Structure Characterization of WO₃/ZrO₂ Catalysts by Raman Spectroscopy

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WO₃/ZrO₂ catalysts prepared by different methods are distinct in their catalytic behaviour. In this work, WO₃/ZrO₂ catalysts prepared by impregnating Zr(OH)₄ and crystallized ZrO₂, and then calcining at selected temperatures were characterized by means of qualitative and quantitative Raman spectroscopy. The results showed that ZrO₂ in WO₃/ZrO₂ obtained from crystallized ZrO₂ (referred to as WZ) is monoclinic, whereas ZrO₂ in WO₃/ZrO₂ obtained from Zr(OH)₄ (referred to as WZH) is in a metastable tetragonal phase as long as the WO₃ content is high enough. In both WZ and WZH, WO₃ is dispersed on ZrO₂ as a monolayer, and the dispersion capacity per 100 m² of ZrO₂ is in good agreement with that estimated from the close-packed monolayer model. However, since the specific surface areas of WZH samples are larger than those of WZ samples, the dispersion capacity per gram of ZrO₂ of WZH is larger than that of WZ. A chemical reaction may occur between WO₃ and the surface of Zr(OH)₄ (or tetragonal ZrO₂) at high temperature, and then some superacid sites are created on the surface of the WZH sample.

INTRODUCTION

Any acid can be termed a superacid if its acidity is stronger than that of 100% H₂SO₄, i.e. ß H₂SO₄ < -12.0.¹² The catalytic activity of superacids is surprisingly high.² Solid superacids have some additional advantages as catalysts, e.g. no corrosion of the reactor and freedom from environmental problems in disposing of the catalyst.³ Therefore, superacids may have better application prospects than those of traditional acids. In 1988, Arata and Hino³⁻⁵ reported that solid superacid could also be synthesized by supporting WO₃ or MoO₃ on ZrO₂ under special preparation conditions. Since its active component is not easy to run off and it can remain stable at high temperatures and in a solid-liquid system, it may have better application prospects than those of the sulphate-promoted Fe₃O₄, TiO₂ and ZrO₂ superacids.

The main facts about the WO₃/ZrO₂ superacid system that have been reported so far are as follows:⁴⁻⁵
1. Superacid can be obtained only by impregnating amorphous Zr(OH)₄ instead of crystalline ZrO₂ with ammonium metatungstate solution.
2. It has been shown by X-ray diffraction that metastable tetragonal ZrO₂ is the major form in WO₃/ZrO₂, when Zr(OH)₄ is first impregnated with ammonium metatungstate solution and then calcined, whereas ZrO₂ obtained by calcining pure Zr(OH)₄ at the same temperature is monoclinic.
3. The sample calcined at 800°C with a W content of 15 wt% has the greatest activity.

Many questions, particularly regarding the existing states of WO₃ in WO₃/ZrO₂, are still open. Our group reported⁶⁻⁷ that the spontaneous monolayer dispersion of many oxides and salts on supports is a widespread phenomenon. When an oxide-support mixture is heated at a high enough temperature, it can usually be observed that the oxide has been dispersed on the surface of the support. The maximum monolayer dispersion capacity can be estimated by using the simple close-packed monolayer model.⁶⁻⁷ However, is WO₃ dispersed on ZrO₂ as a monolayer in WO₃/ZrO₂ superacid? What is its dispersion capacity? How do the preparation conditions affect its structure? All of these problems are worth studying. In this work, the effects of the preparation method, the content of WO₃ and the calcination temperature on the structure of WO₃/ZrO₂ were studied by means of Raman spectroscopy. Their phase composition, including the surface dispersion phase, was studied by qualitative and quantitative Raman spectroscopy. The results obtained help in understanding much better the structure of this system.

EXPERIMENTAL

Sample preparation

Four groups of the samples were prepared from high-purity ZrOCl₂·8H₂O and (NH₄)₆H₂W₁₂O₄₀ according to the following procedures. The WO₃ contents in each group were 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.50 and 0.65 g per gram of ZrO₂.

Zr(OH)₄ precipitate was obtained by adding 3.3 m ammonia solution to 0.6 m ZrOCl₂ solution to give pH 9–10, then the resultant white precipitate was filtered and washed repeatedly with distilled water until the filtrate gave a negative test for Cl⁻ ions. The precipitate was heated at 120°C for 24 h and then divided into two parts. One part was calcined at 500°C for 12 h and then impregnated with solutions with predetermined amounts of ammonium metatungstate and calcined at...
Table 1. Specific surface areas of the samples

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<th>WO₃ content/g per gram of ZrO₂</th>
<th>Specific surface area m² g⁻¹ ZrO₂</th>
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500 or 800 °C for 12 h. The samples obtained were designated as WZ5 and WZ8, respectively.

The other part of Zr(OH)₄ heated only at 120 °C was impregnated with solutions of (NH₄)₂H₂W₁₈O₄₀, then dried and calcined at 500 or 800 °C for 12 h. The samples obtained were designated as WZH5 and WZH8, respectively.

The BET surface areas of the samples were determined by nitrogen adsorption at −196 °C using an ST-03 surface area-pore volume analyzer. The specific surface area of ZrO₂ calcined at 550 °C is 70 m² g⁻¹. The BET surface areas of the other samples are listed in Table 1.

The surface acidity of the sample was determined by using the Hammett indicator method. The samples were heated under a pressure of 10⁻² Pa and at 450 °C for 1 h. After cooling, the samples were exposed to an indicator vapour. If some superacid sites exist with $H_0$ less than or equal to the $pK_a$ of an indicator, the colour of the surface of the sample will change. The results showed that there were some superacid sites with $H_0 \leq -13.75$ on the surface of WZH8 (the indicator used was 2,4-dinitrotoluene with $pK_a = -13.75$). No superacid sites were found on the surfaces of WZH5, WZ5 and WZ8.

**Raman spectroscopic analysis**

Raman spectra were acquired on a Ramanor U-1000 double monochrometer with 1800 grooves mm⁻¹ holographic gratings. A Spectra-Physics Stabilite-2016 argon ion laser was used to supply 514.5 nm exciting radiation. A power of ca. 100 mW was employed. The slit width was 1 cm⁻¹. The wavenumber accuracy of the recorded spectra was ±2 cm⁻¹. The powdered samples were pressed into wafers and rotated at high speed in order to reduce the damage of the heat effect on the sample.

In quantitative Raman determinations, KNO₃ was chosen as an internal standard.²

**RESULTS AND DISCUSSION**

**Qualitative results**

The Raman spectrum of pure ZrO₂ calcined at 800 °C is shown in Fig. 1(a). Comparison with a published spectrum⁹ indicates that monoclinic ZrO₂ is dominant. Its characteristic peaks are at 220, 332, 380, 474, 620 and 640 cm⁻¹. Figure 1(b), (c) and (d) show the Raman spectra of WZ8 samples with different WO₃ contents, from which we can see that monoclinic ZrO₂ is pre-

![Figure 1. Raman spectra of WZ8 samples with different WO₃ contents. (a) ZrO₂; (b) 0.05 g WO₃; (c) 0.10 g WO₃; (d) 0.15 g WO₃ per gram of ZrO₂.](image-url)
dominantly present, there is a broad band at 996 cm$^{-1}$ and the greater the content of WO$_3$, the larger is the area of this band. Referring to published spectra of WO$_3$/TiO$_2$ and WO$_3$/Al$_2$O$_3$, we can recognize that it is the characteristic band of a monolayer dispersion of WO$_3$, and is due to the symmetrical stretching mode of W=O. Further, the characteristic peaks of crystalline WO$_3$ $^{11,12}$ (808, 720, 328 and 276 cm$^{-1}$) appear when the content of WO$_3$ is beyond a certain level.

These results are proof that WO$_3$ can be dispersed on ZrO$_2$ in a monolayer dispersion state, and crystalline WO$_3$ appears only when the content of WO$_3$ is beyond the monolayer capacity of WO$_3$ on ZrO$_2$.

A similar phenomenon occurs in the WZ$_5$ series calcined at 500°C (see Fig. 2). What is different is that besides the monolayer dispersion phase, a small amount of crystalline WO$_3$ can be detected even in the samples with low WO$_3$ contents (i.e. 0.05 and 0.10 g WO$_3$ per gram of ZrO$_2$). The reason might be that if part of the (NH$_4$)$_6$H$_2$WO$_{12}$O$_{40}$ decomposes before being dispersed completely and forms crystalline WO$_3$, the resultant crystalline WO$_3$ would disperse further during calcination at 800°C. However, as the samples are calcined at 500°C, the dispersion of the crystalline WO$_3$ is difficult owing to its high melting point and therefore it remains crystalline in the samples. Moreover, it should be noted that the band of monolayer WO$_3$ shifts to ca. 962 cm$^{-1}$. This phenomenon demonstrates that the wavenumber of the monolayer band depends on the calcination temperature, which is in agreement with the literature.$^{10,12}$

Figure 3 shows the Raman spectra of WZH$_8$ samples that are similar to those of WZ$_8$ in some ways: there is only a broad band at 996 cm$^{-1}$ which represents the monolayer dispersion phase when the content of WO$_3$ is below its monolayer capacity. The characteristic peaks of crystalline WO$_3$ appear only when the content of WO$_3$ is higher than a certain level. However, there are some differences between WZH$_8$ and WZ$_8$:

(a) A considerable portion of ZrO$_2$ exists in a metastable tetragonal phase, and its characteristic peaks at about 268, 325, 478 and 648 cm$^{-1}$ (Ref. 9) are rather broad. The overall spectrum is different from that of monoclinic ZrO$_2$, and the peaks at 268 and 325 cm$^{-1}$ and those of monoclinic ZrO$_2$ do not overlap, and so they can be used as standards to determine the existence of metastable tetragonal ZrO$_2$ in the system and to estimate its content. From Fig. 3, it can be seen that a considerable amount of monoclinic ZrO$_2$ exists in the sample with a WO$_3$ content of 0.10 per gram of ZrO$_2$. However, the tetragonal ZrO$_2$ is predominantly present when the content of WO$_3$ is 0.15 g per gram of ZrO$_2$. There are similar characteristics in WZH$_5$.

It has been reported$^{13}$ that ZrO$_2$ can exist in three phases: monoclinic, tetragonal and cubic. The monoclinic ZrO$_2$ is stable below 1170°C, the tetragonal phase is observed at 1170-2370°C and the cubic phase is stable from 2370°C up to its melting point. However, the tetragonal phase ZrO$_2(t)$ is stabilized by a crystallite size effect, i.e. it can be stable from room temperature to 1170°C provided that its crystallites are below a certain critical size. In this case, it is referred as metastable tetragonal ZrO$_2$.

Zirconia, the catalyst support, involves mainly two phases: ZrO$_2(m)$ and metastable tetragonal ZrO$_2$. With a small size, the metastable tetragonal ZrO$_2$ has a larger specific surface area, and its Raman peaks are broader. This is the case for WZH samples.

(b) In addition to the characteristic peaks of crystalline WO$_3$, a small peak at 580 cm$^{-1}$ can be observed when the WO$_3$ content of the sample is more than 0.20 g per gram of ZrO$_2$. This peak is not observed in the spectra of samples of WZ$_5$, WZ$_8$ and WZH$_5$. This peak appears only in the sample prepared by using Zn(OH)$_4$.
as support and then calcining at 800 °C. We think that a new W—O—Zr species might be formed between WO₃ and ZrO₂ under the preparation conditions used, and it might be responsible for the superacidity of WZH8. This phenomenon is more obvious in the MoO₃/ZrO₂ system.¹⁵ This might be why there are no superacid sites in WZH5 although ZrO₂ in them is tetragonal, and a larger amount of dispersed WO₃ can be accommodated owing to their high specific surface areas.

Quantitative measurement

KNO₃ was used as an internal standard⁴,¹⁶ and mixed with the sample in an appropriate ratio. The peak areas of monolayer WO₃ at 996 cm⁻¹, crystalline WO₃ at 808 cm⁻¹ and KNO₃ at 1050 cm⁻¹ were measured, and then normalized as the peak-area ratios of the first two peaks to the last peak as there are equal amounts of KNO₃ and ZrO₂ in the sample. The ratios are regarded as the relative contents of monolayer dispersion and crystalline WO₃ phase. The spectra were accumulated several times. Figure 4 shows an example.

Figure 5 gives the quantitative Raman results for WZ8 and WZH8 samples. It can be seen that when the content of WO₃ in WZ8 is low, WO₃ exists in the form of a monolayer phase, the content of which increases with increase in WO₃ content. After the content of WO₃ has reached a certain value, the content of the monolayer phase does not change and crystalline WO₃ appears, and its content increases gradually with increase in total WO₃ content. The plots showing the relationship between the relative content of monolayer WO₃, the relative content of crystalline WO₃ vs. total WO₃ content, exhibit a change of slope which occurs at the same total WO₃ content. At this point, the maximum monolayer capacity is 0.11 g WO₃ per gram of ZrO₂, i.e. 0.20 g WO₃ per 100 m² of ZrO₂ (the surface area of the sample is 52 m² g⁻¹), which is consistent with the theoretical close-packed monolayer dispersion capacity, 0.19 g per 100 m² of ZrO₂.⁶,⁷ This result indicates that WO₃ can form a nearly perfect monolayer on the surface of ZrO₂.

The quantitative result for WZH8 [see Fig. 5(b)] is similar to that for WZ8. The change of slope corresponds to a WO₃ content of 0.17 g per gram of ZrO₂, which seems higher than that of WZ8. However, the surface area of the sample is about 75 m² g⁻¹ ZrO₂, and therefore the monolayer capacity is about 0.23 g WO₃ per 100 m² of ZrO₂, only slightly higher than its theoretical capacity. We have noted that the change of point of the quantitative curve of the monolayer phase is not so definite for WZH8, and the content of the monolayer phase decreases slowly with increasing WO₃ content when the total content of WO₃ is above the threshold. The small band at 580 cm⁻¹ in the Raman spectra of this series of samples may be due to the formation of a new species that is produced by the reaction between Zr(OH)₄ (or tetragonal ZrO₂) and the active component at 800 °C.

Figure 3. Raman spectra of WZH8 samples with different WO₃ contents. (a) ZrO₂; (b) 0.10 g WO₃; (c) 0.15 g WO₃; (d) 0.20 g WO₃; (e) 0.30 g WO₃ per gram of ZrO₂.
The quantitative Raman curves for the WZ5 and WZH5 series of samples are similar to those of the WZ8 series, the only difference being that the characteristic peak of crystalline \( \text{WO}_3 \) appears when the content of \( \text{WO}_3 \) is lower than the threshold derived from the quantitative curve. As stated above, this is because the dispersion equilibrium has not really been established in the system calcined at 500°C.

**CONCLUSIONS**

\( \text{ZrO}_2 \) in \( \text{WO}_3/\text{ZrO}_2 \) obtained by impregnating crystallized \( \text{ZrO}_2 \) is monoclinic, but in \( \text{WO}_3/\text{ZrO}_2 \) obtained by impregnating \( \text{Zr(OH)}_4 \) it is metastable tetragonal provided that \( \text{WO}_3 \) content is high enough.
WO₃ in WO₃/ZrO₂ exists on the surface of ZrO₂ as a monolayer phase no matter whether ZrO₂ or Zr(OH)₄ is used in the impregnation process, and its dispersion threshold is in agreement with the theoretical close-packed monolayer dispersion capacity.

Some kind of chemical binding is formed between Zr(OH)₄ (or tetragonal ZrO₂) and WO₃ at high temperature. This might be responsible for the superacidity of the sample prepared by impregnating Zr(OH)₄ and then calcining it at 800 °C.

Acknowledgement

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REFERENCES