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Application of cyclic voltammetry in heterogeneous catalysis: NO decomposition and reduction

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Abstract

It is reported that cyclic voltammetry (CV) is a strong tool to investigate catalytic reactions not only in homogeneous catalysis, but also in heterogeneous catalysis. The application of CV measurements in homogeneous catalysis is illustrated through investigation of NO removal (NO reduction and decomposition), which is an urgent task of today in environment catalysis. Results of our study indicate that both the area of redox peak and the symmetry of redox potentials of catalyst are important parameters in determining the catalytic activity, but each has his strong point in different reactions (NO reduction and decomposition). We suggest that CV is a powerful means to select catalysts for NO_x removal.

Keywords: Perovskite-like oxides; Cyclic voltammetry; NO removal; Redox potential

1. Introduction

For a catalytic reaction, two steps should be involved. One is oxidation; the other is reduction. An excellent catalyst, accordingly, should exhibit the ability both to reduction and to oxidation. Namely, the catalytic performance and the redox potentials of the catalyst are related closely. Hence, measurement of the redox potentials of a catalyst is useful before investigating the nature of a catalytic reaction. This concept has obtained great success in homogeneous catalysis. However, no literature related to this aspect has been reported in heterogeneous catalysis (for example, gas–solid reactions) to our knowledge. Part of the reasons are due to the difficulty in measuring the redox potentials of catalysts (especially solid-state oxides [1]).

Recently, NO_x removal from combustion sources received much attention and has become one of the most important projects in environment catalysis, because of the harm NO_x caused [2,3]. However, although this subject has been researched for many years, there is still no effective method to solve this problem. One of the reasons is that there is no suitable catalyst for use. Hence, to find a suitable catalyst that can be used for NO_x removal is an urgent task of today in environment catalysis.

Previously, we reported that perovskite-like mixed oxides ($LaSrCuO_4$ [4] and $LaSrNiO_4$ [5]) were active and potential catalysts for NO removal (NO reduction and decomposition, respectively). In this work, we demonstrated why $LaSrCuO_4$ showed the best activity in NO reduction and $LaSrNiO_4$ showed the best activity in NO decomposition by correlating the catalytic perfor-

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mance with the redox potentials of catalysts. Results of study shown here indicated that redox potentials of catalyst are also an important parameter in determining the catalytic activity, and hence suggest that CV is a powerful means to select catalyst used for NO_x removal. The present results also showed that CV is a strong tool to investigate catalytic reaction not only in homogeneous catalysis, but also in heterogeneous catalysis.

2. Experimental

The preparation and activity measurement of the two series perovskite-like oxides ($La_{1-x}Sr_xCuO_4$, $x = 0$, 0.5, 1.0, and $LaSrMO_4$, M = Co, Ni, Cu) is reported in our previous papers [4,5].

The cathode was made in the following way: we mixed the sample (powder) with a dimethylformamide (DMF) solution containing 2% polytetrafluoroethylene (PTFE) and agitated them to form a cream. The mixture was then rolled into sheet and cut into pellets. The working electrode was prepared by putting a cathode pellets between two pieces of nickel mesh and pressing softly. The electrode then was vacuum-dried at 373 K for 24 h before using. Cyclic voltammetric measurement of the electrode was performed in 1 mol dm^{-3} $LiClO_4$/PC (propanediol carbonate) electrolyte solution using a three-electrode cell (type DH-1, China) as described elsewhere [1,6]. Lithium metal and lithium fragment were used as counter and reference electrode, respectively. The potential was swept between 4.4 and 1.0 V vs. Li/0.1MLi^+ at a speed of 10 mV/s.

3. Results and discussion

Some physical properties of the samples are listed in Table 1. It is seen that all the samples are single A_2BO_4 type with tetragonal or orthorhombic structures, which suggests that the catalysts are pure phases. The average valence of Cu in $LaSrCuO_4$ and $La_{1.5}Sr_{0.5}CuO_4$ is in the same, although the Sr content in $LaSrCuO_4$ is twice as that in $La_{1.5}Sr_{0.5}CuO_4$. This suggests that the maximum oxidative state of Cu in this system is +2.24 no matter how much of La is replaced by Sr. For $LaSrCuO_4$, the decreasing charge caused by the excess substitution of Sr^{2+} for La^{3+} might be compensated totally by increasing the amount of non-stoichiometric oxygen. While for $LaSrNiO_4$ and $LaSrCoO_4$, the average valence of Ni and Co could reach a higher oxidative state (2.68 and 2.85, respectively), but the amount of non-stoichiometric oxygen is lower. In all, for all the samples, the average valence of metal (Co, Ni, Cu) is in inverse proportion to the amount of non-stoichiometric oxygen.

The catalytic activity of NO reduction and decomposition is also listed in Table 1. For NO reduction reaction, which is performed at low temperatures ($T = 400$ °C), it is seen that the catalytic activity of the samples increased with increasing the non-stoichiometric oxygen, in sequence of $LaSrCuO_4 > LaSrNiO_4 > La_{1.5}Sr_{0.5}$- $CuO_4 > LaSrCoO_4 > La_2CuO_4$. This suggests that the oxygen vacancy related closely to the active center and has a large influence on NO reduction reaction. The more the number of oxygen vacancies are, the more the amount of NO adsorbed on the catalyst can be. As a result, there are more opportunities for NO reduction reaction to occur, which results in the high activity. The detailed reaction steps are described as follows [7]:

$$M^{3+} - [\,] - M^{2+} + NO = M^{3+} - NO^- - M^{3+} \quad (1)$$

$$2M^{3+} - NO^- - M^{3+} = 2M^{3+} - O^- - M^{3+} + N_2 \quad (2)$$

$$M^{3+} - O^- - M^{3+} + CO = M^{3+} - [\,] - M^{2+} + CO_2 \quad (3)$$

where M represents Co, Ni, or Cu; "[ ]" represents the oxygen vacancy. After NO adsorption and dissociation, the oxygen left on catalyst will be removed by reducing agent (CO, see reaction (3)). That is to say, oxygen removal is easily carried out in NO reduction reaction, because of the existence of reducing agent. The crucial step of the reaction, then, becomes to be the adsorption and dissociation of NO, which relates greatly to the non-stoichiometric oxygen. As a result, $LaSrCuO_4$ showed the highest activity in NO reduction reaction.

Table 1
Physical properties and catalytic performance of $La_{2-x}Sr_xCuO_4$ ($x = 0$, 0.5, 1) and $LaSrMO_4$ (M = Co, Ni, Cu)

Catalysts	Structure	SSA (m^2/g)	Average valence	Non-stoichiometry oxygen	NO conversion (%)[a]	NO conversion (%)[b]	Reductive potential (V)	Oxidative potential (V)	ΔE (V)[c]
La_2CuO_4	Orthorhombic	2.5	2.02	+0.01	1.0	1.9	2.49	3.35	0.86
$La_{1.5}Sr_{0.5}CuO_4$	Tetragonal	2.4	2.24	−0.13	60.0	9.8	2.0	2.9	0.9
$LaSrCuO_4$	Tetragonal	2.6	2.24	−0.38	96.8	34.3	1.30	3.13	1.77
$LaSrCoO_4$	Orthorhombic	2.3	2.85	−0.06	39.9	20.3	–	2.15	–
$LaSrNiO_4$	Tetragonal	2.7	2.68	−0.16	80.1	94.7	2.75	3.25	0.5

[a] NO reduction (reducing agent: CO) at 400 °C.
[b] NO decomposition at 850 °C.
[c] ΔE: the difference between oxidative and reductive potential.