo) atomic ratio of 0.5: (a) fresh and (b) after reaction.

$Ce_2(MoO_4)_3$ and CeO_2 peaks in the fresh sample, an additional new peak assigning to crystalline Ce_2O_3 is found in the sample after reaction, indicating the fact that a part of CeO_2 in the fresh sample has been reduced to Ce_2O_3 during reaction. LRS spectra of these samples are shown in Fig. 2, from which one can see that after reaction there is a remarkable decrease in the intensity of the band at 464 cm^{-1} assigning to CeO_2 [27], suggesting the disappearance of an appreciable amount of CeO_2 on the surface of the fresh sample during reaction. Thus, it seems reasonable to conclude that the excess CeO_2 in the ultrafine Ce–Mo oxide does participate into the reaction, and is partly reduced to Ce_2O_3.

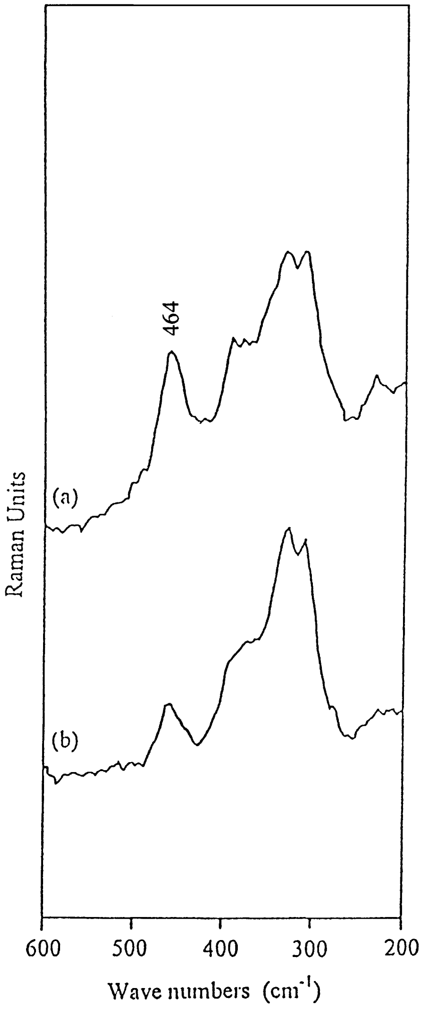


Fig. 2. LRS spectra of the ultrafine Ce–Mo oxide with a Ce/(Ce + Mo) atomic ratio of 0.5: (a) fresh and (b) after reaction.

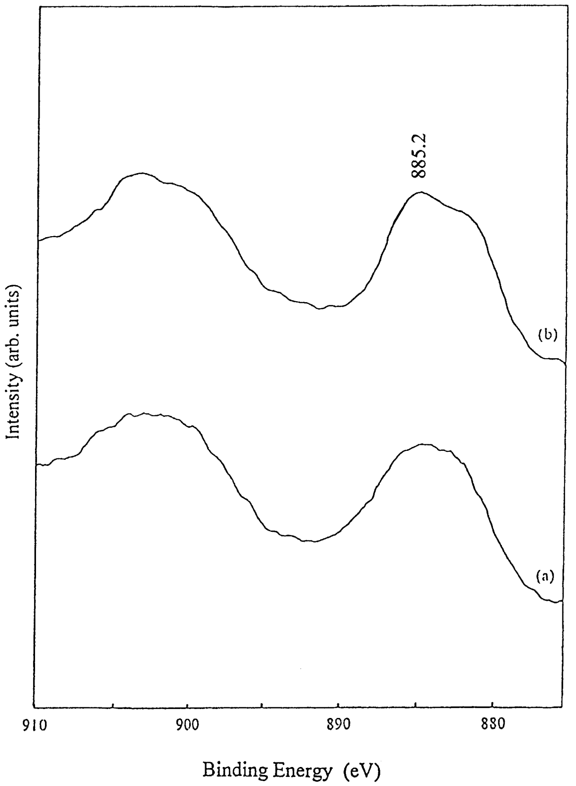
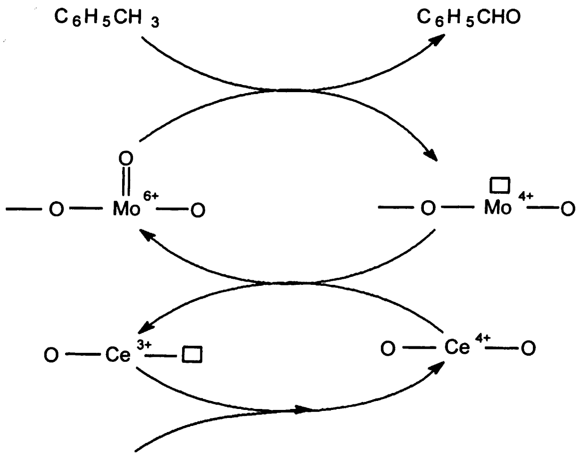


Fig. 3. $Ce_{(3d5/2)}$ XPS spectra of the ultrafine Ce–Mo oxide with a Ce/(Ce + Mo) atomic ratio of 0.5: (a) fresh and (b) after reaction.

To get a deeper insight on the surface constitution of these samples, their $Ce_{(3d5/2)}$ XPS profiles are shown in Fig. 3. The $Ce_{(3d5/2)}$ binding energies for the related compound have been reported in the literature [28], i.e. 881.8 eV for CeO_2, 880.6, and 884.8 eV for Ce_2O_3 (the intensity of 884.8 is much stronger than that of 880.6) as well as 881.6 and 885.4 eV for $Ce_2(MoO_4)_3$, respectively. As can be seen from Fig. 3, after reaction there is a remarkable increase on the peak intensity at ca. 885.2 eV. The result suggests that during reaction a part of Ce^{4+} ions on the surface of the catalyst may be reduced to Ce^{3+} ions. In addition, the $Mo_{(3d5/2)}$ XPS profiles of these samples have indicated a shift of the $Mo_{(3d5/2)}$ binding energy from 232.5 to 232.0 eV with no obvious change of the peak shape, suggesting that some of the Mo^{6+} ions on the sample surface have been partially reduced, i.e. Mo^{6+} and Mo ions of lower valence co-exist on the surface of the particles.

Recently cerium oxide and CeO_2-supported materials have come under intense scrutiny as structural and/or electronic promoters as well as catalysts for related catalytic reactions [29]. It is argued that the oxygen vacancies in the fluorite crystal structure of CeO_2 are mobile with the formation of the dominant point defects playing an important role in the partial oxidation reaction. As indicated above, although pure CeO_2 is a well-known catalyst for the complete oxidation of toluene, the excess CeO_2 in the ultrafine Ce–Mo oxide with a Ce/(Ce + Mo) atomic ratio of 0.5 can greatly enhance the reactivity for the partial oxidation of toluene to benzaldehyde. Together with the results we reported previously [20], i.e. that the main reactive sites for this reaction are the terminal Mo=O bonds in $Ce_2(MoO_4)_3$, it might be proposed that the Mars–van Krevelen cycle can be used to understand the cooperative effect of $Ce_2(MoO_4)_3$ and CeO_2 in the ultrafine Ce–Mo oxide for the partial oxidation of toluene to benzaldehyde [30]:



where (□) denotes a lattice oxygen vacancy. When the lattice oxygen ions on $Ce_2(MoO_4)_3$ are being used for the partial oxidation of toluene to occur, the Mo^{6+} ions are being reduced to a lower valence state, e.g. Mo^{4+}, with the creation of lattice oxygen vacancies. Meanwhile, the CeO_2 co-existed with $Ce_2(MoO_4)_3$ provides its lattice oxygen anions to the lattice oxygen vacant sites on $Ce_2(MoO_4)_3$ by oxygen spillover with the transformation of Ce^{4+} to Ce^{3+}, which was then reoxidized to Ce^{4+} by gas oxygen. In other words, the promotional effect of CeO_2 is originated from its capability in compensating the lattice oxygen vacant sites formed on the ultrafine $Ce_2(MoO_4)_3$ during reaction; and the redox cycle of CeO_2, i.e. between Ce^{3+} and Ce^{4+} is accomplished by the implementation of its lattice oxygen from gas phase. These arguments might explain why the catalytic reactivity for the partial oxidation of toluene to benzaldehyde can be remarkably improved by the existence of a small amount of excess CeO_2 in the ultrafine Ce–Mo oxide. However, as pure CeO_2 is active in the complete oxidation of toluene, too much CeO_2 in the catalyst will inevitably result in the decrease of the selectivity to benzaldehyde. These conclusions are consistent with the experimental results listed in Table 2, i.e. with the increase of Ce/(Ce + Mo) atomic ratio to values >0.5, the selectivity of the catalysts drops obviously, although the conversion of toluene is even increased.

To explore the reason that large Ce–Mo oxide particles with similar composition, but prepared by the conventional coprecipitation method have a rather low selectivity for the above reaction, a comparative study on the XRD patterns of the Ce–Mo oxide with an atomic ratio of 0.5 prepared by the coprecipitation method is shown in Fig. 4. For the fresh sample, its XRD patterns are similar to those of the ultrafine Ce–Mo oxide, i.e. the existence of both $Ce_2(MoO_4)_3$ and CeO_2 is obvious, however, a distinct difference is the absence of the new species corresponding to Ce_2O_3 in this catalyst after reaction. The result seems to suggest that the promotion effect in providing lattice oxygen from the excess CeO_2 to $Ce_2(MoO_4)_3$ is much weaker in this sample than that of the corresponding ultrafine oxide, which might be due to the relatively uneven distribution of the Ce and Mo components in the precipitate precursor and accordingly in the final catalyst prepared by the coprecipitation method. The uneven distribution of the components as well as the larger size of the particles might lead to a loose contact between the excess CeO_2 and $Ce_2(MoO_4)_3$, preventing the CeO_2 from participating the redox cycle of the $Ce_2(MoO_4)_3$ reactive phase. Moreover, as shown in Table 3, the surface Ce/Mo atomic ratio of the large Ce–Mo oxide particles is about 30% higher than that of ultrafine Ce–Mo oxide particles, the severe surface enrichment of the ceria species in the sample might contribute to its high toluene conversion, but low

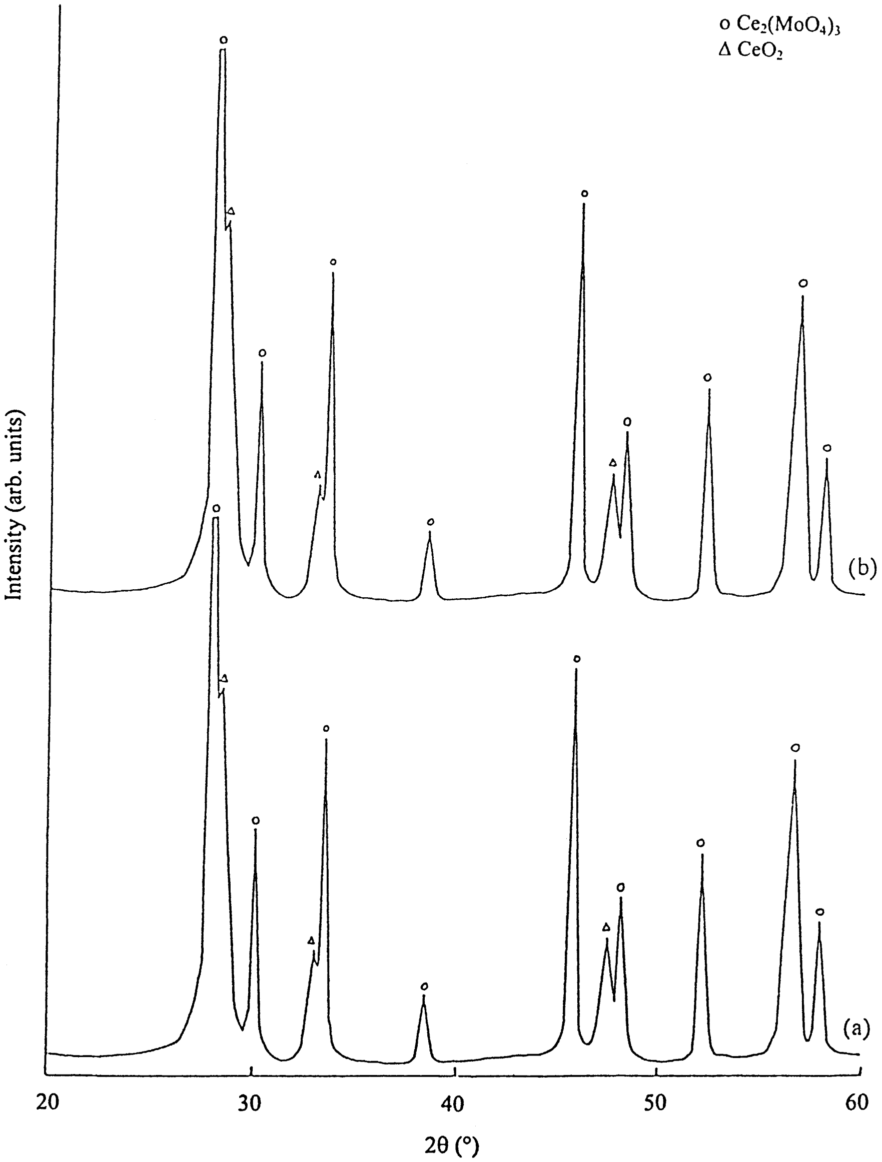


Fig. 4. XRD patterns of the Ce–Mo oxide with a Ce/(Ce + Mo) atomic ratio of 0.5 prepared by the coprecipitation method: (a) fresh and (b) after reaction.

selectivity to benzaldehyde. This may account for the reactivity results shown in Table 3, i.e. the toluene conversion of the large oxide particles is similar to that of ultrafine oxide particles, but the selectivity to benzaldehyde is much lower. In contrast, for the case of the ultrafine Ce–Mo oxide prepared by the sol–gel method, the Ce and Mo components in the gel precursor are better mixed on a molecular scale and the excess CeO_2 species are evenly distributed and closely contact with the active $Ce_2(MoO_4)_3$ species, which result in the pronounced promotion effect of the excess CeO_2 through participating the redox cycle of $Ce_2(MoO_4)_3$ species, resulting in the higher selectivity for the partial oxidation of toluene to benzaldehyde.

4. Conclusions

Preparation method and oxide composition have a strong impact on the structure and reactivity of the Ce–Mo oxide catalysts. In comparison with the rather large Ce–Mo oxide particles prepared by the conventional coprecipitation method, sol–gel process can produce ultrafine Ce–Mo oxide particles with better reactivity for the partial oxidation of toluene to benzaldehyde. Ultrafine Ce–Mo oxide particles with a Ce/(Ce + Mo) atomic ratio of 0.50 thus prepared have the highest selectivity and yield of benzaldehyde. The mechanism of the above reaction can be described by Mars–van Krevelen cycle, the excess CeO_2 works as a promoter by releasing its lattice oxygen to the oxygen vacant sites formed on the $Ce_2(MoO_4)_3$ species during reaction. As evidenced by XRD, XPS and laser Raman results, the co-existence of a small and appropriate amount of CeO_2 with $Ce_2(MoO_4)_3$ in the ultrafine Ce–Mo oxide is critical in improving the selectivity to benzaldehyde; in contrast, due to the uneven distribution of CeO_2 and $Ce_2(MoO_4)_3$ as well as the larger particle size in the Ce–Mo oxide prepared by the conventional coprecipitation method, the excess CeO_2 is difficult to get involving into the redox cycle of the $Ce_2(MoO_4)_3$ reactive species, and in addition the surface enrichment of cerium component on the surface of this catalyst tends to increase its activity for the complete oxidation of toluene and results in its lower selectivity for the partial oxidation of toluene.

Acknowledgements

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References

[1] US Patent 3387036 (1969).
[2] US Patent 3658875 (1972).
[3] US Patent 3948995 (1976).
[4] Chem. Eng. News 13 (July 4, 1977).
[5] J.E. Germain, R. Laugier, C.R. Acad. Sci. Ser. C 276 (1973) 1349.
[6] K. van der Wiele, P.J. van den Berg, J. Catal. 39 (1975) 437.
[7] M. Ai, T. Ikawa, J. Catal. 40 (1975) 203.
[8] N.K. Nag, T. Fransen, P. Mars, J. Catal. 68 (1981) 77.
[9] B. Jonson, B. Rebenstorf, R. Larsson, S.L.T. Andersson, S.T. Lundin, J. Chem. Soc., Faraday Trans. I 82 (1986) 767.
[10] S.L.T. Andersson, J. Chem. Soc., Faraday Trans. I 82 (1986) 1537.
[11] B. Jonson, B. Rebenstorf, R. Larsson, S.L.T. Andersson, J. Chem. Soc., Faraday Trans. I 84 (1988) 1897.
[12] B. Jonson, B. Rebenstorf, R. Larsson, S.L.T. Andersson, J. Chem. Soc., Faraday Trans. I 84 (1988) 3363.
[13] B. Jonson, B. Rebenstorf, R. Larsson, S.L.T. Andersson, J. Chem. Soc., Faraday Trans. I 84 (1988) 3547.
[14] H. Zhang, W. Zong, X. Duan, X. Fu, J. Catal. 129 (1991) 426.
[15] H.K. Matralis, C. Papadopoulou, C. Kordulis, A.A. Elguezabal, V.C. Corberan, Appl. Catal. A: Gen. 126 (1995) 365.
[16] A.A. Elguezabal, V.C. Corberan, Catal. Today 32 (1996) 265.
[17] J.S. Yoo, Appl. Catal. A: Gen. 143 (1996) 29.
[18] F. Konietzni, H.W. Zanthoff, W.F. Maier, J. Catal. 188 (1999) 154.
[19] S. del Val, M.L. Granados, J.L.G. Fierro, J. Santamaria-Gonzalez, A. Jimenez-lopez, J. Catal. 188 (1999) 203.
[20] W. Kuang, Y. Fan, K. Chen, Y. Chen, J. Catal. 186 (1999) 310.
[21] P. Mars, D.W. van Krevelen, Chem. Eng. Sci. Suppl. 3 (1954) 41.
[22] Z. Zhong, Q. Yan, X. Fu, J. Gong, J. Chem. Soc. Chem Commun. (1996) 1745.
[23] Q. Liang, K. Chen, W. Hou, Q. Yan, Appl. Catal. A: Gen. 166 (1998) 191.
[24] G.M. Pajonk, Appl. Catal. 72 (1991) 217.
[25] D.A. Ward, E.I. Ko, Ind. Eng. Chem. Res. 34 (1995) 421.
[26] W. Kuang, Y. Fan, K. Yao, Y. Chen, J. Solid State Chem. 140 (1998) 354.
[27] G.W. Graham, W.H. Weber, C.R. Peters, R. Usmen, J. Catal. 130 (1991) 310.
[28] T.L. Barr, C.G. Fries, F. Cariati, J.C.J. Bart, N. Giordano, J. Chem. Soc., Dalton Trans. (1983) 1825.
[29] A. Trovarelli, Catal. Rev.-Sci. Eng. 38 (1996) 439.
[30] Y. Fan, W. Kuang, Y. Chen, Stud. Surf. Sci. Catal. 112 (1997) 121.