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Short Communication

# Modification of $Co/Al_2O_3$ with Pd and Ce and their effects on benzene oxidation

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ABSTRACT

Palladium and cerium oxide promoted $Co/Al_2O_3$ catalysts were prepared and used for oxidation of benzene. Influence of Pd, Ce and Co/Ce molar ratios on the properties and catalytic performance was investigated. The results indicated that addition of palladium and cerium oxide could provide active oxygen species to cobalt oxide and make $Co_3O_4$ particles better dispersed on $Al_2O_3$, thus enhancing oxidation ability of the catalyst. High catalyst activity is mainly attributed to better dispersed $Co_3O_4$ on $Al_2O_3$, smaller $Co_3O_4$ crystallites and larger $CeO_2$ crystallites which can strengthen the interaction among PdO, $CeO_2$ and $Co_3O_4$.

## 1. Introduction

Volatile organic compounds (VOCs) are considered as a major pollutant in indoor and outdoor air. One of the techniques available for destructive removal of VOCs is catalytic oxidation [1–3]. Base metal oxides, noble metals and their combinations deposited on conventional supports such as $Al_2O_3$, $SiO_2$, etc., have shown to be efficient for this reaction [4]. Cerium oxide, as oxygen storage material, not only possesses high oxygen storage capacity (OSC), but also improves the dispersion of the metal. Consequently, it is feasible to develop oxidation catalysts mainly consisting of cobalt and cerium oxides [5,6]. As catalysts, Co–Ce mixed oxides have been applied in many reactions, such as methanol oxidation [7], $CH_4$ combustion [8], diesel soot oxidation [9] and VOC combustion [10]. During these reactions, a catalytic synergistic effect between cobalt and cerium oxides is observed. Moreover, it is believed that oxidation activity of base metal oxide catalysts can be prominently enhanced by addition of a small amount of Pd, which is called active-phase enhancement. Nowadays, more and more studies are focusing on the catalysts with combination of noble metal and base metal oxides for oxidation applications [11–14].

The object of our research is to study the influence, activity of Co catalysts with addition of Pd and Ce. This paper extended the development of cobalt oxide catalysts by the addition of Pd and Ce that have an excellent activity in benzene oxidation, higher than that of Co–Ce or Pd–Ce catalysts. The catalysts were characterized by XRD, BET surface area and TPR techniques.

## 2. Experimental

### 2.1. Catalyst preparation

A series of $Co/Al_2O_3$, $Co–Ce/Al_2O_3$ catalysts was prepared with an aqueous solution containing appropriate amount of $Co(NO_3)_2 \cdot 6H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ respectively via wet co-impregnation technique. $Pd/Co–Ce/Al_2O_3$ catalysts were prepared by wet impregnation with an aqueous of $H_2PdCl_4$ as metal precursors. The impregnated samples were reduced by hydrazine hydrate, filtered and washed with a large amount of deionized water until free of chlorides. Then the samples were dried at 110 °C for 3 h and calcined at 400 °C for 2 h. The content of Pd and Co for all catalysts is 0.2 and 10 wt.% respectively.

### 2.2. Catalyst activity determination

Benzene oxidation was carried out in a microreactor at a space velocity of 20,000 $h^{-1}$. Reactive flow (125 ml/min) was composed of air and gaseous benzene (1000 ppm). Catalyst (40–60 mesh) was loaded in quartz reactor and bed volume was about 0.375 ml. Benzene conversion was analyzed by on-line gas chromatography (Shimadzu, GC-14C) with a SE-30 capillary column.

### 2.3. Catalyst characterization

X-ray diffraction (XRD) was performed on a Rigaku D/max2550 PC. Diffraction patterns were recorded with Cu Kα radiation (300 mA, 40 kV). The average crystallite size of $Co_3O_4$ and $CeO_2$ was calculated by Scherrer equation from width at half height of line profiles corresponding to crystal plane (3 1 1) and (1 1 1) respectively.

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BET surface area of the samples was obtained from $N_2$ adsorption isotherms at −195.8 °C using a Tristar II 3020 apparatus of Micromeritics Company. Prior to adsorption measurements, the samples were outgassed at 250 °C under vacuum for 4 h.

Temperature programmed reduction (TPR) was performed on CHEMBET-3000. Prior to $H_2$-TPR measurement, 50 mg catalyst was pretreated at 300 °C in air for 0.5 h, and then temperature was decreased to −30 °C. The reductive gas was a mixture of 5 vol.% $H_2$ in Ar (40 ml/min), which was purified using deoxidizer and silica gel. Amount of hydrogen uptakes during reduction was measured by a thermal conductivity detector, and effluent $H_2O$ formed during $H_2$-TPR was absorbed with a 5 A molecular sieve.

## 3. Results and discussion

### 3.1. Catalytic activity

The conversion results of benzene in catalysts with and without Pd and Ce are reported in Fig. 1. In case of $Co/Al_2O_3$, the conversion is negligibly low and it was less than 90% even at 440 °C. And for Co–Ce (12:1)/$Al_2O_3$, the conversion are more than 98% at 420 °C, so adding Ce obviously improves activity of $Co/Al_2O_3$. For $Pd/Co/Al_2O_3$, temperature of complete benzene oxidation is 310 °C. As can be observed, with addition of Pd, benzene oxidation activity of $Co/Al_2O_3$ is enhanced to a great extent. Pd/Co–Ce (12:1)/$Al_2O_3$ is the most active one among them, and a complete conversion of benzene can be achieved at about 250 °C.

Effect of Co/Ce molar ratios on benzene oxidation over $Pd/Al_2O_3$ is shown in Fig. 2. From the results it can be deduced that Co/Ce molar ratios have impact on catalytic activity of $Pd/Al_2O_3$. Incorporation of Co within ceria lattice may bring a lot of lattice defects and enhance mobility of lattice oxygen to the surface to be activated, thus enhancing activity of the catalysts [15]. The catalyst shows a relatively low activity when Co/Ce ratio is 3, which is caused by the fact that Co is active species while Ce acts as a promoting component. The catalyst activity is decreased when Co/Ce molar is 12, because decrease of $CeO_2$ amount results in lack of oxygen vacancies. Therefore, catalyst with proper Ce content exhibits high activity. Pd/Co–Ce (6:1)/$Al_2O_3$ exhibits the highest activity, and temperature for complete benzene conversion using this catalyst is about 210 °C. It is important to stress that Pd/Co–Ce/$Al_2O_3$ was active between 140 and 250 °C. In this temperature range, the conversion was higher than some reported Co or Pd–Ce catalysts for benzene oxidation [16–18].

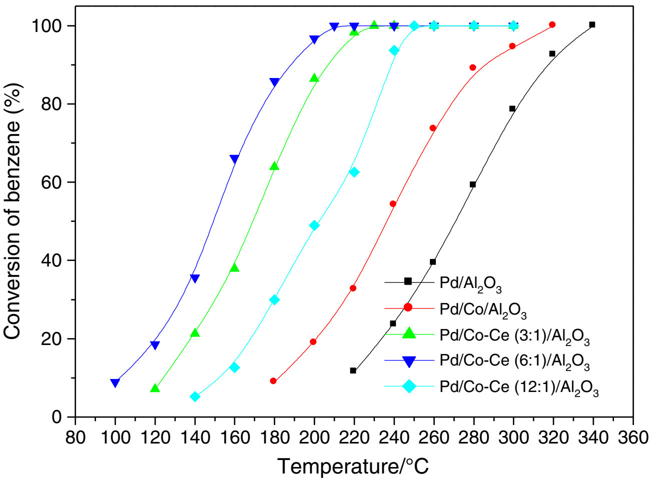

**Fig. 2.** Effect of Co/Ce molar ratios on benzene oxidation over the catalysts.

### 3.2. XRD

Fig. 3 shows XRD patterns between 20 and 80° of the samples. The peaks characterizing $Co_3O_4$ crystal can be seen in the pattern of $Co/Al_2O_3$, but become weaker in patterns of Co–Ce (6:1)/$Al_2O_3$ and Pd/Co–Ce (6:1)/$Al_2O_3$. According to Scherrer equation [19], crystallite size of pure $Co_3O_4$ is calculated as 26.5 nm, while for $Co/Al_2O_3$, Co–Ce (6:1)/$Al_2O_3$ and Pd/Co–Ce (6:1)/$Al_2O_3$ they are 18.5, 14.7 and 14.6 nm, respectively. The results indicate that addition of Ce and Pd promotes dispersion of $Co_3O_4$ particles and make crystal size of $Co_3O_4$ smaller. The peaks characterizing PdO crystals cannot be seen in XRD pattern of Pd/Co–Ce (6:1)/$Al_2O_3$, which is probably due to the fact that content of Pd doped in catalyst is too low, highly dispersed on surface of $Al_2O_3$ support. What's more, the average crystallite sizes of $CeO_2$ for Co–Ce (6:1)/$Al_2O_3$ and Pd/Co–Ce (6:1)/$Al_2O_3$ are 15.8 and 27.6 nm respectively. From Fig. 3 it can be seen that after impregnation of Pd, diffraction peaks of $CeO_2$ in Pd/Co–Ce (6:1)/$Al_2O_3$ is obviously increased and larger $CeO_2$ crystallites are formed. From catalyst activity and XRD results, we suggest that better dispersed $Co_3O_4$ on $Al_2O_3$, smaller $Co_3O_4$ crystallites and larger $CeO_2$ crystallites are the key factors to enhance the catalytic activity of the catalysts.

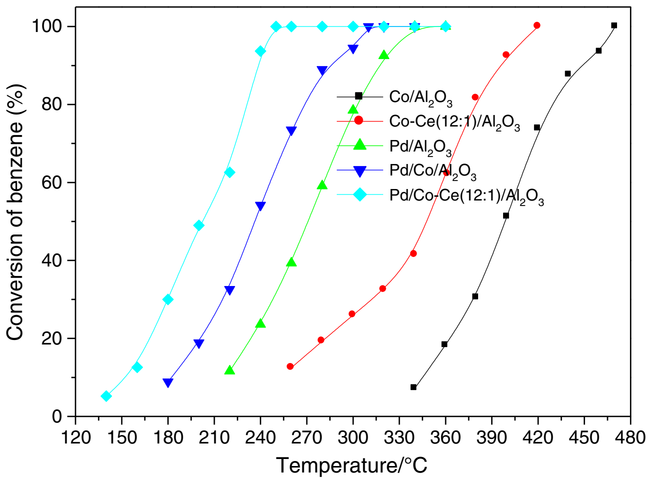

**Fig. 1.** Temperature dependence of benzene conversion over the catalysts: effect of adding Pd and Ce on $Co/Al_2O_3$.

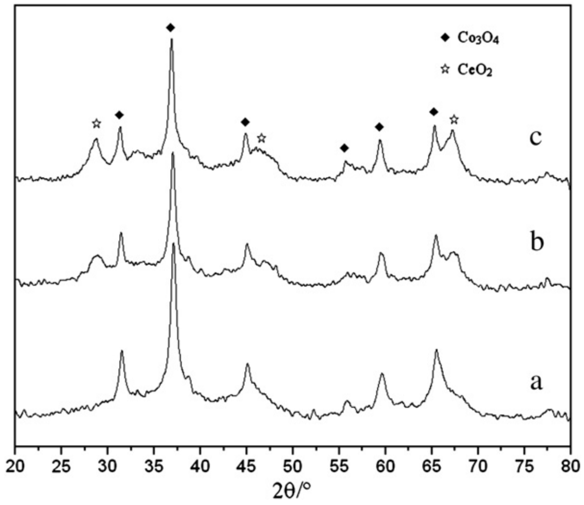

**Fig. 3.** XRD patterns of the catalysts between 20 and 80°: (a) $Co/Al_2O_3$; (b) Co–Ce (6:1)/$Al_2O_3$; (c) Pd/Co–Ce (6:1)/$Al_2O_3$.