

Characterization of TiO₂-ZrO₂ and Isopropanol Catalytic Conversion

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Abstract: A series of TiO₂-ZrO₂ composite oxides were prepared by a coprecipitation method, and were characterized by N₂ adsorption, XRD, TEM, microcalorimetric adsorption of NH₃ and CO₂, and infrared spectra of ammonia adsorption. In comparison with the single metal oxide, amorphous composite oxides could be observed with mesoporous structure and higher BET surface area ($S_{\text{BET}}=218 \text{ m}^2\cdot\text{g}^{-1}$). Although the initial adsorption heat for all these samples did not vary significantly, composite oxides possessed more Brønsted acid sites than the single oxide. With an increase in the incorporated amount of titania, the number of basic sites on the surface of composite oxides decreased. In the absence of O₂, the values of selectivity for propene exceeded 90% for all these catalysts *via* isopropanol catalytic conversion, revealing that each of the samples had a strong surface acidity. However, in the presence of O₂, 70%–85% selectivity for acetone was obtained for TiO₂ and ZrO₂, suggesting that redox properties were predominant over acidity. Due to the formation of composite oxides, selectivity for propene increased to about 70%, whereas selectivity for acetone decreased to about 30%, indicating that the acidity was enhanced and the redox property was weakened.

Key Words: TiO₂-ZrO₂; Isopropanol catalysis; Surface acidity/basicity; Redox property

The unique properties of TiO₂ and ZrO₂ had resulted in the wide interests in the catalytic circles. However, when each of them is used as the carrier of catalyst, the disadvantages of the smaller surface area and poor stability against sintering appeared. In general, TiO₂-ZrO₂ composite oxides gave relatively the larger surface area and the stronger acidity and used as the carrier, apparently, which is superior to the single oxide. Thus, in recent years, TiO₂-ZrO₂ composite oxides have received increasing attention as catalyst carriers and have been widely applied to important catalytic reactions, such as the auto-exhaust DeNO_x^[1], the hydrodesulfurization^[2], the decomposition of chlorofluorocarbons^[3], and the vapor-phase Beckmann rearrangement of cyclohexanone oxime^[4,5], the hydrogenation, as well as hydrotreatment^[6]. The synthesis methods for TiO₂-ZrO₂ composite oxides mainly include the coprecipitation^[1,4,5,7], the homogeneous precipitation^[2,6], and the sol-gel (includes metal alkoxide hydrolysis preparation)^[3,8–10]. Mao *et al.*^[11] studied the influence of the

above-mentioned three preparation methods on the conversion of cyclohexanone oxime to caprolactam over B₂O₃/TiO₂-ZrO₂ (molar fraction of TiO₂: 50%). The results indicated that TiO₂-ZrO₂ composite oxides was prepared from coprecipitation, the BET surface area (S_{BET}) was the smallest, $171 \text{ m}^2\cdot\text{g}^{-1}$, but as the sample came from the homogeneous precipitation the S_{BET} was the largest, $221 \text{ m}^2\cdot\text{g}^{-1}$, however, the coprecipitation method is easily operated, thus the obtained catalyst, B₂O₃/TiO₂-ZrO₂, exhibited the best catalytic activity, selectivity, and stability. Therefore, in the present study coprecipitation method was selected to prepare TiO₂-ZrO₂ composite oxides with a S_{BET} of $218 \text{ m}^2\cdot\text{g}^{-1}$, which is close to the value obtained from the homogeneous precipitation method^[11]. The prepared composite oxides were characterized by N₂ adsorption, TEM, XRD, the microcalorimetric adsorption, the infrared spectra of ammonia adsorption, and the isopropanol (IPA) catalysis under the presence of oxygen or the absence of oxygen conditions to have an insight into the physico-chemical

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properties and the IPA catalytic conversion. In this article, composite oxides have not yet been found in the published reports to characterize the surface acidity/basicity of $\text{TiO}_2\text{-ZrO}_2$ using the microcalorimetric adsorption.

1 Experimental

1.1 $\text{TiO}_2\text{-ZrO}_2$ preparation

A certain amount of TiCl_4 was dissolved into a certain amount of absolute ethanol solution, followed by an addition of $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$ according to the desired molar ratio, and then a homogeneous solution was obtained. In a cold bath at 273 K, the above solution was gradually dropped into an excess amount of aqueous ammonia (15%, w) with a certain amount of PEG-400 under vigorous stirring. The value of pH was adjusted to 9–10. After aging of 24 h at ambient temperature, precipitates were filtered, washed with deionized water to remove chloride ions (detected by $0.1 \text{ mol}\cdot\text{L}^{-1}$ AgNO_3 solution), and then washed twice with absolute ethanol. The $\text{TiO}_2\text{-ZrO}_2$ precursors were prepared after the precipitate was dried for 10 h at 383 K. Finally, the precursors were calcined in the flowing air for 2 h at 773 K, and then a series of different compositions of $\text{TiO}_2\text{-ZrO}_2$ composite oxides were obtained.

1.2 $\text{TiO}_2\text{-ZrO}_2$ characterization

The S_{BET} of samples were determined by N_2 adsorption at the temperature of liquid N_2 using the BET method on the homemade apparatus. Before measurement, the sample (0.2–0.3 g) was degassed at 673 K for 2 h.

X-ray diffraction (XRD) was performed on a Rigaku D/Max-RA X-ray diffractometer equipped with $\text{Cu } K_\alpha$ radiation ($\lambda=0.15418 \text{ nm}$). The applied voltage and current were 40 kV and 40 mA, respectively. The scanning rate was $10 \text{ (}^\circ\text{)}\cdot\text{min}^{-1}$.

TEM images were obtained by a JEOL JSM 2100 electron microscope using an accelerating voltage of 200 kV.

N_2 adsorption/desorption isotherms and the pore size distribution plots of the samples were determined by nitrogen adsorption on a Micromeritics ASAP-2020 type instrument. Before adsorption, the samples performed the vacuum treatment at 573 K.

The microcalorimetric adsorption measurements were performed with a Tian-Calvet heat-flux apparatus. Before the microcalorimetric measurements, the samples were evacuated, introduced O_2 at room temperature (66.7 kPa), heated to 673 K and held for 1 h, evacuated for 10 min again, and then again introduced O_2 (66.7 kPa) at 673 K and held for 1 h. Finally, evacuated at 673 K for 1 h, the vacuum degree was about $1.33\times 10^{-3} \text{ Pa}$. The probe molecules, NH_3 and CO_2 were used for the measurements of surface acidity and basicity and were purified by a process of freeze-out-gassed-melted. The microcalorimetric adsorption was performed at 423 K, and the measured results were revised by the sensitivity factor.

The infrared spectra of ammonia adsorption were measured with a Bruker IFS66V FTIR spectrophotometer. A sample of 15–20 mg was pressed to form a self-supporting wafer with a diameter of 13 mm, and then was set in an IR cell connecting with a vacuum system. The sample treatments were the same as those for the microcalorimetric adsorption measurement. The spectrum of wafer was recorded as a background after the proper treatment of the wafer. The spectrum was recorded when 2 kPa of NH_3 was introduced into the IR cell, then the adsorption process was performed for 20 min, and then the system was evacuated for 10 min. A spectrum of adsorbed species was obtained by subtracting the background spectrum of the wafer. The recorded spectrum was obtained by 40 scans, and the resolution was 4 cm^{-1} .

1.3 Catalytic reaction

IPA catalytic reaction under the presence of oxygen or the absence of oxygen conditions was performed in a fixed-bed glass tube reactor (8 mm internal diameter), respectively. At normal pressure, IPA was introduced to the reaction zone by carrier gas by a glass saturator filled with IPA maintained at 295 K. In the absence of oxygen, the highly pure N_2 at $60 \text{ mL}\cdot\text{min}^{-1}$ was used as the carrier gas, whereas in the presence of oxygen, the carrier gas of air at $60 \text{ mL}\cdot\text{min}^{-1}$ was used. About 0.1 g sample (20–40 meshes) was loaded for the reaction. IPA and reaction products (propylene (PPE), acetone (ACE), diisopropylether (DIPE)) were measured by an online GC900A gas chromatograph equipped with the hydrogen flame ionization detector and a PEG 20000 packed column.

2 Results and discussion

2.1 S_{BET} , XRD, TEM, and N_2 adsorption

Fig.1 gave the S_{BET} results of $\text{TiO}_2\text{-ZrO}_2$ composite oxides with different compositions. It is clearly observed that the S_{BET} of composite oxides were higher than that of any single oxide. After the addition of a small amount of ZrO_2 into TiO_2 , the S_{BET} showed an apparent increase. When the content of TiO_2 was 75%, the S_{BET} was the largest. Whereas when the content of TiO_2 varied from 50% to 75%, the change in S_{BET} was not

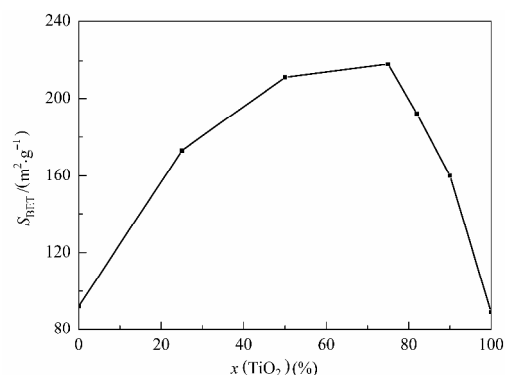


Fig.1 Effect of composition of $\text{TiO}_2\text{-ZrO}_2$ on S_{BET}

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