

## Infrared and Raman Characterization of V<sub>2</sub>O<sub>5</sub> on Zirconia Modified with WO<sub>3</sub> and Activity for Acid Catalysis

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**Abstract**—Vanadium oxide supported on zirconia modified with WO<sub>3</sub> was prepared by adding Zr(OH)<sub>4</sub> powder into a mixed aqueous solution of ammonium metavanadate and ammonium metatungstate followed by drying and calcining at high temperatures. The characterization of prepared catalysts was performed by using FTIR, Raman, and XRD. In the case of calcination temperature at 773 K, for samples containing low loading V<sub>2</sub>O<sub>5</sub> below 18 wt%, vanadium oxide was in a highly dispersed state, while for samples containing high loading V<sub>2</sub>O<sub>5</sub> equal to or above 18 wt%, vanadium oxide was well crystallized due to the high V<sub>2</sub>O<sub>5</sub> loading on the surface of ZrO<sub>2</sub>. The ZrV<sub>2</sub>O<sub>7</sub> compound was formed through the reaction of V<sub>2</sub>O<sub>5</sub> and ZrO<sub>2</sub> at 873 K, and the compound decomposed into V<sub>2</sub>O<sub>5</sub> and ZrO<sub>2</sub> at 1,073 K, these results were confirmed by FTIR and XRD. Catalytic tests for 2-propanol dehydration and cumene dealkylation have shown that the addition of WO<sub>3</sub> to V<sub>2</sub>O<sub>5</sub>/ZrO<sub>2</sub> enhanced both catalytic activity and acidity of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/ZrO<sub>2</sub> catalysts. The variations in catalytic activities for both reactions are roughly correlated with the changes of acidity.

Key words: V<sub>2</sub>O<sub>5</sub> on ZrO<sub>2</sub>, FTIR and Raman, Acid Catalysis, 2-Propanol Dehydration, Cumene Dealkylation

### INTRODUCTION

Vanadium oxides are widely used as catalysts in oxidation reactions, e.g., the oxidation of sulfur dioxide, carbon monoxide, and hydrocarbons [Miyata et al., 1989; Lakshmi et al., 1999; Sachtler, 1971]. These systems have also been found to be effective catalysts for the oxidation of methanol to methylformate [Busca et al., 1987] and for the selective catalytic reduction of nitrogen oxide [Armor, 1992; Alemany et al., 1995]. Much research has been done to understand the nature of active sites, the surface structure of catalysts as well as the role played by the promoter of the supported catalysts, using infrared (IR), X-ray diffraction (XRD), electron spin resonance (ESR) and Raman spectroscopy [Busca et al., 1987; Elmi et al., 1989; Miyata et al., 1987; Cavani et al., 1988]. So far, silica, titania, zirconia and alumina [Hatayama et al., 1991; Arco et al., 1990; Centi et al., 1991; Scharf et al., 1991; Sohn et al., 1996] have been commonly employed as the vanadium oxide supports.

Recently, metal oxides modified with sulfur compounds have been studied as strong solid acid catalysts [Ward and Ko, 1994; Kustov et al., 1994], especially sulfate promoted zirconia containing iron or manganese as promoters [Hsu et al., 1992; Wan et al., 1996] or noble metals to inhibit deactivation [Iglesia et al., 1993; Ebitani et al., 1991]. The high catalytic activity and small deactivation upon the addition of noble metals can be explained by both the elimination of coke by hydrogenation and hydrogenolysis [Vaudagna et al., 1997], and the formation of Brønsted acid sites from H<sub>2</sub> on the catalysts [Ebitani et al., 1991]. Recently, several workers reported

zirconia-supported tungsten oxide as an alternative material in reactions requiring strong acid sites [Sohn and Bae, 2000; Barton et al., 1999; Scheithauer et al., 1998; Arata, 1990; Hino and Arata, 1987]. Several advantages of tungstate, over sulfate, as dopant include that it does not suffer from dopant loss during thermal treatment and it undergoes significantly less deactivation during catalytic reactions [Larsen et al., 1996]. However, comparatively few studies have been reported on binary oxide, vanadium oxide-tungsten oxide supported on zirconia. This paper describes Infrared and Raman characterization of V<sub>2</sub>O<sub>5</sub> supported on zirconia and modified with WO<sub>3</sub>, and catalytic activity for acid catalysis. For this purpose, the 2-propanol dehydration and cumene dealkylation are used as test reactions.

### EXPERIMENTAL SECTION

#### 1. Catalysts Preparation

Precipitate of Zr(OH)<sub>4</sub> was obtained by adding aqueous ammonia slowly into an aqueous solution of zirconium oxychloride (Aldrich) at room temperature with stirring until the pH of the mother liquor reached about 8. The precipitate thus obtained was washed thoroughly with distilled water until chloride ion was not detected by AgNO<sub>3</sub> solution, and was dried at room temperature for 12 h. The dried precipitate was powdered below 100 mesh.

Catalysts containing various vanadium oxide content and modified with WO<sub>3</sub> were prepared by adding Zr(OH)<sub>4</sub> powder into a mixed aqueous solution of ammonium metavanadate (NH<sub>4</sub>VO<sub>3</sub>) (Aldrich) and ammonium metatungstate [(NH<sub>4</sub>)<sub>6</sub>(H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>)·nH<sub>2</sub>O] (Aldrich) followed by drying and calcining at high temperatures for 1.5 h. This series of catalysts were denoted by their weight percentage of V<sub>2</sub>O<sub>5</sub> and WO<sub>3</sub> and calcination temperature. For example, 4V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub>(773) indicated the catalyst containing 4 wt% V<sub>2</sub>O<sub>5</sub>

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<sup>‡</sup>This paper is dedicated to Professor Baik-Hyon Ha on the occasion of his retirement from Hanyang University.

and 15 wt% WO<sub>3</sub> calcined at 773 K.

## 2. Procedure

2-Propanol dehydration was carried out at 433 and 453 K in a pulse microreactor connected to a gas chromatograph. Fresh catalyst in the reactor made of 1/4 in. stainless steel was pretreated at 673 K for 1 h in the nitrogen atmosphere. Pulses of 1  $\mu$ l 2-propanol were injected into a N<sub>2</sub> gas stream which passed over 0.05 g of catalyst. Packing material for the gas chromatograph was Diethyleneglycol succinate on Shimalite and column temperature was 423 K. Catalytic activity for 2-propanol dehydration was represented as mole of propylene produced per gram of catalyst. Conversion was taken as the average of the first to sixth pulse values. Cumene dealkylation was carried out at 673-723 K in the same reactor as above. Packing material for the gas chromatograph was Benton 34 on chromosorb W and column temperature was 403 K. Catalytic activity for cumene dealkylation was represented as mole of benzene produced from cumene per gram of catalyst. Conversions for both reactions were taken as the average of the first to sixth pulse values.

FTIR absorption spectra of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/ZrO<sub>2</sub> powders were measured by KBr disk method over the range 1,200-400 cm<sup>-1</sup>. The samples for the KBr disk method were prepared by grinding a mixture of the catalyst and KBr powders in an agate mortar and pressing them in the usual way, where the ratio of KBr to catalysts was 20. FTIR spectra of ammonia adsorbed on the catalyst were obtained in a heatable gas cell at room temperature with a Mattson Model GL 6030E spectrophotometer. The self-supporting catalyst wafers contained about 9 mg/cm<sup>2</sup>. Prior to obtaining the spectra the samples were heated under vacuum at 673-773 K for 1.5 h.

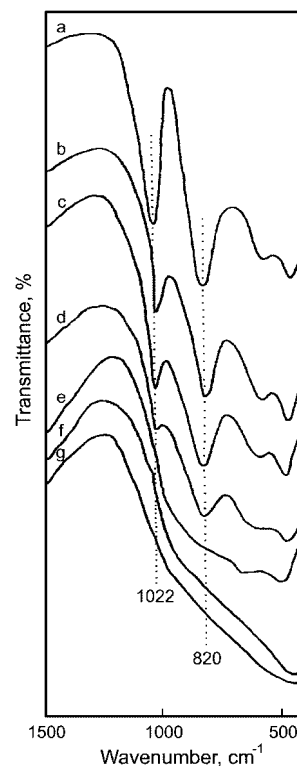
The FT-Raman spectra were obtained with a Bruker model FRA 106 A spectrometer equipped with an InGaAs detector and a Nd:YAG laser source with a resolution of 4 cm<sup>-1</sup>. The laser beam was focused onto an area 0.1 $\times$ 0.1 mm<sup>2</sup> in size of the sample surface; a 180 $^\circ$  scattering geometry was used.

Catalysts were checked in order to determine the structure by means of a Joel Model JDX-8030 diffractometer, employing CuK $\alpha$  (Ni-filtered) radiation. The specific surface area was determined by applying the BET method to the adsorption of N<sub>2</sub> at 77 K.

## RESULTS AND DISCUSSION

### 1. Infrared and Raman Spectra

Fig. 1 shows IR spectra of V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> (773) catalysts with various V<sub>2</sub>O<sub>5</sub> contents calcined at 773 K for 1.5 h. Although with samples below 18 wt% of V<sub>2</sub>O<sub>5</sub>, definite peaks were not observed, the absorption bands at 1,022 and 820 cm<sup>-1</sup> appeared for 18V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub>, 23V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub>, 28V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> and pure V<sub>2</sub>O<sub>5</sub> containing high V<sub>2</sub>O<sub>5</sub> content. The band at 1,022 cm<sup>-1</sup> was assigned to the V=O stretching vibration, while that at 820 cm<sup>-1</sup> was attributable to the coupled vibration between V=O and to V-O-V [Mori et al., 1987]. Generally, the IR band of V=O in crystalline V<sub>2</sub>O<sub>5</sub> showed at 1,020-1,025 cm<sup>-1</sup> and the Raman band at 995 cm<sup>-1</sup> [Miyata et al., 1989; Bjorklund et al., 1989]. The decrease in crystallinity of V<sub>2</sub>O<sub>5</sub>, i.e., the formation of the amorphous phase for V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/ZrO<sub>2</sub> of a low vanadium loading, is attributed to formation of the vanadate species dispersed on ZrO<sub>2</sub> in a monolayer; this results in the distortion of the structure, i.e., a weakening of the V=O bond.

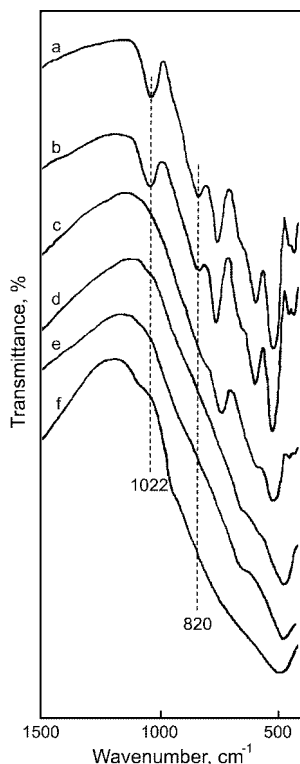


**Fig. 1. Infrared spectra of catalysts calcined at 773 K: (a) V<sub>2</sub>O<sub>5</sub>, (b) 28V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub>, (c) 23V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub>, (d) 18V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub>, (e) 12V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub>, (f) 8V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub>, and (g) 4V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub>.**

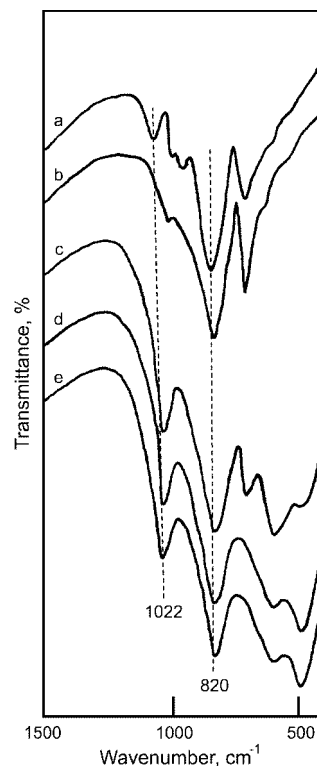
Consequently, the distorted structure brings about a shift of the band due to the V=O stretching vibration from 1,022 cm<sup>-1</sup> to lower wave number [Miyata et al., 1987]. Roozeboom et al. [Roozeboom et al., 1980] have investigated the V<sub>2</sub>O<sub>5</sub> species supported on various supporters by Raman spectroscopy and temperature-programmed reduction; they concluded that the band at 970 cm<sup>-1</sup> is due to surface vanadate species present as a two-dimensional monolayer.

The intensity of the V=O absorption gradually decreased with decreasing V<sub>2</sub>O<sub>5</sub> content, although the band position did not change. As shown in Fig. 1, the catalysts at vanadia loadings below 18 wt% gave no absorption bands due to crystalline V<sub>2</sub>O<sub>5</sub>. This observation suggests that vanadium oxide below 18 wt% is in a highly dispersed state. It was reported that high V<sub>2</sub>O<sub>5</sub> loading on the surface of zirconia is well crystallized and observed in the spectra of IR and solid state <sup>51</sup>V NMR [Sohn et al., 1996].

As shown in Fig. 1, for 4V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> and 12V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> calcined at 773 K the crystalline V<sub>2</sub>O<sub>5</sub> was not observed in their IR spectra, suggesting the high dispersion of V<sub>2</sub>O<sub>5</sub> on the surface of zirconia as the amorphous phase. However, it is necessary to examine the formation of crystalline V<sub>2</sub>O<sub>5</sub> as a function of calcination temperature. Variation of IR spectra against calcination temperature for 4V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> is shown in Fig. 2. There were no V=O stretching bands at 1,022 cm<sup>-1</sup> from 673 to 973 K of the calcination temperature, indicating no formation of crystalline V<sub>2</sub>O<sub>5</sub>. However, as shown in Fig. 2, V=O stretching bands due to crystalline V<sub>2</sub>O<sub>5</sub> at 1,073 and 1,173 K appeared at 1,022 cm<sup>-1</sup> together with lattice vibration bands of V<sub>2</sub>O<sub>5</sub> and WO<sub>3</sub> below 900 cm<sup>-1</sup> [Park et al., 2000; Highfield and Moffat, 1984]. The formation of crystal-



**Fig. 2.** Infrared spectra of  $4V_2O_5-15WO_3/ZrO_2$  calcined at (a) 1,173 K, (b) 1,073 K, (c) 973 K, (d) 873 K, (e) 773 K, and (f) 673 K.

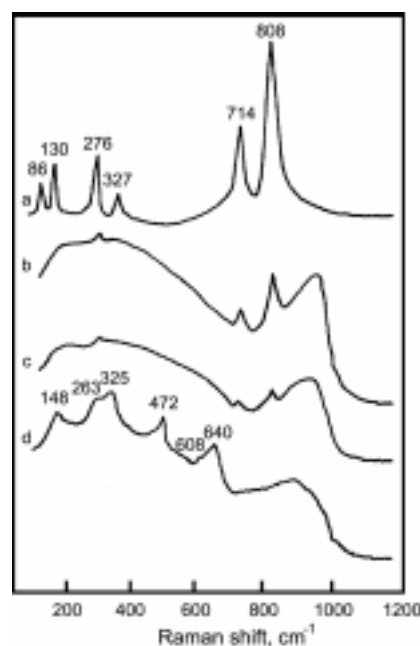


**Fig. 3.** Infrared spectra of  $28V_2O_5-15WO_3/ZrO_2$  calcined at (a) 1,073 K, (b) 973 K, (c) 873 K, (d) 773 K, and (e) 673 K.

line  $V_2O_5$  at above 1,073 K can be explained in terms of the decomposition of  $ZrV_2O_7$  compound which was formed through the reaction of  $V_2O_5$  and  $ZrO_2$  at 873-973 K. In this study, on X-ray diffraction patterns described later, the cubic phase of  $ZrV_2O_7$  was observed in the samples calcined at 873 K and for sample calcined at 1,173 K the  $ZrV_2O_7$  phase disappeared due to the decomposition of  $ZrV_2O_7$ , leaving the  $V_2O_5$  phase and the monoclinic phase of  $ZrO_2$ . In fact, it is known that the formation of  $ZrV_2O_7$  from  $V_2O_5$  and  $ZrO_2$  occurs at 873 K of calcination temperature and the  $ZrV_2O_7$  decomposes into  $ZrO_2$  and  $V_2O_5$  at 1,073 K [Sohn et al., 1996; Roozeboom et al., 1980]. In separate experiments, variation of IR spectra against calcination temperature for  $12V_2O_5-15WO_3/ZrO_2$  (not shown in the Figure) was similar to that for  $4V_2O_5-15WO_3/ZrO_2$  as shown in Fig. 2.

Fig. 3 shows IR spectra of  $28V_2O_5-15WO_3/ZrO_2$  catalysts calcined at 673-1,073 K for 1.5 h. Unlike  $4V_2O_5-15WO_3/ZrO_2$  and  $12V_2O_5-15WO_3/ZrO_2$  catalysts, for  $28V_2O_5-15WO_3/ZrO_2$  crystalline  $V_2O_5$  appeared at a lower calcination temperature from 673 K to 873 K, and consequently V=O stretching band was observed at  $1,022\text{ cm}^{-1}$ . This is because high  $V_2O_5$  loading on the surface of  $ZrO_2$  is well crystallized [Sohn et al., 1996]. However, at 973 K all  $V_2O_5$  reacted with  $ZrO_2$  and changed into  $ZrV_2O_7$  so that V=O stretching at  $1,022\text{ cm}^{-1}$  disappeared completely, as shown in Fig. 3. At 1,073 K of calcination temperature some of the  $ZrV_2O_7$  decomposed into  $V_2O_5$  and  $ZrO_2$  and then V=O stretching band due to the crystalline  $V_2O_5$  was again observed at  $1,022\text{ cm}^{-1}$ .

Raman spectroscopy is a valuable tool for the characterization of dispersed metal oxides and detects vibrational modes of surface and bulk structures. In order to analyze the nature of the surface



**Fig. 4.** Raman spectra of (a)  $WO_3$ , (b)  $4V_2O_5-20WO_3/ZrO_2$  (773), (c)  $4V_2O_5-10WO_3/ZrO_2$  (773), and (d)  $4V_2O_5-5WO_3/ZrO_2$  (773).

species, laser Raman measurements of bulk  $WO_3$  and  $V_2O_5-WO_3/ZrO_2$  samples calcined at 773 K were made. Fig. 4 shows spectra of bulk  $WO_3$  and  $4V_2O_5-WO_3/ZrO_2$  (773) samples with different  $WO_3$  loadings under ambient condition. The  $WO_3$  structure is made up of distorted  $WO_3$  octahedra. Bulk  $WO_3$ , obtained by calcining am-

monium metatungstate at 773 K, shows the main bands in good agreement with data previously reported [Salvati et al., 1981; Sohn and Park, 1998]. The major vibrational modes of WO<sub>3</sub> are located at 808, 714, and 276 cm<sup>-1</sup>, and have been assigned to the W-O stretching mode, the W-O bending mode, and the W-O-W deformation mode, respectively [Chan et al., 1984]. Zhao et al. have observed the formation of WO<sub>3</sub> crystallites only when the monolayer capacity of WO<sub>3</sub> on zirconia has been exceeded [Zhao et al., 1996]. In this work the tungsten oxide exceeding the monolayer capacity of the zirconia support forms crystalline WO<sub>3</sub> under ambient conditions at elevated temperature. The crystalline WO<sub>3</sub> was also observed in the XRD patterns described below. So, as shown in Fig. 4(d), for 4V<sub>2</sub>O<sub>5</sub>-5WO<sub>3</sub>/ZrO<sub>2</sub> (773) no bands corresponding to WO<sub>3</sub> crystallites appear, indicating that WO<sub>3</sub> is in a highly dispersed state. In view of Fig. 4, a monolayer capacity for WO<sub>3</sub> seems to be between 5 and 10 wt%. As described in IR spectra, the catalysts at vanadia loadings below 18 wt% gave no absorption bands due to crystalline V<sub>2</sub>O<sub>5</sub>. As shown in Fig. 4, for the samples containing 4% V<sub>2</sub>O<sub>5</sub> no bands due to V<sub>2</sub>O<sub>5</sub> crystalline were observed, showing good agreement with the results of IR spectra.

The molecular structure of the supported tungsten oxide species depends on the loading. Several authors observed that the nature of surface tungsten species on Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and ZrO<sub>2</sub> depends on the amount of WO<sub>3</sub>. For low tungsten loading there appear tetrahedrally coordinated tungsten oxide species; for high tungsten loading octahedral polymeric WO<sub>3</sub> species appear in addition to the tetrahedral ones [Sohn and Park, 1998; Engweiler et al., 1996; Vaudagna et al., 1998]. As shown in Fig. 4, at low tungsten loading tetrahedrally coordinated tungsten oxide species (at ~935 cm<sup>-1</sup>) are predominantly formed, while with increased loading polytungstate species with an octahedral environment become predominant (at 965-985 cm<sup>-1</sup>). The frequency of Raman features (1,000-940 cm<sup>-1</sup>), the maximum of which shifts slightly upwards on increasing vanadium content, is assigned to the V=O stretching mode of vanadyl species in a hydrated form [Alemany et al., 1995; Ramis et al., 1990]. Therefore, the broad band observed in the 930-990 cm<sup>-1</sup> region in Fig. 4 will be interpreted as an overlap of three characteristic bands (two tungsten oxide species and one vanadyl species). Tetragonal zirconia is expected to yield a spectrum consisting of six Raman bands with frequencies at about 148, 263, 325, 472, 608 and 640 cm<sup>-1</sup>, while monoclinic zirconia exhibits the characteristic features at 180, 188, 221, 380, 476, and 637 cm<sup>-1</sup> [Mercera et al., 1990; Scheithauer et al., 1998]. Therefore, as shown in Fig. 4(d), 4V<sub>2</sub>O<sub>5</sub>-5WO<sub>3</sub>/ZrO<sub>2</sub> sample exhibits the characteristic features of tetragonal zirconia, indicating no transformation of ZrO<sub>2</sub> from tetragonal to monoclinic. For high tungsten loading samples calcined at 773 K in Fig. 4(b and c), zirconia is amorphous to X-ray diffraction described below. The Raman spectrum of amorphous zirconia is characterized by a very weak and broad band at 550-600 cm<sup>-1</sup> [Schild et al., 1991]. Therefore, the Raman band of amorphous zirconia in Figs. 4 and 5 is not well observed by overlapping of other bands.

We will discuss the Raman spectra of the series of V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> (773) samples containing different V<sub>2</sub>O<sub>5</sub> loadings, which are shown in Fig. 5. For both samples, 22V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> and 18V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> the spectra displayed bands at 144, 196, 284, 304, 406, 484, 528, 702 and 996 cm<sup>-1</sup> all of which are characteristic of crystalline V<sub>2</sub>O<sub>5</sub> [Dines et al., 1991]. These results are in good

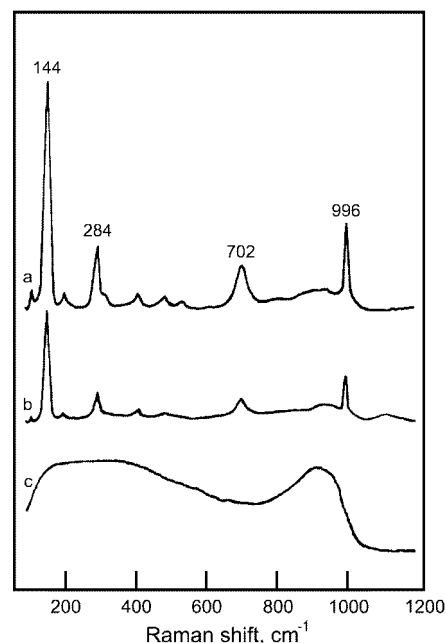


Fig. 5. Raman spectra of (a) 22V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> (773), (b) 18V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> (773), and (c) 8V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> (773).

agreement with those of the IR mentioned above. The 996 cm<sup>-1</sup> band is assigned to the vibration of the short vanadium oxygen bond normally regarded as a V=O species [Dines et al., 1991]. However, for 8V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> containing low V<sub>2</sub>O<sub>5</sub> loading, no bands due to crystalline V<sub>2</sub>O<sub>5</sub> are observed, indicating high dispersion of V<sub>2</sub>O<sub>5</sub> on the ZrO<sub>2</sub> surface. A broad band containing a maximum at 940 cm<sup>-1</sup> is associated with the overlap of three characteristic bands by two tungsten oxide species and one vanadyl species discussed above.

The IR spectra in Figs. 1-3 have been taken in contact with air and KBr pressed disks. The Raman spectra in Figs. 4 and 5 have been taken in air by using the sample powders. To examine the structure of metal oxides supported on ZrO<sub>2</sub> under dehydration conditions, IR spectra of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/ZrO<sub>2</sub> samples (self-supporting wafers) were obtained in a heatable gas cell after evacuation at 773 K for 1.5 h. The IR spectra for 4V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> and 18V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub>(773) are presented for the range, 1,200-800 cm<sup>-1</sup> in Fig. 6. For 4V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> and 18V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> samples, the IR band at 1,012 cm<sup>-1</sup> after evacuation at 773 K is due to the W=O stretching mode of the tungsten oxide complex bonded to the ZrO<sub>2</sub> surface [Sohn and Park, 1998; Barton et al., 1999]. As shown in Fig. 6, these W=O bands due to wolframyl species only appear on evacuated samples, being undetectable on wet samples. This can be rationalized by assuming that the adsorption of water causes a strong perturbation of the corresponding tungsten oxide species, with a consequent strong broadening and shift down of these bands which become almost undetectable [Gutierrez-Alejandre et al., 1998]. The IR band at 1,012 cm<sup>-1</sup> matches the Raman absorption at 1,015 cm<sup>-1</sup> [Vuurman et al., 1991]. However, the band at 1,015 cm<sup>-1</sup> in Figs. 4 and 5 was not observed because Raman spectra were recorded under ambient conditions. These isolated tungsten oxide species are stabilized through multiple W-O-Zr bonds between each tungsten oxide species and the zirconia surface [Scheithauer et al., 1998; Barton et al., 1999]. Zhao et al. observed, in the Raman spec-

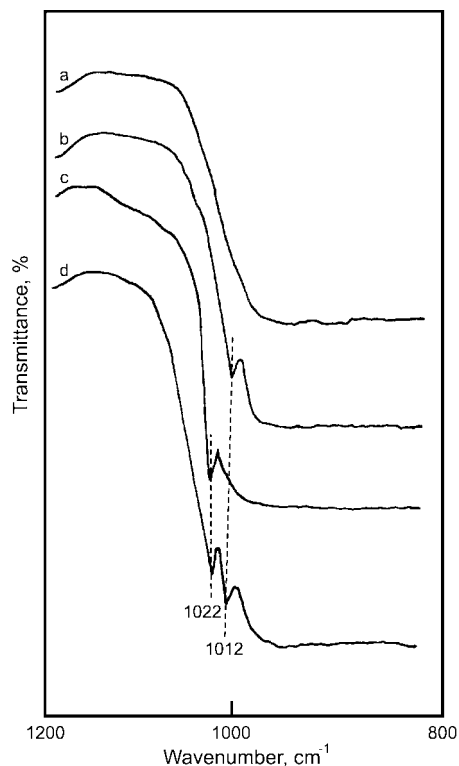


Fig. 6. IR spectra of 4V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> evacuated at (a) 298 K and (b) 773 K, and of 18V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> evacuated at (c) 298 K and (d) 773 K.

trum of WO<sub>x</sub>-ZrO<sub>2</sub>, a band at 580 cm<sup>-1</sup>, assigned to a W-O-Zr species [Zhao et al., 1996]. Upon dehydration at elevated temperature, the hydrated surface metal oxide species are unstable and decompose to form dehydrated surface metal oxide species by direct interaction with the surface OH groups of support, giving the formation of metal-oxygen-support bond [Kim et al., 1996].

For 18V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> sample the band at 1,022 cm<sup>-1</sup> is due to the V=O stretching vibration of crystalline V<sub>2</sub>O<sub>5</sub> as mentioned above, because V<sub>2</sub>O<sub>5</sub> loading exceeding the formation of monolayer on the surface of ZrO<sub>2</sub> is well crystallized [Sohn et al., 1996]. Therefore, with 4V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> the definite peak due to the crystalline V<sub>2</sub>O<sub>5</sub> is undetectable, explaining that vanadium oxide loading below 18 wt% is in a highly dispersed state.

## 2. Crystalline Structure of Catalyst

The crystalline structures of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/ZrO<sub>2</sub> calcined in air at different temperatures for 1.5 h were examined. For the 4V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> as shown in Fig. 7, ZrO<sub>2</sub> is amorphous to X-ray diffraction up to 673 K, with a tetragonal phase of ZrO<sub>2</sub> at 773-873 K, a two-phase mixture of the tetragonal and monoclinic ZrO<sub>2</sub> forms at 973 K, and a monoclinic phase of ZrO<sub>2</sub> at 1,073-1,173 K. Three crystal structures of ZrO<sub>2</sub>, tetragonal, monoclinic and cubic phases have been reported [Larsen et al., 1997; Afansiev et al., 1994].

On the other hand, V<sub>2</sub>O<sub>5</sub> for 4V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> and 12V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> is amorphous to X-ray diffraction up to 773 K, indicating that vanadium oxide is in a highly dispersed state and showing a good agreement with the results of IR in Fig. 1. In separate XRD experiments, the cubic phase of ZrV<sub>2</sub>O<sub>7</sub> began to be observed in the sample of 12V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> calcined at 873 K and the

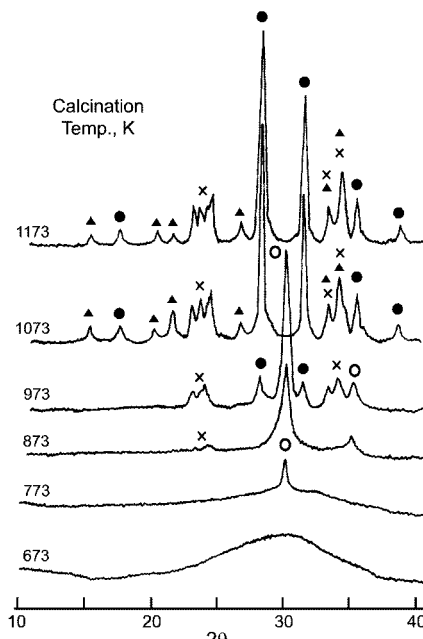


Fig. 7. X-ray diffraction patterns of 4V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> calcined at different temperatures. ○, tetragonal phase ZrO<sub>2</sub>; ●, monoclinic phase ZrO<sub>2</sub>; ▲, V<sub>2</sub>O<sub>5</sub>; ×, WO<sub>3</sub>.

peak intensities of ZrV<sub>2</sub>O<sub>7</sub> increased to some extent at 973 K (not shown in the Fig.). However, for samples calcined at 1,073-1,173 K the ZrV<sub>2</sub>O<sub>7</sub> phase disappeared due to the complete decomposition of ZrV<sub>2</sub>O<sub>7</sub> [Roozeboom et al., 1980], leaving only the crystalline V<sub>2</sub>O<sub>5</sub> phase and the monoclinic phase of ZrO<sub>2</sub>. The triclinic phase of crystalline WO<sub>3</sub> due to the decomposition of ammonium metatungstate was observed in the samples calcined at 873-1,173 K.

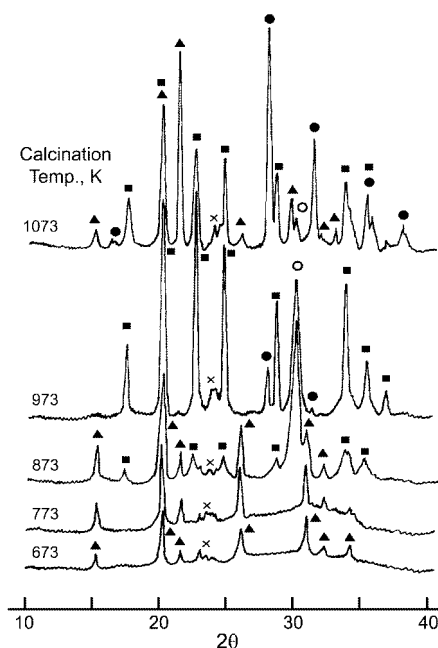


Fig. 8. X-ray diffraction patterns of 28V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> calcined at different temperatures. ○, tetragonal phase ZrO<sub>2</sub>; ●, monoclinic phase ZrO<sub>2</sub>; ▲, V<sub>2</sub>O<sub>5</sub>; ■, ZrV<sub>2</sub>O<sub>7</sub>; ×, WO<sub>3</sub>.

However, as shown in Fig. 7, for the sample of 4V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> the crystalline ZrV<sub>2</sub>O<sub>7</sub> on X-ray diffraction pattern was not observed at 873 K of calcination temperature. This indicates that for 4V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub>, the ZrV<sub>2</sub>O<sub>7</sub> crystallites formed are less than 4 nm in size, that is, beyond the detection capability of the XRD technique [Sohn et al., 1996].

As shown in Fig. 8, in the case of 28V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> containing high content of V<sub>2</sub>O<sub>5</sub> the crystalline V<sub>2</sub>O<sub>5</sub> phase was observed even at 673 K of low calcination temperature, indicating that high V<sub>2</sub>O<sub>5</sub> loading on the surface of ZrO<sub>2</sub> is well crystallized [Sohn et al., 1996]. These results are in good agreement with that of IR in Fig. 3 described above. From 873 K of calcination temperature V<sub>2</sub>O<sub>5</sub> began to react with ZrO<sub>2</sub> to form ZrV<sub>2</sub>O<sub>7</sub> compound and at 973 K the crystalline V<sub>2</sub>O<sub>5</sub> phase disappeared completely, due to the consumption of V<sub>2</sub>O<sub>5</sub> for the formation of ZrV<sub>2</sub>O<sub>7</sub> compound. However, at 1,073 K, the crystalline V<sub>2</sub>O<sub>5</sub> phase was observed again through the decomposition of ZrV<sub>2</sub>O<sub>7</sub> compound [Sohn et al., 1996], as shown in Fig. 8. For 28V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> ZrO<sub>2</sub> was amorphous to X-ray diffraction up to 773 K, with a tetragonal phase of ZrO<sub>2</sub> at 873 K, and a two-phase mixture of the tetragonal and monoclinic forms at 973-1,073 K. From 673 K of calcination temperature the crystalline WO<sub>3</sub> phase was observed due to the decomposition of ammonium metatungstate.

### 3. Surface Properties

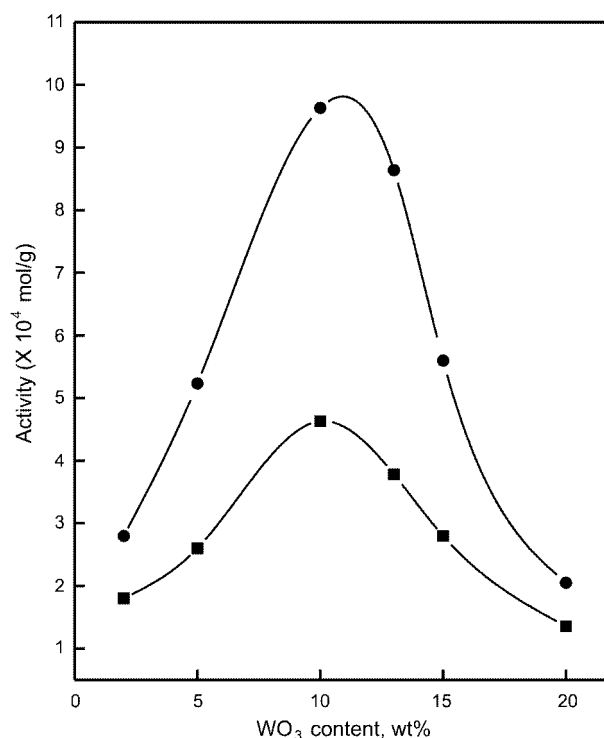
The specific surface areas of some samples calcined at 673 and 773 K for 1.5 h are listed in Table 1. The presence of vanadium oxide and tungsten oxide influences the surface area in comparison with the pure ZrO<sub>2</sub>. Specific surface areas of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/ZrO<sub>2</sub> samples are larger than that of pure ZrO<sub>2</sub> calcined at the same temperature. It seems likely that the interaction between vanadium oxide (or tungsten oxide) and ZrO<sub>2</sub> protects catalysts from sintering [Sohn et al., 1996].

Infrared spectroscopic studies of ammonia adsorbed on solid surfaces have made it possible to distinguish between Brønsted and Lewis acid sites [Sohn et al., 2002; Larrubia et al., 2000]. The IR spectra of ammonia adsorbed on 4V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> calcined at 973 K and evacuated at 673 K for 1 h indicated the presence of both Brønsted and Lewis acid sites. Other samples having different vanadium content also showed the presence of both Lewis and Brøn-

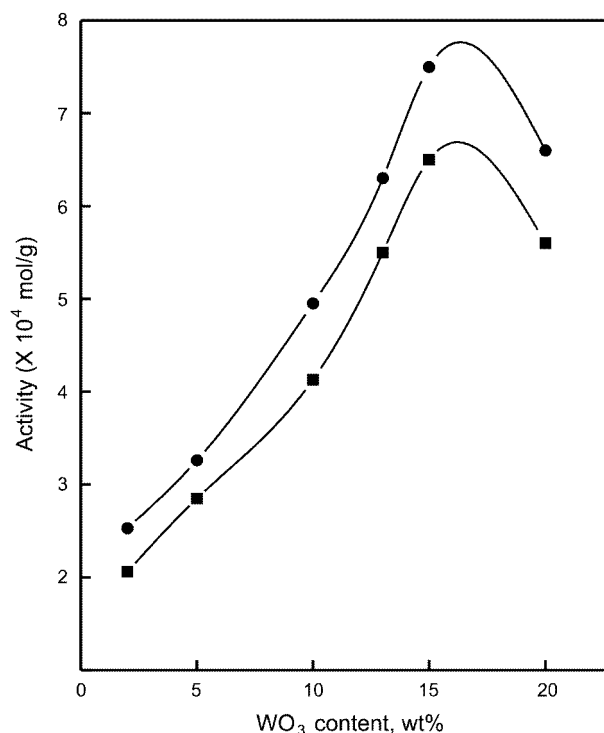
**Table 1. Specific surface areas of some V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/ZrO<sub>2</sub> samples calcined at 673 K and 773 K**

Catalysts	Surface area (m <sup>2</sup> /g, 673 K)	Surface area (m <sup>2</sup> /g, 773 K)
ZrO <sub>2</sub>	185	122
0.4V <sub>2</sub> O <sub>5</sub> -15WO <sub>3</sub> /ZrO <sub>2</sub>	235	207
1V <sub>2</sub> O <sub>5</sub> -15WO <sub>3</sub> /ZrO <sub>2</sub>	239	211
4V <sub>2</sub> O <sub>5</sub> -5WO <sub>3</sub> /ZrO <sub>2</sub>	238	198
4V <sub>2</sub> O <sub>5</sub> -10WO <sub>3</sub> /ZrO <sub>2</sub>	246	212
4V <sub>2</sub> O <sub>5</sub> -15WO <sub>3</sub> /ZrO <sub>2</sub>	224	201
4V <sub>2</sub> O <sub>5</sub> -20WO <sub>3</sub> /ZrO <sub>2</sub>	218	196
8V <sub>2</sub> O <sub>5</sub> -15WO <sub>3</sub> /ZrO <sub>2</sub>	201	198
12V <sub>2</sub> O <sub>5</sub> -15WO <sub>3</sub> /ZrO <sub>2</sub>	217	188
18V <sub>2</sub> O <sub>5</sub> -15WO <sub>3</sub> /ZrO <sub>2</sub>	206	176
20V <sub>2</sub> O <sub>5</sub> -15WO <sub>3</sub> /ZrO <sub>2</sub>	171	149
28V <sub>2</sub> O <sub>5</sub> -15WO <sub>3</sub> /ZrO <sub>2</sub>	144	106

sted acids. Therefore, these V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/ZrO<sub>2</sub> samples can be used as catalysts for Lewis or Brønsted acid catalysis.



**Fig. 9. Catalytic activity of 4V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/ZrO<sub>2</sub> (1023) for 2-propanol dehydration as a function of WO<sub>3</sub> content. ●, 453 K; ■, 433 K.**



**Fig. 10. Catalytic activity of 4V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/ZrO<sub>2</sub> (1023) for cumene dealkylation as a function of WO<sub>3</sub> content. ●, 723 K; ■, 673 K.**

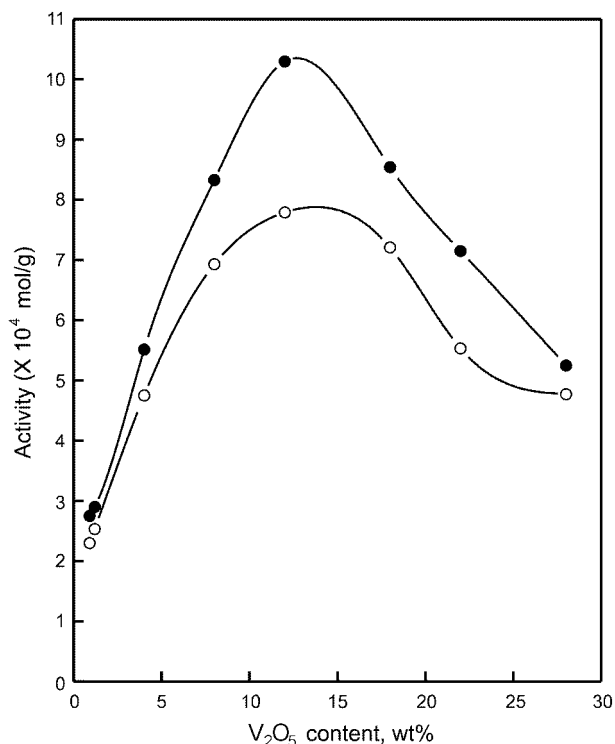
**Table 2. Acidity of  $4V_2O_5$ - $WO_3$ / $ZrO_2$  (1023) containing different  $WO_3$  contents**

Catalysts	Acidity ( $\mu\text{mol/g}$ )
$4V_2O_5$ - $2WO_3$ / $ZrO_2$	26.3
$4V_2O_5$ - $5WO_3$ / $ZrO_2$	31.7
$4V_2O_5$ - $10WO_3$ / $ZrO_2$	40.2
$4V_2O_5$ - $13WO_3$ / $ZrO_2$	27.1
$4V_2O_5$ - $15WO_3$ / $ZrO_2$	24.9
$4V_2O_5$ - $20WO_3$ / $ZrO_2$	18.8

#### 4. Catalytic Activities for Acid Catalysis

It is also interesting to examine how the catalytic activity of an acid catalyst depends on its acidic properties [Lee and Rhee, 1997; Yuan et al., 2002]. The catalytic activities for the 2-propanol dehydration and cumene dealkylation are measured and the results are illustrated as a function of  $WO_3$  content in Figs. 9 and 10, respectively. The addition of  $WO_3$  to  $4V_2O_5$ / $ZrO_2$  up to 10-15 wt% caused the increases in the catalytic activities for both reactions. The increases of catalytic activities for both reactions are due to the increase of acidic sites. In separate experiments, the acidity of the catalysts, as determined by the amount of  $NH_3$  irreversibly adsorbed at 503 K [Sohn et al., 1996; Sohn and Park, 1998], increased with the addition of  $WO_3$  to  $4V_2O_5$ / $ZrO_2$ , as listed in Table 2. In view of Table 2 and Figs. 9 and 10, the variations in catalytic activities for both reactions are roughly correlated with the changes of acidity. The differences of catalytic activities for both reactions against acidity are due to the difference of necessary acid strength for both reactions to occur. In fact, it has been known that 2-propanol dehydration takes place very readily on weak acid sites, while cumene dealkylation does on relatively strong acid sites [DeCanio et al., 1986]. In view of the catalytic data shown in Figs. 9 and 10 for 2-propanol dehydration and cumene dealkylation reactions, where the reaction temperatures were 433-453 K for the former and 673-723 K for the latter, it is clear that 2-propanol dehydration takes place more readily than cumene dealkylation. Recently, Toda et al. reported that the addition of  $WO_3$  to  $V_2O_5$  series catalysts led to an increase of the number of both Lewis and Brønsted acidic sites [Toda et al., 1999]. From the IR results of  $V=O$  bands they also reported that the majority of  $WO_3$  incorporated onto the  $V_2O_5$ / $ZrO_2$  catalysts seems to be intercalated between vanadia and zirconia [Toda et al., 1999]. It has been also reported that for  $V_2O_5$ - $WO_3$ / $TiO_2$  catalyst the electronic interaction between V and W oxides surface species may occur through oxygen bridging of the polyhedra and/or through the conduction band of  $TiO_2$  [Alemony et al., 1995]. The former possibility is consistent with the formation of mixed  $W_xV_yO_z$  species and with the detection of relatively isolated  $VO^{2+}$  ions that are slightly different from those monitored over  $V_2O_5$ / $TiO_2$  by EPR.

Considering the correlation between acidity and catalytic activities for 2-propanol dehydration and cumene dealkylation, and the experimental results of other investigators [Alemony et al., 1995; Toda et al., 1999; Paganini et al., 1997], it is suggested that the increase of acidic sites and their strength may be attributable to electronic and structural interaction between vanadium oxide and tungsten oxide species on the  $ZrO_2$  surface. Evidence for the existence of interaction between vanadium oxide and tungsten oxide species has also been provided by acidic catalytic tests for 2-propanol de-



**Fig. 11. Catalytic activity of  $V_2O_5$ - $15WO_3$ / $ZrO_2$  (1023) for 2-propanol dehydration and cumene dealkylation as a function of  $V_2O_5$  content. ●, 453 K for 2-propanol dehydration; ○, 673 K for cumene dealkylation.**

hydration and cumene dealkylation. The catalytic tests for both reactions have shown that the addition of  $WO_3$  to  $V_2O_5$ / $ZrO_2$  enhanced both catalytic activity (Figs. 9 and 10) and acidity of  $V_2O_5$ - $WO_3$ / $ZrO_2$  catalysts.

The catalytic activities of  $V_2O_5$ - $15WO_3$ / $ZrO_2$  for the 2-propanol dehydration and cumene dealkylation are measured and the results are illustrated as a function of  $V_2O_5$  content in Fig. 11, where reaction temperatures are 453 K for the 2-propanol dehydration and 673 K for the cumene dealkylation. The catalytic activities for both reactions increased with the  $V_2O_5$  content, giving maxima at 12% of  $V_2O_5$ , and then the activities decreased. We measured the acidity of  $V_2O_5$ - $15WO_3$ / $ZrO_2$  as a function of  $V_2O_5$  content. However, the variations in catalytic activities for both reactions were not correlated with the changes of acidity. Therefore, it is concluded that the increased catalytic activities up to 12% of  $V_2O_5$  are not because of the increased acidity. This result may be attributed to the fact that for  $V_2O_5$ - $15WO_3$ / $ZrO_2$  catalysts vanadium oxide up to 12 wt% is in a highly dispersed state or that the electronic interaction between V and W oxides species may occur through the intercalation of  $WO_3$  between vanadia and zirconia [Toda et al., 1999; Alemony et al., 1995].

Catalytic activities of  $4V_2O_5$ - $10WO_3$ / $ZrO_2$  are plotted as a function of calcination temperature for 2-propanol dehydration in Fig. 12. The activities increased with the calcination temperature, giving a maximum at 973 K and then the activities decreased. Catalytic activities of  $12V_2O_5$ - $15WO_3$ / $ZrO_2$  for cumene dealkylation are also plotted as a function of calcination temperature in Fig. 13. The activities also exhibited a maximum at 1,023 K. The decrease of activi-

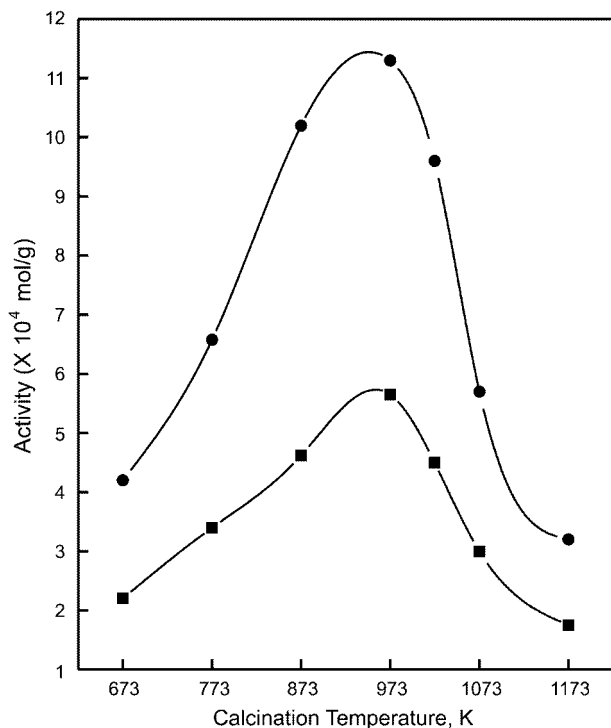


Fig. 12. Catalytic activity of 4V<sub>2</sub>O<sub>5</sub>-10WO<sub>3</sub>/ZrO<sub>2</sub> for 2-propanol dehydration as a function of calcination temperature. ●, 453 K; ■, 433 K.

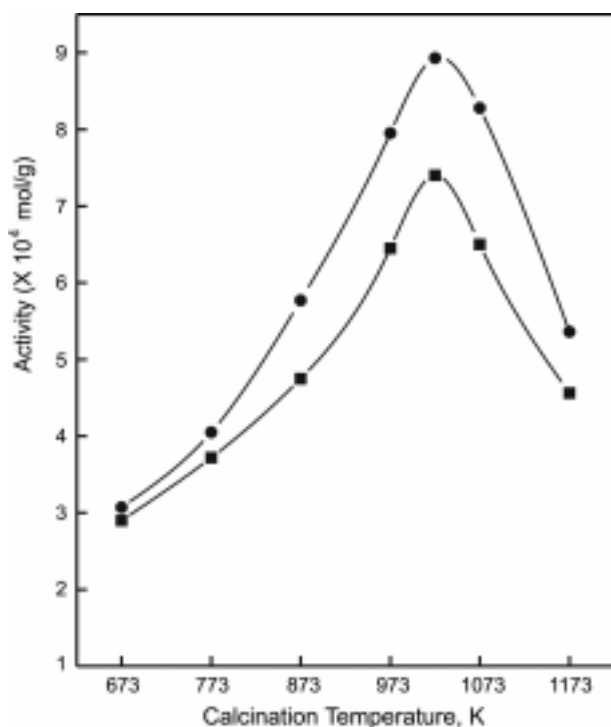


Fig. 13. Catalytic activity of 12V<sub>2</sub>O<sub>5</sub>-15WO<sub>3</sub>/ZrO<sub>2</sub> for cumene dealkylation as a function of calcination temperature. ●, 723 K; ■, 673 K.

ties for both reactions above 973-1,023 K can be probably attributed to the fact that the surface area and acidity above 973-1,023 K

decrease with the calcination temperature [Sohn and Park, 2002].

## CONCLUSIONS

On the basis of the results of FTIR, Raman and XRD, at low calcination temperature of 773 K vanadium oxide up to 12 wt% was well dispersed on the surface of zirconia. However, high V<sub>2</sub>O<sub>5</sub> loading (equal to or above 18 wt%) on the surface of zirconia was well crystallized. The ZrV<sub>2</sub>O<sub>7</sub> compound was formed through the reaction of V<sub>2</sub>O<sub>5</sub> and ZrO<sub>2</sub> at 873 K and the compound decomposed into V<sub>2</sub>O<sub>5</sub> and ZrO<sub>2</sub> at 1,073 K, which was observed in the spectra of FTIR and XRD. The W=O bands (1,012 cm<sup>-1</sup>) due to wolframyl species strongly suggests that they interact with the zirconia via W-O-Zr bonds. It is suggested that the increase of acidic sites and their acid strength may be attributable to electronic and structural interaction between vanadium oxide and tungsten oxide species on the ZrO<sub>2</sub> surface. The variations in catalytic activities for 2-propanol dehydration and cumene dealkylation are roughly correlated with the changes of acidity.

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