Promoting effect of Pt addition to V_2O_5/ZrO_2 catalyst on reduction of NO by C_3H_6

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The effect of Pt addition to a V_2O_5/ZrO_2 catalyst on the reduction of NO by C_3H_6 has been studied by FTIR spectroscopy as well as by analysis of the reaction products. Pt loading promoted the catalytic activity remarkably. FTIR spectra of NO adsorbed on the catalysts doped with Pt show the presence of two different types of Pt sites, Pt oxide and Pt cluster, on the surface. The amount of these sites depends on Pt contents and the catalyst state. Pt atoms highly disperse on the surface as Pt oxide at low Pt content, being aggregated into Pt metal clusters by increasing Pt amount or reducing the catalysts. The spectral behavior of V=O bands on the surface also supports the formation of Pt clusters. It is concluded that Pt promotes the NO–C_3H_6 reaction through a reduction–oxidation cycle between its oxide and cluster form.

KEY WORDS: promoting effect; Pt addition; V_2O_5/ZrO_2 catalysts; NO reduction; C_3H_6; Pt cluster; FTIR

1. Introduction

Catalytic removal of NO_x emissions has been the subject of extensive investigation in environmental protection [1,2]. Concerning automotive NO_x emissions, the platinum group metals are practically used in the three-way catalysts to reduce NO. Among them the highest activity of NO reduction has been reported with the Pt-based catalysts [3]. In the selective catalytic reduction (SCR) of NO by NH_3, vanadium oxide, though it is a key component for practical catalysts, has been found to be less active for the SCR of NO by light hydrocarbons (HC-SCR) [2]. Monolayer vanadium oxide catalysts, however, have a great possibility for the HC-SCR of NO through their unique characters and interactions with support materials [4].

We have already reported the adsorption and decomposition of NO_x [5] and the reduction of NO by C_2H_4 [6] over vanadium oxides layered on zirconia prepared by a gas phase method. Recently, we have found a considerable promoting effect of Ca doping to the V_2O_5/ZrO_2 catalysts on the reduction of NO by C_3H_6 [7]. In the present work, the effect of platinum on reduction of NO by C_3H_6 over a V_2O_5/ZrO_2 catalyst has been investigated by FTIR spectroscopy as well as by the analysis of the reaction products.

2. Experimental

Details of the preparation of the V_2O_5/ZrO_2 catalysts have been described previously [8]. A vanadium oxide loading of 2.0 wt% (V2Z) was estimated to be the theoretical monolayer content on the ZrO_2 support [8]. Two types of Pt-doped V_2O_5/ZrO_2 catalysts (atomic ratio; Pt/V = 0.1 and 0.2) were obtained with a small amount of hydrogen hexachloroplatinate(IV) hexahydrate solution by a similar dry impregnation method, as described in [8,9]. Two kinds of Pt-doped ZrO_2 catalysts were also prepared by the same manner, containing 0.44 and 0.88 wt% of Pt (corresponding to that of Pt-doped V_2O_5/ZrO_2 catalyst).

The catalysts are designated as PtxV2Z or PtxZ (x = 1 and 2), where x is ten times the atomic ratio of Pt/V and means the amount of Pt corresponding to Pt1V2Z and Pt2V2Z. The BET surface area of the support and the catalysts were as follows: ZrO_2 28, V2Z 31, Pt1Z 24, Pt2Z 27, Pt1V2Z 30 and Pt2V2Z 29 $m^2\ g^{-1}$.

The chlorine atoms incorporated onto the catalyst may inhibit the reaction and/or the catalyst itself. In order to remove the chlorine atoms, a catalyst disk (20 mm diameter, *ca*. 100 mg) was reduced under circulation of hydrogen (*ca*. 1.3 kPa) at 673 K before use. Then, the disk was degassed in vacuum at 723 K for 30 min, followed by circulation of oxygen (*ca*. 4 kPa) at the same temperature. After this oxidation pretreatment was repeated twice, the disk was cooled to room temperature (RT) in oxygen.

In situ FTIR spectra were recorded on a Shimadzu FTIR-8600PC by a transmission method using a conventional closed-circulation system. The products were analyzed by a Shimadzu GC-MS QP-5000 with a Porapak Q column. Details of the apparatus and procedures have been described in the previous work [7].

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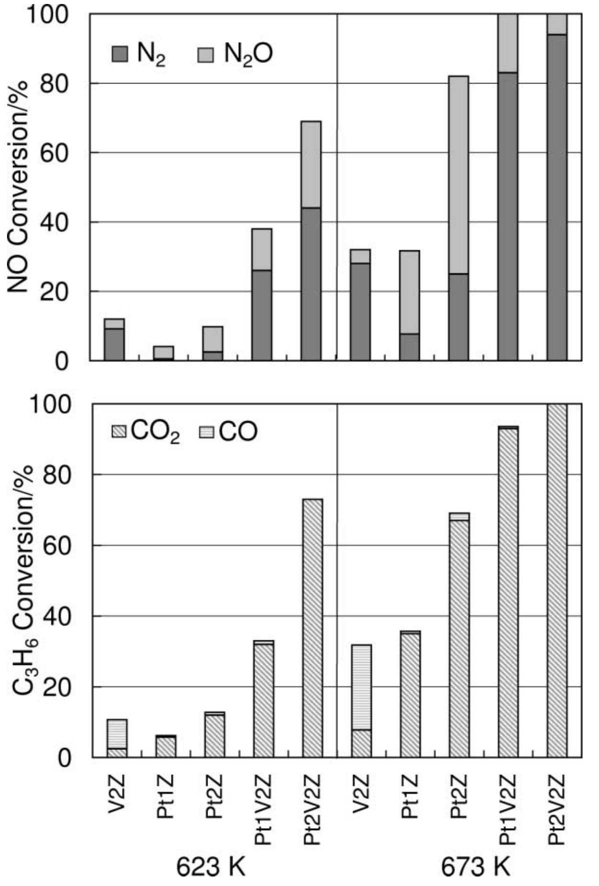

Figure 1. Products in the reaction of NO (*ca.* 1.2 kPa) and C_3H_6 (*ca.* 130 Pa) on the catalysts at 623 and 673 K for 30 min with a closed circulation method.

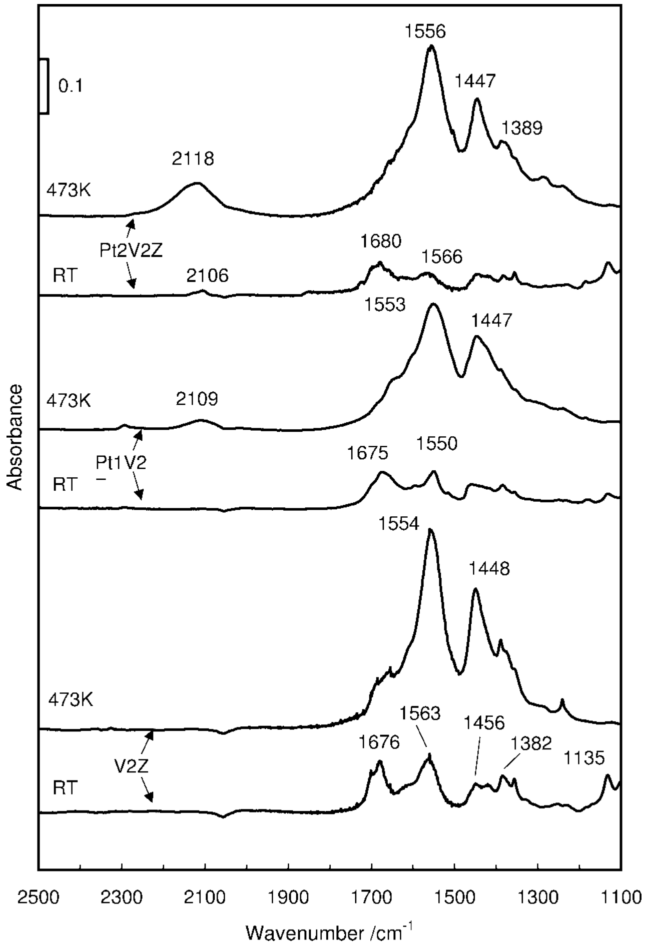

Figure 2. FTIR spectra of pre-oxidized V2Z, Pt1V2Z and Pt2V2Z after circulation of a gaseous mixture of NO (*ca.* 1.2 kPa) and C_3H_6 (*ca.* 130 Pa) at RT and 473 K for 30 min.

3. Results and discussion

3.1. Reaction products of NO + C_3H_6 on catalysts

The reaction of NO with C_3H_6 was carried out at 623 and 673 K for 30 min over oxidized V2Z, Pt1Z, Pt2Z, Pt1V2Z and Pt2V2Z by a closed circulation method. The results are shown in figure 1. The products consisted of N_2, N_2O, CO and CO_2. No other compounds including –CN, –CNO group or chlorine atom were detected except for water, which was not measured though it formed in these experiments. It should be noted that no significant conversion occurred on ZrO_2 support at 623 and 673 K (below 10% at most).

The conversions of both NO and C_3H_6 on V2Z, Pt1Z and Pt2Z were low (below 13%) at 623 K. While those on Pt1V2Z and Pt2V2Z increased linearly with increasing Pt loading at 623 K. At 673 K, the conversion on Pt1Z was comparable with that on V2Z. Those on Pt2Z, Pt1V2Z and Pt2V2Z were significantly high at 673 K. The experimental condition under the closed circulation method is different from the practical one. The above results, however, suggest that Pt is an excellent promoter for the V_2O_5/ZrO_2 catalyst in this reaction. The selectivity to CO_2 also increased on the Pt-doped catalysts owing to the strong interaction of Pt with CO. The selectivity to N_2O at 623 and 673 K increased on Pt-doped catalysts with the exception of Pt2V2Z. It is well known that the catalysts including Pt produce a lot of N_2O in the HC-SCR of NO [1,2]. At 673 K the smaller selectivity of N_2O on Pt2V2Z compared with that on Pt1V2Z shows the decomposition of N_2O to form N_2 during the circulation over the catalyst.

3.2. IR spectra of NO + C_3H_6 on oxidized catalysts

A gaseous mixture of NO and C_3H_6 was introduced and circulated for 30 min on oxidized V2Z, Pt1V2Z and Pt2V2Z at various temperatures (RT to 673 K). The resulting FTIR spectra at room temperature and 473 K are shown in figure 2. Each spectrum in the region 2500–1100 cm^{-1} in figures 2–4 is seen after subtraction of the catalyst itself together with the gas phase.

At room temperature (RT), bands appeared at 1705 (shoulder), 1676, 1563, 1456, 1382, 1355 and 1135 cm^{-1} on V2Z. The bands around 1676 cm^{-1} together with the 1135 cm^{-1} band have already been attributed to carbonyl species, such as propanal or acetone formed by the reaction of C_3H_6 with surface vanadate, in the previous report [7]. Increasing temperature of V2Z led to the decrease of these bands in intensity. The bands at 1563, 1456, 1382 and

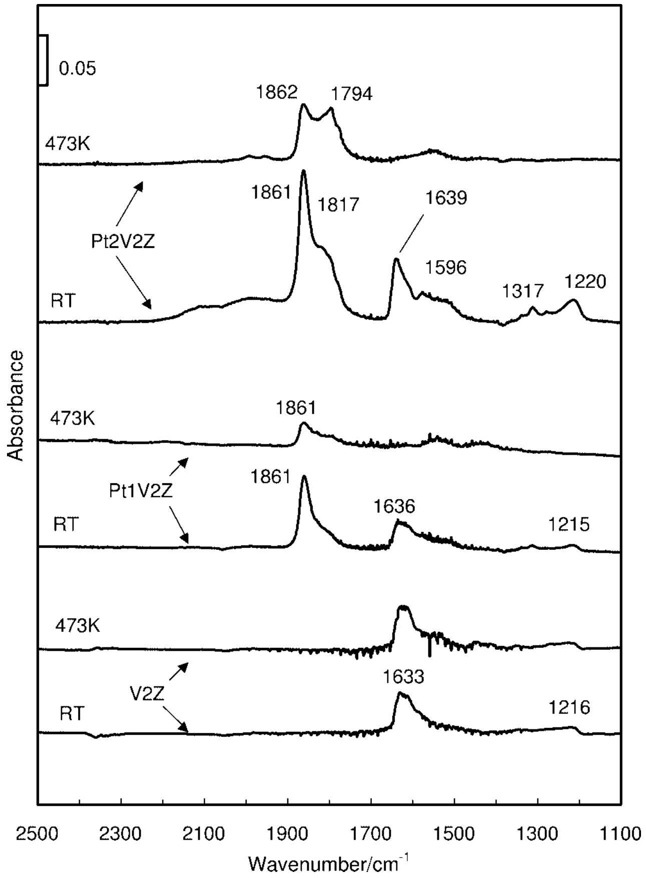

Figure 3. FTIR spectra of the pre-oxidized V2Z, Pt1V2Z and Pt2V2Z after circulation of NO (*ca.* 650 Pa) at RT and 473 K for 30 min.

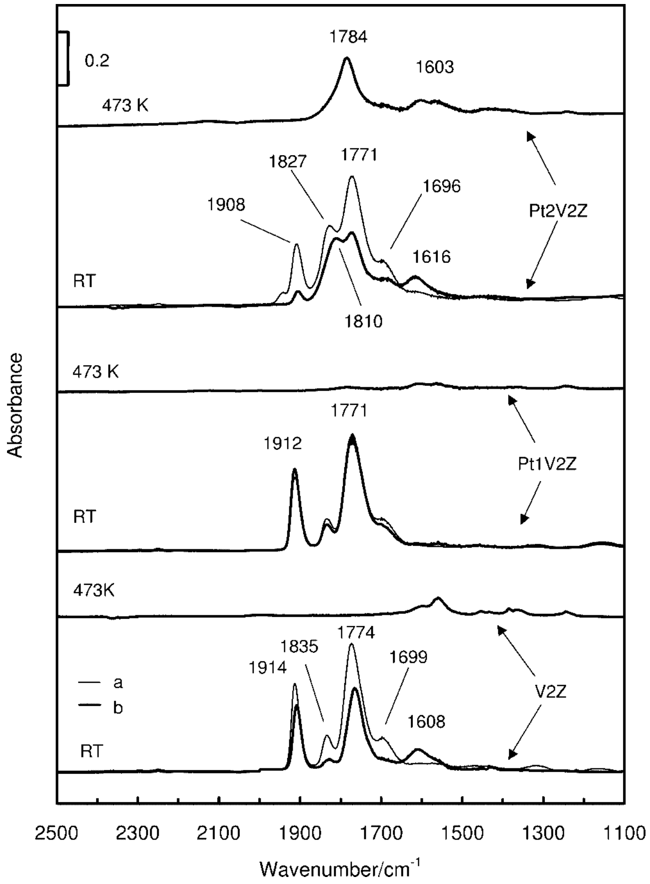

Figure 4. FTIR spectra of the pre-reduced V2Z, Pt1V2Z and Pt2V2Z after circulation of NO (*ca.* 650 Pa) at RT for 10 min (a) and 15 h (b) and at 473 K for 30 min.

1355 cm^{-1}, being intensified at 473 K with a few shifts at the 1554 and 1448 cm^{-1} peaks, are due to carboxylate species, such as acetate or formate species adsorbed on the V2Z surface [6,7].

On Pt1V2Z and Pt2V2Z at room temperature, the bands due to the carbonyl species were rather weak in comparison with those on V2Z, suggesting that Pt doping onto the catalysts reduced the amount of surface vanadate. A new band at 2106 cm^{-1} appeared on Pt2V2Z at room temperature and intensified at 473 K. In addition, a similar band appeared at 2109 cm^{-1} on Pt1V2Z at 473 K. The introduction of C_3H_6 alone onto Pt2V2Z led to the appearance of bands at 2109 and 2014 cm^{-1} at 473 K and adsorbed CO on Pt-doped V_2O_5/ZrO_2 showed several bands in the range of 2200–2050 cm^{-1} at various temperatures in the separate experiments (not shown in the figure). Thus, these bands are attributable to surface CO species associated with surface Pt although there is a possibility for the presence of cyanide species, which shows a ν(–CN) band in the same region, as reported on Pt/Al_2O_3 [10].

We have already reported that this reaction proceeds *via* the redox mechanism, *i.e.*, C_3H_6 reduces the catalyst and NO re-oxidizes it, in the case of V2Z [6,7]. The above results support that the similar mechanism is applicable on Pt-doped V_2O_5/ZrO_2 catalysts. The spectral results in figure 2, however, did not clarify the interaction of NO with the surface of catalysts so the adsorption of NO alone on pre-oxidized and pre-reduced catalysts was examined.

3.3. IR spectra of NO adsorbed on oxidized catalysts

Figure 3 shows the spectra after circulating gaseous NO (*ca.* 650 Pa) for 30 min on oxidized V2Z, Pt1V2Z and Pt2V2Z at room temperature and 473 K. A broad band at 1633 cm^{-1} together with a weak band at 1216 cm^{-1} appeared on V2Z at room temperature. The bands at 1633 and 1216 cm^{-1} are already attributed to ν(N=O) and $\nu(NO_2)$ of surface nitrate species of a bridge type on V2Z, respectively [7]. A shoulder peak at 1620 cm^{-1} suggests the presence of adsorbed NO_2 on the surface [11]. The bands of the nitrate species hardly changed on V2Z at 473 K, suggesting that the nitrate species on V2Z are stable around these temperatures. The bands at 1636 and 1215 cm^{-1} of the nitrate species on Pt1V2Z were rather weak in intensity compared with those on V2Z and disappeared at 473 K. While, in addition to the strong bands of the nitrate species at 1639 and 1220 cm^{-1}, bands appeared at 1596 and 1317 cm^{-1} on Pt2V2Z, suggesting formation of another type of nitrate species correlated to the surface Pt species. These bands almost disappeared at 473 K.

On Pt1V2Z at room temperature, a sharp band appeared at 1861 cm^{-1} together with a shoulder band at *ca*. 1817 cm^{-1}, which were not observed on V2Z. The 1861 cm^{-1} band reduced in intensity on Pt1V2Z at 473 K. Pt2V2Z also showed an intense sharp band at 1861 cm^{-1} with a clear shoulder peak at 1817 cm^{-1} at room temperature. The 1861 cm^{-1} band on Pt2V2Z reduced in intensity and shifted slightly at 473 K. While a band at 1794 cm^{-1} clearly appeared as decreasing the 1861 cm^{-1} band. It seems that the shoulder band at 1817 cm^{-1} shifted into an isolated band at 1794 cm^{-1} with reducing its intensity slightly.

The above bands can be assigned to the nitrosyl species adsorbed on the surface Pt sites since they were strongly correlated with the Pt addition to the catalysts. As regards the nature of Pt surface sites, Rochester *et al.* reported that NO adsorbed on surface Pt atoms with oxygen atoms existing at adjacent surface sites on Pt/Al_2O_3 gave an IR band at 1847 cm^{-1}[12]. The band at 1935 cm^{-1} has been already assigned to molecular adsorption of NO on a partly oxidized Pt surface on Pt/SiO_2 [13]. Thus, the band at 1861 cm^{-1} can be assigned to the nitrosyl species adsorbed on $Pt^{\delta+}$ sites, partially oxidized Pt atoms, or Pt oxides on the surface of V_2O_5/ZrO_2 catalyst. Metal nitrosyl complex, in general, shows a band of linear NO coordinated to a single metal atom in the region of 1830–1700 cm^{-1}. In the cases of metallic Pt surface, an IRAS study showed the bands between 1820 and 1840 cm^{-1} of linear NO adsorbed on a defect site of Pt(111) [14]. Therefore, the band at 1817 cm^{-1} at room temperature and that at 1794 cm^{-1} at 473 K on the catalysts with Pt are attributable to nitrosyl species adsorbed on metallic Pt^0 sites, Pt clusters, on the surface.

3.4. IR spectra of NO adsorbed on reduced catalysts

The catalysts were reduced by H_2 at 673 K after the oxidation pretreatment in order to examine in detail the nature of adsorbed sites on the surface. Figure 4 shows the spectra of the reduced catalysts after the circulation of NO at room temperature and 473 K.

Immediately after adsorption of NO on reduced V2Z at room temperature, four significant bands appeared at 1914, 1835, 1774 and 1699 cm^{-1}. These bands are already assigned to several types of nitrosyl species coordinated to unsaturated vanadium species on the surface [5]. The prolonged adsorption of NO on V2Z at room temperature led to the reduction of these bands and the simultaneous appearance of a new band at 1608 cm^{-1} attributed to NO_2 species, indicating that the oxidation activity of V2Z still exists even after this reduction treatment. The nitrosyl bands almost disappeared while very weak bands due to nitrate species appeared together with decreasing of the band due to NO_2 species at 473 K.

After NO adsorption on reduced Pt1V2Z at room temperature, the similar bands as observed on V2Z appeared at slightly lower frequencies and hardly changed for 15 h. Upon raising the catalyst temperature to 473 K, these bands almost disappeared. No band due to NO_2 species appeared on reduced Pt1V2Z at room temperature and 473 K, showing that this catalyst does not oxidize the nitrosyl species to form NO_2 or nitrate species. It is noticed that the bands due to NO adsorbed on Pt sites (Pt oxide and Pt cluster) were not observed on reduced Pt1V2Z.

After introduction of NO at room temperature for 10 min on Pt2V2Z, the corresponding bands of nitrosyl species appeared at 1908, 1827, 1771 and 1696 cm^{-1} though the intensity of the band at 1827 cm^{-1} was about two times that at 1835 cm^{-1} on V2Z. The band at 1827 cm^{-1} shifted to 1810 cm^{-1} with a slight decrease in intensity at room temperature for 15 h. Other bands considerably decreased in intensity and, at the same time, the band of NO_2 species appeared at 1616 cm^{-1}, indicating that increasing of Pt amount recovered the oxidation ability of the catalyst. The 1810 cm^{-1} band disappeared while the strong band at 1784 cm^{-1} remained at 473 K, suggesting that NO adsorbs strongly on Pt2V2Z.

It seems that the band at 1810 cm^{-1} is not due to nitrosyl species on unsaturated vanadium sites but that on Pt^0 cluster sites. The band at 1784 cm^{-1} is also assigned to nitrosyl species adsorbed on Pt^0 cluster sites since the nitrosyl bands coordinated to vanadium sites usually disappeared at this temperature. This band corresponds to the 1794 cm^{-1} band on oxidized Pt2V2Z, as shown in figure 2, but the intensity is *ca*. four times stronger than that of the 1794 cm^{-1} band. Primet *et al.* reported that the wavenumber of the IR band of linear NO adsorbed on Pt/Al_2O_3 decreased from 1815 to 1780 cm^{-1} as the Pt particle size increases from 1.5 to 3.5 nm [15]. Thus, the observed lower shift of the nitrosyl band from 1794 to 1784 cm^{-1} shows that Pt^0 cluster sites enlarged their size by the reduction treatment of the catalysts. The different intensities of nitrosyl bands on Pt clusters between oxidized and reduced Pt2V2Z catalysts may suggest that the cluster size is varying with the states of catalyst during the reaction.

3.5. IR spectra of surface V=O species of the catalysts

Figure 5 shows the FTIR spectra in the V=O region (1100–900 cm^{-1}) of the catalysts after the oxidation pretreatment. The spectra were redrawn by superposition in order to clarify the difference of the catalysts.

In the previous papers [7,8], we have analyzed the V=O band region of the V2Z catalyst and reported the band assignments. Since the V2Z catalyst used in this experiment was essentially the same as described in the previous works, the similar assignments are applicable to the V2Z catalyst (figure 5(a)) as follows. The bands at 1043 and 1036 cm^{-1} are assigned to the V=O species in the top layer on multilayered vanadium oxides and similar species in the monolayer vanadium oxides on ZrO_2, respectively. The band at 1021 cm^{-1} is due to the bulk V=O species in the second or third layer. That at 1054 cm^{-1} is attributable to the minor V=O species owing to the surface heterogeneity.

As shown in figure 5 (b) and (c), the intensities of these V=O bands on Pt1V2Z were considerably decreased by the addition of Pt while those on Pt2V2Z were increased with increasing amount of Pt. The relative integrated intensity of

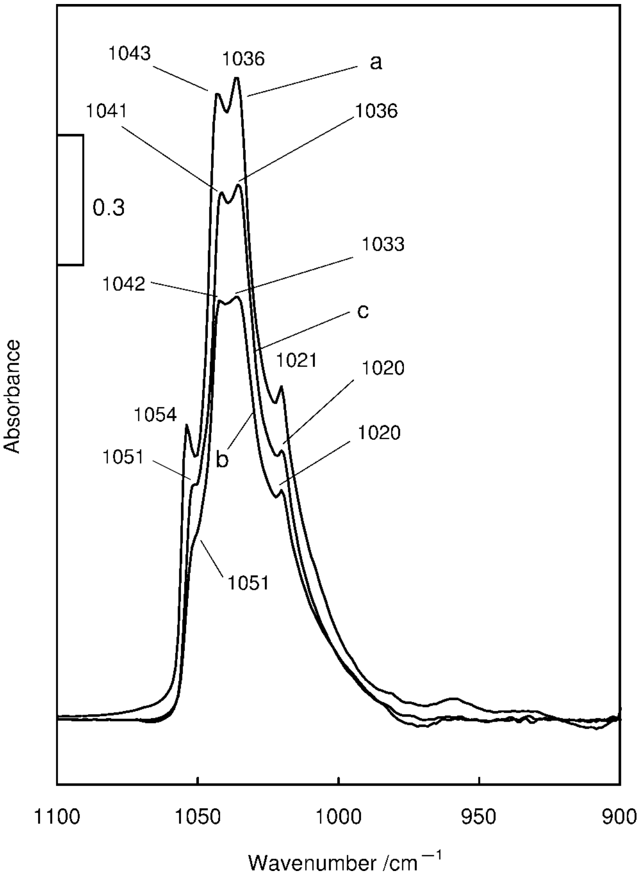

Figure 5. FTIR spectra of the V=O band region after oxidation treatment at 723 K of (a) V2Z, (b) V2Pt1Z and (c) V2Pt2Z.

the total V=O bands was 100% for V2Z, 69% for Pt1V2Z and 83% for Pt2V2Z, respectively. However, the position of each peak hardly changed compared with that on V2Z, suggesting little effect of Pt on the quality of each V=O species left on the catalyst. The above behavior clearly shows that Pt atoms highly disperse to form the Pt oxide on the surface at low Pt content (Pt/V = 0.1). Consequently, Pt addition reduces the amount of V=O species on the surface and weakens the oxidation ability of the catalyst in the case of Pt1V2Z. As Pt loading increases (Pt/V = 0.2), Pt atoms are aggregated to form the metallic clusters on the surface of the catalyst, which leads to the increase of the V=O species and recovers the oxidation capability in the case of Pt2V2Z.

As described in sections 3.3 and 3.4, the amount and the nature of nitrosyl species adsorbed on Pt sites depends on the contents of Pt as well as the surface state of oxidative or reductive on the catalysts. On Pt1V2Z and Pt2V2Z with an oxidation pretreatment or in the oxidative atmosphere, $Pt^{\delta+}$ sites or Pt oxide on the surface play an important role in the adsorption of NO as nitrosyl species and in the decomposition of nitrosyl and nitrate species. On Pt2V2Z with a reduction pretreatment or in the reductive environment, the formation of Pt^0 sites or Pt cluster by the aggregation from $Pt^{\delta+}$ sites contributes to the redox reaction through the reproduction of the V=O species. Therefore, it is concluded that Pt promotes the reduction of NO by C_3H_6 through a reduction–oxidation cycle between its oxide and cluster form.

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