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The double peaks and symmetric path phenomena in the catalytic activity of Pd/Al_2O_3-TiO_2 catalysts with different TiO_2 contents

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ABSTRACT

Physicochemical properties of Pd/Al_2O_3-TiO_2 catalysts with different amounts of TiO_2 contents were investigated by XRD, nitrogen adsorption-desorption, FTIR, NH_3-TPD, H_2-TPR and XPS techniques. Catalysts of different compositions were tested in the ethanol oxidation reaction to study the effects of TiO_2 contents. Double peaks and symmetric path phenomena were observed at certain temperatures with the increase in TiO_2 contents. The symmetric peak phenomena and the diverse activity fluctuations have been ascribed to the controlling factors such as temperature and compositions. With the increase in TiO_2 content, the surface area, adsorbed oxygen contents and surface acid quantity decreased gradually. The large surface area and adsorbed oxygen contents were conducive to the performance, while increased acid amounts were not beneficial for ethanol oxidation. At 150 and 175 °C, Pd/AT(X[1]) ($X < 50$) catalysts performed better in ethanol oxidation because of the main factors of surface area and adsorbed oxygen. Owing to the stronger effects of acid quantity compared to other factors, Pd/AT(X) ($X < 50$) catalysts showed lower catalytic performance at 200 and 225 °C. The higher contents of low-temperature acid in the NH_3-TPD results and the larger difference between Pd^0 and Pd^{2+} in XPS analyses were the origins of the double peaks of higher activity for the Pd/AT20 and Pd/AT80 catalysts.

1. Introduction

Volatile organic compounds (VOCs), which are emitted from various industrial, commercial and domestic sources, are considered to be major contributors to air pollution and formation of photochemical smog [1]. Ethanol is one of the most common alcohols and is widely used as a solvent, as well as in biomedicine and in the printing industry [2]. With the increasing drive for sustainable energy, ethanol (C_2H_5OH) has been used as an additive or substitute for gasoline for ethanol-fuelled vehicles to improve the octane number and reduce emissions of carbon monoxide (CO) from automotive exhaust [3]. However, the unburned ethanol and released acetaldehyde in the exhaust gases are becoming new challenges [4].

Catalytic oxidation is one of the most effective techniques for the elimination of VOCs in which the VOCs can be oxidized into carbon dioxide and water at much lower temperatures, and no secondary pollution products are generated [5]. The supported noble metal catalysts have been demonstrated to be promising catalysts for this process because of their high activities at low temperatures, even at room temperature [6]. The Pd-supported catalysts have been extensively studied [7], since palladium has been found to be a prospective material for practical applications in the total combustion of VOCs owing to its high activity at a relatively low temperature, tolerance to moisture [8] and higher resistance to thermal sintering in an oxidizing environment than platinum [9].

The intrinsic basicity associated with a supported catalyst plays a crucial role in catalytic performance. Okumura et al. [10] have suggested that use of Pd with a support would profoundly affect in the generation of active species and change the catalytic performance of Pd. For Pt and Pd catalysts, the commonly used supports are Al_2O_3, ZrO_2, CeO_2, SiO_2 and TiO_2, among others [11–13]. The composite oxide supports attracted widespread attention for their advantages to utilize properties associated with multiple materials so as to overcome the disadvantages observed while using a single oxide as support. Gutiérrez-Alejandre [14] and Ramirez [15] demonstrated that the TiO_2-Al_2O_3 binary oxide could overcome the disadvantages of the low surface of the TiO_2 support and show the advantages of the high activity of the TiO_2 as well as the high thermal stability of Al_2O_3. El All and El-Shobaky [16] indicated that the TiO_2/Al_2O_3 composite possessed higher electric conductivity compared to the pure oxides. Wang

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[1] Pd/AT(X): Pd/Al_2O_3-TiO_2($X = X$ wt% of TiO_2).

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et al. [17] reported that the catalytic activity and selectivity of the Ni_2P/TiO_2-Al_2O_3 catalyst increased significantly compared to the corresponding Ni_2P catalysts supported by a single oxide. The support properties are mainly affected by the compositional changes. The combustion activity of the Pd-supported zeolite catalysts was found to be relatively dependent on the Al concentration and structures of the zeolite [18]. Shee et al. [19] discovered that a titania-alumina mixed oxide support with a small amount of alumina showed high catalytic activity for propane conversion. Li et al. [20] found that the reducibility of the precursors as well as the surface electronic properties of the Ni_2P catalysts were affected by the addition of TiO_2. Song et al. [21] stated that the incorporation of Ti resulted in proper Lewis acidity of the Ni_2P/Ti-MCM-41 catalyst and improved its HDS catalytic activity.

When a heterogeneous catalytic reaction passes through one catalytic species then there is one activation process leading to a single peak process. In the previous work from our laboratory, Yang et al. [22] investigated the catalytic activity of Pd/γ-Al_2O_3-TiO_2 with variation on the amount of Al_2O_3. In such case double catalytic activity peaks were observed for which the optimal value of ethanol conversion was observed for the two compositions of catalyst having respective compositions Pd/Al(0.05)-Ti and Pd/Al(0.90)-Ti. The double peak process may arise due to the composition of Supplementary material. When the support composition changes, it naturally results in modification of the dominant properties, under such a situation the double peaks might appear. We have chosen to explore ethanol conversion with a binary oxide system of Al_2O_3-TiO_2 where Al_2O_3 in anticipation of double peak process. This system is expected to show the double peaks because regardless of whether the Al_2O_3 or TiO_2 is used as the main support component, the catalyst should maintain favorable conditions for ethanol conversion.

Although the double peaks were observed in the work of Yang [22], the concept of double peaks was only proposed without the detailed interpretation and discussion regarding the origins of this phenomenon. In this work, a series of Pd/Al_2O_3-TiO_2 catalysts with TiO_2 contents ranging from 0% to 100% were prepared and tested for the ethanol oxidation reaction. Several characterization methods were used to study the structures and properties of the catalysts. The main purpose of our research was to investigate and interpret the relationship between the effects of the TiO_2 contents on the physicochemical properties of catalysts and the double peaks for ethanol oxidation.

2. Experimental section

2.1. Preparation of catalysts

The alumina sol (aluminium isopropoxide), titania sol (tetrabutyl titanate) and mixed sol were prepared by the sol-gel method [7]. The sols were dried at 50 °C and 110 °C in an oven for 12 h, respectively, and were then calcined at 500 °C in air for 5 h (the heating rate was 2 °C min^{-1}). With the increase in the TiO_2 contents, the attained supports were denoted as A100, AT20, AT40, AT50, AT60, AT80 and T100 (A-Al_2O_3, T-TiO_2). The corresponding weight percentage of TiO_2 was 0%, 20%, 40%, 50%, 60%, 80% and 100%, respectively.

1.0 wt% Pd (Palladium Chloride) was loaded on the supports as the active component by the impregnation method. The solution was stirred continuously at room temperature for 24 h and dried by evaporation at 80–85 °C and then dried in an oven for 12 h at 110 °C. Subsequently, the dry powders were ground and then calcined at 500 °C in air for 5 h. The samples were defined as Pd/A100, Pd/AT20, Pd/AT40, Pd/AT50, Pd/AT60, Pd/AT80 and Pd/T100 corresponding to the supports.

2.2. Characterizations of catalysts

X-ray diffraction (XRD) measurements were carried out with a Rigaku D/max 2500 diffractometer by using Ni-filtered Cu-K_α radiation with a step size of 0.03° in the 2θ range of 5–80°.

N_2 adsorption-desorption isotherms were obtained by a Micromeritics ASAP 2020 analyser. Prior to the measurements, samples were degassed at 200 °C and 6.67×10^{-2} Pa vacuum pressure for 4 h.

Fourier transformed infrared spectroscopy (FT-IR) analyses were performed using a NICOLET360 spectrometer. The spectra of the solids were obtained using KBr pellets. The vibrational transition frequencies were reported in wavenumbers (cm^{-1}).

NH_3-TPD tests were performed on the XQ TP-5080 catalyst characterization apparatus. Prior to the experiments, 100-mg samples were pretreated at 400 °C for 0.5 h under a constant He flow rate of 30 mL min^{-1}. The adsorption of NH_3 was operated in the flow of NH_3 at 50 °C for 0.5 h, followed by He purging for 0.5 h to remove the NH_3 of physical adsorption. The desorption process was carried out from 50 to 800 °C at a rate of 10 °C min^{-1} with flowing He (30 mL min^{-1}).

H_2-TPR experiments were also performed using the XQ TP-5080 catalyst characterization apparatus. A total of 50 mg of catalysts was pretreated at 400 °C by flowing N_2 of 50 mL min^{-1} for 40 min. After being cooled to room temperature, a feed gas mixture of 5 vol% H_2 in N_2 was fed to the reactor at a flow rate of 50 mL min^{-1} and the temperature was raised to 950 °C at a rate of 10 °C min^{-1}.

X-ray photoelectron spectra (XPS) were obtained using an ESCALAB 250 multifunctional electronic energy spectrometer using Al-K_α (150 W) as the X-ray source. All element binding energies were referenced to the standard energy of C 1s at 284.6 eV, and the estimated error was ± 0.1 eV.

2.3. Oxidation of ethanol

The oxidation reaction was carried out in a continuous-flow fixed-bed reactor (Ø = 6 mm) at atmospheric pressure. The straight quartz tube reactor shrank in the middle to hold 300 mg of catalysts (40–60 mesh) every time. The reactants were fed by the continuous bubble method at room temperature, and the feed gas was a mixture of 0.5 vol% C_2H_5OH, 2.0 vol% O_2 and the balance of N_2 with a flow rate of 145 mL min^{-1} and WHSV: 33.36 h^{-1}. An online gas chromatograph (HXSP, GC-950) with two FID detectors was used to analyse the products from the reactor. The first FID detector was applied to the detection of methane, acetaldehyde, ethyl acetate and ethanol after the separation of the column filled with DNP (20%). The other detector incorporated a methanator and was used to analyse CO, CH_4 and CO_2 through a TDX-01 column. Ethanol conversion (X_i) and product selectivity (S_i) were calculated according to:

$$X_i = [(C_{i,in} - C_{i,out})/C_{i,in}] \times 100\%$$

where $C_{i,in}$ and $C_{i,out}$ are the peak areas of ethanol before the reaction and in combustion products.

$$S_i = [(n_j \bullet C_{j,out})/\sum (n_j \bullet C_{j,out})] \times 100\%$$

where $C_{j,out}$ is the concentration of the products and n_j is the carbon atom ratio of products to reactants.

3. Results and discussion

3.1. Activity of ethanol oxidation

Ethanol conversion and CO_2 selectivity could be used to evaluate the catalytic performance of different catalysts in the ethanol oxidation reaction. As shown in Fig. 1, the two parameters increased with increasing temperature varying from 75 °C to 500 °C and did not decrease at high temperatures where the high reactivity and stability of the samples was obtained. Furthermore, all catalysts (except for Pd/A100) converted above 90% ethanol at 250 °C. With the exception of Pd/A100 and Pd/T100, which exhibited lower reactivity at some