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Effect of cobalt precursors on the dispersion, reduction, and CO oxidation of $\text{CoO}_x/\gamma\text{-Al}_2\text{O}_3$ catalysts calcined in N_2

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ABSTRACT

The present work tentatively investigated the effect of cobalt precursors (cobalt acetate and cobalt nitrate) on the physicochemical properties of $\text{CoO}_x/\gamma\text{-Al}_2\text{O}_3$ catalysts calcined in N_2 . XRD, Raman, XPS, FTIR, and UV–vis DRS results suggested that $\text{CoO}/\gamma\text{-Al}_2\text{O}_3$ was obtained from cobalt acetate precursors and CoO was dispersed on $\gamma\text{-Al}_2\text{O}_3$ below its dispersion capacity of $1.50 \text{ mmol}/(100 \text{ m}^2 \gamma\text{-Al}_2\text{O}_3)$, whereas $\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ was obtained from cobalt nitrate precursors and Co_3O_4 preferred to agglomerate above the dispersion capacity of $0.15 \text{ mmol}/(100 \text{ m}^2 \gamma\text{-Al}_2\text{O}_3)$. Compared with $\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$, $\text{CoO}/\gamma\text{-Al}_2\text{O}_3$ catalysts were difficult to be reduced and easy to desorb oxygen species at low temperatures and presented high activities for CO oxidation as proved by $\text{H}_2\text{-TPR}$, $\text{O}_2\text{-TPD}$, and CO oxidation model reaction results. A surface incorporation model was proposed to explain the dispersion and reduction properties of $\text{CoO}/\gamma\text{-Al}_2\text{O}_3$ catalysts.

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1. Introduction

Cobalt oxide supported on $\gamma\text{-Al}_2\text{O}_3$ ($\text{CoO}_x/\gamma\text{-Al}_2\text{O}_3$) catalysts are of great importance for their extensive applications in Fischer–Tropsch (FT) synthesis [1–3], NO_x reduction [4–8], CO oxidation [9–12], VOC removal [13–15], etc. It is suggested that the catalytic performances of $\text{CoO}_x/\gamma\text{-Al}_2\text{O}_3$ catalysts in these reactions are mainly related to the dispersion, valence and interaction of surface cobalt species with $\gamma\text{-Al}_2\text{O}_3$, which are dependent on the preparation conditions including cobalt precursors, calcination temperature and atmosphere, etc. [16–21]. Among these factors, cobalt precursors could greatly influence the type and dispersion of cobalt species. As a result, some research groups have comparatively studied the influence of cobalt acetate and cobalt nitrate on the dispersion and interaction of cobalt oxide with the support [18,22,23]. As Okamoto et al. [18] concluded, $\text{CoO}_x/\gamma\text{-Al}_2\text{O}_3$ catalysts prepared from cobalt acetate showed the bigger $\text{Co}^{2+}/\text{Co}^{3+}$ proportion and higher cobalt dispersion than from cobalt nitrate. Chae et al. [22] pointed out that the size of alumina increased for $\text{CoO}_x/\text{Al}_2\text{O}_3$ prepared from cobalt nitrate, but was almost changeless from cobalt acetate. Girardon et al. [23] found that cobalt nitrate decomposed into Co_3O_4 crystallites, whereas cobalt acetate

decomposed into barely reducible cobalt silicate in Co/SiO_2 catalysts. However, these studies focused on the structure and properties of supported cobalt oxide catalysts calcined in air. Therefore, one question that should be answered is the dispersion capacity and surface state of cobalt species from different precursors on the surface of Al_2O_3 .

As reported elsewhere, calcination atmosphere also significantly influences the decomposition products of cobalt acetate [19,23,24]. In the absence of the support, the decomposition products of cobalt acetate are mainly CoO in N_2 and Co_3O_4 in air [24]. Although cobalt nitrate decomposes into Co_3O_4 both in air and in inert gas [23,25], Sietsma and co-workers [26] have shown that changing the calcination atmosphere could improve the dispersion of cobalt oxide from cobalt nitrate on SBA-15. However, to our knowledge, little attention has been paid to comparing the effect of cobalt precursors on the components, dispersion capacity, redox properties, and CO oxidation activities of $\text{CoO}_x/\gamma\text{-Al}_2\text{O}_3$ catalysts calcined in N_2 . Another aspect, the surface structure of $\text{CoO}_x/\gamma\text{-Al}_2\text{O}_3$ catalysts is still not very clear. We believe that more detailed experimental research will be helpful for further understanding the dispersion and surface structure of cobalt oxide on $\gamma\text{-Al}_2\text{O}_3$ and their related redox and catalytic properties.

In this work, a series of $\text{CoO}_x/\gamma\text{-Al}_2\text{O}_3$ catalysts were prepared by impregnating cobalt acetate or cobalt nitrate on $\gamma\text{-Al}_2\text{O}_3$ and calcining them in N_2 . They were characterized by XRD, LRS, XPS, FTIR, UV–vis DRS, $\text{H}_2\text{-TPR}$, $\text{O}_2\text{-TPD}$, and CO oxidation model

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reactions. The studies have mainly focused on (1) exploring the influence of precursors on the components, dispersion, redox properties, and CO oxidation activities of $\text{CoO}_x/\gamma\text{-Al}_2\text{O}_3$ catalysts calcined in N_2 ; (2) trying to understand the surface structures of $\text{CoO}_x/\gamma\text{-Al}_2\text{O}_3$ catalysts and establish the structure–property relationship. Based on our previous work [27], a surface incorporation model has been proposed to explain the dispersion and properties of $\text{CoO}_x/\gamma\text{-Al}_2\text{O}_3$ catalysts.

2. Materials and methods

2.1. Catalysts preparation

$\gamma\text{-Al}_2\text{O}_3$ was purchased from Fushun Petrochemical Institute in China and calcined at 750 °C for 5 h in air before being used for catalyst preparation. Its BET surface area is 158.2 m^2g^{-1} . $\text{CoO}_x/\gamma\text{-Al}_2\text{O}_3$ catalysts were prepared by wet impregnation of $\gamma\text{-Al}_2\text{O}_3$ with an aqueous solution containing required amounts of $\text{Co}(\text{Ac})_2$ (0.1 mol L^{-1}) or $\text{Co}(\text{NO}_3)_2$ (0.1 mol L^{-1}). The mixture was vigorously stirred for 1 h. After that, it was heated to 100 °C to vaporize the water in the oil bath. The resulting materials were dried at 110 °C overnight in the oven, and then calcined at 450 °C in N_2 for 5 h. The cobalt loading amounts were varied from 0.1 to 3.0 and 0.1 to 1.2 $\text{mmol}/(100\text{ m}^2\ \gamma\text{-Al}_2\text{O}_3)$ for $\text{Co}(\text{Ac})_2$ or $\text{Co}(\text{NO}_3)_2$, respectively. For simplicity, the resultant catalysts were denoted as $x\text{Co}(\text{A})/\text{Al}$ or $x\text{Co}(\text{N})/\text{Al}$, where x referred to the amount of $\text{Co}^{x+}/(100\text{ m}^2\ \gamma\text{-Al}_2\text{O}_3)$, and A or N referred to $\text{Co}(\text{Ac})_2$ or $\text{Co}(\text{NO}_3)_2$ precursor, respectively; e.g., 06Co(N)/Al corresponded to the catalyst prepared by impregnation of $\text{Co}(\text{NO}_3)_2$ with cobalt loading amount of 0.6 $\text{mmol}/(100\text{ m}^2\ \gamma\text{-Al}_2\text{O}_3)$.

2.2. Catalysts characterization

XRD patterns were recorded on a Philips X'pert Pro diffractometer using Ni-filtered $\text{Cu K}\alpha$ radiation (0.15418 nm). The X-ray tube was operated at 40 kV and 40 mA.

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

FTIR spectra were collected on a Nicolet 5700 FTIR spectrometer, working in the range of wavenumbers 400–4000 cm^{-1} at a resolution of 4 cm^{-1} (number of scans, 32). The samples were mixed with KBr and pressed into self-supporting disks for IR characterization at room temperature. The IR spectra were obtained by subtracting the KBr spectrum from each specific spectrum.

XPS measurements were performed on a Thermo ESCALAB 250 high performance electron spectrometer using monochromatized $\text{Al K}\alpha$ ($h\nu = 1486.6\text{ eV}$) as the excitation source. A binding energy (BE) of 284.6 eV for the $\text{C}1s$ level was used as an internal reference.

UV–vis diffuse reflectance spectra (UV–vis DRS) were recorded in the range of 200–800 nm by a Shimadzu UV-2401 spectrophotometer with BaSO_4 as reference.

H_2 -TPR was carried out in a quartz U-tube reactor connected to a thermal conduction detector (TCD) with $\text{H}_2\text{-Ar}$ mixture (7.3% H_2 by volume) as the reductant. A 50 mg sample was used for each measurement. Before switching to the $\text{H}_2\text{-Ar}$ stream, the sample was pretreated in a N_2 stream at 100 °C for 1 h and then cooled to room temperature. TPR started at 100 °C at a rate of 10 °C min^{-1} .

O_2 -TPD was performed in a conventional temperature programming system equipped with a TCD for analysis. The catalyst sample (50 mg) was pretreated in helium (99.995%) at 100 °C for 1 h. Then the oxygen adsorption proceeded with pure oxygen at 200 °C for 1 h. After cooling to room temperature, the system was purged in helium for 1 h. Then the O_2 -TPD measurement was performed using helium (30 mL min^{-1}) as carrier gas. The temperature was increased at a rate of 10 °C min^{-1} from room temperature to 600 °C.

2.3. Catalytic activity tests

The activities of the $\text{CoO}_x/\gamma\text{-Al}_2\text{O}_3$ catalysts in the $\text{CO} + \text{O}_2$ reaction were measured in a flow microreactor with a gas composition of 1.6% CO , 20.8% O_2 , and 77.6% N_2 by volume at a space velocity of 72,000 $\text{mL g}^{-1}\text{ h}^{-1}$ and 50 mg catalyst was used for each measurement. The catalysts were pretreated in a N_2 stream at 100 °C for 1 h before being switched to the reaction gas stream. Tail gas was analyzed using a gas chromatograph with a TCD. Two columns for gas separation were used: the one packed with 13X molecular sieve (30–60 M) for separating O_2 , N_2 , and CO and the other packed with Porapak Q for separating CO_2 .

3. Results and discussion

3.1. Structural characterization

3.1.1. XRD and LRS results

Fig. 1 shows XRD patterns of $\text{Co}(\text{A})/\text{Al}$ and $\text{Co}(\text{N})/\text{Al}$ samples with different cobalt loading amounts and the pattern of $\gamma\text{-Al}_2\text{O}_3$ support for comparison. As shown in Fig. 1A, no typical diffraction peak of crystalline cobalt oxide can be observed for $\text{Co}(\text{A})/\text{Al}$ samples when the cobalt loading amount is below 1.6 $\text{mmol}/(100\text{ m}^2\ \gamma\text{-Al}_2\text{O}_3)$. It suggests that the cobalt oxide species have been highly dispersed on $\gamma\text{-Al}_2\text{O}_3$. As the cobalt loading amounts increase from 1.6 to 3.0 $\text{mmol}/(100\text{ m}^2\ \gamma\text{-Al}_2\text{O}_3)$, the XRD peaks of crystalline CoO ($2\theta = 36.5^\circ$, 42.4° , and 61.5°) [JCPDS (Card No. 78-0431)] appear and their intensities increase with the cobalt loading amounts, implying the formation of crystalline CoO besides the dispersed one. In Fig. 1B, when the cobalt loading amount is below 0.2 $\text{mmol}/(100\text{ m}^2\ \gamma\text{-Al}_2\text{O}_3)$, only the diffraction peaks of $\gamma\text{-Al}_2\text{O}_3$ support can be observed for $\text{Co}(\text{N})/\text{Al}$ samples. As the cobalt loading amount reaches 0.4 $\text{mmol}/(100\text{ m}^2\ \gamma\text{-Al}_2\text{O}_3)$, the characteristic peaks of crystalline Co_3O_4 ($2\theta = 31.3^\circ$ and 36.8°) [JCPDS (Card No. 80-1541)] appear and their intensities increase with the cobalt loading amounts. Accordingly, XRD quantitative analysis is employed to determine their dispersion capacities [28,29]. The results indicate that the dispersion capacities of cobalt oxide from cobalt acetate and cobalt nitrate are 1.50 and 0.15 $\text{mmol}/(100\text{ m}^2\ \gamma\text{-Al}_2\text{O}_3)$, respectively, as recorded in Figs. 2A and B. As similar systems, they are found to be comparable to the dispersion capacities of MO (NiO , MgO , ZnO) and MO_2 (ThO_2 , CeO_2) supported on $\gamma\text{-Al}_2\text{O}_3$, respectively [27,30–32].

LRS characterization has been used to further confirm the dispersion performance of cobalt oxides supported on $\gamma\text{-Al}_2\text{O}_3$. As shown in Fig. 3A, no apparent Raman band of cobalt oxide can be observed for 01 and 02Co(A)/Al samples, indicating that the cobalt oxide species are highly dispersed on $\gamma\text{-Al}_2\text{O}_3$. The spectra of 06 and 12Co(A)/Al samples are predominated by three broad bands at 469, 600, and 674 cm^{-1} , respectively. These bands are assigned to characteristic vibrations of dispersed surface cobalt oxide species [33,34]. But in the case of 16 and 20Co(A)/Al samples, several new bands appear at 188, 469, 507, 600, and 674 cm^{-1} , respectively. Combined with the above XRD results, they should be assigned to the crystalline CoO , which are supported by previous reports [34,35]. In Fig. 3B, no apparent Raman band appears for 01Co(N)/Al sample, indicating that the cobalt oxide species are highly dispersed on $\gamma\text{-Al}_2\text{O}_3$. When the cobalt loading amount increases to 0.2 $\text{mmol}/(100\text{ m}^2\ \gamma\text{-Al}_2\text{O}_3)$, several strong Raman bands are observed at about 186, 464, 512, 600, and 663 cm^{-1} for 02, 06, and 12Co(N)/Al samples, which should be attributed to crystalline Co_3O_4 [34,36].

3.1.2. XPS results

To further reveal the chemical states and dispersion properties of cobalt oxide on $\gamma\text{-Al}_2\text{O}_3$, XPS measurements are carried out.

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