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Surface Acidic and Redox Properties of V–Ag–O/TiO_2 Catalysts for the Selective Oxidation of Toluene to Benzaldehyde

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Abstract Previous work showed that the V–Ag–O complex oxides exhibited quite good catalytic behavior for the selective oxidation of toluene to benzaldehyde. In this work, TiO_2 was added into V–Ag–O by co-precipitation with a sol–gel method. Structural characterizations using X-ray diffraction and Fourier transform infrared spectroscopy indicated the phases of $Ag_2V_4O_{11}$, $Ag_{1.2}V_3O_8$ and TiO_2 in the V–Ag–O/TiO_2 before the reaction. No complex oxide phases involving titanium were observed. Thus, the addition of TiO_2 seemed to generate the interfaces between TiO_2 and the silver vanadates. The $Ag_2V_4O_{11}$ and part of $Ag_{1.2}V_3O_8$ were converted into $Ag_{0.68}V_2O_5$ and metallic Ag during the reaction. The results of temperature programmed reduction, microcalorimetric adsorption of NH_3 and isopropanol probe reaction in air revealed that the addition of TiO_2 might increase both the surface acidity and redox ability of the catalysts. The increased redox ability seemed to improve the activity for the oxidation of toluene, but the increased surface acidity might lead to the decrease of selectivity to benzaldehyde. The V–Ag–O/TiO_2 with 20% TiO_2 exhibited significantly improved catalytic behavior for the selective oxidation of toluene to benzaldehyde, as compared to the un-promoted V–Ag–O catalyst. The conversion of toluene reached 7.3% over the V–Ag–O/20%TiO_2 at 613 K with 95% selectivity to benzaldehyde.

Keywords V–Ag–O complex oxide catalysts · Silver vanadates · TiO_2 support · Selective oxidation of toluene to benzaldehyde · Surface acidity · Redox ability

1 Introduction

Benzaldehyde is a widely used raw material for the synthesis of many other valuable chemicals such as medicines, flavors, food and pesticides [1]. In the current industrial practice, it is produced by the hydrolysis of benzal chloride or by the partial oxidation of toluene in liquid phase. Benzaldehyde produced by chlorination of toluene followed by hydrolysis contains chlorine, which can not be used as the raw material for the production of medicines, food and flavors. In addition, the process involving Cl_2 causes environmental pollutions and equipment corruptions. On the other hand, the process of liquid phase selective oxidation of toluene usually produces benzoic acid as the main product and benzaldehyde is only produced as a by-product (about 2–3%). Since benzaldehyde is more costly than benzoic acid [2], higher selectivity to benzaldehyde is desired. In the process of gas phase oxidation of toluene, the contact time might be decreased and thus the further oxidation of benzaldehyde might be reduced so that high selectivity to benzaldehyde might be achieved [3–17]. However, no commercial plants are currently available for the production of benzaldehyde from the oxidation of toluene by air in gas phase, due to the low activity and/or selectivity. Studies are still undergoing for screening the proper catalysts for the improved catalytic behavior.

During the past decades, researches have been continuing for the selective oxidation of toluene to benzaldehyde. Pure vanadium oxide (V_2O_5) was tested for the partial oxidation of toluene, but the conversion of toluene and the

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selectivity to benzaldehyde were low over the V_2O_5. Studies were carried out on supports as well as promoters, such as SiO_2, TiO_2, K and Ag to modify the surface properties of the catalysts, in order to improve the catalytic activity for the selective oxidation of toluene [6, 8–10, 15]. Supporting of vanadium oxides on TiO_2 might increase the surface areas of supported vanadium species and the interfaces between vanadium oxides and TiO_2 which have been considered as active surfaces for the selective oxidation of toluene [13]. In addition, our earlier work [9, 10] showed that the addition of silver to V_2O_5 greatly decreased the surface acidity and increased redox ability of the catalysts, leading to the increased conversion of toluene and the selectivity to benzaldehyde. In this work, TiO_2 was added into the V–Ag–O and the V–Ag–O/TiO_2 catalysts were studied for the selective oxidation of toluene.

A series of V–Ag–O/TiO_2 catalysts were prepared by the sol–gel method with TiO_2 of 5, 10, 20, 40 and 80% by weight when V/Ag atomic ratio was fixed at 2/1. Various techniques such as X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) were employed to characterize the phases and structures of the catalysts. In particular, the surface acidic and redox properties of the catalysts were determined by the techniques of microcalorimetric adsorption of ammonia, TPR and isopropanol probe reactions and were correlated with the catalytic behavior for the selective oxidation of toluene to benzaldehyde.

2 Experimental

2.1 Preparation of Catalysts

A series of catalysts were prepared by the sol–gel method. According to the desired proportion of V, Ag, and TiO_2, V_2O_5 (8 g citric acid per 1 g V_2O_5) and $Ti(OC_4H_9)_4$ were dissolved in alcohol, respectively. $AgNO_3$ was dissolved in water. The solutions of vanadium oxides and $AgNO_3$ were then added with constant stirring to the alcohol solution of $Ti(OC_4H_9)_4$ at the same time. After stirred for 1 h, a green sol was formed and it was distilled and dried in a water bath at 353 K overnight (about 12 h) until the gel was formed. After being further dried at 393 K for 12 h, the sample was calcined in a muffle furnace at 673 K for 5 h. The sample was then pelletized, crushed and sieved to 20–40 meshes for the catalytic tests.

2.2 Characterization of Catalysts

The surface areas were measured by N_2 adsorption at the temperature of liquid N_2 employing the BET method. The phases present in the catalysts were determined by X-ray diffraction (XRD) using the X'TRA diffractometer with a CuKα radiation source ($\lambda = 0.15418$ nm) and a graphite monochromator. The applied voltage and current were 40 kV and 40 mA, respectively. The FTIR spectra were recorded with a Brucker Vector 22 FTIR spectrophotometer. The samples were mixed with KBr and pressed into self-supporting wafers for the FTIR measurements. TPR was performed by using a quartz U-tube reactor loaded with about 50 mg of a sample. A mixture of N_2 and H_2 (5.13% H_2 by volume) was used and the flow rate was maintained at 40 mL/min. The hydrogen consumption was monitored using a thermal conductivity detector (TCD). The reducing gas was first passed through the reference arm of the TCD before entering the reactor. The reactor exit was directed through a trap filled with $Mg(ClO_4)_2$ (to remove water) and then to the second arm of the TCD. The temperature was raised at a programmed rate of 10 K/min from 303 to 1173 K.

Microcalorimetric adsorption of NH_3 was carried out on a Tian–Calvet heat-flux apparatus. The microcalorimeter was connected to a gas handling and volumetric adsorption system, equipped with a Baratron capacitance manometer (MKS, USA) for precision pressure measurement. The differential heat of adsorption versus adsorbate coverage was obtained by measuring the heats evolved when doses of a gas (2–5 μmol) were admitted sequentially onto the catalyst until the surface was saturated by the adsorbate. Ammonia with a purity of 99.99% was used. Before microcalorimetric measurements, the samples were typically dried under vacuum, calcined in 67 kPa O_2, and evacuated, respectively, at 673 K for 1 h. The microcalorimetric adsorption was performed at 423 K.

2.3 Measurements of Catalytic Reactions

The probe reaction was carried out in a fixed-bed glass tube reactor (ϕ12). About 100 mg of a sample was loaded for the reaction. Isopropanol was introduced to the reaction zone by bubbling air (60 mL/min) through a glass saturator filled with isopropanol maintained at 295 K. Isopropanol and reaction products were analyzed by an online gas chromatograph, using a PEG 20 M packed column connected to an FID. Each catalyst was pretreated by heating in air at 673 K for 1 h and then cooled in air flow to the reaction temperature.

The reaction of selective oxidation of toluene was performed by using a U-tube fixed-bed microreactor (ϕ12) loaded with a sample of about 0.5 g with 20–40 meshes. The reactants were fed into the reactor by bubbling air through a glass saturator filled with toluene maintained at 330 K. The tail gas was analyzed by using an on-line gas chromatograph. The organic compounds were separated by an FFAP capillary column and detected by an FID while

CO_x was detected by using a Hayesep D packed column and a TCD.

3 Results and Discussion

Figure 1 shows the XRD patterns of the V–Ag–O/TiO_2 catalysts before and after the reaction for the selective oxidation of toluene. Silver vanadates ($Ag_{1.2}V_3O_8$ and $Ag_2V_4O_{11}$) and a small amount of TiO_2 (rutile) were the main phases of the V–Ag–O/TiO_2 catalysts containing 10–40% TiO_2. The intensity of TiO_2 increased while that of $Ag_{1.2}V_3O_8$ decreased with the increase of TiO_2 content from 10 to 40%. $Ag_2V_4O_{11}$ and part of $Ag_{1.2}V_3O_8$ were reduced to metallic Ag and $Ag_{0.68}V_2O_5$ while the TiO_2 remained during the reaction for the selective oxidation of toluene. Since no titanium was involved in the formation of complex oxides, we expressed the catalysts as V–Ag–O/TiO_2, as if TiO_2 played the function of a support. Thus, the XRD results indicated that the V–Ag–O/TiO_2 catalysts were easily reduced during the reaction, especially the silver containing phases. The V–Ag–O/TiO_2 catalyst with 80% TiO_2 exhibited only anatase TiO_2 without any other phases detected before and after the reaction for the selective oxidation of toluene, implying the well dispersed vanadium and silver species on the surface of TiO_2 when the contents of vanadium and silver were low [18, 19]. In addition, TiO_2 existed as anatase when its content was high while as rutile when its content was low in the V–Ag–O/TiO_2. This seemed to suggest a promoting effect of vanadium oxides for the phase change from anatase to rutile [20]. In fact, the diffraction peaks of rutile VO_2 and $TiVO_4$ overlap with that of rutile TiO_2, and thus some rutile VO_2 and $TiVO_4$ might be formed in the V–Ag–O/TiO_2 catalysts with 10–40% TiO_2. However, the bulk atomic ratio of V/Ag was two and the atomic ratios of V/Ag in the main phases of $Ag_{1.2}V_3O_8$ and $Ag_2V_4O_{11}$ detected in the catalysts were significantly greater than two, implying that vanadium was most likely combined with silver as V–Ag–O complex oxides. Thus, it was unlikely that vanadium existed as rutile VO_2 and $TiVO_4$ in the V–Ag–O/TiO_2 catalysts.

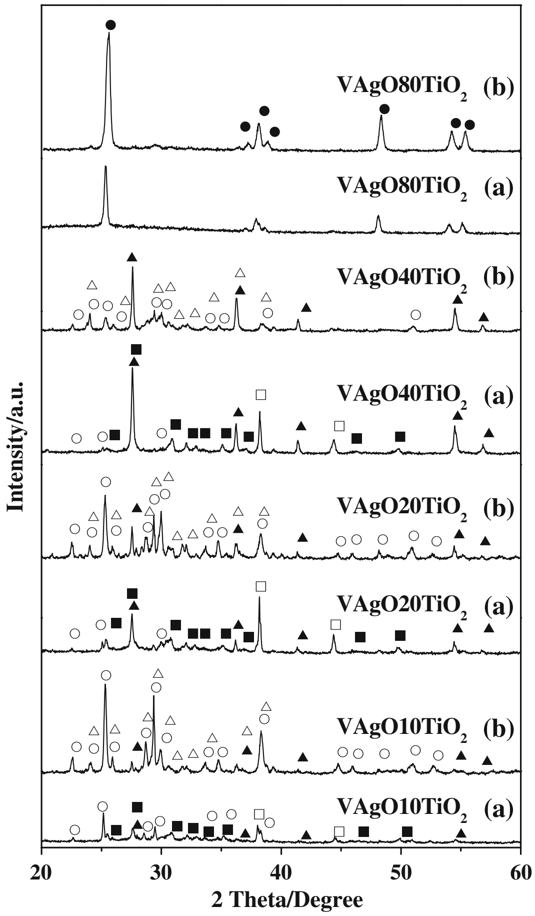

Fig. 1 X-ray diffraction patterns of V–Ag–O/TiO_2 catalysts with different TiO_2 content before **b** and after **a** the reaction of selective oxidation of toluene. The symbols used for the phases are as follows: ● TiO_2 (anatase), ○ $Ag_{1.2}V_3O_8$, Δ $Ag_2V_4O_{11}$, ▲ TiO_2 (rutile), ■ $Ag_{0.68}V_2O_5$, □ Ag

Figure 2 presents the FTIR spectra for the V–Ag–O/TiO_2 catalysts before and after the reaction. The FTIR spectra of the catalyst containing 10% TiO_2 consists six absorption peaks at 971, 921, 885, 836, 740 and 525 cm^{-1} before the reaction. The FTIR peaks at 971, 921 and 885 cm^{-1} belong to V=O double bond vibrations of $Ag_2V_4O_{11}$ and $Ag_{1.2}V_3O_8$ [21–23]. The peak at 885 cm^{-1} can also be assigned to the Ti–O vibration [24]. The peak at 836 cm^{-1} was originated from the vibration of V–O–V unit. The two peaks located at 740 and 525 cm^{-1} were due to the vibrations of the V–O and Ti–O bonds [25], respectively. With the increase of TiO_2 from 10 to 40%, the peak at 836 cm^{-1} for the vibration of V–O–V decreased, while the peak at 740 cm^{-1} for V–O increased. Meanwhile, the peak at 525 cm^{-1} belonging to Ti–O was broadened. These results indicated the increased dispersion of vanadium species with the increase of TiO_2 content. After the reaction for the selective oxidation of toluene, the peak around 920 cm^{-1} (for V=O vibration in $Ag_2V_4O_{11}$ and $Ag_{1.2}V_3O_8$) disappeared while that around 970 cm^{-1} (also for V=O vibration in silver vanadates) decreased, indicating the conversion of $Ag_2V_4O_{11}$ and $Ag_{1.2}V_3O_8$ to $Ag_{0.68}V_2O_5$, in consistence with the results of XRD. For the V–Ag–O/TiO_2 catalyst with 80% TiO_2, the broad peak at 500–950 cm^{-1} belongs to Ti–O–Ti vibration of anatase [24, 26]. The peaks at 968 and 927 cm^{-1} might indicate the existence of some small crystallites or non-crystalline grains of $Ag_2V_4O_{11}$ and $Ag_{1.2}V_3O_8$ since no such phases were detected by XRD for the V–Ag–O/80%TiO_2. After the reaction, the peak at 927 cm^{-1} disappeared while that

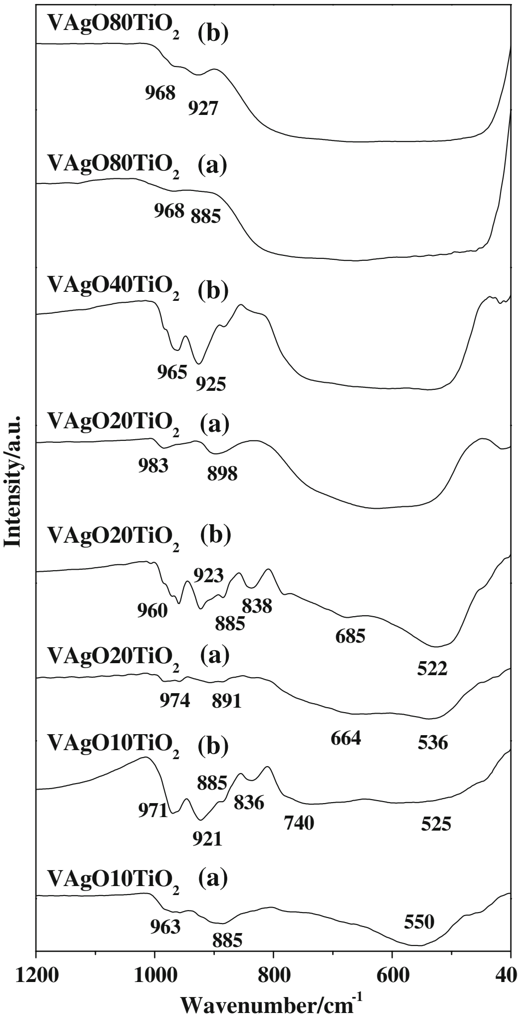

Fig. 2 FTIR of V–Ag–O/TiO$_2$ catalysts with different TiO$_2$ content before **b** and after **a** the reaction of selective oxidation of toluene

at 968 cm^{-1} decreased, indicating the same phase changes occurred in the V–Ag–O/80%TiO$_2$ as in the other V–Ag–O/TiO$_2$ catalysts.

According to the XRD and FTIR results discussed above, it was demonstrated that $Ag_2V_4O_{11}$, $Ag_{1.2}V_3O_8$ and TiO$_2$ were the main phases in the V–Ag–O/TiO$_2$ catalysts containing 10–80% TiO$_2$ before the reaction. No evidences for the formation of phases of Ag–Ti–O and V–Ti–O complex oxides. $Ag_2V_4O_{11}$ and part of $Ag_{1.2}V_3O_8$ were reduced to $Ag_{0.68}V_2O_5$ and metallic silver during the reaction for the selective oxidation of toluene.

Figure 3 shows the TPR profiles of the catalysts. Five peaks occurred at 626, 672, 704, 785 and 821 K for the reduction of V–Ag–O without the presence of TiO$_2$. The peak at 626 K may be assigned to the reduction of surface V–Ag–O complex oxides while the other four peaks might be due to the sequential reductions: silver vanadates → Ag+V_6O_{13} → V_2O_4 → V_2O_3+ undetected solid solution→ crystalline V_2O_3 [27]. The TPR profiles of the V–Ag–O/TiO$_2$ catalysts are similar to that of V–Ag–O. According to the XRD and FTIR results, $Ag_2V_4O_{11}$, $Ag_{1.2}V_3O_8$ and TiO$_2$ were the main phases in the V–Ag–O/TiO$_2$ catalysts. Since TiO$_2$ was not reduced in the TPR conditions employed in this work, the TPR peaks might be due to the reductions of silver vanadates and the reduction process seemed similar to that of V–Ag–O without the presence of TiO$_2$. However, the addition of TiO$_2$ seemed to decrease the reduction temperatures. For example, the main reduction peak decreased from 672 K (0% TiO$_2$) to 651 K (80% TiO$_2$), indicating the improved redox abilities of the V–Ag–O/TiO$_2$ catalysts.

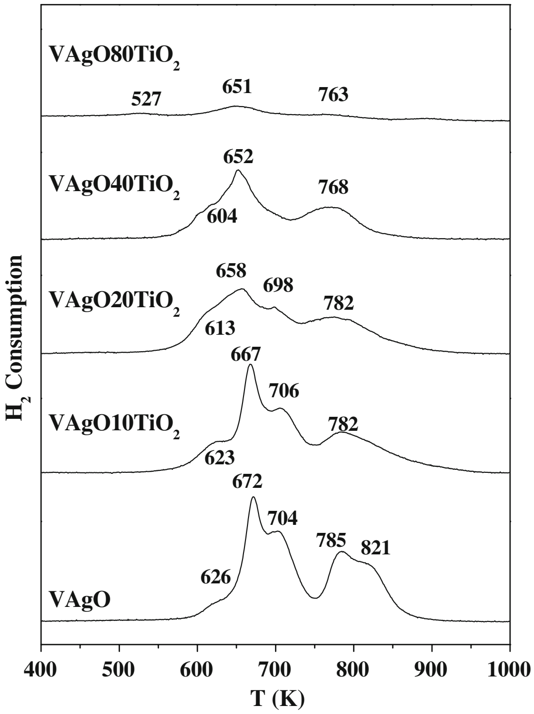

Fig. 3 TPR profiles of V–Ag–O/TiO$_2$ catalysts with different TiO$_2$ content

The surface acidity of metal oxides may play an important role in selective oxidation of hydrocarbons. The technique of microcalorimetric adsorption of ammonia was employed in this work to titrate the surface acidity of the V–Ag–O/TiO$_2$ catalysts. Figure 4 shows the results. The V–Ag–O/TiO$_2$ catalysts containing 20% and 40% TiO$_2$ possessed weak surface acidity with the initial adsorption heat of about 35 and 55 kJ/mol, respectively. The V–Ag–O/TiO$_2$ catalyst containing 80% TiO$_2$ exhibited much stronger surface acidity with the initial heat of 140 kJ/mol for the adsorption of ammonia. It has been reported [18, 28] that the acidity of V_2O_5/TiO$_2$ was stronger than that of V_2O_5, but the acidity of V–Ag–O was much weaker than that of V_2O_5 [10]. As compared to V–Ag–O [10], the surface acidity of V–Ag–O/TiO$_2$ increased due to the presence of TiO$_2$. However, owing to the presence of Ag,

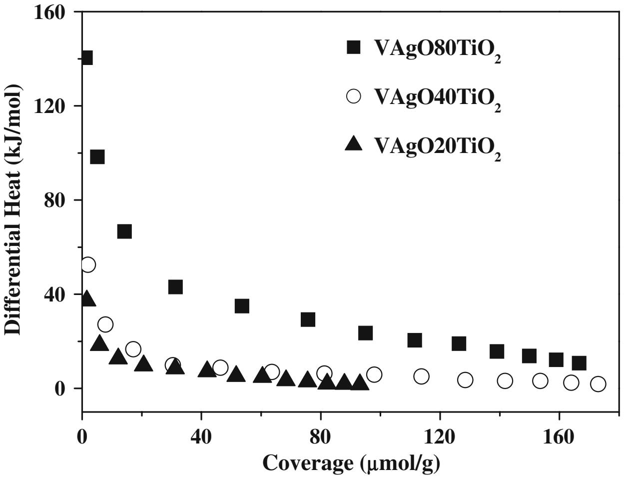

Fig. 4 Differential heats versus coverage for NH_3 adsorption at 423 K on the V–Ag–O/TiO_2 catalysts

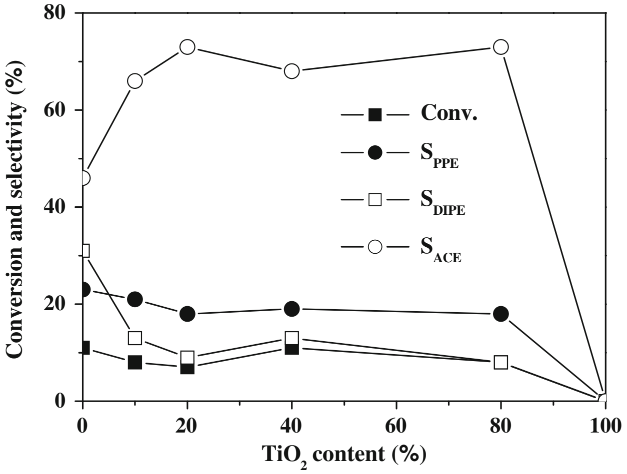

Fig. 5 Conversion of isopropanol and selectivity to propylene (S_{PPE}), diisopropyl ether (S_{DIPE}), and acetone (S_{ACE}) on the V–Ag–O/TiO_2 catalysts with different TiO_2 content in air at 453 K

the acidity of V–Ag–O/TiO_2 was significantly weaker than that of V_2O_5/TiO_2 [18]. The relative strengths of the surface acidity and redox ability of the V–Ag–O/TiO_2 catalysts might be important in determining the catalytic behavior for the selective oxidation of toluene.

The probe reaction of isopropanol in air was employed to characterize the surface acidic and redox properties of the metal oxide catalysts. Figure 5 shows the results obtained at 453 K. TiO_2 itself did not exhibit any activity for the reaction at the conditions used. Similar conversions of isopropanol (around 10%) were observed for the V–Ag–O and V–Ag–O/TiO_2 catalysts at 453 K. The apparent feature was that the addition of TiO_2 increased the selectivity to acetone while decreased the selectivity to diisopropyl ether. Since isopropanol is dehydrated to propylene and diisopropyl ether on acidic sites while it is oxidatively dehydrogenated to acetone on redox sites, the increase in the selectivity to acetone implied the enhanced redox ability of the V–Ag–O/TiO_2 catalysts upon the addition of TiO_2. This agrees with the TPR results discussed above. Moreover, since the results of microcalorimetric adsorption of ammonia revealed the increased surface acidity upon the addition of TiO_2, the results of isopropanol probe reaction indicated that the enhancement of the redox ability might be more than that of surface acidity upon the addition of TiO_2. Since the conversion of isopropanol in air probes acid and redox sites simultaneously, the relative selectivity to dehydration (propylene and diisopropyl ether) and oxidatively dehydrogenation products (acetone) might be used to describe the relative strengths of surface acidity and redox ability of the catalysts. The results in Fig. 5 showed that the V–Ag–O/TiO_2 seemed to exhibit stronger redox ability than surface acidity.

The results of selective oxidation of toluene over the series of catalysts at 613 K were presented in Table 1. TiO_2 itself did not show any activity for the reaction at the conditions used, and the V–Ag–O exhibited 5.3% conversion of toluene with high selectivity (92%) to benzaldehyde. With the increase of TiO_2 content in the V–Ag–O/TiO_2, the conversion of toluene was increased. Meanwhile, the selectivity to benzaldehyde was also increased with the increase of TiO_2 content up to 20%. This is apparently due to the enhanced surface redox ability of the catalyst without the significant increase of its surface acidity when 20% TiO_2 was added. Thus, the V–Ag–O/TiO_2 with 20% TiO_2 exhibited significantly improved catalytic performance with 7.3% conversion of toluene and 95% selectivity to benzaldehyde, as compared to the unpromoted V–Ag–O catalyst. Addition of more TiO_2 led to the significantly decreased selectivity to benzaldehyde. This is due to the significantly increased surface acidity that promoted the further oxidation of benzaldehyde to benzoic acid and then to CO_x. It has been reported [5, 11, 29] that

Table 1 Conversion of toluene on V–Ag–O/TiO_2 catalysts with different TiO_2 content

TiO_2%	Surface area (m^2/g)	Conv.%	Selectivity (%)		
			Benzaldehyde	Benzoic acid	Total
0	4	5.3	92	0	92
5	9	5.5	93	0	93
10	10	6.5	92	0	92
20	11	7.3	95	0	95
40	14	11	63	0	63
80	20	25	18	15	33
100	35	0	–	–	–

toluene and benzaldehyde were strongly adsorbed on the acid sites, leading to the complete oxidation to CO_x.

4 Conclusions

Structural characterizations and catalytic tests showed that the active phases for the selective oxidation of toluene to benzaldehyde might be some silver vanadates in the V–Ag–O/TiO_2. No complex oxide phases involving titanium were found in the V–Ag–O/TiO_2 catalysts before and after the reaction. The addition of TiO_2 seemed to produce some interfaces between TiO_2 and the silver vanadates that enhanced the surface redox ability and acidity of the catalysts. In addition, the content of TiO_2 in the V–Ag–O/TiO_2 affected the relative strengths of surface acidity and redox ability of the catalysts, which in turn influenced the catalytic behavior for the selective oxidation of toluene to benzaldehyde. Specifically, when the content of TiO_2 was lower than 20%, the enhancement of redox ability was much more than that of surface acidity and therefore, the addition of TiO_2 showed the positive effect for the reaction. On the other hand, the addition of TiO_2 more than 20% might significantly increase the surface acidity of the catalysts so that the added TiO_2 might play a negative effect on the selectivity to benzaldehyde. The V–Ag–O/TiO_2 with 20% TiO_2 seemed to exhibit significantly improved catalytic performance for the selective oxidation of toluene to benzaldehyde, as compared to the un-promoted V–Ag–O catalyst. The conversion of toluene reached 7.3% over the V–Ag–O/20%TiO_2 at 613 K with 95% selectivity to benzaldehyde.

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