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Acidity of co-precipitated SiO_2-ZrO_2 mixed oxides in the acid-catalyzed dehydrations of *iso*-propanol and formic acid

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ABSTRACT

SiO_2-ZrO_2 is an interesting class of binary mixed oxide systems, but its acidity has not been intensively linked to the catalytic activity in the dehydration reactions. Thus, SiO_2-ZrO_2 mixed oxides with the Si/(Si + Zr) ratio ranging from 0 to 1 were synthesized via a coprecipitation method and their physicochemical properties including acid characteristics were investigated. As a result of pyridine adsorbed FT-IR and *iso*-propanol (IPA)-TPD, the type, quantity, concentration, and strength of acid site were largely dependent on the molar composition of SiO_2-ZrO_2 mixed oxides, where they reached maximum at the Si/(Si + Zr) molar ratio of 0.7. Furthermore, it was found that the catalytic activity was proportional to the acid strength in the decomposition of IPA, while the quantity of Brønsted acid sites was a principal contributor to the activity in the decomposition of formic acid.

1. Introduction

Catalysts containing acidic functionalities are widely used in a range of chemical reactions, including the dehydration of alcohols [1–4] and formic acid [3,5,6], isomerization [7,8], cracking [9,10], pyrolysis [11], oxidative dehydrogenation [12,13], and the polymerization of alkenes [14–16]. Since most acid-catalyzed reactions occur at the catalyst surface, the number of exposed acidic sites is an important factor in determining the catalytic activity. However, in certain acid-catalyzed chemical reactions, not only the number, but also the type of acidic site (i.e., Lewis or Brønsted) can have a significant influence on the catalytic behavior. As such, determination of the numbers and types of acid centers on catalyst surfaces is of particular importance in the optimization of certain acid-catalyzed reactions.

It is well known that mixed oxide catalysts exhibit a very distinctive properties compared to single oxides from which they are composed, with examples including SiO_2-Al_2O_3 [17,18], SiO_2-TiO_2 [7,8,19], SiO_2-MgO [20], TiO_2-ZrO_2 [19], Al_2O_3-ZrO_2 [21,22], and SiO_2-ZrO_2 [2,7,8,21,23–27]. In particular, in the case of SiO_2-ZrO_2, although pure ZrO_2 has demonstrated extensive usability as a unique metal oxide that exhibits acidic, basic, oxidizing, and reducing properties [7,21], it tends to possess a low Brunauer–Emmett–Teller (BET) surface area [2,21] and only Lewis acid properties [1,2,8]. In addition, pure SiO_2 does not contain any acidic sites due to its construction from strong covalent bonds [2]. In contrast, in the SiO_2-ZrO_2 binary mixed oxide system, new acidic sites including the Brønsted acid sites can be developed depending on the preparation methods and conditions, and the atomic compositions. As aforementioned, variations in surface acidity of SiO_2-ZrO_2 mixed oxide have been reported in several previous literatures [2,7,8,21,24–27], however in most articles, only focus on the relationship between surface acidity and physicochemical properties depending on experimental variables. In contrast, not many cases have reported that acidic characteristics of SiO_2-ZrO_2 catalysts directly correlate to catalytic performance for the specific reaction [2].

Thus, we herein reported the synthesis of binary SiO_2-ZrO_2 mixed oxide catalysts via a co-precipitation method, and subsequent determination of the quantities and types of acidic sites in these catalysts as a function of atomic compositions. Pyridine-adsorbed infrared spectroscopy (Py-IR) was employed to measure the quantities and types of acid centers, while the temperature-programmed desorption of *iso*-propanol (IPA-TPD) was conducted to determine the acidic strength of the catalysts. In addition, the physicochemical properties of the catalysts were measured by X-ray diffraction (XRD), N_2-sorption, energy-dispersive X-ray spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS), and the results were correlated with the development of acidic properties on the catalyst surface. Furthermore, the decomposition reactions of IPA and formic acid were used as model reactions to closely analyze the effects of the acidic characteristics on specific

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catalytic reactions. Finally, we discussed the variation in the catalyst acidic properties for the SiO_2-ZrO_2 mixed oxide system in the context of the atomic composition, and examined how such acidic functions operated in the above catalytic reactions.

2. Experimental

2.1. Catalyst preparation

The Si-Zr mixed oxide catalysts were prepared via a co-precipitation method with different molar ratios of Si/(Si + Zr) ranging from 0 to 1. More specifically, the desired quantities of zirconia nitrate ($ZrO(NO_3)_2 \cdot 2H_2O$, 99%, JUNSEI) and tetraethyl orthosilicate ($C_8H_{20}O_4Si$, 98%, Acros Organics) were dissolved in mixture of 17 vol% deionized water and 83 vol% ethanol at room temperature, and a 28 wt% solution of NH_4OH (SK Chemicals) was added dropwise to give a pH of 9.5. The resulting suspension was aged at 75 °C for 48 h under reflux, after which the obtained precipitate was washed with deionized water, and dried at 60 °C for 24 h. Finally, the dried samples were calcined at 500 °C for 6 h under an air flow. The final products were labeled as xSi-Zr, where x indicates the Si/(Si + Zr) molar ratio in the mixed oxide.

2.2. Characterization

XRD measurements were carried out on a D8 Discover with GADDS (Bruker AXS) diffractometer using Cu Kα radiation. The BET surface areas, total pore volumes, and pore diameters of the calcined samples were determined from the physical adsorption of N_2 at −196 °C using an ASAP 2020 (Micromeritics) after sample pretreatment at 250 °C for 5 h under vacuum. The BET surface areas were determined using the BET method in the P/P_0 range of 0.05–0.2. In addition, the pore size distribution of each catalyst was calculated using the Barrett-Joyner-Halenda (BJH) method from a desorption branch of the isotherm, and the total pore volumes were calculated from the quantity of N_2 adsorbed at $P/P_0 = 0.99$. Scanning electron microscopy (SEM) was carried out on an LEO-1530 (Carl Zeiss) instrument equipped with an EDS to observe the morphology and atomic composition of the catalyst.

Py-IR analysis was performed on a Nicolet 6700 spectrometer (Thermo Scientific). Prior to analysis, a portion of the sample (30 mg) was pressed into a self-supported disk and pretreated at 300 °C for 1 h under vacuum. Subsequently, pyridine (5 μL) was injected for 15 min at 150 °C then evacuated for 30 min under vacuum. All Py-IR spectra were recorded with 32 scans and a resolution of 4 cm^{-1}. From Py-IR analysis, the Lewis and Brønsted acid densities were quantified using the bands at 1444 and 1540 cm^{-1}, respectively, using previously reported empirical formulae [28] (integrated molar extinction coefficients = 2.22 and 1.67 cm μmol^{-1} for the Lewis and Brønsted acid sites, respectively).

$$\text{C (Pyridine on Lewis acid sites)} = 1.42 \cdot \text{IA (L)}\, R^2/W; \tag{1}$$

$$\text{C (Pyridine on Brønsted acid sites)} = 1.88 \cdot \text{IA (B)} \cdot R^2/W; \tag{2}$$

where C is the acid site number on a per-gram-catalyst basis ($\mu mol\ g_{cat}^{-1}$), IA (L or B) the integrated absorbance of the band (1444 or 1540 cm^{-1}) ascribed to Lewis or Brønsted acid site, R the radius of the catalyst disk (cm), and W the weight of the disk (mg).

IPA-TPD measurement was performed using quadrupole mass spectrometry (GSD301, Pfeiffer vacuum) according to the following procedure. The sample (0.05 g) was loaded into a U-shaped quartz reactor and pretreated at 300 °C for 1 h under a flow of Ar (30 $cm^3\ min^{-1}$). After cooling to room temperature, IPA was adsorbed on the catalyst surface under a flow of 3% IPA/Ar (30 $cm^3\ min^{-1}$) for 30 min, followed by removal of the physisorbed IPA in an Ar flow for 30 min. Subsequently, the sample was heated to 400 °C with a heating rate of 10 °C min^{-1} under a flow of Ar (30 $cm^3\ min^{-1}$), and evolved mass fragments were recorded. The surface electronic states of the Si-Zr mixed oxide catalysts were identified by XPS using a PHI Quantera-II (ULVAC-PHI) photoelectron spectrometer (Al Kα radiation; $h\nu = 1486.6$ eV), and XPS spectra were calibrated using the binding energy of adventitious carbon (i.e., C 1s, 284.6 eV). To further interpret the XPS results, peak-fitting and deconvolution of the O 1s, Zr $3d_{5/2}$, and Si 2p spectra were carried out using the Gaussian–Lorentzian curve-fitting method after background subtraction by the Shirley method.

2.3. Catalytic activity tests

2.3.1. IPA decomposition

Prior to IPA decomposition experiments, all catalysts (0.1 g per reaction) were pretreated under a flow of N_2 (50 $cm^3\ min^{-1}$) for 1 h at 400 °C in a fixed-bed quartz reactor. After pretreatment, the reactor was cooled to 180 °C, and the isothermal reaction was allowed to proceed for 9 h at a fixed partial pressure of 3 kPa IPA balanced with N_2 (total flow rate = 50 $cm^3\ min^{-1}$). The obtained dehydration products were analyzed by an online gas chromatograph (Varian 3800) equipped with a CP-Volamine capillary column (60 m × 0.32 mm) and an FID detector. The conversion of IPA and the selectivities to propylene and diisopropyl ether (DIPE) were defined as follows:

$$Conversion\,(\%) = \frac{F_{\text{IPA}}\ reacted}{F_{\text{IPA}}\ fed} \times 100\%\ ; \tag{3}$$

$$\text{Selectivity}(\%) = \frac{F_i}{\sum F_i(product)} \times 100\%\ ; \tag{4}$$

where F_{IPA} and F_i are the molar flow rates of IPA and the product *i* (i.e., propylene or DIPE).

2.3.2. Formic acid decomposition

The formic acid (HCOOH) decomposition reaction was carried out with 0.1 g of the catalyst in the identical reaction system as described for the IPA decomposition reaction. After pretreatment at 400 °C for 1 h under a flow of Ar (100 $cm^3\ min^{-1}$), the reactor was cooled to 230 °C, and the isothermal reaction was performed under a 5 kPa HCOOH/Ar balanced feed stream (total flow rate = 100 $cm^3\ min^{-1}$). The resulting decomposition products were analyzed by an online gas chromatography (Varian 3800) equipped with a HayeSep Q column (80 m × 100 mm) and a TCD detector. The conversion of formic acid was calculated using the following equation:

$$Conversion\,(\%) = \frac{F_{\text{HCOOH}}\ reacted}{F_{\text{HCOOH}}\ fed} \times 100\%\ ; \tag{5}$$

where F_{HCOOH} is the molar flow rate of formic acid.

3. Results and discussion

3.1. General properties of SiO_2-ZrO_2 mixed oxides

Following the successful preparation of the Si-Zr mixed oxide catalysts composed of various Si/(Si + Zr) molar ratios, we initially examined their XRD patterns after calcination at 500 °C for 6 h. As shown in Fig. S1A, the characteristic peaks of pure ZrO_2 were detected at 2θ = 30.1, 35.3, 50.4, and 60.2°, which corresponded to a tetragonal crystalline structure (JCPDS No. 50-1089). However, the Si-Zr mixed oxides expressed a low degree of crystallinity, namely X-ray amorphous phase. This is due to introduction of Si species into the Zr matrix stabilized the tetragonal phase of ZrO_2. For confirmation, the samples were calcined at a much higher temperature of 900 °C for 6 h, and all SiO_2-ZrO_2 mixed oxides exhibited the tetragonal ZrO_2 crystallites compared to pure ZrO_2 showing mixed monoclinic and tetragonal phases. In addition, the tetragonal characteristic peaks of ZrO_2 became less intense as the content of SiO_2 increased (see Fig. S1B). It is known that the ZrO_2 can exist in monoclinic, tetragonal, and cubic crystal structures, and the development of the crystalline structure is largely