Journal of Colloid and Interface Science 509 (2018) 334–345

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Regular Article

Effect of precursors on the structure and activity of $CuO\text{-}CoO_x/\gamma\text{-}Al_2O_3$ catalysts for NO reduction by CO

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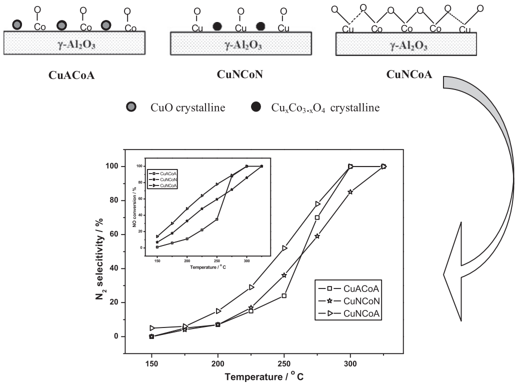
GRAPHICAL ABSTRACT

Precursors significantly influence the structures and catalytic performances of $CuO\text{-}CoO_x/\gamma\text{-}Al_2O_3$ catalysts for NO reduction by CO.



ARTICLE INFO

Article history:
Received 3 July 2017
Revised 2 September 2017
Accepted 7 September 2017
Available online 8 September 2017

Keywords:
Precursors
Homogeneously dispersed
$CuO\text{-}CoO_x/\gamma\text{-}Al_2O_3$
Synergistic effect
NO reduction by CO

ABSTRACT

Catalytic reduction of NO by CO was studied over a series of $CuO\text{-}CoO_x/\gamma\text{-}Al_2O_3$ catalysts prepared by co-impregnation with different copper and cobalt precursors (acetate and nitrate) to evaluate the structure–activity relationship. The obtained samples were characterized in detail by means of XRD, LRS, XPS, H_2-TPR and in situ FT-IR technologies. Results indicate that copper oxide is agglomerated while cobalt oxide is dispersed on $\gamma\text{-}Al_2O_3$ for the catalyst prepared from copper acetate and cobalt acetate precursors (CuACoA); $Cu_xCo_{3\text{-}x}O_4$ spinel is formed and agglomerated on the catalyst prepared from copper nitrate and cobalt nitrate precursors (CuNCoN); while both copper oxide and cobalt oxide could be homogeneously dispersed for the catalyst prepared from copper nitrate and cobalt acetate precursors (CuNCoA), which exhibits the best activity for NO reduction by CO. Probably the synergistic effect between dispersed copper oxide and cobalt oxide is propitious to the oxygen transfer, which could be the reason for its high activities. Finally, a possible reaction mechanism was tentatively proposed to explore the different catalytic performances in NO reduction by CO model reaction.

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http://dx.doi.org/10.1016/j.jcis.2017.09.031
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1. Introduction

Nitrogen oxides (NO_x), generated in combustion processes (stationary and mobile sources), are generally believed to be one of the important atmospheric pollutants to threat ecological environment and human health [1]. The catalytic reduction of NO_x has been a popular subject in environmental catalysis field. Especially, the reaction of NO reduction by CO has attracted more attention due to the simultaneous transformation of NO and CO to nontoxic N_2 and CO_2 for the purification of vehicle exhaust [2]. In addition, it is also a typical model reaction in three-way catalysis (TWC) to study the adsorption and desorption process of reactants. Noble metal catalysts have been extensively reported for this reaction [3–6]. However, due to their scarcity, high cost and poor thermal stability, many efforts have been devoted to employing catalysts containing transition metal oxides to substitute noble metals.

Transition metal copper oxides-based catalysts show excellent catalytic performance in the reduction of NO by CO [7–13]. Nevertheless, it was found that unitary copper oxide still showed unsatisfactory activity for NO reduction at low temperature. Therefore, many studies were performed to improve the catalytic efficiency by utilizing the binary metal oxides catalysts containing Cu-Co or Cu-Mn mixed oxides due to the synergistic interaction between Cu and Co (or Mn) [14–23]. For example, Liu et al. studied CuO-$CoO_x/Ce_{0.67}Zr_{0.33}O_2$ or CuO-$MnO_x/Ce_{0.67}Zr_{0.33}O_2$ catalysts for NO reduction by CO and found that the catalysts prepared by co-impregnation copper nitrate and cobalt nitrate or copper nitrate and manganese acetate on $Ce_{0.67}Zr_{0.33}O_2$ support were more active than stepwise impregnation binary metal oxides catalyst or CuO/$Ce_{0.67}Zr_{0.33}O_2$ catalyst due to the strong interactions between the copper oxide and cobalt/manganese oxide species [14,15].

Precursors have significant influence on the dispersion, oxidation states and catalytic activities of supported metal oxides during the impregnation process. For example, Sun et al. have studied the effect of manganese precursors on the catalytic performances of CuO-MnO_x/TiO_2 catalysts prepared by co-impregnation of copper acetate and manganese acetate or nitrate on TiO_2 support and have found the catalyst prepared from manganese nitrate precursor is more active since the formation of the surface synergetic oxygen vacancy (SSOV) (Cu^+–□–Mn^{3+}) in the CuMn(N)/TiO_2 catalyst is easier than that (Cu^+–□–Mn^{2+}) in the CuMn(A)/TiO_2 catalyst [20]. Li et al. have reported the effect of precursors (manganese nitrate and manganese acetate) on the surface manganese species and activities of MnO_x/TiO_2 catalysts for NO reduction and have found that the higher low-temperature activity of MnO_x/TiO_2 from Mn $(Ac)_2$ precursor is attributed to higher surface Mn concentration and the surface Mn_2O_3 species [24]. We have studied the effect of cobalt precursors on the structure and catalytic performance of $CoO_x/\gamma\text{-}Al_2O_3$ catalysts for CO oxidation and have found that CoO/$\gamma\text{-}Al_2O_3$ catalyst prepared from cobalt acetate precursor exhibit better dispersion and catalytic performances than $Co_3O_4/\gamma\text{-}Al_2O_3$ catalyst prepared from cobalt nitrate precursor [25]. However, to our knowledge, little attention has been paid to comparing the effect of copper and cobalt precursors on the structure and catalytic performances of CuO-$CoO_x/\gamma\text{-}Al_2O_3$ catalysts for NO reduction by CO in the previous research.

In this work, a series of CuO-$CoO_x/\gamma\text{-}Al_2O_3$ catalysts were prepared by co-impregnation on $\gamma\text{-}Al_2O_3$ with different copper and cobalt precursors (acetate and nitrate). CuO/$\gamma\text{-}Al_2O_3$ and $CoO_x/\gamma\text{-}Al_2O_3$ catalysts were also prepared from different nitrate and acetate precursors for comparison. The effects of copper and cobalt precursors on the structures, reduction properties and catalytic performances of CuO-$CoO_x/\gamma\text{-}Al_2O_3$ catalysts were investigated by XRD, LRS, XPS, H_2-TPR and NO + CO reaction. In situ FT-IR was also employed to investigate the interaction between the reactants and these catalysts. A possible reaction mechanism was tentatively proposed to explore the different catalytic performances in NO reduction by CO model reaction.

2. Experimental

2.1. Catalysts preparation

$\gamma\text{-}Al_2O_3$ was purchased from Fushun Petrochemical Institute in China, and calcined at 750 °C for 5 h before catalyst preparation. Its BET surface area is 158.2 $m^2 \cdot g^{-1}$. CuO/$\gamma\text{-}Al_2O_3$ and $CoO_x/\gamma\text{-}Al_2O_3$ catalysts were prepared by wet impregnation of $\gamma\text{-}Al_2O_3$ with aqueous solutions of $Cu(Ac)_2$ or $Cu(NO_3)_2$ and $Co(Ac)_2$ or Co$(NO_3)_2$, respectively. CuO-$CoO_x/\gamma\text{-}Al_2O_3$ catalysts were prepared by co-impregnation with the mixed solutions of $Cu(Ac)_2$ and $Co(Ac)_2$, $Cu(NO_3)_2$ and $Co(NO_3)_2$, $Cu(NO_3)_2$ and $Co(Ac)_2$, respectively. The loading amounts of copper or/and cobalt were 0.6 mmol/100 m^2 $\gamma\text{-}Al_2O_3$. The samples were dried at 110 °C overnight, and then calcined at 450 °C in muffle for 5 h. For simplicity, the resultant catalysts are denoted as CuA, CuN, CoA, CoN, CuACoA, CuNCoN, and CuNCoA, respectively. In which, A and N referred to the acetate and nitrate precursor, respectively.

2.2. Catalysts characterization

X-ray diffraction (XRD) patterns were recorded on a Philips X'pert Pro diffractometer using Ni-filtered Cu Kα radiation (0.15418 nm). The X-ray tube was operated at 40 kV and 40 mA.

Laser Raman spectra (LRS) were recorded by using Renishaw invia spectrometer. Raman excitation at 514.5 nm was provided by Ar^+ laser. A laser power of 20 mW at the sample was applied.

X-ray photoelectron spectroscopy (XPS) analysis was performed on a PHI 5000 VersaProbe system, using monochromatic Al Kα radiation (1486.6 eV) operating at an accelerating power of 15 kW. Before the measurement, the sample was outgassed at room temperature in a UHV chamber ($<5 \times 10^{-7}$ Pa). The sample charging effects were compensated by calibrating all binding energies (BE) with the adventitious C 1s peak at 284.6 eV. This reference gave BE values with accuracy at ±0.1 eV.

H_2-temperature programmed reduction (H_2-TPR) experiments were performed in a quartz U-type reactor connected to a thermal conductivity detector (TCD) with Ar-H_2 mixture (7.0% H_2 by volume) as a reductant. 50 mg sample was used for each measurement. Before switched to the Ar-H_2 stream, the sample was pretreated in a N_2 stream at 100 °C for 1 h. TPR started from 100 °C at a rate of 10 $°C \cdot min^{-1}$.

In situ Fourier transform infrared (FT-IR) spectra of CO or/and NO adsorbed on catalysts were recorded on a Nicolet 5700FT-IR spectrometer at a resolution of 4 cm^{-1} (number of scans, 32). In situ FT-IR spectra for NO or/and CO in IR cell (equipped with KBr windows) were recorded at various target temperature as background for each test. The catalysts (~10 mg) were mounted in a quarts IR cell and pretreated at 100 °C for 1 h, followed by flowing N_2 atmosphere. After cooled to room temperature, the sample wafers were exposed to a controlled stream of CO-He (10% of CO by volume) or/and NO-He (5% of NO by volume) at a rate of 5.0 $ml \cdot min^{-1}$ for 30 min. Desorption/reaction studies were performed by heating the adsorbed species at different temperatures. All of the presented spectra were obtained by subtraction of the corresponding background reference.

2.3. Catalytic performances measurement

The catalytic performances of these catalysts for NO reduction by CO model reaction were determined under steady state,