Journal of Energy Chemistry 25 (2016) 375–380

Contents lists available at ScienceDirect

Journal of Energy Chemistry

journal homepage: www.elsevier.com/locate/jechem

http://www.journals.elsevier.com/journal-of-energy-chemistry/

Catalytic activity and crystal structure modification of Pd/γ-Al_2O_3–TiO_2 catalysts with different Al_2O_3 contents☆

Chengwu Yang[a], Qian Zhang[a], Jun Li[a], Ruirui Gao[a], Zhe Li[a,*], Wei Huang[b]

[a] College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, Shanxi, China
[b] Key Laboratory of Coal Science and Technology, Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan 030024, Shanxi, China

ARTICLE INFO

Article history:
Received 12 June 2015
Revised 30 October 2015
Accepted 30 October 2015
Available online 15 January 2016

Keywords:
Ethanol complete oxidation
Al_2O_3/TiO_2 ratio
Double peaks phenomenon
Calcination temperature

ABSTRACT

Pd/γ-Al_2O_3–TiO_2 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_2 adsorption–desorption, FTIR, XRD and XPS were conducted, and the effects of Al_2O_3 content on the surface area, phase transformation and structural properties of TiO_2 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_2O_3/TiO_2 ratio and calcination temperature. Al_2O_3 can effectively prevent the agglomeration of TiO_2 and this can be ascribed to the formation of Al–O–Ti chemical bonds in Al_2O_3–TiO_2 crystals. Binding energy and Pd surface concentration of the catalysts were modified apparently, which may also lead to catalyst activity changes.

1. Introduction

Titanium dioxide and aluminum oxide have been widely used in various catalysis fields and nanotechnology researches. TiO_2 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_2O_3, a widely used ceramic material with many different polymorphs like δ, η, γ and α phases, has been synthesized by many new methods [7–9]. Alumina also shows numerous applications in catalysis, optics, biomedicine, etc.

TiO_2 and Al_2O_3 have been used for a wide application independently while each has its individual deficiencies and limitations. Al_2O_3 suffers a decrease in the activity for many applications and TiO_2 tends to confront lower surface area and reduced thermal stability [10,11]. TiO_2–Al_2O_3 nano-composites can combine the advantages of individual oxide supports, giving better high-temperature stability, a stronger surface acid, and better textural properties. TiO_2–Al_2O_3 mixed oxides have been found applications in petroleum hydrotreatment [12], selective oxidation [13], and catalytic reduction of NO_x [14].

Moreover, TiO_2–Al_2O_3 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_2 or TiO_2–Al_2O_3 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_2O_3 in Pd/TiO_2 catalysts improved the total oxidation of ethanol [20]. In the present work, a series of TiO_2–Al_2O_3 nanocomposites with different Al_2O_3 ratios were synthesized and characterized. The effect of different Al_2O_3/TiO_2 ratios on the catalytic performance for ethanol oxidation and crystal structural, particle size and morphology of Pd/Al_2O_3–TiO_2 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_2O_3–TiO_2 catalysts for the first time.

☆ This work was supported by Shanxi Provincial Science and Technology Projects (No. 20140313002-2) and the National Natural Science Foundation of China (No. 21073131).

* Corresponding author. Tel/Fax: +86 351 6018975.
E-mail address: lizhe@tyut.edu.cn (Z. Li).

http://dx.doi.org/10.1016/j.jechem.2016.01.011
2095-4956/

2. Experimental

2.1. Carrier and catalyst preparation

The Al_2O_3–TiO_2 composite supports were prepared by a sol–gel method. Titania and alumina sols were prepared separately, and then mixed together to obtain Al_2O_3–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 TiO_2 and pure Al_2O_3 supports were prepared in a similar method. Pd/Al_2O_3–TiO_2 catalysts were prepared by a wet-impregnation method, and all the samples contained 1 wt% Pd. The Al_2O_3(x)–TiO_2 (where $x = 0$, 0.05, 0.50, 0.90, and 1 of mass ratio) composite is denoted as Al(x)–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% C_2H_5OH, 5 vol% O_2, and a balance of N_2. The flow rate was 100 mL/min of total gas and the gas hourly space velocity (GHSV) was 24,000 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: $X_i = [(C_{i,in} - C_{i,out})/C_{i,in}] \times 100\%$, $Y_j = (C_{j,out}/C_{i,in}) \times 1/n \times 100\%$. 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

N_2 adsorption–desorption isotherms for pure TiO_2 and the modified 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 N_2 cooled MCT detector. The full spectra with wave numbers ranged from 400 to 4000 cm^{-1} with a 4 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 Cu $K\alpha$ radiation. Intensities of the diffraction peaks were recorded in the 2θ range of 10°–80° with a step size of 0.01°, and the scanning speed was 8 °/min. The X-ray photoelectron spectroscope (XPS) using a ESCALAB 250 multi-purpose electronic energy spectrometers with 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 Pd/γ-Al_2O_3–TiO_2 catalysts (500 °C) with different Al_2O_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

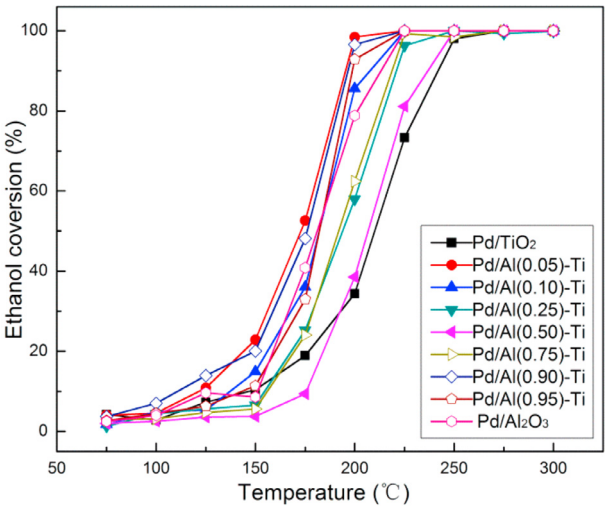

Fig. 1. Ethanol conversion over Pd/TiO_2, Pd/γ-Al_2O_3 and Pd/Al–Ti catalysts.

results show that the effect of Al_2O_3/TiO_2 ratio on catalytic performance is obvious. The catalysts Pd/Al(0.05)–Ti and Pd/Al(0.90)–Ti presented the best catalytic performance comparing to Pd/γ-Al_2O_3, Pd/TiO_2 and other Pd/Al–Ti catalysts. For instance, the optimal value of ethanol conversion appeared on Pd/Al(0.05)–Ti and Pd/Al(0.90)–Ti was over 90% at 200 °C. However, the conversion for Pd/γ-Al_2O_3 was less than 80% and for Pd/Al(0.50)–Ti and Pd/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 Pd/γ-Al_2O_3–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 Pd/γ-Al_2O_3–TiO_2 catalysts to CO_2. From the results it can be seen that CO_2 selectivity of samples exhibits a similar phenomenon or trend to the ethanol conversion. The catalysts Pd/Al(0.05)–Ti and Pd/Al(0.90)–Ti presented the best CO_2 selectivity, and could reach over 90% of the ultimate conversion. Moreover, the main by-products obtained on the Pd/γ-Al_2O_3–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.

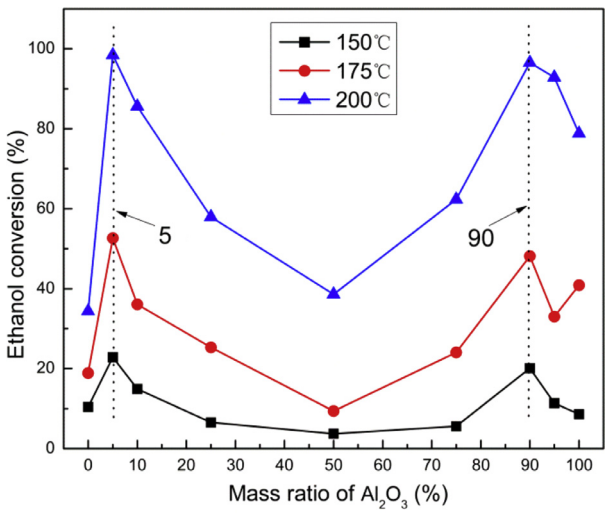

Fig. 2. Catalytic performance for the oxidation of ethanol over Pd/γ-Al_2O_3–TiO_2 catalysts with different Al_2O_3 ratios.