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Catalytic oxidation of CO over $Cu_xCe_{1-x}O_{2-x}$/SBA-15/FeCrAl monolithic catalysts

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ABSTRACT

A series of $Cu_{0.5}Ce_{0.5}O_{1.5}$/SBA-15/FeCrAl with the $Cu_{0.5}Ce_{0.5}O_{1.5}$ contents from 10 wt% to 60 wt% and 50 wt% $Cu_xCe_{1-x}O_{2-x}$/SBA-15/FeCrAl (x = 0–1) catalysts were prepared. The structure of the catalysts was characterized using X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and temperature-programmed reduction (TPR). The catalytic activity of the catalysts for the oxidation of CO was evaluated. The results indicated that for the $Cu_{0.5}Ce_{0.5}O_{1.5}$/SBA-15/FeCrAl catalysts CuO was observed when $Cu_{0.5}Ce_{0.5}O_{1.5}$ loading is more than 40 wt%. For the 50%$Cu_xCe_{1-x}O_{2-x}$/SBA-15/FeCrAl catalysts, when x is in the range of 0–0.9, CeO_2 or Cu-Ce oxides were observed. When x is more than 0.5, CuO was observed. There were the strong interactions among CuO, CeO_2 and the FeCrAl support, and they affected the catalytic activity of the catalysts. In all catalysts, the 50%$Cu_{0.5}Ce_{0.5}O_{1.5}$/SBA-15/FeCrAl catalyst exhibited the best catalytic activity. CO can be completely oxidized at 160 °C.

1. Introduction

Recently, the catalytic oxidation of CO is considered as immense importance due to its applications in pollution control devices for vehicle exhaust, indoor air cleaning, fuel cells, and carbon dioxide lasers [1,2]. Precious metal catalysts, such as Pt, Pd, Ru, Rh and Au, have been widely studied for CO catalytic oxidation and showed high catalytic activities [3,4]. However, the high cost and the limited availability of the precious metals has encouraged researchers to look for alternative catalysts. In particular, CuO-CeO_2 composite catalysts have been reported as highly active for CO oxidation. A strong interaction between copper and ceria has been reported to be responsible for the high activity of these CuO-CeO_2 catalysts [5].

The newly achieved SBA-15 has high surface area, uniform pore structure, and narrow pore size distribution [6]. These unique features offer new possibilities for obtaining highly dispersed metal catalysts. Therefore it has attracted much attention as a catalyst support. On the other hand, the conventional fixed-bed reactors loaded with catalyst pellets have high pressure drops and high gradient of temperature thus depressed the activity of the catalysts. Nowadays, monolithic catalysts, especially using the FeCrAl alloy foils as the catalyst supports, have increasingly drawn the attention of researchers. The monolithic catalysts have distinct advantages: the much lower pressure drops, the lower capacity of mass and heat transfer, the higher resistance to thermal shocks [7]. Especially, for the reactions with high space velocity, such as CO catalytic oxidation reaction, the metallic monolithic catalysts have a promising application.

In this work, a series of $Cu_{0.5}Ce_{0.5}O_{1.5}$/SBA-15/FeCrAl with the $Cu_{0.5}Ce_{0.5}O_{1.5}$ contents from 10 wt% to 60 wt% and 50%$Cu_xCe_{1-x}O_{2-x}$/SBA-15/FeCrAl (x = 0–1) metal monolithic catalysts were prepared. The structure of catalysts was characterized by XRD, XPS and TPR. The catalytic activity of catalysts for CO oxidation was evaluated.

2. Experimental

2.1. Catalyst preparation

The metallic monolithic catalysts were prepared using the FeCrAl alloy foils (OC404, Sandvik Steel, Sweden) as supports. The alloy foils were rolled into several cylinders in different diameters and 50 mm in length. The supports were pretreated successively in basic, acidic and ethanol solution, then thoroughly rinsed in deionized water, and finally the pretreated supports were calcined at 950 °C for 15 h in air. In order to improve the adhesion between the washcoat layers and the heat-treated metallic supports, a boehmite primer sol was used as first washcoat layer, then dried at room temperature in air and thereafter at 120 °C for 3 h, and calcined at 500 °C for 4 h, and the monolithic support (Al_2O_3/FeCrAl) was formed. SBA-15 was synthesized according to the method described in the literature [8]. The $Cu_{0.5}Ce_{0.5}O_{1.5}$/SBA-15 and $Cu_xCe_{1-x}O_{2-x}$/SBA-15 samples were prepared by co-impregnation of pure SBA-15 with an aqueous solution of copper nitrate and cerium nitrate. Then, the slurry of the $Cu_{0.5}Ce_{0.5}O_{1.5}$/SBA-15

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Table 1
Compositions and particle size of the catalysts.

Catalyst	Composition	D_{CuO}[a] (nm)	$D_{\mathrm{CeO_2}}$ or $D_{\mathrm{CuCeO_x}}$[a] (nm)
1#	10%$Cu_{0.5}Ce_{0.5}O_{1.5}$/SBA-15/FeCrAl	n.d.[b]	9.9
2#	20%$Cu_{0.5}Ce_{0.5}O_{1.5}$/SBA-15/FeCrAl	n.d.[b]	9.7
3#	30%$Cu_{0.5}Ce_{0.5}O_{1.5}$/SBA-15/FeCrAl	n.d.[b]	9.7
4#	40%$Cu_{0.5}Ce_{0.5}O_{1.5}$/SBA-15/FeCrAl	34.1	9.8
5#	50%$Cu_{0.5}Ce_{0.5}O_{1.5}$/SBA-15/FeCrAl	28.6	9.8
6#	60%$Cu_{0.5}Ce_{0.5}O_{1.5}$/SBA-15/FeCrAl	35.0	9.6
7#	50%CuO/SBA-15/FeCrAl	25.4	–
8#	50%$Cu_{0.9}Ce_{0.1}O_{1.1}$/SBA-15/FeCrAl	22.9	10.7
9#	50%$Cu_{0.7}Ce_{0.3}O_{1.3}$/SBA-15/FeCrAl	28.1	9.7
10#	50%$Cu_{0.3}Ce_{0.7}O_{1.7}$/SBA-15/FeCrAl	n.d.[b]	9.8
11#	50%$Cu_{0.1}Ce_{0.9}O_{1.9}$/SBA-15/FeCrAl	n.d.[b]	10.5
12#	50%CeO_2/SBA-15/FeCrAl	–	10.6

[a] Calculated from XRD measurements.
[b] Not detected.

and $Cu_xCe_{1-x}O_{2-x}$/SBA-15 was coated on the Al_2O_3/FeCrAl monolithic supports, dried at room temperature in air and thereafter at 120 °C for 3 h, and then calcined at 500 °C for 4 h. The coating procedure should be repeated to achieve the desired coating amount. Finally, the $Cu_{0.5}Ce_{0.5}O_{1.5}$/SBA-15/FeCrAl with the $Cu_{0.5}Ce_{0.5}O_{1.5}$ content from 10 wt% to 60 wt% and $Cu_xCe_{1-x}O_{2-x}$/SBA-15/FeCrAl (x = 0–1) catalysts with the $Cu_xCe_{1-x}O_{2-x}$ content of 50 wt% were obtained. The compositions of the catalysts were listed in Table 1.

2.2. Catalytic activity measurements

CO catalytic oxidation experiments were performed in a conventional quartz flow reactor (i.d., 8 mm; length, 300 mm) at atmospheric pressure. The mixture gas was 1 vol.% CO in air, with a gas hourly space velocity of 36,000 ml/g h. The reaction was stabilized for 30 min at the required temperature, and the outlet products were measured with on-line gas chromatography (Beijing East & West Electronics Institute, GC-4000A). The catalyst temperature was controlled with a K-type thermocouple placed in the vicinity of the catalyst bed. In every case, carbon dioxide and water were the only reaction products detected along the whole experiments.

2.3. Catalysts characterization

The phase structure of the samples was characterized by XRD using a Rigaku D/Max 2500 VB2 + /PC diffractometer with a Cu Kα radiation operating at 200 mA and 40 kV. XPS experiments were carried out on an ESCALAB250 instrument (Thermo Electron Co.) using Al Kα as the exciting radiation at the constant pass energy of 50 eV. Binding energies were calibrated using the carbon present as a contaminant (C 1s = 285.0 eV). The surface atomic compositions of all samples were calculated from photoelectron peak areas for each element after correction for instrument parameters. Temperature-programmed reduction (TPR) experiments were performed using a Thermo Electron Corporation TPD/R/O 1100 series Catalytic Surfaces Analyzer equipped with a TC detector. Samples were preheated with 10 vol.% O_2/He mixture heating 20 °C/min up to 500 °C, then cooling down to room temperature in flowing N_2, and thereafter reduced with 5 vol.% H_2/N_2 mixture heating 10 °C/min up to 1000 °C. Water produced by the sample reduction was condensed in a cold trap before reaching the detectors. Only H_2 was detected in the outlet gas confirming the effectiveness of the cold trap.

3. Results and discussion

3.1. Catalytic activity

The catalytic activity over $Cu_{0.5}Ce_{0.5}O_{1.5}$/SBA-15/FeCrAl catalysts is presented in Fig. 1(A). It can be observed that the loading of $Cu_{0.5}Ce_{0.5}O_{1.5}$ had a significant influence on the catalytic activity of the catalysts. The catalytic activity was significantly enhanced with the increase in $Cu_{0.5}Ce_{0.5}O_{1.5}$ loading from 10 wt% to 40 wt%. As the loading of $Cu_{0.5}Ce_{0.5}O_{1.5}$ increased from 40 wt% to 50 wt%, there was only slight increase in catalytic activity. The 50%$Cu_{0.5}Ce_{0.5}O_{1.5}$/SBA-15/FeCrAl catalysts exhibited the highest catalytic activity with CO conversion of 10% at 66 °C. The CO can be completely oxidized at 160 °C.

Fig. 1(B) shows catalytic performance for CO oxidation over the 50%$Cu_xCe_{1-x}O_{2-x}$/SBA-15/FeCrAl catalysts. As observed, the catalytic activity of CO oxidation over both 50%CeO_2/SBA-15/FeCrAl (12#) and 50%CuO/SBA-15/FeCrAl (7#) were quite low. For catalyst 12#, T_{10} and T_{90} were 360 °C and 537 °C, respectively; while for catalyst 7#, T_{10} and T_{90} were 214 °C and 319 °C, respectively. The activities of 50%$Cu_xCe_{1-x}O_{2-x}$/SBA-15/FeCrAl (x = 0.1–0.9) catalysts were much higher than that of catalyst 12# or 7#. The catalytic activities of the 50%$Cu_xCe_{1-x}O_{2-x}$/SBA-15 (x = 0.1–0.9) catalysts were closely related to the Cu/Ce molar ratios. When x = 0.3 and 0.5, the catalysts exhibited the similar catalytic activity. However, further increasing the Cu content ($x > 0.5$) resulted in the decrease of the catalytic activity. On the basis of the activity results, it indicated that the excessive copper would decrease the activity of catalysts.

3.2. XRD

The XRD patterns of FeCrAl metal support and $Cu_{0.5}Ce_{0.5}O_{1.5}$/SBA-15/FeCrAl monolithic catalysts are presented in Fig. 2(A). For

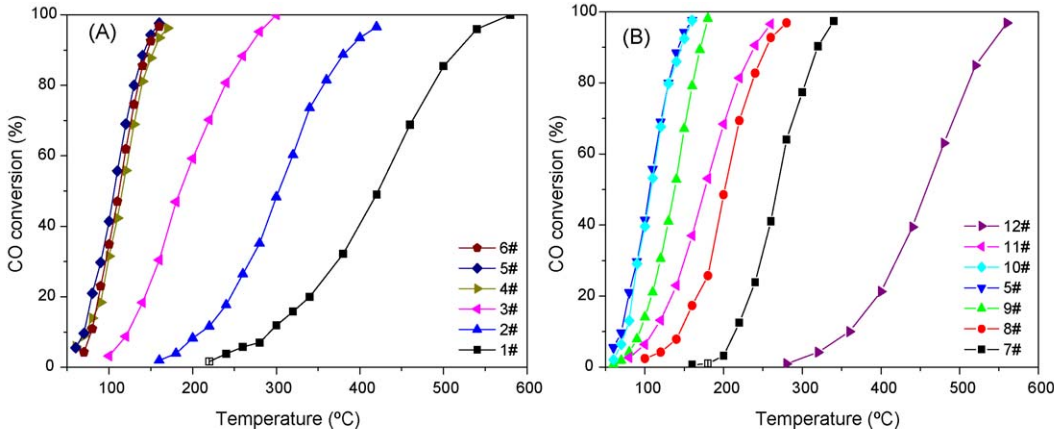

Fig. 1. CO catalytic oxidation over the monolithic catalysts: (A) $Cu_{0.5}Ce_{0.5}O_{1.5}$/SBA-15/FeCrAl catalysts; (B) 50%$Cu_xCe_{1-x}O_{2-x}$/SBA-15/FeCrAl catalysts.