Studies on the redox behaviour of La$_{1.867}$Th$_{0.100}$CuO$_4$ and its catalytic performance for NO decomposition

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La$_{1.867}$Th$_{0.100}$CuO$_4$ was prepared by means of the citric acid complexing method. The reduction–oxidation (redox) properties of this composite oxide have been investigated by using the XRD, TGA, EPR, TPD, and SEM methods. The fresh (non-reduced) La$_{1.867}$Th$_{0.100}$CuO$_4$ catalyst is single phase with tetragonal K$_2$NiF$_4$-type structure. There were three reduction steps observed over La$_{1.867}$Th$_{0.100}$CuO$_4$ in the temperature ranges of 25–100, 100–300, and 300–500 °C, respectively. After reduction at 300 °C, the material still retained its original single phase but there were oxygen vacancies generated in the lattice. After reduction at 500 °C, it decomposed to a mixture of oxides. In the course of reduction, trapped electrons were generated. During the oxidation of the reduced sample, O$_2^-$ was detected. Apparently, oxygen vacancies are able to stabilise O$_2^-$ on the surface of the catalyst. NO adsorption on both the fresh and reduced La$_{1.867}$Th$_{0.100}$CuO$_4$ samples generated NO radicals and O$_2^-$ species. On a La$_{1.867}$Th$_{0.100}$CuO$_4$ sample reduced at 300 °C [-O$_2$NO$_2$]$^{2-}$ was generated in NO adsorption and decomposed to N$_2$ and O$_2^-$ at ca. 730 °C. After reduction, the O$_2^-$ inside the La$_{1.867}$Th$_{0.100}$CuO$_4$ lattice became more mobile and participated in the decomposition of [O$_2$NO$_2$]$^{2-}$. The fresh (non-reduced) La$_{1.867}$Th$_{0.100}$CuO$_4$ sample with cation defects in its lattice shows higher NO decomposition activity than the fresh La$_2$CuO$_4$ sample in which there are no cation defects. The 300 °C-reduced La$_{1.867}$Th$_{0.100}$CuO$_4$ with cation defects and oxygen vacancies is more active than the fresh one for NO decomposition. The redox action between Cu$^+$ and Cu$_2^+$ is an essential process for NO decomposition.

Keywords: La$_{1.867}$Th$_{0.100}$CuO$_4$, redox behaviour, NO decomposition

1. Introduction

Perovskite type (ABO$_3$) mixed oxides are known to be active catalysts for NO$_x$ reduction and ammonia oxidation [1,2]. They are thermally stable (up to 1000 °C) and can accommodate lattice defects such as oxygen vacancies, A-site deficiencies, and B ions of variable oxidation states. The perovskite-like A$_2$BO$_3$ mixed oxides of K$_2$NiF$_4$ structure are thermally more stable than ABO$_3$ and have been described as novel catalysts for ammonia oxidation and NO$_x$ elimination [3–5]. In general, in ABO$_3$ and A$_2$BO$_3$, A is a rare earth element and B is a transition metal; the oxidation state of B is 2$^+$ and 3$^+$, respectively, in the two compounds. Besides noble metals such as Pt, Pd, Ru, and Rh, copper is also a common component in DeNO$_x$ catalysts. Unlike LaMnO$_3$, LaFeO$_3$, LaCoO$_3$, and LaNiO$_3$, the compound LaCuO$_3$ is unstable because it is difficult to keep a high concentration of Cu$^{3+}$ in the bulk of LaCuO$_3$. In contrast, La$_2$CuO$_4$ is very stable [5]. The working oxidation state of copper for the DeNO$_x$ reaction is unclear. For the Cu-ZSM-5 catalysts, Cu$^+$ was thought to be an active center [6,7]. London et al. suggested that NO decomposition is associated with a redox between Cu$^+$ and Cu$^0$ [8]. Mizuno et al. reported that Cu$^{2+}$ is an active center for NO decomposition [9]. The role played by oxygen in the NO decomposition reaction is a topic of controversy [10]. Most of the DeNO$_x$ catalysts are SCR (selective catalytic reduction) catalysts. The SCR process needs additional reductant(s) such as hydrocarbons, CO, H$_2$ or NH$_3$; this leads to the production of secondary pollutants such as oxygenated hydrocarbons, CO, CO$_2$, N$_2$O or cyanate and isocyanate compounds [10]. The direct catalytic decomposition of NO to N$_2$ and O$_2$ is highly desirable because no additional reactant is needed for the reaction. However, up to now, no suitable material has been obtained to catalyse the reaction under actual exhaust conditions [10–12]. The influence of cation defects on the catalytic activity of NO decomposition was rarely reported. The radius of Th$^{4+}$ (0.94 Å) is smaller than that of La$^{3+}$ (1.23 Å). The substitution of Th$^{4+}$ for La$^{3+}$ is possible. Based on such an understanding, we synthesised La$_{1.867}$Th$_{0.100}$CuO$_4$ as a catalyst for NO decomposition. According to the La$_{1.867}$Th$_{0.100}$CuO$_4$ stoichiometry, 1.65% of the A-site ions are defects. The activity of the catalyst for NO decomposition has been investigated as related to the intrinsic defect properties of the material.

2. Experimental

2.1. Catalyst preparation

The catalyst was prepared by the citric acid complexing method: lanthanum, thorium, and copper nitrates in a
desired molar ratio were dissolved in a citric solution at 80 °C with constant stirring until a viscous gel was formed. The gel was decomposed abruptly to very fine powder (ca. 10 nm) at around 300 °C. The furnace temperature was then raised (20 °C min\(^{-1}\)) to 500 °C and the catalyst was heated at this temperature in air for 5 h. After being pressed and ground, the catalyst was calcined at 950 °C for 12 h.

2.2. Characterisation

The metal-ion composition of the catalyst was determined by titration against standardised solution of EDTA. The oxidation state of copper in the catalyst was measured by means of the iodometry method \([13,14]\). Together with the known contents of La\(^{3+}\) and Th\(^{4+}\), the data were used to estimate the non-stoichiometric amount of oxygen in the sample.

XRD measurements were carried out on a Rigaku D-Max Rotaflex instrument with Cu Kα radiation and Ni filter. BET specific areas were measured on a Nova 1200 instrument. The samples were first treated in a vacuum for 2 h at 400 °C before BET measurements.

H\(_2\)-TGA was performed on a Rigaku thermoanalyser. For each measure, 40 mg of fresh (non-reduced) sample was used. A mixture of 10% H\(_2\)–90% He (flow rate 20 ml min\(^{-1}\)) was passed through the sample. The temperature range studied was from 20 to 500 °C and the heating rate was 10 °C min\(^{-1}\).

EPR spectra were recorded at −196 °C with a Jeol spectrometer operating in the X-band and calibrated with DPPH (\(g = 2.004\)). The sample (0.1 g) was placed in a self-made quartz cell in which the sample could be treated under different atmospheres at various temperatures. Before performing the EPR studies over fresh or 300 °C-reduced La\(_{1.867}\)Th\(_{0.105}\)CuO\(_4\), we He-purged (flow rate 20 ml min\(^{-1}\)) the sample at 800 °C for 1 h and then cooled it down to 25 °C in He. For NO adsorption, NO (3000 ppm with He being the carrier gas, flow rate 20 ml min\(^{-1}\)) was introduced into the quartz cell at a desired temperature for 1 h. The NO-TPD experiments of fresh and the 100 \(\%\) Cu-reduced La\(_{1.867}\)Th\(_{0.105}\)CuO\(_4\) were repeated. A mixture of 10% H\(_2\)–90% He (flow rate 20 ml min\(^{-1}\)) was passed through the sample. The temperature range studied was from 20 to 500 °C and the heating rate was 10 °C min\(^{-1}\).

For the redox studies of La\(_{1}\)Th\(_{0}\)CuO\(_4\) \((1.23 \text{ Å})\), the substitution of Cu\(^{3+}\) for La\(^{3+}\) in the lattice is possible. Due to the substitution of Th\(^{4+}\) for La\(^{3+}\), the concentration of Cu\(^{3+}\) in La\(_{1.867}\)Th\(_{0.105}\)CuO\(_4\) is lower than that in La\(_2\)CuO\(_4\). One can envision that besides the cation defects, there was an excess amount of oxygen in La\(_{1.867}\)Th\(_{0.105}\)CuO\(_4\). Catalytic activity evaluation was carried out with 0.3 g of sample packed in a quartz microreactor. Prior to the test, the sample was treated at 650 °C under a He flow to eliminate water and carbonates. The decomposition of NO was performed between 200 and 800 °C (heating rate 2 °C min\(^{-1}\)). The reaction feed was 3000 ppm NO in He and the total GHSV was 7500 h\(^{-1}\). Catalytic activity was measured 0.5 h after performance stabilisation. The effluent gases (N\(_2\), NO, and N\(_2\)O) were analysed by gas chromatography and mass spectrometry. Before evaluating the catalytic activity of the reduced sample, we carried out the CD\(_3\)I-TPD procedure to eliminate surface hydrogen. After three cycles of CD\(_3\)I-TPD treatments, we observed no more CD\(_3\)H. It is an indication that most of the surface hydrogen has been eliminated.

3. Results and discussion

3.1. Redox behaviours of catalyst

Based on the data obtained according to the titration methods, the composition of La\(_{1.867}\)Th\(_{0.105}\)CuO\(_4\) is actually La\(_{1.867}\)Th\(_{0.105}\)CuO\(_{4.005}\) whereas that of La\(_2\)CuO\(_4\) is La\(_2\)CuO\(_{4.008}\) (table 1). The radius of Th\(^{4+}\) (0.94 Å) is smaller than that of La\(^{3+}\) (1.23 Å), the substitution of Th\(^{4+}\) for La\(^{3+}\) in the lattice is possible. Due to the substitution of Th\(^{4+}\) for La\(^{3+}\), the concentration of Cu\(^{3+}\) in La\(_{1.867}\)Th\(_{0.105}\)CuO\(_4\) is lower than that in La\(_2\)CuO\(_4\). One can envision that besides the cation defects, there was an excess amount of oxygen in La\(_{1.867}\)Th\(_{0.105}\)CuO\(_4\) (La\(_{1.867}\)Th\(_{0.105}\)CuO\(_{4.005}\) : cation defect).

The XRD results of fresh and the 100 °C-reduced La\(_{1.867}\)Th\(_{0.105}\)CuO\(_4\) samples are listed in table 1.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu(^{3+})/Cu (%)</th>
<th>Surface (m(^2)/g)</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>La(_2)CuO(_4)</td>
<td>1.5</td>
<td>2.8</td>
<td>La(_2)CuO(_4) \text{0.008})</td>
</tr>
<tr>
<td>La(<em>{1.867})Th(</em>{0.105})CuO(_4)</td>
<td>1.0</td>
<td>3.5</td>
<td>La(<em>{1.867})Th(</em>{0.105})CuO(_4) \text{0.005})</td>
</tr>
</tbody>
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