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A novel CO conversion catalyst

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A novel CO conversion catalyst, $Sm_2Cu_{2/3}Nb_{4/3}O_7$ with a pyrochlore structure, has been synthesized. Catalytic oxidation of carbon monoxide on the catalyst can occur at about 50°C. The conversion efficiency will be close to 100% at near 300°C. $Sm_2Cu_{2/3}Nb_{4/3}O_7$ is an insulator. The possible effect of variation of the valence states of Sm, Cu and Nb ions in the compound on the oxidation reaction of carbon monoxide has also been discussed.

Keywords: CO conversion catalyst, pyrochlore compound

Some pyrochlore compounds possess a catalytic property for the oxidation of carbon monoxide [1,2]. Some Cu-containing compounds, such as superconducting cuprates, have also a certain catalytic activity for direct decomposition of nitrogen monoxide [3]. Therefore, to investigate whether some Cu-containing pyrochlore compounds can possess a better catalytic activity not only for oxidation of carbon monoxide, but also for direct decomposition of nitrogen monoxide will be very interesting for exploring new catalysts.

However, to date, only a few Cu-containing pyrochlore compounds have been reported [4]. Perhaps this may be mainly attributed to the conventional method to synthesize pyrochlore compounds. According to this method, the mixture of several metal oxides or carbonates must undergo a high temperature treatment process over 1000°C. But, CuO will be decomposed at about 1000°C, hence, it may be very difficult to synthesize Cu-containing pyrochlore compounds by using this method. Recently, some perovskite, spinel and pyrochlore compounds can be synthesized at a lower temperature by means of a wet chemical method, such as the citrate process. We have also synthesized a novel Cu-containing pyrochlore compound $Sm_2Cu_{2/3}Nb_{4/3}O_7$ by the wet chemical method and we have found that this compound does possess a certain catalytic activity for the oxidation reaction of carbon monoxide. Here, we shall give a simple description of the synthesis process of this compound and some preliminary results of catalytic reaction experiments of the oxidation of carbon monoxide on $Sm_2Cu_{2/3}Nb_{4/3}O_7$.

First, aqueous solutions of niobium oxalate, samarium nitrate and copper nitrate are prepared and the concentrations of niobium, samarium and copper in the solutions are calibrated. The aqueous solutions of samarium nitrate, copper nitrate and niobium oxalate are mixed in an accurate stoichiometric ratio of $Sm : Cu : Nb = 3 : 1 : 2$. A certain amount of citric acid and ethylenediamine is added into the above mixed solution. Then, water is evaporated from the mixed solution with stirring at about 90°C until a blue viscous sol is obtained. The sol is further dehydrated in a vacuum oven and heated at about 300°C in a muffle furnace to yield an amorphous citrate precursor. At last, the precursor undergoes heat decomposition at 500°C for about 5 h and is calcined at 950°C for 8 h. The resultant product is a very fine grey powder. Characterization by powder X-ray diffraction has demonstrated that the product is a single-phase compound and possesses a pyrochlore structure. Generally, the crystal structure of the pyrochlore compound with a general formula $A_2B_2O_7$ belongs to a cubic system. However, the pyrochlore compound with a general formula $A_2B'_{2/3}B''_{4/3}O_7$ may have hexagonal or tetragonal symmetry and may possess a superstructure because of lattice distortion [5]. We have found that $Sm_2Cu_{2/3}Nb_{4/3}O_7$ has a tetragonal symmetry and a large cell structure. The lattice parameters are $a = 1.4658$ nm and $c = 1.7602$ nm. Electric measurements indicate that $Sm_2Cu_{2/3}Nb_{4/3}O_7$ is an insulator. The resistivity of the compound is larger than $10^5\ \Omega$ cm, even at 300–500°C.

Catalytic experiments on the oxidation of carbon monoxide over $Sm_2Cu_{2/3}Nb_{4/3}O_7$ have been performed in a continuous flow microreactor with a fixed bed. The amount of $Sm_2Cu_{2/3}Nb_{4/3}O_7$ used in the experiment is 1.0 g. Space velocity is 8000 h^{-1}. The inert gas is nitrogen. The volume percentage of carbon monoxide in the gas is 2.6%. The ratio of oxygen to carbon monoxide (O to CO) in the gas flow is 1.05. The temperature of the microreactor is gradually increased from room temperature to 500°C. The catalytic activity of $Sm_2Cu_{2/3}Nb_{4/3}O_7$ is measured as the conversion efficiency of carbon monoxide and the conversion of carbon monoxide is determined by gas chromatography. The experimental results are shown in figure 1.

The results show that the oxidation reaction of carbon

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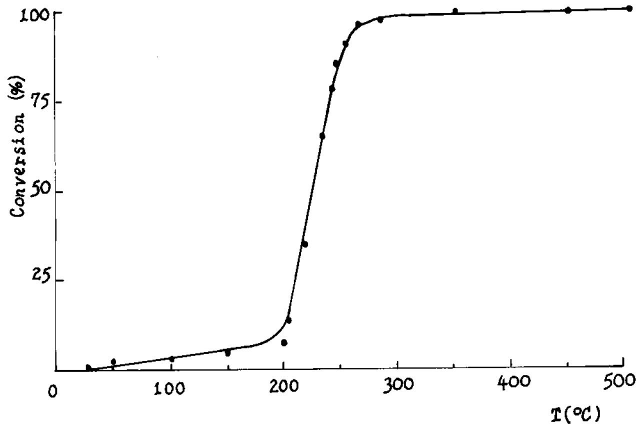

Figure 1. The catalytic activity of $Sm_2Cu_{2/3}Nb_{4/3}O_7$ for oxidation of carbon monoxide plotted as a function of temperature. (SV: 8000 h^{-1}; the volume percentage of CO in nitrogen gas: 2.6%; ratio of O to CO in the gas: 1.05.)

monoxide on $Sm_2Cu_{2/3}Nb_{4/3}O_7$ can occur below 50°C. The activity of the catalyst increases rapidly with temperature at about 200°C and the conversion efficiency approaches 100% at near 300°C. The experimental results demonstrate that the pyrochlore compound $Sm_2Cu_{2/3}Nb_{4/3}O_7$ does possess a certain activity for the catalytic oxidation of carbon monoxide. The holding time of the catalytic reaction at 500°C is over 5 h and no detectable descent in the conversion efficiency of carbon monoxide on $Sm_2Cu_{2/3}Nb_{4/3}O_7$ can be found after 5 h. Perhaps this indicates that $Sm_2Cu_{2/3}Nb_{4/3}O_7$ is a very stable catalyst. It is very well known that most of pyrochlore compounds are very stable under atmospheric conditions at high temperature and some of them are refractory materials.

The reaction mechanism of the oxidation process of carbon monoxide on oxidic catalysts has been supposed [2]. Generally, it is considered that in the first step of reaction, CO is adsorbed on the catalyst surface. The adsorbed CO will give an electron to the valence band of the catalyst to annihilate a hole in the valence band, and, consequently, becomes a CO^+ ion. Then, the adsorbed CO^+ ion reacts with a lattice oxygen to yield an adsorbed carboxylate CO_2^- ion and an oxygen vacancy. The adsorbed CO_2^- gives an electron to the valence band to annihilate a hole in the valence band again, and the resultant gaseous CO_2 leaves the surface of the catalyst. After the formation of gaseous CO_2, an oxygen molecule from the gas phase will get two electrons from the catalyst to yield two holes in the valence band and becomes an adsorbed oxygen anion on the surface of the catalyst. The oxygen anion will occupy the oxygen vacancy in the lattice to generate the lattice oxygen and the hole in the valence band.

Obviously, according to the above mentioned reaction mechanism, the oxidation process of carbon monoxide on the surface of the catalyst must involve the annihilation and generation of a hole in the valence band of the catalyst. For a p-type semiconductor compound, it is not very difficult to annihilate and generate a hole in the valence band due to a smaller energy gap of the compound. However, the fact that $Sm_2Cu_{2/3}Nb_{4/3}O_7$ still possesses a very large resistivity even at a temperature as high as 500°C may indicate that the energy gap between the conduction band and the valence band in the compound is very large. This implies that annihilation or generation of a hole will need more energy. It may be possible, however, that the activation energy in the reaction process of CO conversion on the surface of $Sm_2Cu_{2/3}Nb_{4/3}O_7$ is not very large, because the catalytic oxidation of the carbon monoxide on $Sm_2Cu_{2/3}Nb_{4/3}O_7$ can occur below 50°C. In this case, it can be reasonably assumed that the catalytic conversion process of carbon monoxide on the surface of $Sm_2Cu_{2/3}Nb_{4/3}O_7$ does not involve the annihilation and generation of any hole in the valence band, and may be relating to a variation of valence states of the copper niobium and samarium ions in the compound.

In $Sm_2Cu_{2/3}Nb_{4/3}O_7$, the copper ion and the niobium ion have positive valence of two and five, respectively, and the coordination number of both copper ion and niobium ion is six. The samarium ion is positive trivalent and the coordination number is eight. But the copper ion, niobium ion and samarium ion can also exist in a lower valence state, such as Cu^+, Nb^{4+} and Sm^{2+}. Besides, one of seven oxygen atoms in the general formula $A_2B_2O_7$ of the pyrochlore compound occupies a special position in the lattice, hence, the oxygen atoms in the special position can be partially lost to yield a pyrochlore compound with oxygen deficient structure [6]. Therefore, there may also be some oxygen vacancies on the surface of $Sm_2Cu_{2/3}Nb_{4/3}O_7$. In the lattice, the copper, niobium and samarium ions will lie at the centres of different coordination polyhedra composed of the oxygen atoms, respectively. These polyhedra are connected to each other and share some oxygen atoms in the lattice. If there exists an oxygen vacancy in any polyhedron, the oxygen vacancy will affect not only the coordination structure and the electronic configuration of the cation in the polyhedron with oxygen vacancy, but also the coordination structures and the electronic configurations of the cations in some neighbouring polyhedra. In this case, perhaps, we may consider that the adsorbed CO will give an electron to a Cu^{2+} ion in the polyhedron to yield a Cu^+ ion, and consequently become the adsorbed CO^+ when CO occupies the position of the oxygen vacancy in a coordination polyhedron on the surface of $Sm_2Cu_{2/3}Nb_{4/3}O_7$. Similarly, the adsorbed CO_2^-, which is produced by the reaction of the adsorbed CO^+ with a lattice oxygen, can also give an electron to a Sm^{3+} ion in the polyhedron which is a neighbour of the polyhedron of the above mentioned Cu^+ ion, to yield a Sm^{2+} ion, and consequently form the gaseous CO_2. Whereas, after formation of gaseous CO_2, the oxygen molecule from the gas phase can get electrons from the Cu^+ ion and Sm^{2+} ion in two neighbouring polyhedra, which is produced in the formation process of gaseous CO_2, and yield the adsorbed oxygen anion and Cu^{2+} and Sm^{3+} ion. In this way, the reduction of Cu^{2+} and Sm^{3+} ions will replace the annihilation of the hole in the reaction mechanism of oxidation of carbon monoxide on the surface of oxidic catalysts with p-type semiconducting property. Similarly, the oxidation of Cu^{+} and Sm^{2+} ions will replace the generation of the hole in the valence band.

Although the role of variation of valence states of some rare earth ions in the oxidation reaction of carbon monoxide has been discussed [2], we want to emphasize that not only the samarium ion, but also the copper ion may play a significant role in the oxidation process of carbon monoxide on the surface of $Sm_2Cu_{2/3}Nb_{4/3}O_7$. Very possibly, this is a co-catalytic process of two cations. It is very well known, that the oxide of niobium is a very good catalyst for some oxidation reactions. So, we cannot rule out the role of the niobium ion in the catalytic oxidation process of carbon monoxide on the surface of $Sm_2Cu_{2/3}Nb_{4/3}O_7$. The niobium ion may also play the same role in the above mentioned reaction process, like copper ion or samarium ion. We consider that the investigation which role the copper, niobium and samarium ions will play in the oxidation reaction of carbon monoxide on the surface of $Sm_2Cu_{2/3}Nb_{4/3}O_7$ may be very interesting.

In summary, a novel CO conversion catalyst with a pyrochlore structure has been synthesized by a wet chemical method. $Sm_2Cu_{2/3}Nb_{4/3}O_7$ has a tetragonal symmetry. The catalytic oxidation of carbon monoxide on the surface of $Sm_2Cu_{2/3}Nb_{4/3}O_7$ can occur below 50°C and the conversion efficiency of carbon monoxide will be close to 100% at near 300°C. The catalytic oxidation process of carbon monoxide on the catalyst may not involve the annihilation and generation of a hole in the valence band of the compound, because $Sm_2Cu_{2/3}Nb_{4/3}O_7$ is an insulator. It has been assumed that the variation of valence states of the copper, niobium and samarium ions in the compound may play a significant role in the catalytic process and that a co-catalytic process is very possible.

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