Preparation and Characterization of Tungsten Oxide-Zirconia Catalyst

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Abstract: Tungsten oxide-zirconia catalysts were prepared by drying of powdered Zr(OH)$_4$ with ammonium metatungstate aqueous solution followed by calcining in air at high temperature. The characterization of prepared catalysts was performed using Fourier transform infrared (FTIR), Raman, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and Differential scanning calorimetry (DSC), and by the measurement of surface area. The addition of tungsten oxide up to 20 wt % to zirconia shifted the phase transition of ZrO$_2$ from amorphous to tetragonal to higher temperature due to the interaction between tungsten oxide and zirconia, and the specific surface area and acidity of catalysts increased in proportion to the tungsten oxide content. Since the ZrO$_2$ stabilizes supported tungsten oxide, for the samples equal to or less than 5 wt % tungsten oxide was well dispersed on the surface of zirconia, but for the samples containing 13 wt % or above 13 wt % the triclinic phase of WO$_3$ was observed at any calcination temperature. Upon the addition of only small amount of tungsten oxide (1 wt % WO$_3$) to ZrO$_2$, both the acidity and acid strength of catalyst increased remarkably, showing the presence of Brönsted and Lewis acid sites on the surface of WO$_3$/ZrO$_2$. The high acid strength and large amount of acidity were responsible for the W=O bond nature of complex formed by the interaction between WO$_3$ and ZrO$_2$.

1. Introduction

Supported metal oxides exhibit interesting catalytic behavior depending on the kind of support, the content of active component, and the preparation method [1,2]. Supported tungsten oxide catalysts are used for hydrotreating and for alkene metathesis reactions because of their solid acid properties [3,4] and they are active for the skeletal isomerization of butene [5] and the selective catalytic reduction of nitric oxide with ammonia [6,7]. Much research has been done to understand the nature of active sites and the surface structure of catalysts, as well as the role played by the promoter of the supported catalysts, using IR, ESR, NMR, and Raman spectroscopy [5,8-11]. So far, however, they have been studied mainly on alumina and silica [4,12-15], and only a small amount of work was studied for the ZrO$_2$ support [16,17]. Zirconia is an important material due to its interesting thermal and mechanical properties and so has been investigated as a support and catalysts in recent years. Different papers have been devoted to the studies of ZrO$_2$ catalytic activity in the important reactions such as methanol and hydrocarbon syntheses from CO and H$_2$ from CO$_2$ and H$_2$ [18,19], or from alcohol dehydration [20,21]. Zirconia has been extensively used as a support for metals or incorporated in supports to stabilize them or make them more resistant to sintering [22-24]. ZrO$_2$ activity and selectivity highly depend on the methods of preparation and treatment used. In particular, in the previous papers from this laboratory,
it has been shown that NiO-ZrO₂ and ZrO₂ modified with sulfate ion, and Cr₂O₃-ZrO₂ are very active for acid-catalyzed reactions [25-27]. The high catalytic activities in the above reactions were attributed to the enhanced acidic properties of the modified catalysts, which originate from the inductive effect of S=O or Cr=O bonds of the complexes formed by the interaction of oxides with the sulfate or chromate ions.

It is well known that the dispersion, the oxidation state, and the structural features of supported species may strongly depend on the support. Structure and physicochemical properties of supported metal oxides are considered to be different compared with bulk metal oxides because of their interaction with supports. This paper describes the preparation and characterization of tungsten oxide supported on zirconia. The characterization of the samples was performed by means of Fourier transform infrared (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectra (XPS), Raman, Differential scanning calorimetry (DSC), and by the measurement of surface area.

2. Experimental

2.1. Catalyst Preparation

The precipitate of Zr(OH)₄ was obtained by adding aqueous ammonia slowly into an aqueous solution of zirconium oxychloride at room temperature with stirring until the pH of mother liquor reached about 8. The precipitate thus obtained was washed thoroughly with distilled water until chloride ion was not detected, and was dried at room temperature for 12 h. The dried precipitate was powdered below 100 mesh.

The catalysts containing various tungsten oxide contents were prepared by adding an aqueous solution of ammonium metatungstate [(NH₄)₆(H₂W₁₄O₄₃)nH₂O] to the Zr(OH)₄ powder followed by drying and calcining at high temperatures for 1.5 h in air. This series of catalysts are denoted by their weight percentage of WO₃ and calcination temperature. For example, 10-WO₃/ZrO₂(973) indicates the catalyst containing 10 wt % WO₃ and calcined at 973 K.

2.2. Characterization

FTIR spectra were obtained in a heated gas cell at room temperature using Mattson Model GL6030E spectrophotometer. The self-supporting catalyst wafers contained about 9 mg/cm². Prior to obtaining the spectra the samples were heated under vacuum at 673-773 K for 1.5 h.

The Raman spectra were recorded on a Spex Ramalog spectrometer with holographic gratings.

5145-A line from a Spectra-Physics Model 165 argon-ion laser was used as the exciting source. The spectral shift width was typically 4 cm⁻¹, and laser source powers of approximately 45 mW, measured at the sample, were used.

X-ray photoelectron spectra was obtained with a VG scientific model ESCALAB MK-11 spectrometer. Al Kα and Mg Kα were used as the excitation source, usually at 12 kV, 20 mA. The analysis chamber was at 10⁻⁴ torr or better and the spectra of sample, as fine powder, were analyzed. Binding energies were referenced to the C₁s level of the adventitious carbon at 285.0 eV.

Catalysts were checked in order to determine the structure of the support as well as that of tungsten oxide by means of a Jeol Model JDX-8030 diffractometer, employing Cu Kα (Ni-filtered) radiation.

DSC measurements were performed by a PL-STA model 1500H apparatus in air, and the heating rate was 5 K per minute. For each experiment 10~15 mg of sample was used.

The specific surface area was determined by applying the BET method to the adsorption of N₂ at 77 K. Chemisorption of ammonia was also employed as a measure of the acidity of catalysts. The amount of chemisorption was determined on the basis of irreversible adsorption of ammonia [28,29].

3. Results and Discussion

3.1. Raman and Infrared Spectra

The Raman spectra of WO₃ obtained by calcining ammonium metatungstate at 773 K, 5-WO₃/ZrO₂(973), and 13-WO₃/ZrO₂(973) under ambient conditions are presented in Figure 1. The WO₃ structure is made up of distorted WO₃ octahedra. The major vibrational modes of WO₃ are located at 810, 714, and 276 cm⁻¹, and have been assigned to the W=O stretching mode, the W=O bending mode, and the W-O-W deformation mode, respectively [30]. The Raman spectrum of the 5-WO₃/ZrO₂(973) sample shows a weak and broad band at ~945 cm⁻¹ which is characteristic of tetrahedrally coordinated surface tungsten oxide species [31]. This assignment is in agreement with the WO₃/γ-Al₂O₃ system where combined Raman and XANES data revealed the presence of distorted tetrahedral coordination at low loading [10]. In addition to this 945 cm⁻¹ band, the feature of zirconia at 637, 620, 506, 478, 383, 348, 335, 181, and 180 cm⁻¹ is also present [32].

The molecular structures of the supported tungsten oxide species are also found to depend on the loading. As the loading is increased, the W=O stretching modes shifts upward to 965 cm⁻¹.
cm$^{-1}$ band in the Raman spectrum of the 13-WO$_3$/ZrO$_2$ sample is assigned to the octahedrally coordinated polytungstate species [31]. The shift from 945 cm$^{-1}$ for 5-WO$_3$/ZrO$_2$ to 965 cm$^{-1}$ for 13-WO$_3$/ZrO$_2$ is in agreement with reported Raman spectra [31], and suggest that under ambient conditions different two-dimensional tungsten oxide species may be present in the WO$_3$/ZrO$_2$ samples. At 13% loading three bands also appear in the Raman spectrum at 808, 711, and 276 cm$^{-1}$, showing the presence of crystalline WO$_3$ [33] in addition to the two-dimensional tungsten oxide species (band at 965 cm$^{-1}$). These results are in good agreement with those of XRD in Figures 5 and 6. That is, for 5-WO$_3$/ZrO$_2$ sample the crystalline WO$_3$ phase was not observed, while for 13-WO$_3$/ZrO$_2$ sample the triclinic phase of crystalline WO$_3$ appeared at the calcination temperature of 673-1373 K. It seems likely that for 13-WO$_3$/ZrO$_2$ monolayer coverage has been exceeded and WO$_3$ crystals are also present on the ZrO$_2$ surface.

Raman spectra above were recorded under ambient conditions. To examine the structure of tungsten oxide complex under dehydration conditions, IR spectra of WO$_3$/ZrO$_2$ samples were obtained in a heatable gas cell after evacuation at different temperature for 1 h. The in situ IR spectra for 20-WO$_3$/ZrO$_2$(1023) are presented for the range 1100-900 cm$^{-1}$ in Figure 2(a). The IR single band at 1003-1012 cm$^{-1}$ is due to the symmetrical W=O stretching mode of the tungsten oxide complex coordinated to the ZrO$_2$ surface. As shown in Figure 2, as evacuation temperature increases, the W=O stretching mode shifts upward from 1003 to 1012 cm$^{-1}$, the band shape becomes sharper, and the intensity increases. The same results have been obtained at the other samples. This shows that the dehydration changes the molecular structures and that the two-dimensional tetrahedrally coordinated tungsten oxide species as well as the octahedrally coordinated polytungstate species are converted into the same highly distorted octahedrally coordinated structure as proposed for the WO$_3$/TiO$_2$ system by Wachs and coworkers [31]. The 1012 cm$^{-1}$ IR band matches the Raman absorption at 1015 cm$^{-1}$ [31]. For the WO$_3$/ZrO$_2$ samples evacuated at 673 K, as shown in Figure 3, the band intensity at 1012 cm$^{-1}$ increases with increasing the WO$_3$ content, indicating that the higher the WO$_3$ content, the more the octahedrally coordinated WO$_3$ species.

3.2. Crystalline Structures of Catalysts
The crystalline structures of WO$_3$/ZrO$_2$ calcined in air at different temperatures for 1.5 h were examined.
As shown in Figure 4, ZrO$_2$ was amorphous to X-ray diffraction up to 573 K, with two-phase mixture of the tetragonal and monoclinic forms at 623-873 K, and a monoclinic phase at 973 K. Three crystal structures of ZrO$_2$: tetragonal, monoclinic and cubic phases have been reported [34,35].

However, in the case of supported tungsten oxide catalysts the crystalline structures of samples were different from that of support, ZrO$_2$. For the 5-WO$_3$/ZrO$_2$ as shown in Figure 5, ZrO$_2$ is amorphous up to 623 K. In other words, the transition temperature from the amorphous to tetragonal phase was higher by 50 K than that of pure ZrO$_2$. X-ray diffraction data indicated a two-phase mixture of the tetragonal and monoclinic ZrO$_2$ forms at 673-1073 K, and monoclinic ZrO$_2$ form, at 1173 K. It is assumed that the interaction between tungsten oxide and ZrO$_2$ hinders the transition of ZrO$_2$ from amorphous to tetragonal phase [27,36]. The presence of tungsten oxide strongly influences the development of textural properties with temperature in comparison with pure ZrO$_2$. No phase of tungsten oxide was observed up to 5 wt % at any calcination temperature, indicating a good dispersion of tungsten oxide on the surface of ZrO$_2$ support due to the interaction between them. Moreover, for the sample of 13-WO$_3$/ZrO$_2$, the transition temperature from the amorphous to tetragonal phase was higher by 100 K than that of pure ZrO$_2$. That is, the more the content of tungsten oxide, the higher the phase transition temperature. As shown in Figure 6, for 13-WO$_3$/ZrO$_2$, ZrO$_2$ was amorphous to X-ray diffraction up to 673 K, with a tetragonal phase of ZrO$_2$ at 773 K, a two-phase mixture of the tetragonal and monoclinic ZrO$_2$ forms at 873-1273 K, and monoclinic ZrO$_2$ forms at 1373 K. However, triclinic phase of crystalline WO$_3$ due to the decomposition of ammonium metatungstate was observed in the samples calcined at 673-1373 K.

It is also of interest to examine the influence of tungsten oxide on the transition temperature of ZrO$_2$ from tetragonal to monoclinic phase. In view of X-ray diffraction patterns, the calcination temperatures at which monoclinic phase is observed initially are 623 K for pure ZrO$_2$, 673 K for 5-WO$_3$/ZrO$_2$, 873 K for 13-WO$_3$/ZrO$_2$, respectively. That is, the transition temperature increases with increasing tungsten oxide.
content. Similarly, the calcination temperatures at which only monoclinic phase without tetragonal phase is observed are 973 K for pure ZrO$_2$, 1173 K for 5-WO$_3$/ZrO$_2$, and 1373 K for 13-WO$_3$/ZrO$_2$ respectively. This can be also explained in terms of the delay of transition from tetragonal to monoclinic phase due to the interaction between tungsten oxide and zirconia, in analogy with the delay of transition from amorphous to tetragonal phase described above.

### 3.3. X-ray photoelectron Spectra

Interactions with a support can dramatically change the properties of metals or metal oxides [37]. Figure 7 shows the W 4f spectra of WO$_3$/ZrO$_2$ samples containing different tungsten oxide content and calcined at 973 K. The W 4f$_{7/2}$ binding energy measured for WO$_3$/ZrO$_2$ samples occurred at 36 eV and corresponds to tungsten in the +6 oxidation state (WO$_3$) [38]. The peak at 31.0 eV is characteristic of metallic W [38], indicating the reduction of WO$_3$ during the calcination of precursor for WO$_3$/ZrO$_2$. The results of quantitative analysis for the tungsten oxidation state are listed in Table 1. It is known that there is a very strong interaction between WO$_3$ and Al$_2$O$_3$ so that tungsten oxide species is present as W$^{6+}$ after calcination of WO$_3$/Al$_2$O$_3$ sample. However, for WO$_3$/ZrO$_2$ samples calcined in air, 4f peak due to metallic W in addition to 4f peak due to W$^{6+}$ appears as shown in Figure 7. The difference between WO$_3$/Al$_2$O$_3$ and WO$_3$/ZrO$_2$ seems to be due to the different interaction with supports, Al$_2$O$_3$ and ZrO$_2$. 

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Figure 5. X-ray diffraction patterns of 5-WO$_3$/ZrO$_2$ calcined at different temperatures for 1.5 h: ○, tetragonal phase ZrO$_2$; ●, monoclinic phase ZrO$_2$.

Figure 6. X-ray diffraction patterns of 13-WO$_3$/ZrO$_2$ calcined at different temperatures for 1.5 h: ○, tetragonal phase ZrO$_2$; ●, monoclinic phase ZrO$_2$; ×, triclinic phase WO$_3$. 

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Figure 7. W4f XPS of WO₃/ZrO₂ (973) having different WO₃ contents: (a) 2-WO₃/ZrO₂ (973), (b) 7-WO₃/ZrO₂ (973), (c) 15-WO₃/ZrO₂ (973), and (d) 25-WO₃/ZrO₂ (973).

Table 1. The Relative Amount of W(VI) and W(O) Species for Some Sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relative amount(%)</th>
<th>W(VI)</th>
<th>W(O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-WO₃/ZrO₂ (973)</td>
<td>31.3</td>
<td>68.7</td>
<td></td>
</tr>
<tr>
<td>7-WO₃/ZrO₂ (973)</td>
<td>49.7</td>
<td>50.3</td>
<td></td>
</tr>
<tr>
<td>15-WO₃/ZrO₂ (973)</td>
<td>906</td>
<td>9.2</td>
<td></td>
</tr>
<tr>
<td>25-WO₃/ZrO₂ (973)</td>
<td>69.8</td>
<td>30.2</td>
<td></td>
</tr>
<tr>
<td>15-WO₃/ZrO₂ (773)</td>
<td>93.3</td>
<td>6.7</td>
<td></td>
</tr>
<tr>
<td>15-WO₃/ZrO₂ (1173)</td>
<td>76.3</td>
<td>23.7</td>
<td></td>
</tr>
</tbody>
</table>

In view of Figure 6 and Table 1, the concentration of W(VI) increases with the total tungsten oxide content up to 15 wt %, but for 25-WO₃/ZrO₂ that of W(VI) would rather decreases. For 25-WO₃/ZrO₂, it seems likely that above monolayer coverage crystalline WO₃ exists on the surface of ZrO₂ and can be reduced to metallic W during calcination [31]. The reduction of 15-WO₃/ZrO₂ sample was examined as a function of calcination temperature, and the W 4f spectra are presented in Figure 8. As the calcination temperature increases, the concentration of metallic W increases due to the easy reduction of WO₃ (Table 1). X-ray photoelectron spectroscopy analysis reveals that the reduction of bulk WO₃(W⁵⁺) to metallic tungsten(W⁰) proceeds through intermediate tungsten oxidation states of +5, +4, and +2 [38]. As shown in Figures 7 and 8, however, WO₃/ZrO₂ samples, unlike bulk WO₃, does not exhibit XPS observable intermediate tungsten oxidation states (W⁶⁺, W⁴⁺, and W²⁺) upon calcination, as in the case of the tungsten oxide monolayer supported on alumina. This is thought to be a consequence of the different reaction mechanism from the case of bulk WO₃.

3.4. Thermal Analysis

In X-ray diffraction pattern, it was shown that the structure of WO₃/ZrO₂ was different depending on the calcined temperature. To examine the thermal properties for the precursors of samples more clearly, their thermal analysis was carried out. For pure ZrO₂ the DSC curve showed a broad endothermic peak below 453 K due to water elimination, and a
Table 2. Phase Transition Temperature of ZrO₂ from Amorphous to Tetragonal for Some Precursors of WO₃/ZrO₂ by DSC.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO₂</td>
<td>703</td>
</tr>
<tr>
<td>1-WO₃/ZrO₂</td>
<td>713</td>
</tr>
<tr>
<td>5-WO₃/ZrO₂</td>
<td>719</td>
</tr>
<tr>
<td>10-WO₃/ZrO₂</td>
<td>722</td>
</tr>
<tr>
<td>15-WO₃/ZrO₂</td>
<td>725</td>
</tr>
<tr>
<td>20-WO₃/ZrO₂</td>
<td>727</td>
</tr>
<tr>
<td>25-WO₃/ZrO₂</td>
<td>727</td>
</tr>
<tr>
<td>30-WO₃/ZrO₂</td>
<td>727</td>
</tr>
</tbody>
</table>

A sharp and exothermic peak at 702 K due to the ZrO₂ crystallization [39]. In the case of WO₃/ZrO₂, two additional endothermic peaks appeared at 323 K and 573 K due to the evolution of NH₃ and H₂O decomposed from ammonium metatungstate. However, it is of interest to see the influence of WO₃ on the crystallization of ZrO₂ from amorphous to tetragonal phase. As listed in Table 2, the exothermic peak due to the crystallization of ZrO₂ appeared at 702 K for pure ZrO₂, while for WO₃/ZrO₂ it was shifted to higher temperatures. The shift increased with increasing WO₃ content up to 20 wt % of WO₃. It is considered that the interaction between WO₃ and ZrO₂ retards the transition of ZrO₂ from amorphous to tetragonal phase [27,36]. These results are in agreement with those of X-ray diffraction patterns described above.

3.5. Surface Properties

It is necessary to examine the effect of tungsten oxide on the surface properties of catalysts, that is, specific surface area, acidity, and acid strength. The specific surface areas of samples calcined at 773 K for 1.5 h are plotted as a function of tungsten oxide content in Figure 9. The presence of tungsten oxide strongly influences the surface area in comparison with the pure ZrO₂. Specific surface areas of WO₃/ZrO₂ samples are much larger than that of pure ZrO₂ calcined at the same temperature, showing that surface area increases gradually with increasing tungsten oxide content up to 20 wt % of WO₃. It seems likely that the interaction between tungsten oxide and ZrO₂ protects catalysts from sintering. The dependence of ant sintering effect on tungsten oxide content is clear from Figure 9.

In addition to tungsten oxide content, calcination temperature influences the surface area value. When pure ZrO₂ and some WO₃/ZrO₂ samples are subjected to calcining in air at a given temperature, the results obtained are plotted in Figure 10 as a function of calcination temperature. The antisintering effect of tungsten oxide is greater at lower calcination temperature than at higher temperature. As illustrated in Figure 10, the difference of surface area between pure ZrO₂ and WO₃/ZrO₂ calcined at 1173 K is very small compared with the cases of samples calcined at lower temperatures.

The acid strength of the catalysts was examined by a color change method, using Hammett indicator [40] in sulphuryl chloride. The results are listed in
Table 3. Acid Strength of Some Samples

<table>
<thead>
<tr>
<th>Hammett Indicator</th>
<th>pKa</th>
<th>ZrO₂</th>
<th>2-WO₃/ZrO₂(973)</th>
<th>5-WO₃/ZrO₂(973)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzeneazodiphenylamine</td>
<td>+1.5</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Dicinnamalacetone</td>
<td>-3.0</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Benzalacetophenone</td>
<td>-5.6</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Anthraquinone</td>
<td>-8.2</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>-12.4</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>2,4-Dinitrofluorobenzene</td>
<td>-14.5</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

Figure 11. Acidity of WO₃/ZrO₂(773) against tungsten oxide content.

Table 3. In this table, (+) indicates that the color of the base form was changed to that of the conjugated acid form. ZrO₂ evacuated at 673 K for 1 h has an acid strength H₀≤ +1.5, while 2-WO₃/ZrO₂ and 5-WO₃/ZrO₂ were estimated to have a H₀≤ -14.5, indicating the formation of new acid sites stronger than those of single oxide components. Acids stronger than H₀≤ -11.93, which corresponds to the acid strength of 100% H₂SO₄, are superacids [41]. Consequently, WO₃/ZrO₂ catalysts would be solid superacids. The superacidic property is attributed to the double bond nature of the W=O in the complex formed by the interaction of ZrO₂ with tungstate, in analogy with the case of ZrO₂ modified with chromate and sulfate ion [25-27].

The acidity of catalysts calcined at 773 K, as determined by the amount of NH₃ irreversibly adsorbed at 503 K [28], is plotted as a function of the tungsten oxide content in Figure 11. Although pure ZrO₂ showed the acidity of 0.05 mmol/g, 1-WO₃/ZrO₂ resulted in a remarkable increase in acidity (0.12 mmol/g). As shown in Figure 11, the acidity increases abruptly upon the addition of 1 wt % tungsten oxide to ZrO₂ and then the acidity increases very gently with increasing tungsten oxide content up to 20 wt % of WO₃. In view of Figures 9 and 11, it seems likely that the acidity of WO₃/ZrO₂ samples is correlated to the surface area of samples. Many combinations of two oxides have been reported to generate acid sites on the surface [42,43].

To obtain further information on the generation of acid cites, IR spectral change for the W=O stretching vibration of 20-WO₃/ZrO₂(1023) treated under various conditions at 673 K for 1 h: (a) after evacuation, (b) after reduction of sample (a) with 70 torr of CO, (c) after reduction of sample (a) with 170 torr of CO, and (d) after oxidation of sample (c) with 70 torr of O₂.

Figure 12. IR spectral change for the W=O stretching vibration of 20-WO₃/ZrO₂(1023) treated under various conditions at 673 K for 1 h: (a) after evacuation, (b) after reduction of sample (a) with 70 torr of CO, (c) after reduction of sample (a) with 170 torr of CO, and (d) after oxidation of sample (c) with 70 torr of O₂.
Figure 13. IR spectra of pyridine adsorbed on (a) 2-WO₃/ZrO₂(973), (b) 7-WO₃/ZrO₂(973), (c) 15-WO₃/ZrO₂(973), and (d) 20-WO₃/ZrO₂(973). Gas phase was evacuated at 523 K for 1 h after adsorption.

appeared at 1012 cm⁻¹. However after reduction at 647 K with 70 torr of CO for 1 h the band intensity decreased because W(VI) species was reduced by CO treatment, and the band position shifted downward. Moreover, after reduction with 170 torr of CO the intensity decreased further and the position shifted to 1003 cm⁻¹ [Figure 12(c)]. When the sample(c) was oxidized with 70 torr of O₂ at 647 K for 1 h, the band intensity and position were recovered originally, as shown in Figure 12(d). We also measured the acidity of above samples treated under various conditions. For original 20-WO₃/ZrO₂ sample(a) the acidity was estimated to be 1.62 mmol/g, while for the sample(c) after reduction with 170 torr of CO the acidity was 0.86 mmol/g, indicating the large decrease of acidity. However, when sample(c) was oxidized with 70 torr of O₂ at 647 K for 1 h, the acidity of oxidized sample(d) was nearly recovered and was found to be 1.58 mmol/g. Therefore, it is very clear that there is a good correlation between the acidity of WO₃/ZrO₂ samples and the band intensity of W=O stretching vibration mode at 1012 cm⁻¹. That is, the higher the band intensity of W=O stretching vibration mode at 1012 cm⁻¹, the more the acidity of the sample. The high acid strength and large amount of acidity for WO₃/ZrO₂ catalysts are responsible for the W=O bond nature of complex formed by the interaction between ZrO₂ and WO₃.

Infrared spectroscopic studies of pyridine adsorbed on solid surfaces have made it possible to distinguish between Brønsted and Lewis acid sites [44]. Figure 13 shows the IR spectra of pyridine adsorbed on some WO₃/ZrO₂ samples evacuated at 673 K for 1 h. For WO₃/ZrO₂ the bands at 1543 are the characteristic peaks of pyridinium ion, which are formed on the Brønsted acid sites and the absorption peaks at 1444 cm⁻¹ are contributed by pyridine coordinately bonded to Lewis acid sites [45], indicating the presence of both Brønsted and Lewis acid sites on the surface of WO₃/ZrO₂ samples. As shown in Figure 13, the peak intensity increases with increasing tungsten oxide content, meaning that acidity increases with increasing tungsten content. This result is in good agreement with that of acidity determined by NH₃ adsorption in Figure 11.

4. Conclusions

This paper has shown that a combination of FTIR, Raman, DSC, and XRD can be used to perform the characterization of WO₃/ZrO₂ prepared by drying a mixed solution of ammonium metatungstate and Zr(OH)₄ and calcining in air. The interaction between tungsten oxide and zirconia influence the physicochemical properties of prepared catalysts with calcination temperature. The presence of tungsten oxide delays the phase transitions from amorphous to tetragonal and from tetragonal to monoclinic. The specific surface area and acidity of catalysts increase in proportion to the tungsten oxide content up to 20 wt %. Since the ZrO₂ stabilizes supported tungsten oxide, for the samples equal to or less than 5 wt % tungsten oxide was well dispersed on the surface of zirconia, but for the samples containing 13 wt % or above 13 wt % the triclinic phase of WO₃ was observed at any calcination temperature. Upon the addition of only a small amount of tungsten oxide (1 wt %) to zirconia, both the acidity and acid strength of the catalyst increases remarkably, showing the presence of Brønsted and Lewis acid sites on the surface of WO₃/ZrO₂. The acidity for the WO₃/ZrO₂ is correlated to the intensity of W=O stretching vibration band appearing at 1012 cm⁻¹ in IR spectrum. The high acid strength and large amount of acidity are responsible for the W=O bond nature of complex formed by the interaction between WO₃ and ZrO₂.
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References