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NO SCR with propane and propene on Co-based alumina catalysts prepared by co-precipitation

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Abstract

Homogeneous dispersions and small size of deposited high-content cobalt on alumina were achieved by the co-precipitation method and were well maintained on the cobalt-based binary alumina catalysts with Zn, Ag, Fe, Cu or Ni as modifiers. The component and concentration of deposited cobalt species were characterized by UV–vis, EDX and XPS spectra and found to be greatly related to the Co loading, calcination temperatures and the type of additive metals. The optimal Co loading of 8 wt% and calcination temperatures of 800 °C were demonstrated. With respect to the single cobalt-based alumina catalyst, the surface concentration of Co^{2+} on the binary catalysts with addition of Fe, Cu, Ag or Ni was all reduced and accompanying with part conversion of Co^{2+} to Co_3O_4 on the Fe and Ni-modified catalysts. A slight enhanced surface Co^{2+} concentration was only achieved on the Zn-promoted catalyst. It was also demonstrated that for the case of Cu and Fe the additive metals themselves participated in the activation of propene. The octahedral and tetrahedral Co^{2+} ions were suggested as the common active sites. A maximum deNOx activity of 96% was observed on the 8Co4ZnA800 catalyst at the reaction temperatures of 450 °C, and the catalytic performance on the cobalt-based binary alumina catalysts can be described as fellows: CoZn > CoAg, CoNi > Co Cu > CoFe. Based on the *in situ* DRIFT spectra, different reaction intermediates R–ONO and –NCO besides $–NO_2$ were formed on the 8Co4ZnA800 and 8Co4FeA800 samples, respectively, demonstrating their dissimilar reaction mechanisms.

Keywords: Co-precipitation method; High cobalt content; Homogeneous dispersion; NO SCR

1. Introduction

NOx removal from diesel exhaust and oxygen rich fuel gases still remains as one of major challenges in the area of environmental catalysis [1–3]. Various catalysts containing noble metals [4–6], ion-exchanged zeolites [7–9], and metal oxides [10–16] have been extensively reported. Among them, the metal-supported alumina catalysts have received one of the most attentions due to its high activity and stability. It was demonstrated that alumina was a good candidate due to its additional ability for dispersion of transition metal cations [10,14,17].

Among the alumina-based catalysts, Ag/Al_2O_3 [13,24–28], Cu/Al_2O_3 [3,29–32], Au/Al_2O_3 [33,34], Co/Al_2O_3 [10,17,18,35], Pt/Al_2O_3 [36], Sn/Al_2O_3 [38], Fe/Al_2O_3 [39] and Ni/Al_2O_3 [40] have been testified efficient for NO reduction with C_3H_6 as reductant in excess oxygen, and Co/Al_2O_3 has attracted much recent attention due to its good activity and selectivity to nitrogen [10]. It is well known that the deNOx activity is greatly related to the dispersion of cobalt species that are usually influenced by the preparation method, the Co concentration, alumina source, and calcination temperatures [10,17–19,35,41–43]. Octahedrally and tetrahedrally coordinated Co^{2+} ions were considered as main active sites for the SCR activity of NO, while Co_3O_4 was only active for the combustion of hydrocarbon but not for the SCR reaction [43]. High dispersion of Co^{2+} ions with small particle size was thought to be more effective, since more active sites could probably be provided.

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Some ways have been suggested to improve the dispersion of Co^{2+} ions and to prevent the aggregation of cobalt particles [10,43,60]. One was to avoid the utilization of a nitrate precursor that tends to facilitate the agglomeration of cobalt species and leads to the formation of unselective Co_3O_4-like particles [10,60]. The other way was to decrease the content of cobalt loading (typically <2–5 wt%) reducing the formation possibility of large particles [10,43]. In addition, high calcination temperatures may be an alternative method, because re-dispersion of large cobalt particles can happen with cobalt aluminate $CoAl_2O_4$ formed at high temperatures [43].

Among all the factors influencing the dispersion and size of deposited cobalt species, the catalyst preparation method was known to be one of the most important. Highly dispersed cobalt species have been prepared by the ion-exchange method [61] and wet-impregnation with acetate complexes [60]. In most of cases, the Co/Al_2O_3 catalysts prepared by a sol–gel method were observed to show much better Co dispersion and relatively better NOx SCR activity than those prepared by impregnation, precipitation and co-impregnation [10,11,19]. However, the cobalt content on these catalysts was usually lower than 2 wt%. To provide much more active sites, the cobalt content of catalyst should be further optimized. For the case of Cu/Al_2O_3, it has been demonstrated [29] that the co-precipitation method can ensure homogeneous dispersion of copper ions and a small size of deposited copper species even when the copper content reached as high as 16 wt%. The high concentrated copper has provided more active sites and caused remarkably enhanced deNOx activity. Accordingly, it is also anticipant to extend the co-precipitation method into the dispersion of cobalt species at high content.

In addition, although high activities and stabilities have been achieved in some cases for Co/Al_2O_3 catalysts [20,21], further improvements are necessary to meet the practical demand of NOx removal. The combination of two catalytic species was testified as an efficient method to further improve the catalytic performance utilizing possible synergistic effects of two metals [19,21–23,37,43]. Unfortunately, the exact effect of additive metal on the cobalt component and dispersion is yet not clear and should be studied more systematically.

In this study, high-loading Zn- (Fe-, Ni-, Cu- or Ag-) promoted Co/Al_2O_3 were prepared via co-precipitation and the effect of additive metals on the selective catalytic reduction (SCR) of NO was systematically examined, where propane and propene were selected as reducing agents. Transmission electron microscopy (TEM), energy-dispersive X-ray analysis (EDX), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and UV–vis spectroscopy were employed to characterize the catalysts, and *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was collected for revealing the mechanism.

2. Experimental

2.1. Catalyst preparation

The cobalt-based alumina binary catalysts were prepared by the co-precipitation method. Fe, Ni, Cu, Zn and Ag were selected as potential promoters. Typically, an aqueous solution containing cobalt nitrate, nickel (or iron, copper, zinc, silver) nitrate and aluminum nitrate was first prepared, and then together with aqueous ammonia (10%) was slowly added into 0.05 mol/L NH_4HCO_3 at room temperature while stirring until the pH of the mother liquor reached about 8. The as-formed co-precipitated hydroxides were filtered and washed with distilled water, dried at 110 °C overnight, and finally calcined at 800 °C for 4 h in static air. According to the content of feed metals and calcination temperatures, the as-prepared particles are denoted as *x*Co*y*MeA*T* (*x* and *y* are the feed content of cobalt and the additive metal separately, "A" means alumina support and *T* stands for the calcination temperatures).

The preparation of Co/Al_2O_3 catalysts was similar, and all of which were denoted as *x*CoA*T*.

2.2. Catalytic tests

The activity measurements were carried out in a fixed-bed stainless steel reactor with an inner diameter of 6 mm. The catalyst powder was compacted to pellets and subsequently crushed yielding samples with mesh sizes of 0.350–0.710 mm. Prior to the reaction, the catalyst was pretreated in the reaction feed gas at 550 °C for 1 h. The feed gas mixture contained 1000 ppm NO, 1000 ppm C_3H_8 or C_3H_6, 5% O_2, and helium as the balance gas. The total gas flow rate was 165 $cm^3\ min^{-1}$ and the catalyst mass was about 0.5 g, resulting in a GHSV of about 10 000 h^{-1}. The reaction temperature has been varied from 350 to 550 °C in steps of 50 K. The composition of the product gas was analyzed by using a gas chromatograph (HP 6890 equipped with Porapak Q and Molecular sieve 5 A columns). A Molecular sieve 5 A column was used for the analysis of N_2, O_2 and CO and a Porapak Q column for analysis of N_2O, CO_2 and C_3H_6. The activity data were collected when the catalytic reaction practically reached steady-state conditions at each temperature chosen. The formation of N_2O was found negligible (<10 ppm) and for this reason this product will not be further discussed in the present study.

2.3. Catalyst characterizations

XRD patterns were collected on a Rigaku D/max 2500 powder diffractometer with Cu Kα radiation equipped with a graphite monochromator. The UV–vis spectrum was recorded on a JASCO V-570 UV–vis spectrophotometer in the range of 220–800 nm. TEM images were acquired on a Tecnai G^2 20 S-TWIN transmission electron microscopy with an accelerate voltage of 200 kV. The as-prepared particles were dispersed in water and dropped onto the surface of a carbon membrane and dried at ambient conditions.

In situ DRIFTS measurements were performed on the spectrometer FTS-60 A (BIO-RAD) by using a diffuse reflectance attachment (HARRICK) equipped with reaction chamber that allows heating under gas flow from room temperature to 500 °C. Two hundred and fifty-six single beam spectra have been co-added at a resolution of 2 cm^{-1}. The spectra are presented as Kubelka–Munk function referred to