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Short Communication

A Ce–Cu–Ti oxide catalyst for the selective catalytic reduction of NO with NH_3

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ABSTRACT

A Ce–Cu–Ti complex oxide catalyst for the selective catalytic reduction of NO with NH_3 was prepared by coprecipitation method. XRD and H_2–TPR reveal that the strong interaction between Ce and Cu results in the production of a new active oxygen species with high reducibility at low temperatures. Compared with Ce–Ti oxide catalyst, the Ce–Cu–Ti oxide catalyst produces better performance at the temperatures lower than 350 °C and higher SO_2-resistent ability. H_2O will reduce the SCR activity of Ce–Cu–Ti catalyst at low temperatures while promoting the catalyst performance at temperatures more than 350 °C.

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1. Introduction

Selective catalytic reduction (SCR) with ammonia is regarded as one of the most promising technologies for the abatement of NOx emissions from stationary sources. The anatase supported V_2O_5–WO_3 or V_2O_5–MoO_3 oxides have been widely used for the past few decades [1]. However, several issues have arisen during industrial applications, such as high cost, toxicity and high oxidation of SO_2 to SO_3 of vanadia-based catalyst [2]. Consequently, it is of great necessity and interest to develop a substitute catalyst to the present V-based SCR catalyst with properties of non-toxicity, low cost and less oxidation of SO_2.

Several transitional metals, such as Mn, Fe, Cu and Ce, have been found to be active for SCR of NO with NH_3 [3–9]. Ceria-based oxides with advantages of high oxygen storage capacity and excellent redox properties [10,11] have been attracting much attention. In 1994, Ito et al. [9] proposed that a Ce-exchanged mordenite catalyst was highly active for SCR of NO. After that, the doping of ceria was found to promote the V_2O_5 based catalyst performance for SCR reaction at low vanadium content [12,13]. Wen and He's research proved that Ce–Cu–Mg–Al synergism showed high activity and excellent SO_2 resistance for NO reduction with CO [14]. Mn–Ce mixed oxide also showed high activity at low temperatures [4,5,15]. In recent years, Ce–Ti oxide was found to possess a high SCR activity and an excellent selectivity to N_2 [16–18]. Therefore, Cerium-based oxides seem to be a qualified candidate for the SCR catalyst in the future. However, deactivation of Ce/TiO_2 catalyst by SO_2 may limit its practical application because of the high SO_2 concentration in the flow gas from stationary sources [19]. As a result, the SO_2-resistance of Ce-based catalyst is an urgent issue to be solved. In this study, Ce–Cu–Ti, Ce–Ti and Cu–Ti complex oxides were prepared by coprecipitation. N_2 adsorption, X-ray diffraction (XRD) and H_2 temperature programmed reduction (H_2–TPR) were performed for these catalysts. The influence of SO_2 and H_2O were also investigated.

2. Experimental

2.1. Catalyst preparation

Ce–Cu–Ti, Ce–Ti and Cu–Ti complex oxides were prepared by a conventional coprecipitation. $Ce(SO_4)_2 \cdot 4H_2O$, $Ti(SO_4)_2 \cdot 2H_2O$ and $CuSO_4 \cdot 5H_2O$ were dissolved in exchanged ion water. An ammonia solution was slowly added (less than 0.3 ml/min) for coprecipitation under vigorous stirring until the pH reached 9.5. After washing and filtering to eliminate sulfate ion, the precipitates were firstly dried at 80 °C in a water bath for 4 h, then dried at 50 °C in a vacuum drying oven for 12 h and finally dried at 110 °C for 4 h. The obtained products were calcined at 500 °C in air for 5 h. The Ce–Cu–Ti, Ce–Ti and Cu–Ti complex oxides were designated as CCT, CET and CUT respectively.

2.2. Catalyst characterization

The chemical compositions were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES). Brunauer–Emmett–Teller (BET) surface area was measured by N_2 adsorption at 77 K using a Quantachrome Autosorb-1 instrument. Room-temperature

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X-ray powder diffraction (XRD) measurements were recorded on a Rigaku D/max 2550PC system with CuKa radiation. The temperature programmed reduction with hydrogen (H_2–TPR) was performed on an AutoChem II 2920 instrument manufactured by Micromeritics Corporation. H_2 signal was detected by a thermal conductivity detector (TCD).

2.3. Activity test

The catalytic activity tests for the reduction of NO with NH_3 were carried out in a fixed bed micro-reactor with 0.2 g catalyst samples with particle size of 250–380 μm. The simulated gas for these tests contained 1000 ppm NO, 5 vol.% O_2, and 1000 ppm NH_3 in N_2. The catalytic reactions were carried out at temperatures from 150 to 450 °C under atmosphere pressure, with a total flow rate of 0.8 L min^{-1}. The NO concentrations before and after reaction were determined using a testo 350 pro analyzer manufactured by the Testo Instrument company in Germany.

3. Results and discussion

3.1. Characterizations

Chemical analysis results given by ICP-OES were listed in Table 1. The rest of the catalysts were composed by Ti and O atoms. Table 1 also shows the BET analysis results of CCT, CUT and CCT catalysts. CCT presents the best textural parameters, i.e. the largest specific surface area and pore volume. CET also possesses a large surface area of 123.6 m^2/g. Unlike CCT and CET, CUT only has a small surface area of 14.3 m^2/g and a small pore volume of 0.051 cc/g.

XRD patterns are shown in Fig. 1. For Cu–Ti oxide (CUT) sample, only anatase TiO_2 oxide was detected. This indicates the fine distribution of Cu on the TiO_2 surface. In the pattern of Ce–Ti oxide (CET) catalyst, only weak diffraction peak of anatase TiO_2 was found, which suggests that CeO_2 is highly dispersed on the catalyst surface. No distinctively obvious diffraction peaks of Ce, Cu or Ti appeared for CCT catalyst. The weak X-ray diffraction characteristic of CCT catalyst suggests that this catalyst will be inherently amorphous in structure, and all metal components (Ce, Cu and Ti) are highly dispersed. The XRD pattern of CCT reveals the strong interaction among Ce, Cu and Ti, i.e. the production of the Ce–Cu–Ti complex oxide.

The H_2–TPR results (Fig. 2) provide the oxygen storage capacities of CET, CUT, and CCT catalysts. Oxygen storage capacity (OSC) is a significant parameter to the SCR activity of ceria-based catalysts [10,11]. CUT shows a hydrogen consumption peak at 250 °C due to the reduction of highly dispersed CuO [20]. As reported, pure CeO_2 shows a small peak at 325 °C due to the reduction of surface ceria ion, and bulk CeO_2 reduction occurring above 500 °C [21,22]. CET catalyst possesses a wide peak around 450 °C. This wide ranged peak is due to the stepwise reduction of Ce^{4+} to Ce^{3+}, indicating the highly dispersed CeO_2 on the TiO_2 surface. Three reduction peaks were detected at 200 °C, 250 °C and 560 °C respectively, for the CCT catalyst. The novel peak at 200 °C may attribute to the cooperative effect between Ce and Cu. The addition of CuO to CeO_2 will produce a new type of oxygen species, which can be reduced by hydrogen in a lower temperature. Integral areas of these three curves were also calculated to compare their OSC. The OSC values rank as CCT > CET > CUT.

Table 1
Chemical analysis and BET results for CET, CUT and CCT samples.

	Composition (wt.%)		Surface area (m^2/g)	Total pore volume (cc/g)	Average pore diameter (Å)
	Ce	Cu			
CET	24.6	0	123.6	0.243	78.7
CUT	0	2.57	14.3	0.051	143
CCT	25.4	3.73	170.6	0.458	107

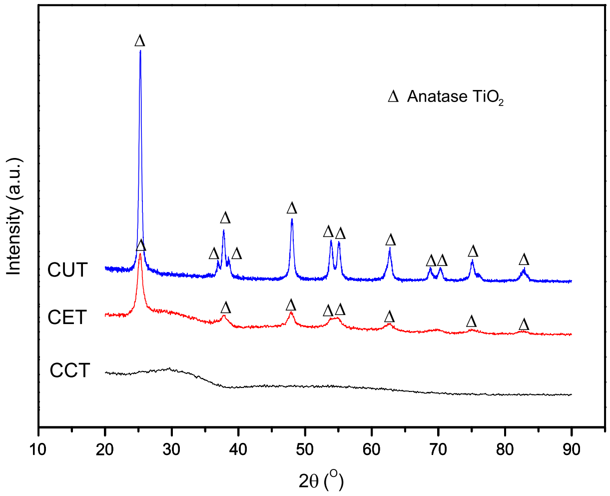

Fig. 1. XRD patterns of CUT, CET and CCT.

3.2. Activity test

Activity tests were carried out for CET, CUT and CCT to compare their SCR performance. The results (Fig. 3) indicate that both CET and CCT show high activities in a wide temperature range. CCT exhibits high NO conversion (>70% at GHSV of 240,000 ml g^{-1} h^{-1}) from 200 to 400 °C in the absence of H_2O and SO_2. The addition of Cu to Ce–Ti catalyst will improve the SCR performance at low temperatures while inhibiting the high temperature performance. This is in accordance with the TPR results that the addition of Cu to Ce–Ti catalyst will improve the surface redox ability at low temperatures, which leads to the promotion of the SCR activity at low temperatures. The low activity of CCT at high temperatures can be observed. The TPR result of CCT has shown the high oxidizing ability of the catalyst, which may probably cause the oxidation of NH_3 to NO at high temperatures in the absence of H_2O and SO_2. A similar result has been found on a Ce–Mn–O catalyst above 300 °C [5]. The productions of N_2O are ignorable, thus not discussed in this section.

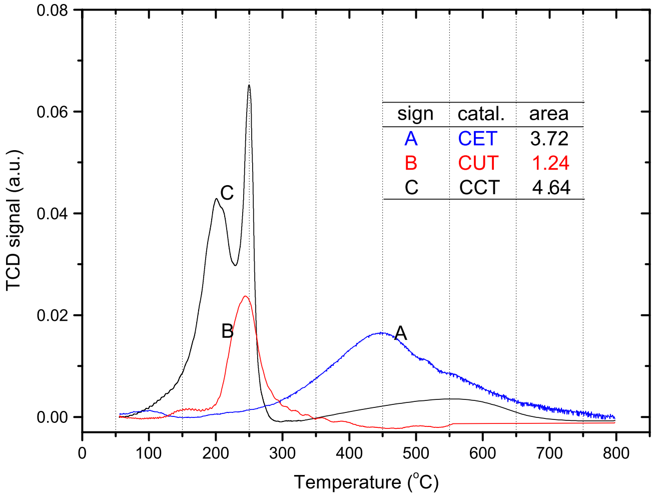

Fig. 2. H_2–TPR profiles for CET, CUT and CCT.

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