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Characterization of acidic and redox properties of Ce–Mo–O catalysts for the selective oxidation of toluene

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Abstract

The surface acidic and redox properties of CeO_2, MoO_3, mechanically mixed CeO_2–MoO_3 and co-precipitated Ce–Mo–O catalysts were characterized by using microcalorimetric adsorption of ammonia and isopropanol (IPA) probe reaction, and the surface properties of these catalysts were correlated with their selectivity for the oxidation of toluene to benzaldehyde and benzoic acid. With the presence of O_2, IPA converted to propylene and diisopropyl ether on acidic sites while converted to acetone on redox sites. It was found that CeO_2 exhibited mainly the redox property while MoO_3 the surface acidity. The IPA probe reaction showed that the mechanically mixed CeO_2–MoO_3 exhibited the surface acidic property, similar to that of MoO_3, indicating that the surface of CeO_2 might be covered by MoO_3 in the mixture upon the calcination at 773 K. On the other hand, the co-precipitated Ce–Mo–O catalyst showed the equivalent acidic and redox properties, and thereby the selectivity to benzaldehyde was greatly enhanced on it as compared to the other catalysts studied in this work.

Keywords: Surface acidity; Redox property; Microcalorimetric adsorption; Isopropanol probe reaction; Selective oxidation of toluene

1. Introduction

The surface acidity/basicity and redox properties of metal oxides play the important roles in catalytic selective oxidation reactions. The surface acidity/basicity can be titrated by basic and acidic probe molecules, as well as by the probe reaction of isopropanol (IPA) conversion [1–3]. On the other hand, the redox property of a metal oxide catalyst can be characterized by using the techniques of TPR/TPO (temperature-programmed reduction/temperature-programmed oxidation) [4]. It is generally true that IPA undergoes the dehydration reaction to produce propylene (PPE) and diisopropyl ether (DIPE) over acidic sites while undergoes the dehydrogenation reaction to produce acetone (ACE) over basic sites [1]. When O_2 is present, IPA can be oxidatively dehydrogenated to ACE. Thus, the oxidative dehydrogenation of IPA may become a probe reaction to characterize the redox properties of metal oxide catalysts. In addition, the presence of O_2 does not seem to affect the dehydration reactions of IPA. Thus, the conversion of IPA with the presence of O_2 may become a probe reaction to characterize the surface acidity and redox properties simultaneously. In this way, the surface acidity and redox property of a metal oxide catalyst can be compared directly, and the dehydration and oxidative dehydrogenation reactions occur on a bi-functional (acidic and redox) surface in a competitive way.

In this work, we studied the surface acidity and redox properties of CeO_2, MoO_3 and two binary oxides Ce–Mo–O prepared via different methods. The surface acidity and redox properties were characterized by microcalorimetric adsorption of ammonia, TPR and IPA probe reactions. These catalysts were also tested for the selective oxidation of toluene to benzaldehyde and benzoic acid, and the catalytic behavior was correlated with the surface acidity and redox properties of the catalysts.

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2. Experimental

CeO_2 and MoO_3 were prepared by calcining $(NH_4)_2Ce(NO_3)_6$ and $(NH_4)_6Mo_7O_{24}\cdot4H_2O$, respectively, at 773 K for 5 h. One binary oxide was prepared by mechanically mixing the two single oxides, and termed as CeO_2–MoO_3. Another binary oxide was prepared by the co-precipitation [5]. Specifically, $(NH_4)_2Ce(NO_3)_6$ and $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ with the molar ratio of 1/1 were dissolved to form an aqueous solution, which was adjusted with NH_4OH solution to pH = 7–8. The solution was evaporated with a rotatory evaporator. The sample was dried and then calcined at 773 K for 5 h. The co-precipitated sample thus obtained was termed as Ce–Mo–O. All the samples were pressed, crashed and sieved to collect the particles with the sizes between 20 and 40 meshes. The mechanically mixed sample was obtained by simply mixing the CeO_2 and MoO_3 with the particles of 20–40 meshes (molar ratio of 1/1).

The surface areas were measured by N_2 adsorption at the temperature of liquid N_2 employing the BET method. The phases present in the catalysts were determined by X-ray diffraction (XRD) using the X′TRA diffractometer equipped with a Cu target and graphite monochromator. TPR measurements were performed by using a quartz U-tube reactor loaded with about 50 mg of a sample. A mixture of N_2 and H_2 (5.13% H_2 by volume) was used and the flow rate was maintained at 40 ml/min. The hydrogen uptake was monitored using gas chromatography with a thermal conductivity detector (TCD). The reducing gas was first passed through the reference arm of the TCD before entering the reactor. The reactor exit was directed through a trap filled with $Mg(ClO_4)_2$ (to remove product water) and then to the second arm of the TCD. The temperature was raised at a programmed rate of 10 K/min from 303 to 1173 K.

Microcalorimetric measurements for the adsorption of NH_3 were carried out using a Tian-Calvet heat-flux apparatus. The microcalorimeter was connected to a gas handling and volumetric adsorption system, equipped with a Baratron capacitance manometer (MKS, USA) for precision pressure measurement. The differential heat of adsorption versus adsorbate coverage was obtained by measuring the heats evolved when doses of a gas (2–5 μmol) were admitted sequentially onto the catalyst until the surface was saturated by the adsorbate. Ammonia with a purity of 99.99% was used. Before microcalorimetric measurements, the samples were typically dried under vacuum, calcined in 66.7 kPa O_2, and evacuated, respectively, at 673 K for 1 h. The microcalorimetric adsorption was performed at 423 K.

The probe reaction was carried out in a fixed-bed glass tube reactor. About 100 mg sample was loaded for the reaction. Isopropanol was introduced to the reaction zone by bubbling air through a glass saturator filled with isopropanol maintained at 295 K. Isopropanol and reaction products were analyzed by an on-line gas chromatograph, using a PEG 20M packed column connected to an FID. Each catalyst was pretreated by heating in air at 673 K for 1 h and then cooled in air flow to the reaction temperature.

The reaction of selective oxidation of toluene was performed by using a U-tube fixed-bed reactor loaded with a sample of about 0.5 g with 20–40 meshes. The reaction was performed at 673 K. The reactants were fed into the reactor by flowing air (62 ml/min) through a glass saturator filled with toluene maintained at 330 K. The tail gas was analyzed by using an on-line gas chromatograph. The organic compounds were separated by an FFAP capillary column and detected by an FID while CO_2 was detected by using a Hayesep D packed column and a TCD.

3. Results and discussion

Fig. 1 presents the XRD patterns for CeO_2 (23 m^2/g), MoO_3 (4 m^2/g), co-precipitated Ce–Mo–O (1.2 m^2/g) and mechanically mixed CeO_2–MoO_3. It is clearly seen that the mechanically mixed sample (after calcination at 773 K) displayed the phases of CeO_2 and MoO_3. No phase change occurred upon the mixing and calcination. The co-precipitated sample exhibited totally different phases. The MoO_3 phase was hardly seen in this sample. The phase of CeO_2 was apparently there and a new phase $Ce_2Mo_4O_{15}$ was formed. Thus, the co-precipitated sample was a mixture of CeO_2 and $Ce_2Mo_4O_{15}$.

Fig. 2 shows the TPR profiles. The CeO_2 exhibited two reduction peaks around 696 and 820 K, corresponding to the reduction of surface Ce^{4+} to Ce^{3+}. The high temperature reduction peak around 1125 K was due to the reduction of bulk Ce^{4+} [6]. The TPR profile of MoO_3 displayed two reduction peaks around 973 and 1040 K, which may be due to the reduction from MoO_3 to MoO_2 and a peak with the temperature higher than 1173 K, which may be attributed to the reduction from MoO_2 to Mo [7]. The mechanically mixed sample CeO_2–MoO_3 had the TPR profile that looked like the overlap of the two TPR profiles of pure CeO_2 and MoO_3. The co-precipitated Ce–Mo–O catalyst displayed totally different TPR profile. Three peaks can be observed for this profile around 880, 1100 and over 1200 K. The peak around 880 K may be due to the reduction of cerium species. This peak shift to higher temperature compared to that of

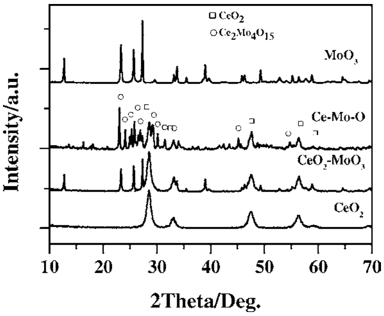

Fig. 1. X-ray diffraction patterns.

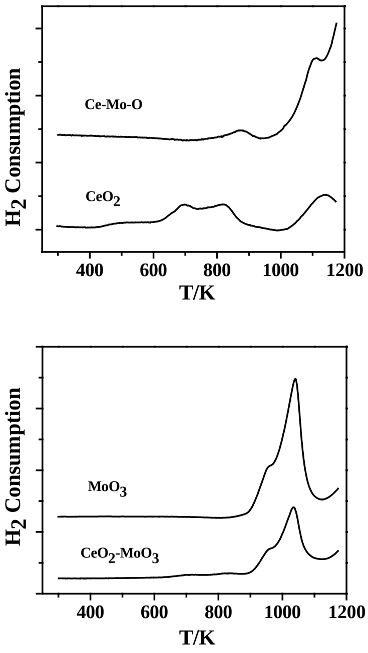

Fig. 2. Temperature-programmed reduction (TPR) profiles.

pure CeO_2, indicating that the presence of molybdenum species retarded the reduction of cerium species. The peak around 1100 K may be due to the reduction of Mo^{6+} to Mo^{4+}, which also shift to higher temperature as compared to the reduction of pure MoO_3 from MoO_3 to MoO_2. The result indicated that the molybdenum in the compound $Ce_2Mo_4O_{15}$ was more difficult to be reduced than in MoO_3. The un-completed peak above 1200 K may be due to the reduction of molybdenum species to metallic Mo.

Microcalorimetric adsorption results are shown in Fig. 3. It is seen that bulk CeO_2 exhibited quite strong surface acidity. The initial heat for ammonia adsorption on the CeO_2 was measured to be about 172 kJ/mol, and the saturation coverage of ammonia on this sample was about 155 μmol/g. The MoO_3 displayed little surface acidity, in consistence with the result of Auroux and Gervasini [8]. The adsorption of ammonia on MoO_3 produced the initial heat lower than 20 kJ/mol. The mechanically mixed CeO_2–MoO_3 sample had the similar surface acidity as CeO_2 while the co-precipitated Ce–Mo–O sample possessed the similar surface acidity as MoO_3, as measured by the microcalorimetric adsorption of ammonia.

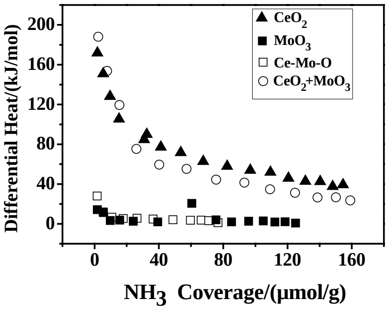

Fig. 3. Differential heat vs. coverage for NH_3 adsorption at 423 K.

Although the result of the probe reaction of IPA conversion depends not only on surface properties, but also on reaction conditions, it does reflect effectively the surface acidic and redox properties of an oxide catalyst. Table 1 gives the results of the probe reaction for the conversion of IPA over the different catalysts studied here at different temperatures with the presence of air. It is seen that the MoO_3 mainly catalyzed the dehydration reactions with the selectivity to PPE (34%) and DIPE (52%). It also catalyzed the oxidative dehydrogenation of IPA to ACE with 14% selectivity. Although the result of microcalorimetric adsorption of ammonia revealed that the MoO_3 had weak surface acidity, the IPA probe reaction clearly showed that the surface acidity of MoO_3 might be more important than its redox property. In contrast, the CeO_2 sample exhibited the selectivity to ACE over 90%. Hence, although the microcalorimetric adsorption of ammonia revealed that the CeO_2 possessed quite strong surface acidity, the IPA probe reaction showed that it mainly displayed the redox property.

The binary metal oxides displayed totally different behavior for the probe reaction. Although the mechanically mixed CeO_2–MoO_3 sample possessed significant amount of CeO_2, the sample mainly exhibited acidic property for the probe reaction. Specifically, the selectivity to PPE, DIPE and ACE over the CeO_2–MoO_3 catalyst was 28, 70 and 2%, respectively. Considering the fact that there was no new phase formed for this sample as revealed by XRD, the only explanation for the results was that there was a thin layer of MoO_3 formed over the CeO_2 in the mixture. In fact, the conversion of IPA over the CeO_2–MoO_3 (21%) was much higher than over the bulk MoO_3 (6.2%) at 473 K. Since the surface area of CeO_2 was significantly higher than that of MoO_3, it was not surprising that the CeO_2–MoO_3 had the higher activity than the bulk MoO_3 for the dehydration of IPA when a thin layer of MoO_3 was formed on the surface of CeO_2. This layer of MoO_3 on the surface of CeO_2 might have been formed during the calcination of the mixed oxide at 773 K, due to the sublimation behavior of MoO_3 at the temperature.

Table 1
Conversion of isopropanol and the selectivity to PPE, DIPE and ACE at different temperatures

Catalyst	*T* (K)	Conversion (%)	Selectivity (%)		
			PPE	DIPE	ACE
MoO_3	453	2.3	34	52	14
	473	6.2	46	44	10
CeO_2	453	1.2	6.5	0	93.5
	473	4	5	0	95
Ce–Mo–O (co-precipitated)	453	1.8	34	26	40
	473	4.5	43	22	35
MoO_3-CeO_2 (mixed)	413	5	11	82	7
	473	21	28	70	2

Table 1 shows that the selectivity to PPE, DIPE and ACE was 34, 26 and 40%, respectively, over the co-precipitated Ce–Mo–O catalyst. Thus, this catalyst exhibited both acidic and redox properties in the comparable extent. In another word, the Ce–Mo–O displayed the redox property of cerium species and also the acidic property of molybdenum species simultaneously. In addition, it seemed that the co-existence of cerium species decreased the surface acidity of molybdenum species since the Ce–Mo–O catalyst exhibited significant selectivity to DIPE, which was taken as to be produced over the weaker acidic sites.

It should be mentioned that the inconsistency for the acidity characterizations of the catalysts studied here demonstrated the limitations of the techniques used. Specifically, the IPA probe reaction seemed to be more sensitive than the microcalorimetric adsorption of ammonia to the change of the surface properties. For example, the microcalorimetric adsorption of ammonia revealed the weak surface acidity of the bulk MoO_3, while the IPA probe reaction indicated the quite strong surface acidity that catalyzed the dehydration of IPA to form PPE. In addition, the microcalorimetric adsorption of ammonia showed the quite strong surface acidity for the mechanically mixed CeO_2–MoO_3 sample, which was due to either the surface acidity of CeO_2 in the mixture or the acidity of the thin layer of MoO_3 on the surface of CeO_2. Since the sample showed the mainly acidic property of MoO_3 for the probe reaction, it was probably that the surface of CeO_2 was covered by the layer of MoO_3, or at least modified by MoO_3. In fact, the production of a significant amount of DIPE indicated the influence of cerium on the acidity of MoO_3 on the surface of CeO_2. In this case, the probe reaction of IPA conversion seemed to be more sensitive than the microcalorimetric adsorption of ammonia in characterizing the change of surface acidity in the mixed oxide.

As was shown in Table 2, the catalysts were tested at 673 K for the selective oxidation of toluene to benzaldehyde and benzoic acid. The MoO_3 exhibited low conversion (1.7%) of toluene with selectivity to benzaldehyde of 18.5% and to benzoic acid of 22.3%, respectively. Although the conversion of toluene was much higher (18.5%) over the CeO_2 than over the MoO_3, the oxidation of toluene on CeO_2 was not selective. Only CO_2 were produced on CeO_2 for the oxidation of toluene at 673 K. The conversion of toluene over the mechanically mixed CeO_2–MoO_3 catalyst was similar to that over the CeO_2. Although the selectivity to benzaldehyde and benzoic acid (5.5%) was low over the mixed oxide, the effect of MoO_3 was apparent as compared to the selectivity over the pure CeO_2. Considering the results of IPA probe reaction over the mixed sample, in can be concluded that the surface of CeO_2 in the mixture might be composed of both cerium and molybdenum oxides. The incorporation of molybdenum oxide onto the surface of CeO_2 increased the selectivity to benzaldehyde and benzoic acid.

The conversion of toluene over the co-precipitated Ce–Mo–O catalyst was 10% at 673 K. The selectivity to benzaldehyde was 64% over the catalyst, which was greatly increased as compared to the other catalysts studied in this work. No benzoic acid was formed on the Ce–Mo–O catalyst that showed low surface acidity as measured by the microcalorimetric adsorption of ammonia. On the other hand, the CeO_2–MoO_3 exhibited the selectivity to benzoic acid when it possessed fairly strong surface acidity, as revealed both by the microcalorimetric adsorption of ammonia and the IPA probe reaction. This implies that the selective oxidation of toluene to benzoic acid may be related to the surface acidity. However, this does not imply that the formation of benzoic acid depends only on the surface acidity. The MoO_3 showed the selectivity to benzoic acid. Although the microcalorimetric adsorption of ammonia revealed that the MoO_3 possessed weak surface acidity, the IPA probe reaction showed that it exhibited the acidic property more than its redox property. Thus, it may be concluded that the relative importance of the surface acidic and redox properties may determine the formation of benzoic acid. The IPA probe reaction clearly indicated that the co-precipitated Ce–Mo–O catalyst displayed equivalent surface acidity and redox ability, although the microcalorimetric adsorption of ammonia indicated its low surface acidity.

CeO_2 is a special oxide that is acidic, basic and redoxic simultaneously. Its redox property exceeds its acidity for the IPA probe reaction. It also displays the oxidation ability for the oxidation of toluene, i.e., only complete oxidation of toluene occurred on CeO_2. However, it also shows basicity by forming the compound $Ce_2Mo_4O_{15}$ with molybdate when it reduces its valent state. With the formation of the compound $Ce_2Mo_4O_{15}$, the oxidation ability of both molybdenum and cerium is decreased, as evidenced by the TPR results. At the same time, the acidity of Mo^{6+} is decreased with the formation of molybdate with Ce^{3+}.

XRD result showed that there were CeO_2 and $Ce_2Mo_4O_{15}$ phases in the co-precipitated Ce–Mo–O catalyst. It is not known right now if there was a synergic effect between the molybdenum and cerium species for the oxidation of toluene. It was suggested that the oxidation of toluene might occurred on Mo^{6+} sites, which itself was reduced to Mo^{4+}. The Mo^{4+} was then oxidized to Mo^{6+} by Ce^{4+}, which itself

Table 2
Selective oxidation of toluene to benzaldehyde and benzoic acid over the catalysts at 673 K

Catalyst	Toluene conversion (%)	Selectivity to benzaldehyde (%)	Selectivity to benzoic acid (%)
MoO_3	1.7	18.5	22.3
CeO_2	18.5	0	0
Ce–Mo–O (co-precipitated)	10	64	0
MoO_3–CeO_2 (mixed)	17.6	4.6	0.9

was reduced to Ce^{3+}. Finally, Ce^{3+} was oxidized to Ce^{4+} by O_2. The above redox steps fulfill the catalytic cycle for the oxidation of toluene, which is usually termed as the Mars-Van Krevelen redox mechanism. Since the pure CeO_2 only exhibited the complete oxidation of toluene, the CeO_2 detected in the co-precipitated Ce–Mo–O catalyst must have been modified by MoO_3. Otherwise, the co-precipitated Ce–Mo–O catalyst would also exhibit the complete oxidation of toluene as the pure CeO_2. The confirmation of the above redox mechanism needs to study the catalytic behavior of the pure $Ce_2Mo_4O_{15}$, which is a subject of further investigation that is currently going on in our lab.

4. Conclusions

In this work, we demonstrated that the combination of the techniques of microcalorimetric adsorption and isopropanol (IPA) probe reaction could provide rich information about the surface acidic and redox properties of metal oxide catalysts for the selective oxidation reactions. Much more information can be obtained by the technique combination than either of them alone. More importantly, the IPA probe reaction carried out with the presence of O_2 can be used to characterize the relative importance of surface acidity and redox ability of a metal oxide catalyst. For example, the microcalorimetric adsorption of ammonia showed the weak surface acidity for the bulk MoO_3, while the IPA probe reaction revealed the significant surface acidity of the MoO_3 for the conversion of IPA to propylene. On the other hand, while the microcalorimetric adsorption of ammonia showed the fairly strong surface acidity for the bulk CeO_2, the IPA probe reaction clearly indicated that CeO_2 exhibited mainly redox property. Interestingly, the IPA probe reaction is sensitive to the slight change of surface property. For example, it revealed that the surface of CeO_2 might be covered by MoO_3 in the mechanically mixed CeO_2–MoO_3 sample after calcination at 773 K, since the sample exhibited the increased dehydration activity even with the presence of O_2. Finally, we demonstrated that the suitable combination of surface acidic and redox properties might be an important factor for the selective oxidation of toluene to benzaldehyde. In fact, while the CeO_2 displayed the complete oxidation of toluene and the MoO_3 showed low activity for the oxidation of toluene, the co-precipitated Ce–Mo–O catalyst, which possessed equivalent surface acidic and redox properties, exhibited greatly enhanced selectivity to benzaldehyde.

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