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Effect of WO_3 in mixed V_2O_5 - WO_3/ZrO_2 catalysts on their surface structures and decomposition of propan-2-ol

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Received 7th December 1998, Accepted 19th January 1999

 V_2O_5 -WO₃/ZrO₂ catalysts prepared by a two-step impregnation method have been studied by FTIR and laser-Raman spectrometry together with a pulse method. Addition of WO₃ to 2 wt.% V_2O_5 /ZrO₂ catalyst increased the activity of propan-2-ol decomposition and the selectivity for propene. On 5 wt.% V_2O_5 /ZrO₂ catalyst the activity was hardly affected but the selectivity for propene was increased by the additive. From the FTIR bands in the region of 1100–900 cm⁻¹, when WO₃ was added to V_2O_5 /ZrO₂ catalysts, the tungsten oxide species was well dispersed on the zirconia support and directly interacted with zirconia to form the bridging layer(s) between the support and vanadate species. Thus, the addition of WO₃ caused the reconstruction of the surface vanadate species. As a result, the surface acidity as well as the catalytic activity changed with the amount of WO₃.

Supported vanadium-containing catalysts are widely used as selective catalysts for the oxidation of various hydrocarbons and in the selective catalytic reduction (SCR) of nitrogen oxides (NOx).^{1,2} Although V₂O₅ is highly active for the SCR reaction, the commercial SCR catalysts contain mixed oxides of V₂O₅ with WO₃ as the major additive. The role of WO₃ is to provide thermal stability to the catalyst and to promote the SCR of NOx. Investigations on the reactivity, structural and physico-chemical characteristics of V₂O₅–WO₃/TiO₂ catalysts have been reported by many workers.^{3–10}

Vuurman *et al.*³ investigated the molecular structures of V_2O_5 -WO₃/TiO₂ mixed samples. They concluded that under dehydrating conditions, both the highly distorted vanadium oxide species and octahedrally coordinated tungsten oxide species are found on the titania surface at a metal oxide loading up to 10% and seem not to be influenced by one another. Paganini *et al.*⁴ reported that a mutual (structure and electronic) interaction exists between the V_2O_5 and WO₃ in the V_2O_5 -WO₃/TiO₂ system. Ramis and Busca⁵ concluded that addition of WO₃ has small effect on the ν (V=O) of V_2O_5 /TiO₂ catalysts. Thus, there are some contradictions about the effect of the WO₃ additive.

 TiO_2 has been widely used as a support in those studies. Interest has recently focused on zirconium oxide as a support because of its amphoteric properties and high thermal stability.^{11–13} Gazzoli *et al.*¹¹ studied the characterisation of the zirconia-supported tungsten oxide system and concluded that the difference in their structure, such as monomeric tungstate or polytungstates, is related not to the pH of the contacting solution but to the surface concentration of tungstate. Indovina¹² investigated the preparation and the characterisation of VO_x/ZrO_2 and reported that the pH of solutions used in the equilibrium adsorption did not affect the nature of surface vanadate species. We have previously studied the reduction of nitric oxide with ethylene over V_2O_5/ZrO_2 catalysts prepared from a gas phase method by using FTIR spectrometry.¹³ From a quantitative analysis of the V=O band in the region of 1100–900 cm⁻¹, it has been concluded that the surface V=O species in the top layer of the catalyst interact with adsorbed species. We have also characterised the difference of the surface V=O species between the monolayer and multi-layer catalysts. However, little work has been carried out on V_2O_5 -WO₃/ZrO₂ systems.

More recently, we have studied the acidic properties of V_2O_5 -WO₃/ZrO₂ catalysts using the adsorption of pyridine by FTIR.¹⁴ In 2 wt.% V_2O_5 /ZrO₂, the number of both Brønsted and Lewis acidic sites increased with the addition of WO₃, while in 5 wt.% V_2O_5 /ZrO₂, only Brønsted acidic sites increased and Lewis acidic sites did not change.

In the present work, the effects of the addition of WO₃ to V_2O_5/ZrO_2 catalysts have been investigated by using FTIR and laser-Raman techniques as well as by the analysis of decomposition products of propan-2-ol. Zirconia shows no IR absorption band above 900 cm⁻¹ which makes it possible to observe the surface species in the region of 1100–900 cm⁻¹ on the V_2O_5 -WO₃/ZrO₂ catalysts. Thus, the correlation between the surface structures of V_2O_5 -WO₃/ZrO₂ catalysts and the activity for propan-2-ol decomposition is discussed in detail.

Experimental

Catalysts preparation

The support used in this study was ZrO_2 (Nippon Shokubai Co., Ltd., 28 m² g⁻¹). The V_2O_5/ZrO_2 catalysts were prepared by a dry impregnation method. In the case of 2 wt.% V_2O_5/ZrO_2 catalyst, a small amount (0.525 g) of ammonium metavanadate was dissolved in 5 cm³ of 1 mol dm⁻³ oxalic acid solution. The solution was added a little at a time onto the powdered ZrO_2 (20.0 g) heated at *ca*. 373 K with stirring. Then the sample was dried at 383 K for 12 h and calcined at

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723 K for 5 h in air. The 5 wt.% V_2O_5/ZrO_2 sample was also prepared by a similar manner.

In the case of 2 wt.% WO_3/ZrO_2 catalysts, a small amount (0.580 g) of ammonium metatungstate was dissolved in 5 cm³ of distilled water. This solution was added dropwise onto the powdered ZrO_2 (20.0 g) heated at *ca.* 373 K with stirring. Then the sample was dried and calcined using the same conditions as mentioned above. The WO_3 content in the samples prepared was 2.0, 5.0 and 8.0 wt.%.

The V_2O_5 -WO₃/ZrO₂ catalysts were prepared by a twostep impregnation method. First the V_2O_5/ZrO_2 catalysts were prepared as described above. Then a small volume (5–10 cm³) of ammonium metatungstate solution was added dropwise onto 20.0 g of finely pulverised V_2O_5/ZrO_2 catalyst heated at 373 K with stirring. These catalysts were dried and calcined using the same conditions as mentioned above.

The catalysts are designated as VxWyZ, where x = vanadium oxide percentage (0, 2.0, 5.0 wt.%); and y = tungsten oxide percentage (0, 2.0, 5.0, 8.0 wt.%). The composition and BET surface area of catalysts are listed in Table 1 together with the number of acidic sites.¹⁴

Propan-2-ol decomposition

Decomposition of propan-2-ol was studied at 443 K by a pulse method, using helium as carrier gas. The catalysts (*ca.* 30 mg) were heated at 723 K for 30 min in a stream of oxygen (*ca.* 101 kPa), followed by heating at 723 K for 30 min in a stream of helium before the reaction. The propan-2-ol pulse (2 μ l) was injected only once and the amount of products were ascertained. The effluent gases were analysed with a Shimadzu GC-4BPT gas chromatograph (GC) with thermal conductivity detection and using a 3 m column of 15% PEG6000 at 333 K.

FTIR and laser-Raman studies

The apparatus used was a conventional closed-circulation system equipped with an IR cell in the circulation loop. A disc of catalyst (20 mm diameter, ca. 100 mg) was placed in the IR cell and the disc temperature was slowly increased from room temperature to 723 K under evacuation and kept at that temperature under oxygen circulation (ca. 10 kPa). This treatment was repeated several times in order to obtain the same surface states of the catalysts as those reported in the experiments of propan-2-ol decomposition.

Fourier-transform infrared (FTIR) spectra were recorded on a Shimadzu FTIR-8100M equipped with a DLATGS detector operating in a single beam mode at 2 cm^{-1} resolution in the region of 4000–400 cm⁻¹. Some spectra were obtained after subtraction of the catalyst itself by using a personal computer (COMPAQ PROLINEA 4/66) with data acquisition and analysis software (Shimadzu Hyper IR). X-Ray diffraction patterns of the catalysts were obtained on a Rigaku RINT 2000 diffractometer using CuKα radiation.

Results

Decomposition of propan-2-ol on V₂O₅-WO₃/ZrO₂

The decomposition of propan-2-ol has been examined at 443 K with a pulse method. The results obtained from the first pulse injection onto the catalysts are shown in Fig. 1. Propan-2-ol decomposes over catalysts to form mainly propene, acetone, water and a small amount of diisopropyl ether. On V2 series catalysts, the addition of WO₃ caused an increase in the amount of propene and a decrease of acetone. The C_3H_6/C_3H_6O ratio was 7.2 on V2W2Z and 1.9 on V2W0Z, respectively. This ratio increased slightly with increasing the tungsten oxide loading over V2 series catalysts.

On V5 series catalysts, the addition of WO₃ led to the increase of the C_3H_6/C_3H_6O ratio slightly while the total amount of products hardly changed. In the case of WO₃/ZrO₂ catalysts, V0W2Z catalyst showed a low catalytic activity, whereas V0W5Z or V0W8Z catalyst showed a high catalytic activity to propene alone.

The catalytic activity of V_2O_5 or WO_3 without the support was also examined in separate experiments. On bulk V_2O_5 , the ratio of C_3H_6/C_3H_6O was *ca*. 8.9 and a large amount of diisopropyl ether was formed, while on bulk WO_3 , mainly propene was formed together with a small amount of diisopropyl ether. Considering that V2 and V5 series catalysts have produced acetone, vanadia species play an important role in acetone formation in the decomposition of propan-2-ol.

It was noticed that the activity and selectivity for decomposition of propan-2-ol were more affected by the addition of WO_3 on V2 series catalysts.

FTIR spectra of propan-2-ol on V₂O₅-WO₃/ZrO₂ catalysts

A small amount of propan-2-ol was introduced onto the V_2O_5 -WO₃/ZrO₂ samples. The resulting spectra are shown in Figs. 2 and 3. The spectra below 1800 cm⁻¹ show the difference between the original and the catalyst itself.

Bands due to adsorbed isopropoxide are observed in the spectra of V2W0Z sample [Fig. 2A(a)]. A band at 1110 cm⁻¹ is assigned to v(C-O) of surface isopropoxide species interacted with Lewis acidic sites. The temperature of the catalyst was raised in stages under evacuation. The alkoxyl band reduced in intensity at 373 K [Fig. 2A(b)]. Simulta-

 $\label{eq:table_$

Catalyst	V ₂ O ₅ -WO ₃ /ZrO ₂		G (Acidic sites ^a /10 ¹⁷ m ⁻²	
	V ₂ O ₅ (%)	WO ₃ (%)	Surface area $/m^2 g^{-1}$	Lewis	Brønsted
V0W0Z	0	0	28	6.1	0.0
V0W2Z	0	2	29	10.0	0.7
V0W5Z	0	5	29	4.7	4.2
V0W8Z	0	8	26	5.9	4.9
V2W0Z	2	0	31	4.5	3.4
V2W2Z	2	2	30	5.3	5.4
V2W5Z	2	5	28	5.5	5.5
V2W8Z	2	8	29	4.7	4.6
V5W0Z	5	0	25	6.0	3.4
V5W2Z	5	2	27	4.8	5.1
V5W5Z	5	5	22	5.8	5.6
V5W8Z	5	8	25	5.3	4.9

^a After pyridine adsorption at room temperature followed by evacuation at 373 K for 30 min.¹⁴



neously, new bands due to acetone coordinated on Lewisacidic sites appeared at 1676 and 1252 cm^{-1} .

The FTIR spectrum of V2W2Z sample [Fig. 2B(a)] exhibits basically the same bands as those of V2W0Z [Fig. 2A(a)], except for the v(C-O) band at 1105 cm⁻¹. At 373 K the spectral behaviour of V2W2Z [Fig. 2B(b)] is almost the same as that of V2W0Z.

Fig. 2C(a) shows the spectra of propan-2-ol adsorbed on V0W2Z. The v(C-O) band of isopropoxide appeared at 1168 and 1117 cm⁻¹. The intensity of the band at 1168 cm⁻¹ is

stronger than that of V2W0Z. In a separate experiment using ZrO_2 alone, the band at 1173 cm⁻¹ appeared after an introduction of propan-2-ol. Two types of isopropoxide are present on the V0W2Z: one interacts with tungsten oxides (1117 cm⁻¹), the other (1168 cm⁻¹) with zirconia. After evacuation at 373 K [Fig. 2C(b)], the bands remained in almost the same position as those in V0W2Z at room temperature. At this temperature, the band at 1676 cm⁻¹ due to acetone appeared on the V2 series catalysts and was completely absent on V0W2Z. The above results show that the isopropoxide species strongly

0.2



С b 1107 а в 1684 b Absorbance 1105 а A 1686 b 1107 а 1800 1600 1400 1200 1000 Wavenumber/cm⁻¹

Fig. 2 FTIR spectra of propan-2-ol on V2W0Z (A), V2W2Z (B) and V0W2Z (C). (a) After introduction of propan-2-ol at 298 K (*ca.* 0.1 kPa for 30 min) followed by 30 min evacuation, (b) followed by 30 min evacuation at 373 K.

Fig. 3 FTIR spectra of propan-2-ol on V5W0Z (A), V5W5Z (B) and V0W5Z (C). (a) After introduction of propan-2-ol at 298 K (*ca.* 0.1 kPa for 30 min) followed by 30 min evacuation, (b) followed by 30 min evacuation at 373 K.

Similar experiments were carried out with V5W0Z, V5W5Z and V0W5Z samples (Fig. 3). Bands due to adsorbed isopropoxide are observed in the spectra of V5 series samples. These bands reduced in intensity at 373 K and bands due to acetone appeared in these samples. In the case of V0W5Z, the bands due to isopropoxide species reduced drastically in intensity by evacuation at 373 K, corresponding with the formation of large amounts of propene in the pulse experiment. Bands due to acetone did not appear in this sample. The v(C-O) band appeared at 1107, 1105 and 1107 cm⁻¹ on V5W0Z, V5W5Z and V0W5Z, respectively.

It was noted that the v(C-O) band shifted to a lower position by adding WO₃. The wavenumber shifted lower by 5 cm⁻¹ in the V2 series and 2 cm⁻¹ in the V5 series, respectively.

FTIR spectra of the V=O and W=O region

Fig. 4 shows the FTIR spectra in the $1100-900 \text{ cm}^{-1}$ region of the V2 series samples. After oxidation treatment for the V2W0Z sample [Fig. 4A(a)], the V=O bands were observed at 1042 and 1035 cm⁻¹ together with weak shoulders at 1052 and 1020 cm⁻¹. When a small amount of propan-2-ol was introduced onto V2W0Z at 298 K [Fig. 4A(b)], the bands at 1052, 1042 and 1035 cm⁻¹ reduced in intensity. Simultaneously a new broad band appeared at 1012 cm⁻¹. The reduction in the intensities of the 1052, 1042 and 1035 cm⁻¹ bands seemed to be accompanied by the appearance of the band at around 1012 cm⁻¹.

Previously, we have reported similar observations using the V_2O_5/ZrO_2 samples prepared by a gas phase method.¹³ In that report, we concluded that the band at 1020 cm⁻¹ was

due to the V=O species of the second or third layer of vanadium oxides and those at 1037 and 1030 cm⁻¹ were due to the V=O species in the top layer. Similar situations would be expected in the present study, *i.e.*; on the V2W0Z sample the bands at 1052, 1042 and 1035 cm⁻¹ were due to the V=O species in the top layer and that at 1020 cm⁻¹ due to similar species in the bulk of vanadia. These bands show the presence of several V=O species which will be discussed below in detail.

The spectrum of the V2W2Z sample [Fig. 4B(a)] shows the V=O band at 1037 cm⁻¹ together with a weak band at 1020 cm⁻¹. It was noticed that the addition of WO₃ changed the doublet bands at 1042 and 1035 cm⁻¹ on V2W0Z into the single band at 1037 cm⁻¹ on V2W2Z. When propan-2-ol adsorbed on V2W2Z the band at 1037 cm⁻¹ reduced in intensity and a band at 1014 cm⁻¹ appeared [Fig. 4B(b)].

The spectral features of V2W5Z and V2W8Z samples in the region above 1000 cm⁻¹ were almost the same compared with that of the V2W2Z sample. The absorption below 950 cm⁻¹ was strong on V2W5Z and became stronger on V2W8Z. Surface coverage has been calculated assuming a monolayer capacity of 4.2 molecules nm⁻² for WO₃.⁸ As a result, a 5 wt.% WO₃/ZrO₂ sample is slightly above monolayer coverage. Therefore, the strong absorption below 950 cm⁻¹, which is directly corresponding to WO₃ loading, supports the formation of bulk WO₃. Thus, bulk WO₃ is generated on V2W5Z and V2W8Z samples.

Fig. 5 shows the FTIR spectra in the region of 1100–900 cm⁻¹ of the V5 series samples. The V=O bands appeared at 1023 cm⁻¹ together with a shoulder band at 1036 cm⁻¹ [Fig. 5A(a)]. This band increased with increasing V_2O_5 loading. After adsorption of propan-2-ol at 298 K, the shoulder band at 1036 cm⁻¹ disappeared, while the band at 1023 cm⁻¹ remained almost constant. For V5W2Z, V5W5Z and V5W8Z samples, as shown in Fig. 5B–5D, the spectral behaviour in



Fig. 5 FTIR spectra of the V=O or W=O stretching region of propan-2-ol adsorbed on V5W0Z (A), V5W2Z (B), V5W5Z (C) and V5W8Z (D). (a) Background, (b) after introduction of propan-2-ol at 298 K (*ca.* 0.1 kPa for 30 min) followed by 30 min evacuation.



Fig. 4 FTIR spectra of the V=O or W=O stretching region of propan-2-ol adsorbed on V2W0Z (A), V2W2Z (B), V2W5Z (C) and V2W8Z (D). (a) Background, (b) after introduction of propan-2-ol at 298 K (*ca.* 0.1 kPa for 30 min) followed by 30 min evacuation.

the region above 980 cm⁻¹ was almost the same compared with that of the V5W0Z sample. For V5W5Z and V5W8Z samples, strong absorption below 950 cm⁻¹ was observed, suggesting the formation of bulk WO₃, as mentioned in the cases of V2W5Z and V2W8Z samples.

The FTIR spectra of WO₃/ZrO₂ catalysts are shown in Fig. 6. In the case of V0W2Z a band appeared at 1011 cm⁻¹ together with shoulder bands at 1007 and 996 cm⁻¹ after the oxidation treatment. The spectrum of V0W5Z catalyst shows the bands at 1019 and 1013 cm⁻¹. For V0W8Z the bands appeared at 1018 and 1009 cm⁻¹ followed by the strong absorption below 960 cm⁻¹. These bands at 1019–996 cm⁻¹ can be assigned to the W=O stretching of wolframyl species.³ After adsorption of propan-2-ol at room temperature on WO₃/ZrO₂ catalysts, these bands drastically reduced in intensity and broad bands around 1010–980 cm⁻¹ appeared in V0W5Z and V0W8Z samples. Since this behaviour could not be seen in V2 and V5 series samples which contained tungsten oxide, wolframyl species were not present on the surface of V2 and V5 series catalysts.

Raman spectra

Fig. 7 shows the Raman spectra in the $1200-200 \text{ cm}^{-1}$ region of various V_2O_5 -WO₃/ZrO₂ catalysts. The spectra of the V2W0Z sample exhibits bands due to the monoclinic phase of the zirconia (645, 620, 485, 386 and 340 cm⁻¹). In the case of the V2W2Z sample, these bands reduced in intensity by WO₃ addition. The spectrum of the V5W0Z sample shows a number of bands, which are attributable to crystalline V_2O_5 (1000, 708, 535, 485, 412, 310 and 290 cm⁻¹). In the case of the V5W5Z sample, these bands due to crystalline V_2O_5 are reduced in intensity.

Considering that the crystalline vanadia phase is more Raman-active than the surface vanadia phase,¹⁶ the above



Fig. 6 FTIR spectra of W=O stretching region of propan-2-ol adsorbed on V0W2Z (A), V0W5Z (B) and V0W8Z (C). (a) Background, (b) after introduction of propan-2-ol at 298 K (*ca.* 0.1 kPa for 30 min) followed by 30 min evacuation.



Fig. 7 Raman spectra of V2W0Z (A), V2W2Z (B), V5W0Z (C), V5W5Z (D) and V0W5Z (E and E').

results show that the V2 and V5 series catalysts are composed mainly of surface vanadate species, although the crystalline V_2O_5 partially exists on the V5 series catalysts.

The spectrum of the V0W5Z sample exhibits bands due to ZrO_2 together with very weak bands at *ca.* 960 and 810 cm⁻¹. In order to clarify the existence of these weak bands, the signal accumulations were increased by eight times (Fig. 7E'). The bands appearing at 967 and 810 cm⁻¹ indicate the terminal W=O of tungsten oxide and crystalline WO₃, respectively. In the same experimental conditions, these bands could not be seen in the V5W5Z sample, since Raman scatterers depend on the colour of the samples; the WO₃/ZrO₂ without V₂O₅ samples are white, the V₂O₅-WO₃/ZrO₂ being dark yellow.

In separate XRD experiments, the results (not shown in the Figure) showed that the peak at 23° (2 θ) due to crystalline WO₃ appeared in V2W5Z, V2W8Z, V5W5Z and V5W8Z samples. Therefore, bulk tungsten oxide species exist in these samples.

Discussion

Acidity and catalytic activity

Recently we have studied the acidic properties of the same catalysts used in this study.¹⁴ As shown in Table 1, V2W0Z and V5W0Z catalysts exhibited both Lewis and Brønsted acidities. The addition of WO₃ to V2 series catalysts led to an increase of the number of both Lewis and Brønsted acidic sites, while only the number of Brønsted acidic sites increased on V5 series catalysts.

Generally, the alcohol decomposes by two parallel reactions: dehydration to propene and/or diisopropyl ether on acidic-type centres and dehydrogenation to acetone on basic redox centres.^{16,17} In the case of V2 series catalysts, the increase of conversion and selectivity to propene are due to the increase of the number of both acidic sites. For V5 series catalysts, the increase of the selectivity to propene seems to depend on the number of Brønsted acidic sites. As shown in Fig. 1, the V0W2Z sample showed less reactivity for propan-2-ol decomposition because it has only Lewis acidic sites. Thus, the propene formation is correlated with not only the quantity of acidic sites but also the quality of them.

The addition of WO_3 onto the catalysts suppressed the formation of acetone, especially in V2W2Z (Fig. 1). However, the amount of acetone did not reduce with increasing amount of WO_3 . Surface vanadate species still exist on the surface irrespective of the impregnation sequence of tungstate species.³

As described above, Figs. 2 and 3 show that the v(C-O) band of the isopropoxide species shifted slightly to a lower wavenumber with increasing amounts of WO₃. Since the wavenumber of the stretching vibration corresponds to the bond energy, the lower shift of v(C-O) indicates the weakening of the C-O bond of the isopropoxide species as well as the strengthening of the Lewis acidic sites on which the isopropoxide species adsorbs. In comparison with both cases of V2W0Z and V5W0Z, the shift of v(C-O) was 5 cm⁻¹ on V2W2Z and 2 cm⁻¹ on V5W2Z. As a result, propene formation increased through the easier cleavage of the C-O bond of the isopropoxide species on V2 series samples.

Structure characterisation of catalysts via the V=O and W=O bands

As described above, there are several bands in the 1100-900 cm⁻¹ spectral region, suggesting the presence of different surface vanadate species. Therefore, we will discuss the surface species in detail by using band separation techniques.¹⁸

Fig. 8A shows the original and separate peaks of the V=O band in the V2W0Z sample after the oxidation treatment. The bands at 970–1070 cm⁻¹ are separated into four peaks (peak

Fig. 8 Band shape analysis of FTIR spectra of V=O bands of V2W0Z (A) and V2W2Z (B) after oxidation treatment. (a) Original peak, (b) separated peak.

Wavenumber/cm⁻¹

950

1, 1052; peak 2, 1042; peak 3, 1035; and peak 4; 1020 cm⁻¹), although the curve fitting is insufficient around 1000 cm⁻¹. Surface coverage has been calculated assuming a monolayer capacity of 2.4 nm^{-2} for V₂O₅.¹⁷ On the V2W0Z sample, the value of 2 wt.% is estimated to be the V₂O₅ content for which the theoretical monolayer is formed on the ZrO₂ support. However, vanadium oxide may aggregate to form a partial multilayer on the support during the calcination procedure.

In a previous study¹³ of V_2O_5/ZrO_2 it was shown that the band at 1030 cm⁻¹ was due to the V=O species in the single layer of vanadium oxide on ZrO_2 and that at 1037 cm⁻¹ was the same species on the top layer on multilayered V_2O_5 . Therefore, the similar assignments are applicable in the case of the V2W0Z sample, i.e., peaks 2 and 3 are assigned to the V=O species of the top layer on multilayered (double or triple layers) vanadium oxide and similar species in the single layer vanadate on ZrO2, respectively. The integrated peak intensities of peaks 2 and 3 are almost the same, suggesting that the amounts of multi- and single-layer vanadate are comparable on the catalyst surface. Peak 1 may be assigned to the V=O species of an another surface vanadate. The heterogeneity of the surface results in these several V=O peaks. Peak 4 is due to the V=O species in the second or third vanadia laver.

In the case of the V2W2Z sample, these bands were also separated into four peaks (Fig. 8B). Addition of WO₃ to V2W0Z leads to the reduction of peak 2 and the increase of peak 3'. The integrated intensity of the reduction of peak 2 corresponds to that of the increase of peak 3', showing that peak 2 in V2W0Z converts into peak 3' in V2W2Z. Consequently, it appears that the doublet bands at 1042 and 1035 cm⁻¹ on V2W0Z changed into the single one at 1037 cm⁻¹ on V2W2Z.

The results suggest that the added WO_3 goes under the vanadia species and interacts directly with the ZrO_2 support. Thus, the vanadia species were reconstructed by the addition of WO_3 and the new V=O species (1037 cm⁻¹) formed over the tungsten oxide species. Consequently, the shifts of the V=O band are explicable.

V2W5Z and V2W8Z samples showed no appreciable change in the V=O band in the top layer and no terminal W=O band irrespective of the amount of WO₃. In addition, the increasing loading of WO₃ led to the appearance of the band below 950 cm⁻¹ due to crystalline WO₃. When WO₃ is incorporated onto the V₂O₅/ZrO₂ catalysts, the majority of WO₃ seems to be intercalated between vanadia and zirconia.

In the case of the V5 series, the band at 1023 cm⁻¹ is in agreement with the V=O band of bulk V₂O₅ (or crystalline V₂O₅), while the 1036 cm⁻¹ band is attributable to the V=O band in the top layer of vanadium oxides in the catalyst, as considered above. The addition of WO₃ hardly affected both the V=O bands in the top layer and of bulk V₂O₅. Although the band due to terminal W=O species appeared at 1019 cm⁻¹ on V0W5Z (Fig. 6B), a similar band could not be observed on V5W5Z (Fig. 5C). Thus, as described in the V2 series, the structure of the vanadia species is also reformed by the added WO₃, being present under the vanadia layers. The influence of WO₃ on the V=O band in the V5 series is little, since the concentration of vanadia is large enough to form multilayer vanadia species in the case of V5 series samples.

Summarising the above considerations, a model of the V2 series catalysts illustrated in Fig. 9 can be proposed. In the absence of tungsten oxide, two types of V=O bond are present on the surface (1042 and 1035 cm⁻¹). The addition of WO₃ led to the reconstruction of vanadia species, resulting in the single V=O bond (1037 cm⁻¹). The V=O species (1042 and 1037 cm⁻¹) possibly convert into Brønsted sites and coordinately unsaturated vanadium ions are Lewis sites in Fig. 9. Thus, both Lewis- and Brønsted-acidic sites increased. The increase of the acidic sites and their strength may be con-





(A)V2W0Z



(B)V2W2Z

O atom O V atom ♥ W atom ● Zr aton

Fig. 9 A model of surface structures of V2W0Z (A) and V2W2Z (B). The numbers in the figure show wavenumber in cm^{-1} .

sidered to be attributable to an electronic interaction between the vanadia and tungstate species.⁴ Tungsten oxide, having a cationic nature,⁵ is distributed over the basic sites of ZrO_2 and repel each other. At low tungstate concentration tungsten is well dispersed on the support owing to repulsion.

In this paper, we focused on the effect of the addition of WO_3 to V_2O_5/ZrO_2 catalysts. The strong interaction of tungsten oxide with the support reconstructs the structure of vanadia species. Considering our preparation methods, this process of intercalation may take place during the calcination of the catalysts. As a result, the surface acidity as well as the catalytic activity changed with the amount of WO_3 .

The authors would like to thank Mr. S. Konishi for carrying out some of the experiments.

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Paper 8/09536A