



# Catalytic activity and crystal structure modification of Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> catalysts with different Al<sub>2</sub>O<sub>3</sub> contents<sup>☆</sup>

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## ABSTRACT

Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> catalysts containing various compositions of titania and alumina were prepared by sol-gel and wet-impregnation methods in attempt to study the particle size, nature of phases, morphology and structure of the composite samples. The ethanol oxidation experiments, N<sub>2</sub> adsorption-desorption, FTIR, XRD and XPS were conducted, and the effects of Al<sub>2</sub>O<sub>3</sub> content on the surface area, phase transformation and structural properties of TiO<sub>2</sub> were investigated. The optimal value of ethanol conversion appeared on Pd/Al(0.05)-Ti and Pd/Al(0.90)-Ti catalysts irrespective of the ethanol oxidation temperature, and we call this as a double peaks phenomenon of catalytic activity. The XRD results reveal that the phase composition and crystallite size of the mixed oxides depend on Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> ratio and calcination temperature. Al<sub>2</sub>O<sub>3</sub> can effectively prevent the agglomeration of TiO<sub>2</sub> and this can be ascribed to the formation of Al-O-Ti chemical bonds in Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> crystals. Binding energy and Pd surface concentration of the catalysts were modified apparently, which may also lead to catalyst activity changes.

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## 1. Introduction

Titanium dioxide and aluminum oxide have been widely used in various catalysis fields and nanotechnology researches. TiO<sub>2</sub> is a suitable material in heterogeneous catalysis, environmental catalysis, photocatalyst, and solar cells for the production of hydrogen and electric energy [1–4] because of its exceptional optical and electronic properties, strong oxidizing power, nontoxicity, chemical stability, and low cost [5,6]. Nanocrystalline Al<sub>2</sub>O<sub>3</sub>, a widely used ceramic material with many different polymorphs like  $\delta$ ,  $\eta$ ,  $\gamma$  and  $\alpha$  phases, has been synthesized by many new methods [7–9]. Alumina also shows numerous applications in catalysis, optics, biomedicine, etc.

TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> have been used for a wide application independently while each has its individual deficiencies and limitations. Al<sub>2</sub>O<sub>3</sub> suffers a decrease in the activity for many applications and TiO<sub>2</sub> tends to confront lower surface area and reduced thermal stability [10,11]. TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> nano-composites can combine the advantages of individual oxide supports, giving better

high-temperature stability, a stronger surface acid, and better textural properties. TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> mixed oxides have been found applications in petroleum hydrotreatment [12], selective oxidation [13], and catalytic reduction of NO<sub>x</sub> [14].

Moreover, TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> structures attracted numerous interests and were used in various applications including catalysis, solar cells, photocatalysis, self-cleaning, etc. [15–17]. Furthermore, a suitable composition of titania-alumina system is necessary to improve the characteristic features of the mixed oxide materials. The influence of the crystal structure of TiO<sub>2</sub> or TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support material on dispersion of Pd nanoparticles and the amount of surface active sites of catalysts was investigated [18,19], and then catalysts activity was modified distinctly.

In previous work, it has been proved that the addition of Al<sub>2</sub>O<sub>3</sub> in Pd/TiO<sub>2</sub> catalysts improved the total oxidation of ethanol [20]. In the present work, a series of TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> nanocomposites with different Al<sub>2</sub>O<sub>3</sub> ratios were synthesized and characterized. The effect of different Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> ratios on the catalytic performance for ethanol oxidation and crystal structural, particle size and morphology of Pd/Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> catalysts has been investigated in details. Furthermore, the structure and properties relationship and calcination temperatures on physical and electrical characteristics of the prepared catalysts were also discussed. As far as we know, this work systematically reports the double peaks phenomenon of the catalytic activity of Pd/Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> catalysts for the first time.

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## 2. Experimental

### 2.1. Carrier and catalyst preparation

The  $\text{Al}_2\text{O}_3$ - $\text{TiO}_2$  composite supports were prepared by a sol-gel method. Titania and alumina sols were prepared separately, and then mixed together to obtain  $\text{Al}_2\text{O}_3$ - $\text{TiO}_2$  [21]. The mixed sol was dried at 50 °C and 110 °C for 12 h, respectively, and then calcined at 500 °C or 700 °C in air for 5 h. Pure  $\text{TiO}_2$  and pure  $\text{Al}_2\text{O}_3$  supports were prepared in a similar method.  $\text{Pd}/\text{Al}_2\text{O}_3$ - $\text{TiO}_2$  catalysts were prepared by a wet-impregnation method, and all the samples contained 1 wt% Pd. The  $\text{Al}_2\text{O}_3(x)$ - $\text{TiO}_2$  (where  $x = 0, 0.05, 0.50, 0.90,$  and 1 of mass ratio) composite is denoted as  $\text{Al}(x)$ - $\text{Ti}-T$ , in which  $T$  corresponds to the calcination temperature in Celsius scale ( $T = 5, 7$  means 500 °C and 700 °C, respectively). In the following text, the  $T$  refers to 500 °C without particular illustration.

### 2.2. Catalytic evaluation

The catalytic properties of the catalysts were evaluated using a fixed-bed reactor connected with an online gas chromatograph. The compositions of ethanol and products were analyzed using a GC-950 apparatus with two FID detectors, one of which incorporated a methanator. Approximately 0.30 g of catalyst was used (40–60 mesh), and the feed gas consisted of 0.5 vol%  $\text{C}_2\text{H}_5\text{OH}$ , 5 vol%  $\text{O}_2$ , and a balance of  $\text{N}_2$ . The flow rate was 100 mL/min of total gas and the gas hourly space velocity (GHSV) was 24,000  $\text{h}^{-1}$ . Ethanol conversion ( $X_i$ ) and the yields ( $Y_j$ ) of by-products and carbon dioxide from ethanol combustion were calculated according to the formulas:  $X_i = [(C_{i,\text{in}} - C_{i,\text{out}})/C_{i,\text{in}}] \times 100\%$ ,  $Y_j = (C_{j,\text{out}}/C_{i,\text{in}}) \times 1/n \times 100\%$ . Where  $C_i$  and  $C_j$  are the concentrations of ethanol and products from ethanol combustion, respectively, and  $n$  is the products and reactants carbon atom ratios. And  $C_i = A_i \times f_i$ ,  $C_j = A_j \times f_j$ , where  $A$  and  $f$  are the peak areas and the relative correction factors of reactants ( $i$ ) or products ( $j$ ), respectively.

### 2.3. Characterization

$\text{N}_2$  adsorption-desorption isotherms for pure  $\text{TiO}_2$  and the modified  $\text{TiO}_2$  composites were measured. The specific surface area was calculated from the adsorption curve using the BET method, and pore size and volume were determined using BJH desorption theoretical model. FTIR spectra were measured in a NEXUS 670-FTIR equipped with a smart collector and a liquid  $\text{N}_2$  cooled MCT detector. The full spectra with wave numbers ranged from 400 to 4000  $\text{cm}^{-1}$  with a 4  $\text{cm}^{-1}$  resolution were recorded. X-ray powder diffraction patterns of the catalysts were recorded with a Rigaku D/max 2500 powder diffractometer operated at 40 kV and 100 mA using  $\text{Cu K}\alpha$  radiation. Intensities of the diffraction peaks were recorded in the  $2\theta$  range of 10°–80° with a step size of 0.01°, and the scanning speed was 8 °/min. The X-ray photoelectron spectrometer (XPS) using a ESCALAB 250 multi-purpose electronic energy spectrometers with  $\text{Al K}\alpha$  (150 W) X-ray source. The XPS data were calibrated based on the standard binding energy of C 1s (284.6 eV). The Pd dispersion was evaluated with a TP-5085 metal dispersion instrument.

## 3. Results and discussion

### 3.1. Catalytic activity evaluation

Fig. 1 shows the ethanol conversion over a series of  $\text{Pd}/\gamma$ - $\text{Al}_2\text{O}_3$ - $\text{TiO}_2$  catalysts (500 °C) with different  $\text{Al}_2\text{O}_3$  ratios at various temperatures. Fig. 2 refers to the oxidation of ethanol that took reaction at 150 °C, 175 °C, and 200 °C, respectively from Fig. 1. The

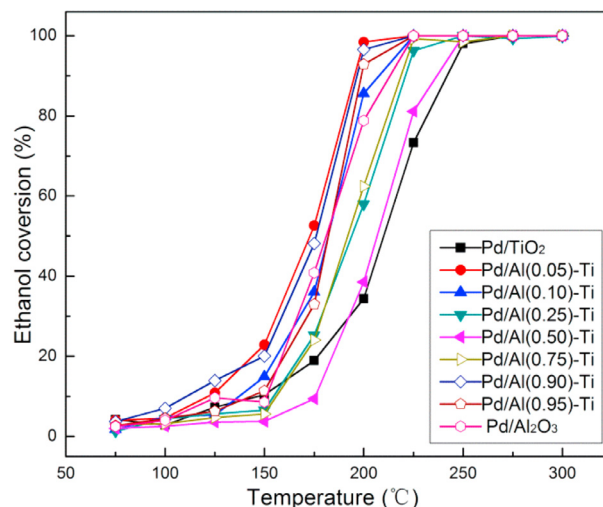


Fig. 1. Ethanol conversion over  $\text{Pd}/\text{TiO}_2$ ,  $\text{Pd}/\gamma$ - $\text{Al}_2\text{O}_3$  and  $\text{Pd}/\text{Al}-\text{Ti}$  catalysts.

results show that the effect of  $\text{Al}_2\text{O}_3/\text{TiO}_2$  ratio on catalytic performance is obvious. The catalysts  $\text{Pd}/\text{Al}(0.05)$ - $\text{Ti}$  and  $\text{Pd}/\text{Al}(0.90)$ - $\text{Ti}$  presented the best catalytic performance comparing to  $\text{Pd}/\gamma$ - $\text{Al}_2\text{O}_3$ ,  $\text{Pd}/\text{TiO}_2$  and other  $\text{Pd}/\text{Al}-\text{Ti}$  catalysts. For instance, the optimal value of ethanol conversion appeared on  $\text{Pd}/\text{Al}(0.05)$ - $\text{Ti}$  and  $\text{Pd}/\text{Al}(0.90)$ - $\text{Ti}$  was over 90% at 200 °C. However, the conversion for  $\text{Pd}/\gamma$ - $\text{Al}_2\text{O}_3$  was less than 80% and for  $\text{Pd}/\text{Al}(0.50)$ - $\text{Ti}$  and  $\text{Pd}/\text{TiO}_2$  was less than 40%. As shown in Fig. 2, it is called the double peaks phenomenon or bimodal structure phenomenon. The double peaks phenomenon was also found on  $\text{Pd}/\gamma$ - $\text{Al}_2\text{O}_3$ - $\text{TiO}_2$  catalysts calcined at 700 °C (data not show), and this discovery may be helpful for the development of more high-performance catalysts.

Fig. 3 presents the selectivity of the  $\text{Pd}/\gamma$ - $\text{Al}_2\text{O}_3$ - $\text{TiO}_2$  catalysts to  $\text{CO}_2$ . From the results it can be seen that  $\text{CO}_2$  selectivity of samples exhibits a similar phenomenon or trend to the ethanol conversion. The catalysts  $\text{Pd}/\text{Al}(0.05)$ - $\text{Ti}$  and  $\text{Pd}/\text{Al}(0.90)$ - $\text{Ti}$  presented the best  $\text{CO}_2$  selectivity, and could reach over 90% of the ultimate conversion. Moreover, the main by-products obtained on the  $\text{Pd}/\gamma$ - $\text{Al}_2\text{O}_3$ - $\text{TiO}_2$  catalysts from ethanol oxidation were acetaldehyde, ethyl acetate, methane, and carbon monoxide. However, the amount of all these by-products could be very little and can be converted completely over 250 °C.

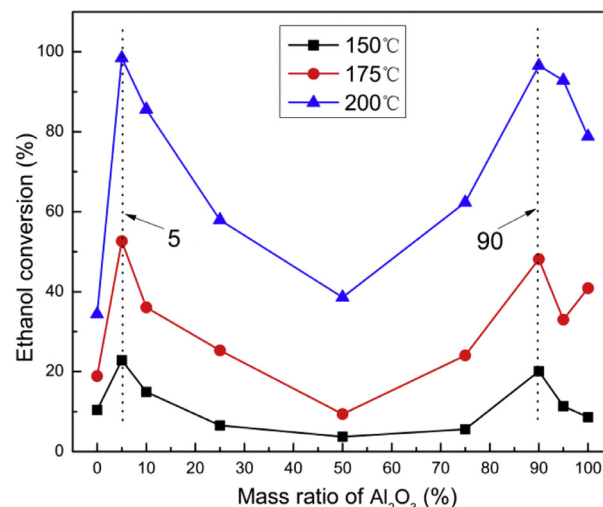


Fig. 2. Catalytic performance for the oxidation of ethanol over  $\text{Pd}/\gamma$ - $\text{Al}_2\text{O}_3$ - $\text{TiO}_2$  catalysts with different  $\text{Al}_2\text{O}_3$  ratios.

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