

Aerobic oxidation of alcohols over Ru-Mn-Ce and Ru-Co-Ce catalysts: The effect of calcination temperature



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ABSTRACT

Two ternary mixed oxides, Ru-Mn-Ce and Ru-Co-Ce, were prepared by a co-precipitation method and used in the aerobic oxidation of alcohols to corresponding aldehydes (ketones). Interestingly, different catalytic results were obtained when these compounds were calcined. The calcination temperature had an adverse effect on the catalytic performance of Ru-Mn-Ce catalysts, while being beneficial to the Ru-Co-Ce catalysts. To illustrate these effects, these materials were characterized using X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), Temperature-programmed reduction (TPR), Electron paramagnetic resonance (EPR) and other techniques. The data showed that ruthenium oxides were uniformly dispersed in the mixed oxides, and phase transformations occur after calcination. Mn_3O_4 was transformed to MnO_2 for the Ru-Mn-Ce catalyst, while $CoO(OH)$ was transformed to Co_3O_4 in the Ru-Co-Ce catalyst. The interactions between ruthenium oxides and Co (Mn)-Ce mixed oxides of the former strengthened while the latter weakened. Calcination decreased the content of adsorbed oxygen and restricted oxygen transfer mechanism in the manganese system, while the opposite effect was observed with the cobalt-containing catalyst. Under optimal reaction conditions, various kinds of alcohols were transformed to corresponding aldehydes (ketones) in high yields over the Ru-Mn-Ce catalyst suggesting these ternary oxides are environmental friendly and economical catalytic systems.

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1. Introduction

Selective oxidation of alcohols to aldehydes (ketones) has been considered as one of the most fundamental organic reactions, with the products widely used in the manufacture of perfumes, agricultural chemicals, and other fine chemicals [1–3]. Environmental and economic concerns lead researchers to require clean oxidation procedures that minimize byproducts and wastes, affected by replacing the conventional stoichiometric methods with atom-efficient catalytic protocols using molecular oxygen as the sole oxidant. Recently many outstanding results have been reported using noble metals (Ru, Pd, Au, etc.) as heterogeneous catalysts

[3–6]. However, these supported catalysts always face the loss of the noble metals, which is a critical issue for the reusability of catalysts.

Much attention has been given to mixed metal oxides (MMOs), usually prepared by a one-pot synthesis method, e.g. the metal doped vanadium phosphorus mixed oxides (M-VPOs) [7,8] and metal doped molecular sieves [9,10]. In these systems, noble metals are doped into the catalysts directly, forming a uniform compound which minimizes synthesis and loss of the metals. Additionally, noble metals also can be put into catalysts by a co-precipitation method, generally uniform mixed oxide (hydroxide) catalysts. These materials containing noble metals are formed when metal precursor solutions are carefully mixed under vigorous stirring, yielding solid precipitates [11,12]. For aerobic oxidative catalysts, most researchers believe that excellent catalytic performance originates from highly dispersed metal components and rich oxygen storage capacity, surface oxygen vacancies and defects, and some

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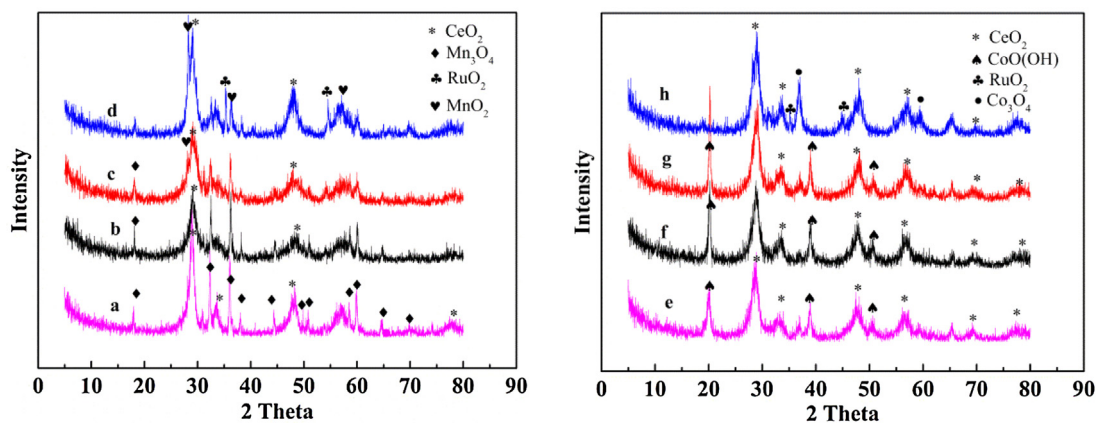


Fig. 1. XRD patterns of catalysts (a) Mn-Ce, (b) Ru-Mn-Ce, (c) Ru-Mn-Ce (300), (d) Ru-Mn-Ce (500) and (e) Co-Ce, (f) Ru-Co-Ce, (g) Ru-Co-Ce (300), (h) Ru-Co-Ce (500).

mixed oxides consisting of cerium oxide, zirconium oxide and iron oxide, have been used for oxidative reactions [13,14].

For MMOs, more active oxygen species can be produced due to the synergistic interaction of different oxides, and they show more excellent catalytic performance than unmixed ones [14,15]. To date, ternary mixed oxides containing noble metals are rarely reported. In this article, Ru-Mn-Ce and Ru-Co-Ce ternary-mixed-oxides were prepared by a co-precipitation method and were investigated as catalysts for aerobic oxidation of alcohols. Interestingly, the calcination temperature has an adverse effect on oxidation of benzyl alcohol over Ru-Mn-Ce catalysts, while being beneficial over the Ru-Co-Ce catalysts.

2. Experimental

2.1. Catalyst preparation

A certain amount of Na_2CO_3 (0.5 M) and NaOH (1.5 M) was slowly dissolved in 30 mL distilled water to produce solution A. Solution B was composed by dissolving 2.2140 g of $\text{Ce}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2.5000 g of $\text{Mn}(\text{CH}_3\text{COO})_2$ ($n_{\text{Ce}}/n_{\text{Mn}} = 0.5$) and 0.317 g of RuCl_3 in 20 mL distilled water. Solution A was then slowly dripped into solution B under vigorous stirring. The resulting solid product was aged in the mother liquor at room temperature for 24 h, and then the dark brown product was filtered, washed with distilled water, and dried at 110°C for 10 h to obtain a black powder. The catalysts were calcined at 300°C and 500°C , yielding materials referred to hereafter as Ru-Mn-Ce, Ru-Mn-Ce (300) and Ru-Mn-Ce (500), respectively. Ru-Co-Ce catalysts were prepared by a similar procedure with $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, the black powders obtained were calcined at 300°C and 500°C , which are signed as Ru-Co-Ce, Ru-Co-Ce (300) and Ru-Co-Ce (500), respectively.

2.2. Catalyst characterization

The morphologies of obtained catalysts were examined by transmission electron microscopy (TEM) (FEI Talos F200X) and scanning electron microscopy (SEM) (JSM-7600F). The crystals of the catalysts were studied by X-ray diffraction (XRD) (X'Pert PRO PANalytical). Specific surface area was measured by N_2 adsorption-desorption experiments at 77 K in an ASAP 2010 instrument. The surface composition was determined by X-ray photoelectron spectroscopy (XPS) (VG ESCALAB210) using a K-Alpha-surface analysis system with monochromatized X-Rays. FT-Infrared spectroscopy was performed on a Bruker Tensor 27 spectrometer. Raman spectra were recorded in a dispersive Horiba Jobin Yvon LabRam HR800 Confocal Raman Microscope with a

20 mW green laser (532.14 nm) without a filter and using a 600 grooves/mm grating. Temperature-programmed reduction (TPR) of catalysts was carried out on a Micromeritics 2920 apparatus. Catalyst samples (60 mg) were heated to 800°C at a rate of $10^\circ\text{C}/\text{min}$ in a H_2 -Ar (5:95) gas flow ($50\text{ cm}^3/\text{min}$). The electron paramagnetic resonance (EPR) spectra were recorded on a Bruker (EMXNano) spectrometer, all spectra were recorded at a power of 0.3 mW, a modulation amplitude of 4 G, and a modulation frequency of 100 KHz. Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis was carried out using a Varian 720ES spectrometer.

2.3. Catalytic studies

A typical example for the oxidation of benzyl alcohol by the Ru-Mn-Ce catalyst is as follows: A mixture of catalyst (0.05 g, Ru 0.03 mmol), benzyl alcohol (4 mmol) and benzotrifluoride (5 mL) was stirred in a 100 mL round-bottom flask equipped with a condenser. All reactions were performed under an oxygen atmosphere using an oxygen balloon. The reaction was initiated by immersing the flask in the oil bath kept at the reaction temperature, and then carried out with vigorous stirring for a certain time. Products were analyzed by a standardized gas chromatograph (GC 9560) with a SE-54 capillary column. For recyclability studies, the used catalyst was washed with water, followed by drying at 110°C , and then subjected to the alcohol oxidation under the same conditions.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 shows the XRD patterns of Mn-Ce, Co-Ce mixed oxides and corresponding Ru-Mn-Ce and Ru-Co-Ce catalysts calcined at different temperatures. As shown in Fig. 1(a–d), the diffraction peaks at $2\theta = 28.6, 33.1, 47.5$ and 56.3° could be assigned to CeO_2 (JCPDS: 43-1002), the intensive and sharp diffractions at $2\theta = 18.0, 28.9, 31.0, 32.3, 36.1, 36.4, 38.0, 44.4, 50.7, 58.5, 59.8$ and 64.7° can be primarily attributed to Mn_3O_4 (JCPDS: 24-0734), the peaks ascribed to the phases of Mn_3O_4 and CeO_2 are obvious and the peaks corresponding to the RuO_2 almost are invisible before the catalysts are calcined. With calcination the peaks corresponding to the Mn_3O_4 are weaker and new peaks assigned to MnO_2 (JCPDS: 50-0866) appear, which indicates that most of the Mn_3O_4 has transformed to MnO_2 after calcination. Meanwhile, the peaks corresponding to RuO_2 (JCPDS: 40-1290) and CeO_2 phases increased with the higher calcined temperature (especially at 500°C), suggesting the RuO_2 and CeO_2 phases segregate and are isolated with the heat

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