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A kind of new pyrochlore compounds with catalytic activity for the oxidation reaction of carbon monoxide and propylene

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A series of new compounds with a formula $RE_2M_{2/3}Nb_{4/3}O_7$ (RE = Nd, Sm, Eu; M = Cu, Co, Zn) have been synthesized by a wet chemical method and the lattice parameters of the compounds have also been determined. The new compounds possess a pyrochlore structure and belong to hexagonal system. Most of the compounds have a certain catalytic activity for the oxidation reaction of carbon monoxide and propylene. The conversion efficiency of carbon monoxide and propylene on the surface of some compounds can be close to 100% at near 450 °C. The compounds are insulator and the resistibility also is larger than 10^5 ohm · cm even if at 500 °C. The compounds are a new kind of oxidation catalysts. The catalytic oxidation process of carbon monoxide and propylene on the surface of the compounds involves the oxidation-reduction of the cations in the compound and the catalytic process is a co-catalytic one. The effects of various metal cations in the compounds on the catalytic activity for the oxidation of carbon monoxide and propylene have been discussed. © *1999 Kluwer Academic Publishers*

1. Introduction

The pyrochlore compounds are one kind of the most important inorganic compounds due to their specially physical and chemical properties [1]. Some pyrochlore compounds, such as the Ru-containing pyrochlore compounds, possess a certain catalytic activity for the oxidation reactions of some compounds [2–5].

There have two different kinds of the cations at the A site and at the B site in the lattice of the pyrochlore compound ($A_2B_2O_7$). For possibility of the existence of any pyrochlore compound, there are two criteria: (1) the ratio of the ionic radius of the cation at the A site to that at the B site must be between 1.46 and 1.80; (2) the chemical valences of various ions must make the compound to be charge neutrality [1, 6]. The cations at the A site and the B site in the lattice can be replaced by the cations with different chemical valence or different oxidation-reduction property to synthesize the various kinds of pyrochlore compounds with different physical or chemical properties, if the criteria can be satisfied. Recently, a lot of pyrochlore compounds with a very complicated composition have been synthesized [7–9]. We have also synthesized some new pyrochlore compounds with a more complex composition by the wet chemical method [10, 11]. Then, we have found that some of the new pyrochlore compounds possess a certain catalytic activity for the oxidation reaction of carbon monoxide and the catalytic oxidation reaction of the carbon monoxide on the surface of $Sm_2Cu_{2/3}Nb_{4/3}O_7$ can occur about 50 °C [12]. It has been reported that some mixed oxides of the transition metals possess a certain catalytic activity for the oxidation reaction of the carbon monoxide and these mixed oxides of the transition metals belong to the p-type semiconductor. Therefore, it is considered that the catalytic oxidation process of carbon monoxide on the surface of the mixed oxides of the transition metal will involve the annihilation and generation of the holes in the valence band of the compounds. However, a lot of pyrochlore compounds are insulator and the resistibility of the new pyrochlore compounds synthesized by us also is larger than 10^5 ohm · cm even if at about 500 °C [10, 11]. Therefore, the energy gap between the conduction band and the valence band of the new pyrochlore compounds must be very large, hence, to annihilate or generate a hole in the valence band will need very large energy. But, the results of the catalytic experiments indicate that the detectable catalytic activity of some new compounds for the oxidation reaction of carbon monoxide can be determined even if at about 30 °C, that is, the activation energy for the catalytic oxidation process of carbon monoxide on the surface of the new pyrochlore compound may be very small. In this case, we can consider that the mechanism for the catalytic oxidation of carbon monoxide on the surface of

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the new pyrochlore compounds must be different from that on the surface of the mixed oxides of the transition metals with a p-type semiconductor property. Hence, we supposed a possible mechanism for the catalytic oxidation process of carbon monoxide on the surface of the new pyrochlore compounds, that is, the catalytic oxidation process of carbon monoxide on the surface of the new pyrochlore compounds may involve the variation of valence state of the metal cations in the compound and the catalytic process may be a co-catalytic one [12].

The results of the X-ray diffraction, the infrared spectra and Mossbauer spectra of the new pyrochlore compounds can indicate, unlike the general pyrochlore compounds, the crystal structure of the new pyrochlore compounds with a formula $RE_2M_{2/3}Nb_{4/3}O_7$ belongs to a hexagonal system due to the lattice distortion, not to a cubic one. Especially, the new pyrochlore compounds may possess a large cell structure, very similar to superstructure [10, 11]. There are three kinds of metal cations in the lattice of the pyrochlore compounds with a formula $RE_2M_{2/3}Nb_{4/3}O_7$ and these metal cations can possess not only the different coordination environment, but also the different oxidation-reduction property. Therefore, to investigate the effect of the various cations with different oxidation-reduction property at different sites in the lattice of the compound on the catalytic activity of the compound for the oxidation reaction of carbon monoxide will be very useful for understanding the catalytic oxidation process of carbon monoxide on surface of the new kind of compounds and for exploring the new pyrochlore compounds with a better catalytic property.

At present, a considerable attention has been paid to the research on the new catalysts without the noble metals for the conversion of the exhaust gases from the vehicle engines. In practically applications, the catalysts for the conversion of the exhaust gases must work for long time at very high temperature, so, the catalysts must be able to bear high temperature. Most of the pyrochlore compounds are refractory materials. Perhaps, the new pyrochlore compounds with a complex composition will be the potential catalysts for the conversion of the exhaust gases. There also are other kinds of gases in the exhaust gases from the vehicle engines, such as remaining hydrocarbons, nitrogen-oxygen compounds and sulfur-oxygen compounds, except for carbon monoxide. In studies of the performance of the catalysts for the conversion of the exhaust gases from the vehicle engines, propylene is often used as a representative compound to simulate all the remaining hydrocarbons. Besides, the catalytic oxidation process of propylene on the surface of some mixed oxides also involves the oxidation-reduction of the cations on the surface of the catalyst [13]. Therefore, in our catalytic experiments, the mixture of carbon monoxide, propylene and oxygen is used as the reaction gas.

Here, we shall give some experimental results about the synthesis, the crystal structures and the preliminary results about the catalytic activities of the series of pyrochlore compounds $RE_2M_{2/3}Nb_{4/3}O_7$ (RE = Nd, Sm, Eu; M = Cu, Co, Zn), as well as some discussions for the effect of the various cations on the catalytic activity of the new pyrochlore compounds for the oxidation reaction of carbon monoxide and propylene.

2. Experimental

All the chemicals used in the synthesis experiments are analytical reagent grade. The series of compounds $RE_2M_{2/3}Nb_{4/3}O_7$ (RE = Nd, Sm, Eu; M = Cu, Co, Zn) are synthesized by a wet chemical method. The synthesis process of the kind of new compounds has been described in detail elsewhere [10, 11]. The resultant products are very fine powder. The morphologies of some resultant products have been observed by transmission electron microscopy and the products are nanocrystalline material. The size of the crystalline particle is about 50–100 nm. The smaller agglomeration phenomenon in the sample can also be observed. However, the surface area of the sample is not determined.

The characterizations of the X-ray diffraction for the new compounds are performed by a D/max-YB X-ray diffractometer, $CuK_{\alpha1}$ radiation; Ni filter; room temperature. The lattice parameters are refined by a least squares refinement program. The calculated lattice parameters of the new compounds are listed in Table I. As an example, the experimental and the calculated spacing d_{hkl} of $Nd_2Cu_{2/3}Nb_{4/3}O_7$ are listed in Table II.

The measurement of electric resistivity of the compounds is carried out by using a Model BD 86-A semiconductor resistivity meter at room temperature and at about 500 °C. The electric measurements indicate that all the new compounds are insulator. Even if at about 500 °C, the electric resistibility of new pyrochlore compounds still is larger than 10^5 ohm · cm.

Catalytic experiments for the oxidation reaction of carbon monoxide and propylene on the surface of the new compounds are carried out by using a continuous flow microreactor with a fixed bed. The amount of the compounds used in the experiment is 1.0 g. The samples are not treated before the experiment. The catalyst is mixed with quartz sand in the weight ratio of 1 : 1 and the volume of the mixture of the catalyst and quartz sand is about 1.5 cm^3. The inert gas is nitrogen gas. The volume percentage of carbon monoxide, propylene and oxygen in the gas is 2.5, 0.1 and 1.75%, respectively. The flow rate of the gas is 300 ml · min^{-1}. The temperature of the microreactor is gradually increased from room temperature to 500 °C. The catalytic activity of the compounds is measured as the conversion

TABLE I The lattice parameters of $RE_2M_{2/3}Nb_{4/3}O_7$ (RE = Nd, Sm, Eu; M = Cu, Co, Zn) (hexagonal system, room temperature)

	The lattice parameters		
Compound	*a* (nm)	*c* (nm)	*V* (nm^3)
$Nd_2Cu_{2/3}Nb_{4/3}O_7$	1.5240	1.8580	3.7372
$Sm_2Cu_{2/3}Nb_{4/3}O_7$	1.5115	1.8592	3.6785
$Eu_2Cu_{2/3}Nb_{4/3}O_7$	1.5034	1.8598	3.6403
$Sm_2Co_{2/3}Nb_{4/3}O_7$	1.5083	1.8557	3.6560
$Sm_2Zn_{2/3}Nb_{4/3}O_7$	1.5125	1.8603	3.6856

TABLE II The experimental data and calculated results for X-ray diffraction of $Nd_2Cu_{2/3}Nb_{4/3}O_7$ (hexagonal system; $a = 1.5240$ nm; $c = 1.8580$ nm)

h, k, l	d_{hkl} (exp)(nm)	d_{hkl} (cal)(nm)	I/I_0
004	0.4662	0.4645	4
402	0.3114	0.3109	26
320	0.3027	0.3028	100
411	0.2846	0.2846	4
323	0.2724	0.2720	19
413	0.2616	0.2612	26
107	0.2598	0.2802	23
306	0.2528	0.2532	9
008	0.2325	0.2322	10
406	0.2260	0.2258	4
431	0.2154	0.2155	4
610	0.2014	0.2013	4
506	0.2004	0.2009	4
524	0.1921	0.1924	5
408	0.1896	0.1899	14
701	0.1876	0.1876	18
532	0.1849	0.1848	34
444	0.1764	0.1763	5
623	0.1753	0.1755	4
801	0.1640	0.1643	8
543	0.1630	0.1630	9
446	0.1621	0.1623	9
720	0.1613	0.1612	8
626	0.1576	0.1576	24
634	0.1563	0.1566	12
805	0.1508	0.1508	9
813	0.1493	0.1499	5
730	0.1486	0.1485	4
734	0.1410	0.1414	4
911	0.1376	0.1380	3
905	0.1366	0.1364	4
549	0.1308	0.1308	5
826	0.1306	0.1306	5
827	0.1262	0.1266	4
931	0.1215	0.1218	7

TABLE III The catalytic activity of $RE_2M_{2/3}Nb_{4/3}O_7$ (RE = Nd, Sm, Eu; M = Cu, Co, Zn) for the oxidation reaction of CO and C_3H_6

	CO		C_3H_6	
Compound	T^a(°C)	η^b	T^a(°C)	η^b
$Eu_2Cu_{2/3}Nb_{4/3}O_7$	230	99	295	96
$Sm_2Cu_{2/3}Nb_{4/3}O_7$	280	99	320	93
$Nd_2Cu_{2/3}Nb_{4/3}O_7$	281	97	299	86
$Sm_2Co_{2/3}Nb_{4/3}O_7$	260	98	390	52
$Sm_2Zn_{2/3}Nb_{4/3}O_7$	>500	26	442	29

[a] Reaction temperature with the conversion 50% of CO or C_3H_6.
[b] Conversion rate of CO or C_3H_6 at 400 °C.

efficiency of carbon monoxide and the completeness of the propylene oxidation. The conversion of carbon monoxide and the oxidation of propylene is determined by a gas chromatography. The holding time of the catalytic reaction is over 3 h and the results of the repeated experiments indicate that any detectable descent in the catalytic activity of the compounds cannot be found. The experimental results about the catalytic activity of the new compounds for the oxidation of carbon monoxide and propylene are summarized in Table III. The temperature dependence curves of the catalytic activity of the compound are also shown in Fig. 1 and Fig. 2, respectively.

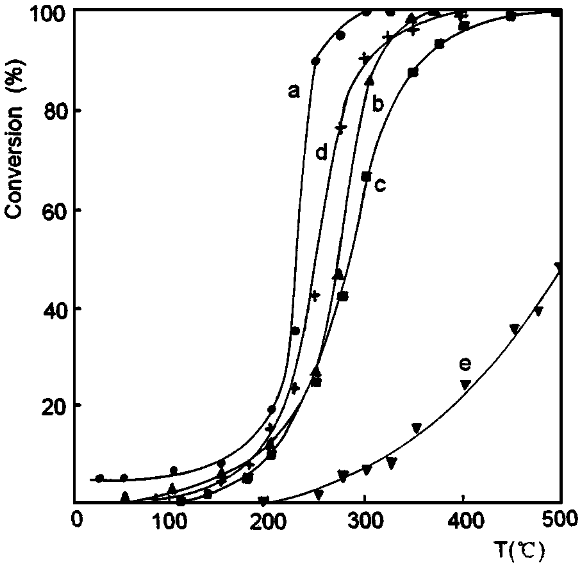

Figure 1 The catalytic activity of $RE_2M_{2/3}Nb_{4/3}O_7$ (RE = Nd, Sm, Eu; M = Co, Cu, Zn) for oxidation of CO plotted as a function temperature. a: $Eu_2Cu_{2/3}Nb_{4/3}O_7$; b: $Sm_2Cu_{2/3}Nb_{4/3}O_7$; c: $Nd_2Cu_{2/3}Nb_{4/3}O_7$; d: $Sm_2Co_{2/3}Nb_{4/3}O_7$; e: $Sm_2Zn_{2/3}Nb_{4/3}O_7$.

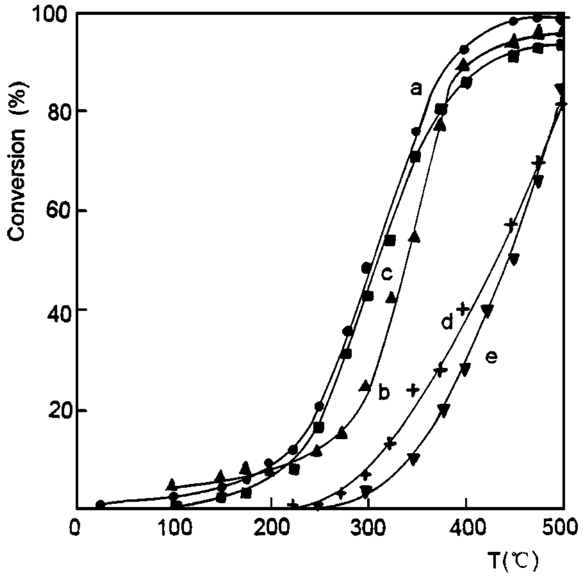

Figure 2 The catalytic activity of $RE_2M_{2/3}Nb_{4/3}O_7$ (RE = Nd, Sm, Eu; M = Co, Cu, Zn) for oxidation of C_3H_6 plotted as a function temperature. a: $Eu_2Cu_{2/3}Nb_{4/3}O_7$; b: $Sm_2Cu_{2/3}Nb_{4/3}O_7$; c: $Nd_2Cu_{2/3}Nb_{4/3}O_7$; d: $Sm_2Co_{2/3}Nb_{4/3}O_7$; e: $Sm_2Zn_{2/3}Nb_{4/3}O_7$.

3. Results and discussions

All the peaks in the X-ray diffraction pattern of each new compound can be very well indexed according to the hexagonal system by a set of lattice parameters. As the results in Table II show, most of the deviations between the calculated spacing d_{hkl} and the experimentally determined spacing d_{hkl} are less than 0.0005 nm. Only few largest deviations between the calculated and the experimental d_{hkl} are larger than 0.001 nm, but, the relative deviation for the largest deviation, also is less than 0.5%. This means that the compounds are single phase. If there is any impurity, its content will also be undetectable in the characterization of the X-ray diffraction for the compounds. In the lattice of the pyrochlore compound $A_2B_2O_7$, the polyhedron about the cation at the A site is composed of eight oxygen anions and the coordination number of the A cation is eight.

The polyhedron about the cation at the B site is composed of six oxygen anions and the coordination number of the B cation is six [1]. The effective ionic radius of the trivalent rare earth cation with eight-coordination is 0.1109, 0.1079 and 0.1066 nm for Nd^{3+}, Sm^{3+} and Eu^{3+}, respectively [14]. As the results in Table I show, although the lattice parameter (a) of the series compounds $RE_2Cu_{2/3}Nb_{4/3}O_7$ decreases and the lattice parameter (c) increases gradually from $Nd_2Cu_{2/3}Nb_{4/3}O_7$, $Sm_2Cu_{2/3}Nb_{4/3}O_7$ to $Eu_2Cu_{2/3}Nb_{4/3}O_7$, respectively, the cell volume (V) of the series compounds $RE_2Cu_{2/3}Nb_{4/3}O_7$ always decreases monotonously with decreasing the ionic radius of the cation at the A site from Nd, Sm to Eu. The lattice parameters a, c and the cell volume (V) of the series compounds $Sm_2M_{2/3}Nb_{4/3}O_7$ always increases monotonously from $Sm_2Co_{2/3}Nb_{4/3}O_7$, $Sm_2Cu_{2/3}Nb_{4/3}O_7$ to $Sm_2Zn_{2/3}Nb_{4/3}O_7$. This just corresponds with the gradual increase in the ionic radius from the Co^{2+}, Cu^{2+} to Zn^{2+} ion [14]. Besides, the Co^{2+} ion in $Sm_2Co_{2/3}Nb_{4/3}O_7$ may be in a low spin state ($t_{2g}^6e_g^1$). The effective ionic radius of the Cu^{2+} and Zn^{2+} ion with six-coordination is 0.073 and 0.074 nm, respectively, and the effective ionic radius of the Co^{2+} ion in the low spin state($t_{2g}^6e_g^1$) is 0.065 nm and that in the high spin state ($t_{2g}^5e_g^2$) is 0.0745 nm [14]. If the Co^{2+} ion in $Sm_2Co_{2/3}Nb_{4/3}O_7$ were in a high spin state ($t_{2g}^5e_g^2$), the parameter a, c and the cell volume of $Sm_2Co_{2/3}Nb_{4/3}O_7$ would have been larger, not smaller, than those of $Sm_2Cu_{2/3}Nb_{4/3}O_7$ and $Sm_2Zn_{2/3}Nb_{4/3}O_7$. The regular variation of the lattice parameter a, c and the cell volume (V) of the series compounds $Sm_2M_{2/3}Nb_{4/3}O_7$ ($M = Co$, Cu, Zn) with increasing the ionic radius of the M cation can also demonstrate that the Co^{2+}, Cu^{2+} to Zn^{2+} ion must be at same site in the lattice of the series of compounds. Perhaps, this regular trend in the variation of the lattice parameters of the compound with the ionic radius of the substitution cation can also demonstrate that the calculations of the lattice parameters for the compounds are reliable and the compounds can be considered to be single phase.

There must have a lot of oxygen vacancies in the surface of the new pyrochlore compounds. This is not only because the new pyrochlore compounds synthesized by a wet chemical method are the nanocrystalline particles and the nanocrystalline particles always possess some deficient structures in the surface region [15, 16], but also because one of the seven oxygen atoms in the pyrochlore compound $A_2B_2O_7$ occupies a special position in the lattice and the special oxygen atom can be partially lost to yield the oxygen vacancy in the lattice [1].

Fig. 1 shows that most of the compounds possess a certain catalytic activity for oxidation reaction of carbon monoxide. The catalytic activity of $Eu_2Cu_{2/3}$ $Nb_{4/3}O_7$ in the series compounds $RE_2Cu_{2/3}Nb_{4/3}O_7$ ($RE = Nd$, Sm, Eu) is the highest. Even if at 25 °C, the catalytic oxidation reaction of carbon monoxide on $Eu_2Cu_{2/3}Nb_{4/3}O_7$ can occur. The catalytic activity of $Sm_2Zn_{2/3}Nb_{4/3}O_7$ in the series compounds $Sm_2M_{2/3}Nb_{4/3}O_7$ ($M = Cu$, Co, Zn) is the lowest. We consider that both the RE cation and the M cation in the new pyrochlore compound can play a role in the catalytic oxidation process of carbon monoxide. Because, if only one kind of the cation in the compound, either the RE^{3+} cations at the A site or the M^{2+} cations at the B site, will play the role in the catalytic oxidation process irrespective of other cations in the compound, one could expect that either the catalytic activity of the series compounds $RE_2Cu_{2/3}Nb_{4/3}O_7$ with different RE^{3+} cation at the A site ($RE = Nd$, Sm, Eu) will always be higher than that of the series compounds $Sm_2M_{2/3}Nb_{4/3}O_7$ with different M^{2+} cation at the B site ($M = Cu$, Co, Zn), or the catalytic activity of the series compounds $Sm_2M_{2/3}Nb_{4/3}O_7$ with different M^{2+} cation at the B site ($M = Cu$, Co, Zn) will always be higher than that of the series compounds $RE_2Cu_{2/3}Nb_{4/3}O_7$ with different RE^{3+} cation at the A site ($RE = Nd$, Sm, Eu). In practice, the catalytic activity of some of the two series of compounds for the oxidation reaction of carbon monoxide is very similar to each other. For example, as the results in Table III show the catalytic activity of $Sm_2Co_{2/3}Nb_{4/3}O_7$ is slightly lower than that of $Eu_2Cu_{2/3}Nb_{4/3}O_7$ but slightly higher than that of $Sm_2Cu_{2/3}Nb_{4/3}O_7$. This indicates that both the RE^{3+} cations at the A site and the M^{2+} cations at the B site in the compounds can have a similar effect on the catalytic activity of the compound.

The experimental results can support the catalytic reaction mechanism about the oxidation process of carbon monoxide on the kind of new pyrochlore compounds supposed by us [12]. According to this catalytic reaction mechanism, in the catalytic oxidation process of carbon monoxide on the surface of the pyrochlore compound $RE_2M_{2/3}Nb_{4/3}O_7$, first, the adsorbed CO will give an electron to the M^{2+} ion or the RE^{3+} ion in $RE_2M_{2/3}Nb_{4/3}O_7$ to yield the M^+ ion or the RE^{2+} ion, and consequently become the adsorbed CO^+ when CO occupies the position of the oxygen vacancy on the surface of $RE_2M_{2/3}Nb_{4/3}O_7$. Similarly, the CO_2^- produced by the reaction of the adsorbed CO^+ with the lattice oxygen can also give an electron to the M^{2+} ion or the RE^{3+} ion in $RE_2M_{2/3}Nb_{4/3}O_7$ to yield the M^+ ion or the RE^{2+} ion and consequently form the gaseous CO_2. Whereas, after the gaseous CO_2 molecule leaves the surface of the compound, the oxygen molecule from the gas phase can get electrons from the M^+ ion or the RE^{2+} ion produced in the formation process of gaseous CO_2 and yield the lattice oxygen and the M^{2+} ion or the RE^{3+} ion. If the catalytic process does be so, the catalytic activity of the compound $RE_2M_{2/3}Nb_{4/3}O_7$ for the oxidation of carbon monoxide must depend on the oxidation-reduction property of the M^{2+} cation at the B site or the RE^{3+} cation at the A site. The more easily the M^{2+} cation or the RE^{3+} cation are reduced, the higher the catalytic activity of $RE_2M_{2/3}Nb_{4/3}O_7$ for the oxidation reaction of carbon monoxide. Because, the Eu^{3+} ion is most easily reduced to the Eu^{2+} ion, $Eu_2Cu_{2/3}Nb_{4/3}O_7$ in the series compounds $RE_2Cu_{2/3}Nb_{4/3}O_7$ ($RE = Nd$, Sm, Eu) possesses the highest catalytic activity for the oxidation of carbon monoxide. Whereas, to reduce the Zn^{2+} ion is much more difficult than to reduce the Co^{2+} ion or the Cu^{2+} ion, hence, the results in Table III show that the catalytic activity of $Sm_2Zn_{2/3}Nb_{4/3}O_7$ for the oxidation of carbon monoxide is the lowest in the series compounds $Sm_2M_{2/3}Nb_{4/3}O_7$ (M = Cu, Co, Zn). Obviously, the experimental results can demonstrate that the catalytic oxidation process of carbon monoxide on the surface of the new pyrochlore compounds does be related to the oxidation-reduction property of both the cations at the A site and the cation at the B site. The experimental results can also demonstrate the catalytic oxidation process of carbon monoxide on the surface of the new pyrochlore compounds is a co-catalytic process. Because, during the total oxidation process from CO to CO_2, each absorbed species must consecutively give two electrons to the compound. However, none of the cations in the compounds, neither the RE^{3+} cation nor the M^{2+} cation, can consecutively receive two electrons and be reduced to the cation in a lower valence state. Therefore, the catalytic oxidation process of each CO molecule on the surface of the new pyrochlore compounds must involve two different cations in the compound, so that each of the two cations can receive only one electron from the absorbed CO or the absorbed CO_2^-, respectively. The two cations may be from both the two RE^{3+} cations at the A site and the two M^{2+} cations at the B site. It also is very possible that one of the two cations is from the RE^{3+} cation at the A site and another from the M^{2+} cation at the B site. In this case, the catalytic oxidation process of carbon monoxide on the surface of these compounds will be a co-catalytic one.

The difference between the catalytic activities of the various new pyrochlore compounds for the oxidation of carbon monoxide will be relating to difference between the oxidation-reduction properties of the cation-pair both at the A site and at the B site in the compounds. For lack of the data of the standard oxidation-reduction potentials of the metal ions in the solid state compounds, we have to refer the general oxidation-reduction properties of the metal cations. Generally, to reduce the Eu^{3+} ion is more easily than to reduce the Sm^{3+} ion, but to reduce the Nd^{3+} ion is much more difficult. So, the catalytic activity of $RE_2Cu_{2/3}Nb_{4/3}O_7$ (RE = Nd, Sm, Eu) for the oxidation of carbon monoxide increases gradually from Nd, Sm to Eu. It may be slightly easily to the Cu^{2+} ion to the Cu^+ ion than to reduce the Co^{2+} ion to the Co^+ ion, but it is rather difficult to reduce the Zn^{2+} ion to the Zn^+ ion, if it is not impossible. So, in the series compounds $Sm_2M_{2/3}Nb_{4/3}O_7$ (M = Cu, Co, Zn), the catalytic activity of $Sm_2Cu_{2/3}Nb_{4/3}O_7$ and $Sm_2Co_{2/3}Nb_{4/3}O_7$ for the oxidation of carbon monoxide is very similar, but the catalytic activity of $Sm_2Zn_{2/3}Nb_{4/3}O_7$ is considerably lower. Although the Nb^{5+} ion can also be reduced to Nb^{3+} ion and the oxide of niobium is very good catalyst for some oxidation reactions, we have noted that catalytic activity of $Sm_2Zn_{2/3}Nb_{4/3}O_7$ in all the pyrochlore compounds is the lowest. Of course, this may be mainly because to reduce the divalent zinc cation is rather difficult. But, if the niobium cation could play a most significant role in the catalytic oxidation process of carbon monoxide, the catalytic activity of $Sm_2Zn_{2/3}Nb_{4/3}O_7$ would not be so lower. Perhaps, the above experimental results can indicate that only the RE-M or M-M ion-pair, not the RE-Nb and M-Nb ion-pair in the the series compounds $RE_2M_{2/3}Nb_{4/3}O_7$, will play the most significant role in the catalytic process. Of course, we cannot rule out that the niobium cation may also have some effects on the catalytic activity of the new pyrochlore compounds. Besides, the fact that the catalytic activity of $Sm_2Zn_{2/3}Nb_{4/3}O_7$ is very low can also imply that the transition metals (M) will play a more important role than the rare earths (RE) in the catalytic oxidation process of carbon monoxide on the surface of the new pyrochlore compounds.

The catalytic oxidation of propylene on the surface of some oxides, such as oxides of bismuth-molybdenum, has been very well studied [13]. It has been known that the catalytic oxidation process of propylene on the mixed oxides will involve the variation of the valence states of the various metal cations in the oxides. If the catalytic oxidation process of the carbon monoxide does be related only to the variation of the valence states of the cations in the new pyrochlore compounds, one can reasonably expect that these pyrochlore compounds must also possess a certain catalytic activity for oxidation process of propylene. As the Fig. 2 shows, indeed, the new compounds can also have a certain catalytic activity for oxidation process of propylene. Like in the catalytic oxidation reaction of carbon monoxide, the catalytic activity of the compounds also varies with the oxidation-reduction property of the rare earth cations (RE) and the transition metal cations (M). Very similarly, the catalytic activity of $Eu_2Cu_{2/3}Nb_{4/3}O_7$ is the highest and that of $Sm_2Zn_{2/3}Nb_{4/3}O_7$ is the lowest for the oxidation reaction of propylene. As above mentioned, the catalytic oxidation process of propylene on some mixed oxides does not involve the annihilation and generation of any hole in the valence band of the oxides, but is related only to the oxidation-reduction of the metal cations in the oxide. The fact that the new pyrochlore compounds also possess a certain catalytic activity for the oxidation of propylene can demonstrate the catalytic reaction mechanism about the oxidation process of carbon monoxide on the new pyrochlore compounds supposed by us. Because the catalytic oxidation process of propylene on the catalysts will undergo several reaction steps, similarly, we can also consider that the catalytic reaction of propylene on the surface of the new pyrochlore compounds may also be a co-catalytic process.

Very interestingly, the catalytic activity of $Sm_2Co_{2/3}Nb_{4/3}O_7$ for the oxidation of propylene is very low, although its catalytic activity for the oxidation of carbon monoxide is very high. Besides, as the results in Table III show, at 400 °C, the conversion of catalytic oxidation of propylene on the surface of $Sm_2Cu_{2/3}Nb_{4/3}O_7$ is the highest. At present, we can not give a reasonable explanation for these experimental phenomena. Perhaps, the catalytic oxidation of propylene on the surface of the new compounds may be a more complicated process. Here, there are only some preliminary experimental results. The possible catalytic oxidation process of propylene on the surface of the new compounds is under research.

4. Conclusions

A kind of new pyrochlore compounds $RE_2M_{2/3}Nb_{4/3}O_7$ (RE = Nd, Sm, Eu; M = Cu, Co, Zn) with a hexagonal symmetry have been found to possess a certain catalytic activity for the oxidation reaction of both carbon monoxide and propylene. The catalytic oxidation process of carbon monoxide and propylene on the surface of the new pyrochlore compounds is related to the variation of the valence states of the cations in the compound. The catalytic activity of the new pyrochlore compound may mainly depend on the oxidation-reduction property of the M-M and RE-M ion-pair in the compounds. The catalytic oxidation process of carbon monoxide and propylene on the surface of the new pyrochlore compounds may be a co-catalytic one.

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