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Study on the reactivity of ultrafine cerium–molybdenum oxide particles in the absence of molecular oxygen

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The state and reactivity of lattice oxygen ions in the ultrafine Ce–Mo oxide particles prepared by the sol–gel method are studied by using X-ray diffraction, laser Raman spectroscopy, temperature-programmed reduction, X-ray photoelectron spectroscopy and pulse microreactor tests. It is found that the lattice oxygen ions in the ultrafine Ce–Mo oxides are the main active species for partial oxidation of toluene to benzaldehyde. By decreasing the size of complex Ce–Mo oxide particles to nanometric scale, the reactivity of lattice oxygen ions can be remarkably improved.

Keywords: ultrafine particles, complex Ce–Mo oxides, reactivity of lattice oxygen ions

1. Introduction

Partial oxidative transformations of hydrocarbons over metal oxide catalysts are currently the main method for the synthesis of a series of important organic oxygenate compounds. In the past decades, mechanisms of these reactions have been extensively studied [1–8]. It is generally recognized that the lattice oxygen ions in the oxide catalysts participate in the formation of partial oxidation products, and thus the nature of lattice oxygen ions is one of the most important parameters influencing catalytic selectivity. However, most of the research works in the area of the oxidative catalysis have been investigated in the presence of molecular oxygen.

In contrast to a large number of studies in the presence of molecular oxygen, little is known about the behavior of lattice oxygen ions in metal oxides for partial oxidation reaction in the absence of molecular oxygen, which may provide new information for explaining the nature of lattice oxygen ions and their reactivity in the presence of molecular oxygen. Compared to the case in the presence of molecular oxygen, due to only the lattice oxygen ions exist on the surface of metal oxides in the absence of molecular oxygen, the role of lattice oxygen ions in partial oxidation of hydrocarbons may be clearly understood.

In our previous report [9], it was found that for partial oxidation of toluene to benzaldehyde in the presence of molecular oxygen, the ultrafine Ce–Mo oxide particles prepared by the sol–gel process exhibited higher catalytic activity than the corresponding large oxide particles prepared by the conventional precipitation method. The aim of this work is to further investigate the state and reactivity of lattice oxygen ions in the ultrafine Ce–Mo oxides in the absence of molecular oxygen.

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 as reported in our previous study [10], in which citric acid was used as a complexing polyfunctional hydroxyacid. Nitrate cerium, ammonium molybdate and citric acid aqueous solutions were prepared separately and then mixed with the molar ratio of citric acid to metallic ions of 1 : 3. The pH of the mixture solutions was adjusted to 0.5 with the addition of nitric acid solution. The above solutions were first kept in a water bath for gelation, and then the gels were dried and calcined. For comparison, the conventional coprecipitation method was also used to prepare complex Ce–Mo oxide [9], in which nitrate cerium aqueous solution was mixed with ammonium molybdate aqueous solution, and the precipitates formed were dried and calcined.

2.2. Partial oxidation of toluene

The toluene oxidation reaction in the absence of molecular oxygen was used as a probe to evaluate the reactivity of lattice oxygen ions in the ultrafine Ce–Mo oxides as reported in our previous study [9]. The reactivity of lattice oxygen ions in the ultrafine Ce–Mo oxides was determined in a pulse microreactor under the conditions of 623 K, 0.2 MPa, helium flow rate of 40 ml min^{-1}, and 0.81 μmol toluene every pulse.

2.3. Characterization

X-ray diffraction patterns were obtained in a Shimadzu 3A diffractometer with Cu Kα radiation (0.15418 nm). The particles' shape and size were elucidated by TEM with a

JEM-100S transmission electron microscope. The BET surface area measurements were performed on a Micromeritics ASAP-2000 instrument (N_2 adsorption at 77 K). The TPR experiments were carried out in a U-type quartz reactor with a heating rate of 10 K/min, and a flow rate of H_2–Ar mixture (5.0 vol% hydrogen) of ca. 30 ml/min. Hydrogen consumption was monitored by a thermal conductivity detector. The pulse microreactor combined with *in situ* Raman spectroscopy experiments were performed using a specially designed *in situ* cell. FT-Raman spectra were taken with a Bruker RSF 100 spectrometer fitted with an InGaAs detector cooled by liquid nitrogen. XPS measurements were performed in a VG ESCALAB MKII spectrometer. Binding energies were referenced to the C_{1s} peak at 284.6 eV.

3. Results and discussion

For partial oxidation of toluene to benzaldehyde in the absence of molecular oxygen the reactivity of lattice oxygen ions (the sum total of benzaldehyde yield per BET surface area) in the ultrafine Ce–Mo oxides with different Ce/(Ce + Mo) atomic ratios is shown in figure 1. For pure CeO_2 and MoO_3 samples, no product is detected under our pulse reaction condition, suggesting that the lattice oxygen ions in CeO_2 and MoO_3 are not a reactive component. However, the ultrafine $Ce_2(MoO_4)_3$ exhibits high benzaldehyde yield, suggesting that cerium molybdate species are the main reactive components. It is interesting to note that the composition of the ultrafine Ce–Mo oxides has great influence on the reactivity of lattice oxygen ions. With the increase of the Ce/(Ce + Mo) atomic ratio, the reactivity of lattice oxygen ions in the ultrafine Ce–Mo oxides is first increased and then decreased rapidly. The maximum reactivity of lattice oxygen ions appears in the vicinity of Ce/(Ce + Mo) = 0.5 for the ultrafine Ce–Mo oxides. As reported in our previous study [9], the maximum benzaldehyde yield for partial oxidation of toluene in the presence of molecular oxygen is reached in the vicinity of Ce/(Ce + Mo) = 0.5 for the ultrafine Ce–Mo oxides. These results indicate that the lattice oxygen ions in the ultrafine Ce–Mo oxides are the main active species for partial oxidation of toluene to benzaldehyde.

The state and reactivity of lattice oxygen ions in the ultrafine Ce–Mo oxide with a Ce/(Ce + Mo) atomic ratio of 0.5 were studied by employing a pulse microreactor combined with *in situ* Raman spectroscopy technique. Figure 2 exhibits the reactivity of lattice oxygen ions in the ultrafine Ce–Mo oxide. It can be seen that for partial oxidation of toluene in the absence of molecular oxygen, benzaldehyde is the main product and the selectivity is as high as ca. 95% every pulse. Compared to the case in the presence of molecular oxygen [9], the selectivity to benzaldehyde is remarkably improved. This reveals that the lattice oxygen ions in the ultrafine Ce–Mo oxide are actually the main active species for partial oxidation of toluene to benzaldehyde. In the absence of molecular oxygen, only the lattice oxygen ions exist on the surface of the oxide, resulting in the high selectivity to benzaldehyde.

The influence of the pulse reaction upon the Raman spectra of the ultrafine Ce–Mo oxide is presented in figure 3. The bands at 750–900 cm^{-1} can be assigned to the stretching vibrations of the bridging oxygen bonds (Mo–O–Ce), and the bands at 900–1000 cm^{-1} to Mo=O stretching vibrations, respectively [11–13]. As shown in figure 2, for the first pulse, the conversion of toluene is 93.3%, and the selectivity of benzaldehyde is 97.1%. This indicates that the lattice oxygen ions on the surface of the fresh sample are very reactive and abundant. From the second to sixth pulses, the selectivity of benzaldehyde almost does not change, but the conversion of toluene decreases to ca. 55.0%. This suggests that the reactive lattice oxygen ions for these pulses may be mainly from the bulk by transferring. As shown in figure 3, after the eighth pulse the relative intensities of the bands to Mo=O stretching vibrations decrease to ca. 80%, while that to Mo–O–Ce stretching vibrations has no marked change. This implies that the lattice oxygen ions on the oxide surface can be

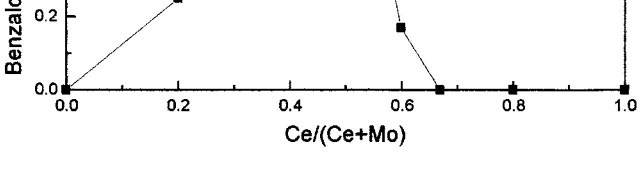

Figure 1. The reactivity of lattice oxygen ions in the ultrafine Ce–Mo oxides.

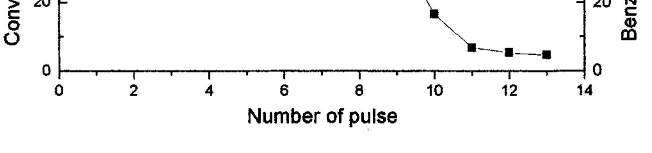

Figure 2. The reactivity of lattice oxygen ions in the ultrafine Ce–Mo oxide with a Ce/(Ce + Mo) atomic ratio of 0.5.

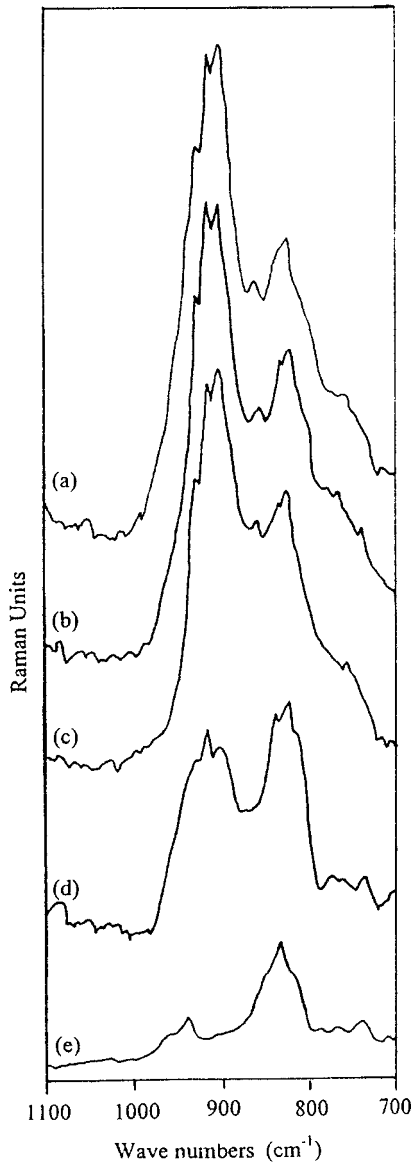

Figure 3. *In situ* LRS spectra of the ultrafine Ce–Mo oxide with a Ce/(Ce + Mo) atomic ratio of 0.5 for the reactivity of lattice oxygen ions: (a) fresh, (b) after the fourth pulse, (c) after the eighth pulse, (d) after the twelfth pulse, (e) after the sixteenth pulse.

mainly replenished after every pulse reaction. After the ninth pulse the conversion of toluene decreases gradually, suggesting that the reactive lattice oxygen species on the oxide surface decrease progressively. After the twelfth pulse the intensities of the bands assigned to Mo=O stretching vibrations decrease to ca. 50%, while that to Mo–O–Ce stretching vibrations decreases to ca. 80%, indicating that the Mo=O sites may be more reactive than the Mo–O–Ce sites. After the sixteenth pulse, no product is detected under our reaction conditions, and the bands assigned to Mo=O stretching vibrations almost disappear, while the intensities of the bands assigned to Mo–O–Ce stretching vibrations decrease to ca. 40%. The above results suggest that the terminal Mo=O bonds may be mainly reactive species during the reaction.

XRD and LRS were used to characterize the ultrafine Ce–Mo oxide with a Ce/(Ce + Mo) atomic ratio of 0.5. The XRD patterns and LRS spectra of the ultrafine Ce–Mo oxide are shown in figures 4 and 5, respectively. For the fresh sample, both XRD patterns of $Ce_2(MoO_4)_3$ and CeO_2 are observed, indicating that the fresh sample is composed of $Ce_2(MoO_4)_3$ and the excessive CeO_2. After reaction, new XRD patterns are observed which can be assigned to crystalline Ce_2O_3. The peak at ca. $2\theta = 47.5°$ in figure 4(b) may result from the overlap of Ce_2O_3 and $Ce_2(MoO_4)_3$, but can be mainly assigned to Ce_2O_3. As shown in figure 5, it can also be found that compared with the band at ca. 340 cm^{-1} of octahedral Mo^{6+} in a surface polymolybdate [14], the band at 464 cm^{-1} of CeO_2 [15] almost disappears after reaction. These results reveal that the excessive CeO_2 also participates in the reaction, and is partly reduced to Ce_2O_3. As indicated above, the ultrafine Ce–Mo oxide with a Ce/(Ce + Mo) atomic ratio of 0.5 has the highest reactivity of lattice oxygen ions. This implies that although pure CeO_2 is not reactive for partial oxidation of toluene, the excessive CeO_2 in the ultrafine Ce–Mo oxide plays an important role in enhancing the reactivity of lattice oxygen ions.

It is well known that the oxygen vacancies in the fluorite crystal structure of CeO_2 are mobile and form the dominant point defect involved in transport behavior. As reported in our previous study [16], the promotional effect of oxygen spillover from CeO_2 to $Ce_2(MoO_4)_3$ in the ultrafine Ce–Mo oxide with a Ce/(Ce + Mo) atomic ratio of 0.5 resulted in faster compensation of active lattice oxygen species in the $Ce_2(MoO_4)_3$. Thus, it may be considered that while the lattice oxygen ions of $Ce_2(MoO_4)_3$ in the ultrafine Ce–Mo oxide are continuously consumed in the reaction, the lattice oxygen ions of CeO_2 in the ultrafine Ce–Mo oxide may transfer to the surface of $Ce_2(MoO_4)_3$ to replenish the reactive lattice oxygen species. As shown in figures 2 and 3, from the second to sixth pulses, the toluene conversion almost does not change, which may be correlated with a timely replenishing of the lattice oxygen ions on the surface of $Ce_2(MoO_4)_3$ after every pulse reaction. Apparently, the promotional effect of oxygen spillover from CeO_2 to $Ce_2(MoO_4)_3$ in the ultrafine Ce–Mo oxide results in the high reactivity of lattice oxygen ions. However, as pure CeO_2 is not reactive for partial oxidation of toluene, increasing of the amount of CeO_2 in the ultrafine Ce–Mo oxides may result in severe surface enrichment of the cerium component, which may further result in the decrease of the reactivity of lattice oxygen ions. As shown in figure 1, increasing the Ce/(Ce + Mo) atomic ratio to higher than 0.5 results in a rapid decrease of the reactivity of lattice oxygen ions in the ultrafine Ce–Mo oxides.

For comparison, the reactivity of lattice oxygen ions in the ultrafine Ce–Mo oxide with a Ce/(Ce + Mo) atomic ratio of 0.5 prepared by the sol–gel process and the corresponding large oxide particles with the same composition prepared by the coprecipitation method is collected in table 1. It is interesting to note that the benzaldehyde yield

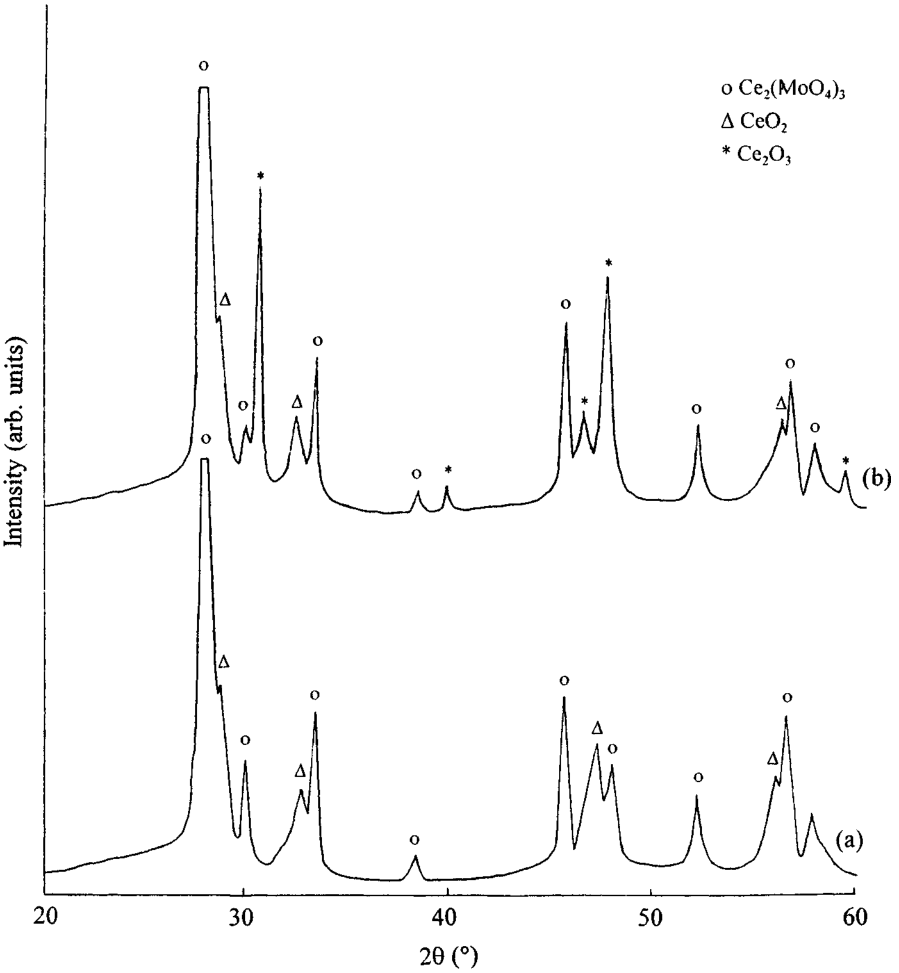

Figure 4. XRD patterns of the ultrafine Ce–Mo oxide with a Ce/(Ce + Mo) atomic ratio of 0.5: (a) fresh, (b) after reaction.

of the ultrafine Ce–Mo oxide is found to be about fifteen times that of the corresponding large oxide particles. This indicates that by decreasing the particle size of complex Ce–Mo oxide to nanometric scale, the reactivity of lattice oxygen ions can be remarkably improved. This result is consistent with their catalytic activity for partial oxidation of toluene to benzaldehyde in the presence of molecular oxygen [9], further suggesting that the lattice oxygen ions in the complex Ce–Mo oxides are the main active species for partial oxidation of toluene to benzaldehyde.

As shown in table 1, it can also be found that there exists severe surface enrichment of the cerium component in the large oxide particles. The surface Ce/Mo atomic ratio of the large oxide particles is much higher than that of the ultrafine oxide particles, which may result in the low reactivity of lattice oxygen ions in the large oxide particles. Compared to the case for the ultrafine Ce–Mo oxide, no new species appear in the XRD pattern of the large oxide particles after the reaction. This reveals that the promotional effect of oxygen spillover from CeO_2 to $Ce_2(MoO_4)_3$ in the large Ce–Mo oxide particles is much weaker than that in the ultrafine oxide particles.

The TPR profiles of the ultrafine Ce–Mo oxide with a Ce/(Ce + Mo) atomic ratio of 0.5 and the corresponding large oxide particles are presented in figure 6. For the ultrafine Ce–Mo oxide, two hydrogen consumption peaks at ca. 783 and 988 K are observed which may be assigned to the reduction of the surface of CeO_2 to Ce_2O_3 [17–19] and the reduction of $Ce_2(MoO_4)_3$ to $Ce_2Mo_3O_9$ [20], respectively. For the large Ce–Mo oxide particles, only one hydrogen consumption peak at ca. 1023 K is observed which may be assigned to the reduction of $Ce_2(MoO_4)_3$ to $Ce_2Mo_3O_9$. This indicates that the reduction of the surface of CeO_2 in the large oxide particles is difficult, which may lead to the poor mobility of the lattice oxygen ions in CeO_2. This results in the weaker promotional effect of oxygen spillover from CeO_2 to $Ce_2(MoO_4)_3$ in the large oxide particles, and further leads to the low reactivity of lattice oxygen ions. Compared with that in the ultrafine oxide particles, the peak maximum of $Ce_2(MoO_4)_3$ in the large oxide particles shifts to higher temperature. The above results indicate that by decreasing the oxide particle size to nanoscale, the Ce–Mo oxide is easier to be reduced to lower valance and the lattice oxygen species in the oxide have a higher mobility. This may lead to the higher reactivity of lattice oxygen ions in the ultrafine oxide particles.

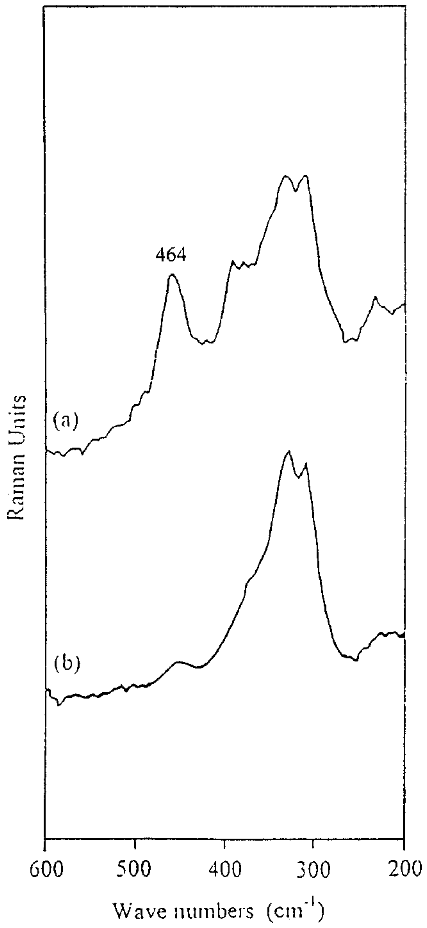

Figure 5. LRS spectra of the ultrafine Ce–Mo oxide with a Ce/(Ce + Mo) atomic ratio of 0.5: (a) fresh, (b) after reaction.

Table 1
The reactivity of lattice oxygen ions in the complex Ce–Mo oxides with a Ce/(Ce + Mo) atomic ratio of 0.5.

	Preparation method	
	Coprecipitation	Sol–gel
Particle size (nm)	>100	20–40
Conversion of toluene[a] (μmol/g)	0.80	17.4
Benzaldehyde selectivity (%)	90.0	98.3
Benzaldehyde yield[a] (μmol/g m^2)	0.06	0.90
Surface Ce/Mo atomic ratio	2.2	1.4

[a] The sum total of every pulse.

4. Conclusion

For partial oxidation of toluene to benzaldehyde, the lattice oxygen ions in the ultrafine Ce–Mo oxides are the main active species, and the Mo=O sites may be more reactive than the Mo–O–Ce sites. The preparation methods and oxide compositions significantly influence the particle size and structure of complex Ce–Mo oxides, and further affect the state and reactivity of lattice oxygen ions in the oxides. It is found that the highest reactivity of lattice oxygen ions in the ultrafine Ce–Mo oxides is reached in the vicinity of Ce/(Ce + Mo) = 0.5, and the reactivity of lattice oxygen ions in the ultrafine Ce–Mo oxide is much higher than that in the corresponding large oxide particles.

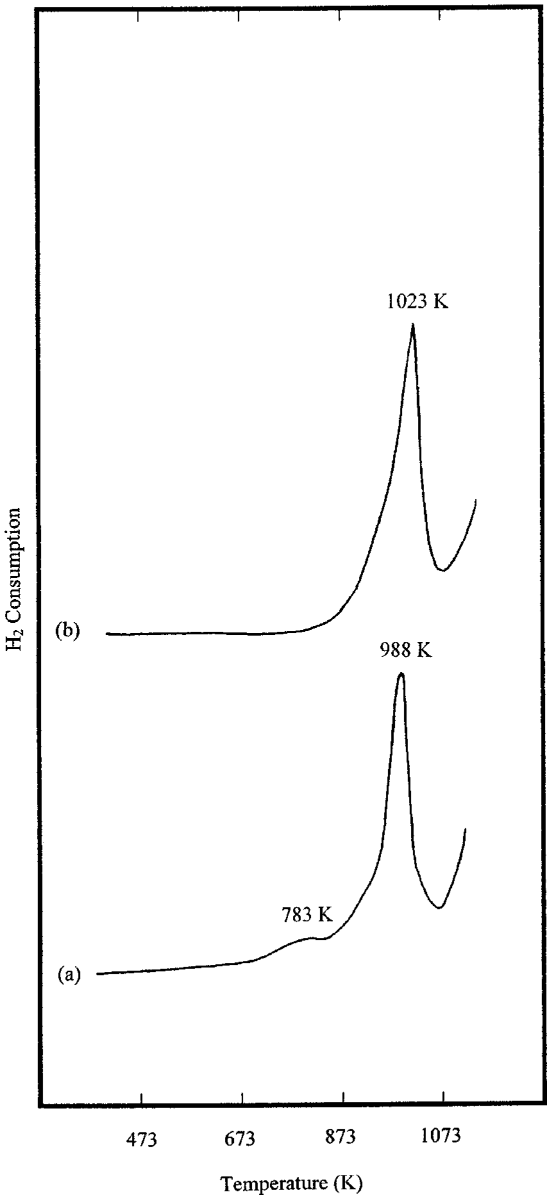

Figure 6. TPR profiles of complex Ce–Mo oxides with a Ce/(Ce + Mo) atomic ratio of 0.5: (a) prepared by the sol–gel method, (b) prepared by the coprecipitation method.

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