

Contents lists available at ScienceDirect

Applied Catalysis A: General



journal homepage: www.elsevier.com/locate/apcata

Preparation and characterization of V-Ag-O catalysts for the selective oxidation of toluene

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ARTICLE INFO

Article history: Received 27 November 2009 Received in revised form 18 January 2010 Accepted 12 February 2010 Available online 26 February 2010

Keywords: Heterogeneous azeotropic distillation drying Silver vanadates Surface acidity Surface redox property Selective oxidation of toluene

ABSTRACT

V-Ag-O complex oxide catalysts with relatively high surface areas of $13-21 \text{ m}^2/\text{g}$ could be prepared by the heterogeneous azeotropic distillation (HAD) method. Specifically, V₂O₅ and AgNO₃ were dissolved in aqueous solution of H₂O₂, followed by evaporation and drying in n-butanol at 353 K. Silver vanadates with highly dispersed nano silver particles in the layered structures of VO_x might be formed during the preparation process, which were then turned into Ag_{0.68}V₂O₅ and metallic silver during the reaction of selective oxidation of toluene at 573 K. Characterizations with microcalorimetric adsorption of NH₃, temperature programmed reduction and isopropanol probe reactions showed that the V-Ag-O catalysts exhibited weaker surface acidity but stronger redox ability than the VO_x, and therefore the better performance for the selective oxidation of toluene to benzaldehyde and benzoic acid. In addition, the V-Ag-O catalysts prepared by the HAD method exhibited much higher activity than its counterpart prepared by the co-precipitation for the conversion of isopropanol and the selective oxidation of toluene to benzaldehyde and benzoic acid in air.

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1. Introduction

Caprolactam is a raw material for the synthesis of nylon 66, an important engineering plastic. In the SNIA process [1-3], toluene is a starting material for the synthesis of caprolactam. The first step of the process is the oxidation of toluene to benzoic acid in liquid phase through the free radical mechanism. Such free radical reaction converts toluene mainly into benzoic acid. Only trace of benzaldehyde is formed during the process. However, benzaldehyde is more costly than benzoic acid since it is an important raw material for the synthesis of many other valuable chemicals such as flavors, medicines and pesticides [4]. Thus, the catalytic oxidation of toluene to benzaldehyde and benzoic acid in gas phase to increase the selectivity to benzaldehyde has received considerable attention [5–19]. However, there is no commercial plant available currently for the production of benzaldehyde and benzoic acid from the oxidation of toluene by air in gas phase due to the low activity and/or selectivity.

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

zaldehyde and benzoic acid were low over the V₂O₅. Supports and promoters, such as SiO₂, TiO₂, K and Ag have been used to modify the surface properties of vanadia catalysts, in order to improve the catalytic behavior for the selective oxidation of toluene [9,10,15]. Our earlier work [20] showed that the addition of Ag and Ni to V₂O₅ greatly decreased the surface acidity and increased redox ability of the catalysts leading to the increased conversion of toluene or the selectivity to benzaldehyde.

Much work has been done to prepare the V-Ag-O complex oxides for lithium batteries and catalysts. The V-Ag-O complex oxides were usually prepared by co-precipitation and solid state synthesis at high temperatures with low surface areas (about $1 \text{ m}^2/\text{g}$) [11,21]. Generally speaking, the increase of surface area increased the number of active sites of a catalyst, leading to the increased catalytic activity.

In our previous work, high surface area mesoporous vanadium oxides (VO_x) were prepared by the heterogeneous azeotropic distillation (HAD) method using n-butanol to decrease the capillary force during drying. The mesoporous VO_x thus prepared might possess surface area of about $180 \text{ m}^2/\text{g}$ and exhibited much higher activity than traditional V₂O₅ for the selective oxidation of toluene to benzaldehyde and benzoic acid [22]. In this work, the same method was used to prepare the V-Ag-O complex oxides with surface areas much higher than $1 \text{ m}^2/\text{g}$ that were tested for the selective oxidation of toluene. The morphologies and structures of these V-Ag-O catalysts were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and transmission electron

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⁰⁹²⁶⁻⁸⁶⁰X/\$ - see front matter © 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.apcata.2010.02.023

microscopy (TEM). The surface acidic and redox properties of the catalysts were determined by the techniques of microcalorimetric adsorption of ammonia, temperature programmed reduction (TPR) and isopropanol probe reactions, and were correlated with the catalytic behavior for the selective oxidation of toluene to benzaldehyde and benzoic acid. A co-precipitated V-Ag-O (V/Ag=2) catalyst was also prepared without the use of n-butanol for the comparison.

2. Experimental

2.1. Preparation of catalysts

Desired amounts of V_2O_5 and $AgNO_3$ were dissolved in 300 ml aqueous solution containing 10% H_2O_2 . The resultant solution was evaporated at 353 K for 15 h, and a brown precipitate was formed. Then, 100 ml n-butanol was added and evaporated again at 353 K for 20 h. A brown powder was obtained and dried at 393 K over night (about 12 h). The samples were pelletized, crushed and sieved to 20–40 meshes for further uses.

2.2. Characterization of catalysts

The surface areas were measured by N₂ adsorption at the temperature of liquid N₂ employing the BET method. The phases present in the catalysts were determined by XRD using the X'TRA diffractometer with a Cu K α 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. TEM measurements were carried out using a JEOL electron microscope (JEM-2010), with an accelerating voltage of 200 keV.

TPR was performed by using a quartz U-tube reactor loaded with about 50 mg of a sample. A mixture of N₂ and H₂ (5.13% H₂ 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(ClO₄)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 NH₃ 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 (1–10 μ mol) 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 evacuated 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 (Ø 12). 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. The reaction was performed at 433 and 453 K with a total space velocity of 12.7 L/(gh) and air/isopropanol=20 (v/v).

The reaction of selective oxidation of toluene was performed by using a U-tube fixed-bed microreactor (Ø 12) 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 reaction was performed at 573-613 K with a total space velocity of 8.9-14.4 L/(gh) and air/toluene=5 (v/v). Products were analyzed after 1 h on-stream when the activity was stabilized, by an online 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. The reaction was performed at different temperatures with 4 h on-stream at a given temperature. The reaction temperature was increased step-wise and then decreased to the first one in order to see the effect of temperature and the stability of a catalyst. The carbon balance was calculated to be between 95-103% according to the amount of toluene introduced into the reactor and the amount of toluene, benzaldehyde, benzoic acid and CO_x detected in the tail gas.

3. Results and discussion

3.1. Textural and structural properties

Table 1 presents the surface areas of the V-Ag-O complex oxides after evacuation at 673 K and reaction for the selective oxidation of toluene at 573 K, respectively. The V-Ag-O oxides prepared by the heterogeneous azeotropic distillation (HAD) method with different V/Ag ratios possessed surface areas of $13-21 \text{ m}^2/\text{g}$ after the evacuation at 673 K or the reaction at 573 K, while the one prepared by the simple co-precipitation method had the surface area of only $\sim 1 \text{ m}^2/\text{g}$. Thus, the HAD method greatly increased the surface areas of V-Ag-O complex oxides, which did not seem to decrease during the reaction of selective oxidation of toluene at 573 K.

Fig. 1 shows the XRD patterns for the V-Ag-O samples dried at 393 K. The XRD pattern of VO_x exhibited a series of diffraction peaks at 6.3°, 12.6°, 19.0° and 31.9°, indicating the layered structure. The layer distance of VO_x was about 1.34 nm, calculated from the diffraction peaks. The structure of VO_x may be layered $V_2O_5 \cdot nC_4H_{10}O$ [22]. The diffraction peaks for the V-Ag-O with different V/Ag ratios were weak, suggesting the small crystallites of or non-crystalline oxides. Three broad diffraction peaks at 26.0°, 29.4° and 50.5° were detected for the V-Ag-O samples with V/Ag = 3 and 4. The peak at 26.0° might belong to a vanadia species, which intensity decreased with content of Ag and disappeared for the V-Ag-O samples with V/Ag=2 and 1.5. The peak at 50.5° was almost not changed with the increase of Ag content, and it might be assigned to the diffraction peak of some vanadia or silver vanadate species. The peak at 29.4° remained, but weakened and broadened with the increase of content of Ag. It might also be ascribed to some silver vanadium complex oxide.

Table 1			
Surface	areas of th	e V-Ag-O	catalysts.

Catalyst	Surface area (m ² /g)		
	Evacuated at 673 K	Reacted at 573 K	
VO _x	183	148 ^a	
V/Ag = 1	21	19	
V/Ag = 1.5	15	13	
V/Ag = 2	13	15	
V/Ag=3	17	13	
V/Ag = 4	19	21	
$V/Ag = 2^{b}$	1	1	

^a Reacted at 593 K.

^b Prepared by the co-precipitation method and calcined at 673 K.



Fig. 1. XRD patterns of V-Ag-O samples dried at 393 K.

In order to understand the phases and phase changes in the V-Ag-O samples, the V-Ag-O (V/Ag = 3) was calcined in N₂ at different temperatures (573–873 K). The XRD patterns of these calcined samples were shown in Fig. 2. With the increase of calcination temperature, the diffraction peaks changed obviously. Before the calcinations, the sample seemed to contained VO_x (26.0° and 50.5°)



Fig. 2. XRD patterns of V-Ag-O (V/Ag = 3) calcinated in N₂ at different temperatures. The phases were assigned according to JCPDS numbers and a reference: $Ag_{0.68}V_2O_5$ (74-2407), $Ag_2V_4O_{11}$ [28] and VO_2 (82-0661).

and $Ag_2V_4O_{11}$ (29.4° and 50.5°). After calcination at 573 K, the peak at 26.0° almost disappeared and the peaks at 29.4° and 50.5° were weakened, suggesting the reaction of VO_x with $Ag_2V_4O_{11}$, probably for the formation of Ag_{0.68}V₂O₅ with poor crystalline since the XRD peaks of $Ag_{0.68}V_2O_5$ became stronger later with the further increase of calcination temperatures. In fact, after calcination at 598 K, two peaks at 30.6° and 49.8° belonging to Ag_{0.68}V₂O₅ appeared which intensities were increased significantly after calcination at 623 K. Calcination at 773 K resulted in the sample with clear and intensive X-ray diffraction peaks. The main phase might be attributed to $Ag_{0.68}V_2O_5$ with the strongest peak at 30.6°. The Ag₂V₄O₁₁ remained for the sample after calcination at 773 K with the peaks at 28.9° , 29.4° , 30.6° and 50.5° . The peak at 27.8° might be assigned to the crystalline VO₂ (M). After calcination at 873 K, the sample contained the main phase of $Ag_{0.68}V_2O_5$ with a small amount of VO_2 (M), while the phase of $Ag_2V_4O_{11}$ disappeared. These XRD results seemed to suggest roughly a process of phase changes during the calcination: The main phase might be Ag₂V₄O₁₁ with some VO_x for the V-Ag-O (V/Ag = 3) dried at 393 K (both were poorly crystallized). With the increase of calcination temperatures, the solid reaction between Ag₂V₄O₁₁ and VO_x occurred, resulting in the formation of crystalline Ag_{0.68}V₂O₅. Meanwhile, the un-reacted VO_x turned to crystalline VO₂ (M).

Fig. 3 displays the XRD patterns for the V-Ag-O catalysts after the reaction of selective oxidation of toluene at 573 K. The original VO_x became V₆O₁₃ with very weak diffraction peaks. Obvious Ag_{0.68}V₂O₅ phase was detected for all the catalysts containing Ag. No other phases were detected for the V-Ag-O with V/Ag = 4 and 3. However, since the V/Ag atomic ratio of Ag_{0.68}V₂O₅ was 2.94, lower than 4, there must be some vanadia species (V₆O₁₃ or VO₂) in the V-Ag-O with V/Ag = 4 that were not detected by XRD due to the small crystallites or non-crystalline grains. With the increase of Ag content, diffraction peaks of metallic Ag were detected for the catalysts with V/Ag = 2 and 1.5, besides the Ag_{0.68}V₂O₅. Different from the V-Ag-O catalysts prepared by the co-precipitation method, in which Ag₂V₄O₁₁, Ag₂V₄O_{11-y}, Ag_{1.2}V₃O₈ existed besides a small amount



Fig. 3. XRD patterns of V-Ag-O catalysts after the reaction of selective oxidation of toluene at 573 K. The phases were assigned according to JCPDS numbers and a reference: Ag (04-0783), Ag_{0.68}V₂O₅ (74-2407), Ag₂V₄O₁₁ [28], Ag₂V₄O_{11-y} [28], Ag_{1.2}V₃O₈ (23-0647) and VO₂ (82-0661). (*) A sample prepared by co-precipitation after the same reaction at 613 K was added for comparison.



Fig. 4. FTIR spectra of V-Ag-O samples dried at 393 K.

of metallic Ag [20], the V-Ag-O catalysts prepared with the HAD method in this work contained only $Ag_{0.68}V_2O_5$ and metallic Ag, after the reaction of selective oxidation of toluene.

Fig. 4 shows FTIR spectra for the V-Ag-O complex oxides dried at 393 K. The VO_x exhibited the typically spectrum of V₂O₅ xero-gel. The peak at 1007 cm⁻¹ was due to the V=O double bond vibration, while the peaks at 763 and 520 cm⁻¹ could be assigned to asymmetric and symmetric vibrations of V–O–V [23]. The peak at 1007 cm⁻¹ shifted to 980 and 960 cm⁻¹ for the samples with V/Ag=4 and 2, respectively, indicating the effect of Ag⁺. In addition, a new peak at 920 cm⁻¹ appeared, which might be ascribed to silver vanadate species. The peak at 1007 cm⁻¹ disappeared for the V-Ag-O with V/Ag=1.5, indicating the complete formation of silver vanadate species.

FTIR spectra for the V-Ag-O catalysts after the reaction of selective oxidation of toluene at 573 K are presented in Fig. 5. Two peaks



Fig. 5. FTIR spectra of V-Ag-O catalysts after the reaction of selective oxidation of toluene at 573 K. (*) A sample prepared by co-precipitation after the same reaction at 613 K was added for comparison.

at 997 and 921 cm⁻¹ were observed for VO_x after the reaction, which could be assigned to V = O vibrations of V_6O_{13} , considering the XRD result above. The complex oxides with high Ag contents (V/Ag=2, 1.5 and 1) displayed two strong absorption peaks at 980 and 900 cm⁻¹, which might be assigned to V=O vibrations in Ag_{0.68}V₂O₅ [24] since XRD showed the phases of Ag_{0.68}V₂O₅ and metallic Ag for the samples after the reaction at 573 K. It was reported [11] that the V-Ag-O complex oxide with V/Ag = 2.16 contained the main phases of Ag_{0.68}V₂O₅ and Ag_{0.8}V₂O₅, and exhibited two strong absorption peaks at 980 and 900 cm⁻¹. The catalysts with low Ag contents (V/Ag=3 and 4) showed three bands around 984, 940–950 and 908–910 cm⁻¹. The peaks around 984 and $908-910 \text{ cm}^{-1}$ might be attributed to $Ag_{0.68}V_2O_5$, too, since they were close to the bands 980 and 900 cm⁻¹ for the samples with V/Ag lower than 2. The peaks around 940–950 cm⁻¹ were difficult to assign, but they seemed to be turned into the band at 900 cm⁻¹ with the increase of silver content. Thus, they might be assigned to V=O vibrations in VO_x affected by the presence of silver. The FTIR spectrum of the V-Ag-O prepared by co-precipitation was quite different from those of the V-Ag-O prepared by the HAD method due to the different phase compositions [20].

The morphology of V-Ag-O complex oxides was established using TEM analysis. The results are presented in Fig. 6. The V-Ag-O with V/Ag=3 dried at 393 K exhibit rods of vanadium oxides with layered structures and highly dispersed silver nano particles of 2-5 nm in diameters (Fig. 6(a and b)), similar to that reported by Sharma et al. [25]. These silver particles could not be detected by XRD due to their small sizes. Such layered structures of rods with highly dispersed silver nano particles remained after the sample was evacuated at 673 K (Fig. 6(c and d)). After the reaction of selective oxidation of toluene at 573 K, the rods remained while the silver nano particles disappeared. Considering that the only phase detected by XRD was Ag_{0.68}V₂O₅ here, the rods observed in Fig. 6(e and f) might be now Ag_{0.68}V₂O₅ with silver cations homogeneously distributed between the layers of VO_x octahedra. On the other hand, the rods disappeared for the V-Ag-O sample with V/Ag = 1.5 after the reaction of selective oxidation of toluene at 573 K. XRD showed $Ag_{0.68}V_2O_5$ and metallic Ag in this sample after the reaction. Thus, the layered structure of rods might be destroyed by the presence of large amount of metallic silver. Accordingly, spherical particles of metallic silver with Ag_{0.68}V₂O₅ might be formed in the V-Ag-O with V/Ag = 1.5 (Fig. 6(h)).

3.2. Surface acidic and redox properties

Fig. 7 shows the TPR profiles for the V-Ag-O samples evacuated at 673 K. The VO_x exhibited one reduction peak at 786 K. With the addition of Ag, two main peaks around 669-686 and 779K were observed for the V-Ag-O samples with V/Ag = 3 and 2. Considering the formation of silver vanadates in the V-Ag-O samples (see XRD results above), the current TPR profiles indicated that the reduction of silver vanadates might be much easier than VO_x . The reduction process of V-Ag-O complex oxides has been studied carefully by the combined techniques of TPR and XRD [20,26]. According to the previous results [20,26], the peaks around 669-686K for the V-Ag-O samples with V/Ag = 3 and 2 might be the reduction of silver vanadates $(Ag_2V_4O_{11} \text{ and } Ag_{0.68}V_2O_5)$ to V_2O_4 and metallic silver, while those with peak temperatures higher than 779K might be attributed to further reduction to V₂O₃. With the increase of silver content, a reduction peak around 594-600 K occurred for the V-Ag-O sample with V/Ag = 1.5 and 1, which might be attributed to the reduction of AgVO₃ [26]. In addition, the V-Ag-O samples prepared by the HAD method might be easier to reduce than that prepared by the co-precipitation method, since the former exhibited lower TPR peaks.



Fig. 6. TEM images for the V-Ag-O (V/Ag = 3) after drying at 393 K (a and b), evacuation at 673 K (c and d) and reaction at 573 K (e and f), as well as for the V-Ag-O (V/Ag = 1.5) after the reaction at 573 K (g and h). The reaction was performed at 573 K for the selective oxidation of toluene.

Fig. 8 shows the results of microcalorimetric adsorption of NH₃ at 423 K on the VO_x and V-Ag-O catalysts. The VO_x exhibited relatively strong surface acidity with the initial heat of 135 kJ/mol and coverage of 650 μ mol/g. Addition of silver decreased the initial heat, indicating the decreased surface acidity. The surface acidity was further weakened when more silver was added. The initial heat

and coverage were only 35 kJ/mol and 100 μ mol/g, respectively, for the adsorption of ammonia on the V-Ag-O sample with V/Ag = 2.

The probe reaction of isopropanol in air was employed to characterize the surface acidic and redox properties of the metal oxide catalysts. Table 2 shows the results. The conversion of isopropanol was high on VO_x (62%) with the high selectivity to propylene and



Fig. 7. TPR profiles of V-Ag-O catalysts prepared by HAD and co-precipitation (*) methods.

diisopropyl ether. Since it is known that isopropanol is dehydrated to propylene and diisopropyl ether on acidic sites and to acetone in air on redox sites, this result indicated that the VO_x exhibited quite strong surface acidity and relatively weak redox ability. With the addition of Ag, the conversion of isopropanol as well as the selectivity to propylene and diisopropyl ether was significantly decreased, implying the decreased surface acidity. However, the selectivity to acetone increased greatly, suggesting the greatly enhanced redox ability upon the addition of silver. When more silver was added, the selectivity to acetone was further increased. The selectivity to acetone might be higher than 65% for the V-Ag-O samples with V/Ag = 2, 1.5 and 1. These results are consistent with those of microcalorimetric adsorption of ammonia and TPR.

Two V-Ag-O samples with V/Ag=2 were compared in Table 2, which were prepared with different methods. The selectivity to acetone was similar (65–68%) for the two samples at 453 K. However,



Fig. 8. Differential heats versus coverage for NH_3 adsorption at 423 K on VO_x and V-Ag-O catalysts evacuated at 673 K.

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Conversion of isopropanol in air over the V-Ag-O catalysts at different temperatures (with the total space velocity of 12.7 L/(gh) and air/isopropanol = 20 v/v).

Catalyst	$T(\mathbf{K})$	Conversion (%)	Selectivity (%)		
			Propene	Diisopropyl ether	Acetone
VO _x	433	62	53	36	11
	453	90	88	12	0
V/Ag = 4	433	13	15	44	41
	453	65	39	28	34
V/Ag = 3	433	12	15	51	35
	453	61	36	35	29
V/Ag = 2	433	5	8	20	73
	453	24	17	18	65
V/Ag=1.5	433	3	5	17	78
	453	11	13	17	69
V/Ag = 1	433	3	9	25	66
	453	14	17	29	54
$V/Ag = 2^{a}$	453	2	18	14	68

 $^a\,$ Prepared by the co-precipitation method and calcined at 673 K. All the catalysts were pretreated in N_2 at 673 K for 2 h before the reaction.

the conversion of isopropanol was much higher over the sample prepared by the HAD method, due to the high surface area, than the one prepared by the co-precipitation method. Thus, the relative strengths of surface acidity and redox ability might be similar for the two samples, but both the surface acidity and redox ability might be significantly enhanced for the sample prepared by the HAD method as compared to the one prepared by the coprecipitation.

3.3. Selective oxidation of toluene

Table 3 presents the results of selective oxidation of toluene over the VO_x and V-Ag-O catalysts. The conversion of toluene was low (2%) over VO_x at 573 K with 48% and 31% selectivity to benzaldehyde and benzoic acid, respectively. With the addition of Ag, the conversion of toluene was increased to 6–9%, indicating the significantly increased catalytic activity. The total selectivity to benzaldehyde and benzoic acid was increased to over 90% at 573 K. Characterizations showed the greatly decreased surface acidity and increased redox ability for the V-Ag-O catalysts as compared to VO_x, which might be the reasons for the increased conversion of toluene and selectivity to benzaldehyde and benzoic acid. It is generally true that the increase of redox ability of VO_x and V-Ag-O increases the

Table 3

Selective oxidation of toluene over the V-Ag-O catalysts at different temperatures (with the total space velocity of 8.9 L/(g h) and air/toluene = 5 v/v).

Catalyst	$T(\mathbf{K})$	Conversion (%)	Selectivity (%)		
			Benzaldehyde	Benzoic acid	Total
VO _x	573	2	48	31	79
	593	4	45	32	77
V/Ag = 4	573	6	37	57	94
V/Ag = 3	573	9	48	45	93
V/Ag = 2	573	8	56	38	94
	593	17	48	40	88
	613	30	26	30	56
V/Ag = 1.5	573	9	61	31	93
V/Ag = 1	573	7	60	31	91
$V/Ag = 2^{a}$	613	5	92	0	92

^a Prepared by the co-precipitation method and calcined at 673 K. All the catalysts were heated from room temperature to the reaction temperature under the flow of reactants (air/toluene=5).

conversion of toluene and the increase of surface acidity favors the selectivity to benzoic acid due to the strong adsorption of toluene and benzaldehyde over acidic surfaces [7,13,22,27]. Thus, more benzoic acid was produced over the V-Ag-O (V/Ag = 2) prepared by the HAD method as compared to that prepared by co-precipitation, since the former possessed relatively stronger surface acidity [20].

The V-Ag-O catalysts with V/Ag = 1-4 seemed to exhibit the similar conversion of toluene (6-9%) and total selectivity to benzaldehvde and benzoic acid (>90%) at 573 K. However, the selectivity to benzaldehyde and benzoic acid was different for the catalysts with different V/Ag ratios. While the catalysts with less silver (V/Ag= 4 and 3) produced more benzoic acid than benzaldehyde, the catalysts with more silver (V/Ag = 2, 1.5 and 1) produced more benzaldehyde than benzoic acid. This might be due to that the catalysts with more silver exhibited weaker surface acidity, but stronger redox ability. Since XRD showed the only phase of $Ag_{0.68}V_2O_5$ in the V-Ag-O catalysts with V/Ag = 4 and 3, but both $Ag_{0.68}V_2O_5$ and metallic Ag in the V-Ag-O catalysts with V/Ag < 2, after the reaction at 573 K, the metallic silver in the catalysts might not be just a spectator. The presence of metallic silver in conjunction with $Ag_{0.68}V_2O_5$ seemed to favor the selective oxidation of toluene to benzaldehyde.

Two V-Ag-O samples with V/Ag=2 prepared with different methods were compared in Table 3 for the selective oxidation of toluene. It is apparent that the catalyst prepared with the HAD method exhibited much higher conversion of toluene than the one prepared by co-precipitation, probably due to that the former possessed significantly higher surface area. The total selectivity to benzaldehyde and benzoic acid was similar for the two catalysts. However, the selectivity to benzaldehyde was much higher on the co-precipitated catalyst than on the one prepared by the HAD method. This might be due to the higher surface area and relatively stronger surface acidity of the catalyst prepared by the HAD method.

Table 4 gives the data for the selective oxidation of toluene collected at different space velocity and temperatures over some V-Ag-O catalysts. Comparing the data in Tables 3 and 4, the increase of space velocity from 8.9 to 14.7 L/(gh) did not seem to decrease the conversion of toluene significantly. However, the selectivity to benzaldehyde seemed to increase with the increase of space velocity. In addition, when the reaction was performed at the relatively high space velocity (14.7 L/(gh)), the total selectivity to benzaldehyde and benzoic acid remained high (decreased only slightly) with the increase of reaction temperature and the conversion of toluene.

By optimizing the catalysts and reaction conditions, good performance for the selective oxidation of toluene to benzaldehyde and benzoic acid could be obtained. For example, the conversion of toluene reached 14% with 93% selectivity to benzaldehyde

Table 4

Selective oxidation of toluene over the V-Ag-O catalysts at different temperatures (with the total space velocity of 14.7 L/(g h) and air/toluene = 5 v/v).

Catalyst	$T(\mathbf{K})$	Conversion (%)	Selectivity (%)		
			Benzaldehyde	Benzoic acid	Total
V/Ag=3	573	9	62	33	95
	583	10	55	40	95
	593	13	40	55	95
V/Ag = 2	573	8	61	33	94
	583	11	56	35	91
	593	13	52	38	90
V/Ag = 1.5	573	9	66	29	95
	583	12	60	34	94
	593	14	58	35	93

The catalysts were heated from room temperature to the reaction temperature under the flow of reactants (air/toluene=5).

(58%) and benzoic acid (35%) over the V-Ag-O with V/Ag=1.5 at 593 K.

4. Summary and conclusions

- (1) V-Ag-O complex oxide catalysts with relatively high surface areas of $13-21 \text{ m}^2/\text{g}$ could be prepared by the heterogeneous azeotropic distillation (HAD) method. In this method, V₂O₅ and AgNO₃ were dissolved in aqueous solution of H₂O₂, followed by evaporation and drying in n-butanol at 353 K. Silver vanadates with highly dispersed nano silver particles in the layered structures of VO_x were formed during the preparation process. After heating in N₂ at 873 K, the sample with V/Ag=3 contained the main phase of $Ag_{0.68}V_2O_5$, which was also the only phase for the sample after the reaction of selective oxidation of toluene at 573 K. In addition, the relatively high surface areas of 13-21 m²/g remained for the V-Ag-O samples after the reaction at 573 K. The V-Ag-O catalysts with high contents of silver (V/Ag < 3) contained the phases of Ag_{0.68}V₂O₅ and metallic silver after the reaction of selective oxidation of toluene at 573 K. The presence of metallic silver and Ag_{0.68}V₂O₅ together seemed to favor the selective oxidation of toluene to benzaldehyde and benzoic acid.
- (2) Characterizations with microcalorimetric adsorption of NH₃, TPR and isopropanol probe reactions showed that the V-Ag-O catalysts exhibited weaker surface acidity but stronger redox ability than the VO_x. On the other hand, the relative strengths of surface acidity and redox ability might be similar for the V-Ag-O samples (with the same V/Ag ratio) prepared by the HAD and co-precipitation methods, but both the surface acidity and redox ability might be significantly enhanced for the sample prepared by the HAD method, due to the significantly increased surface area. Thus, the V-Ag-O with V/Ag = 2 prepared by the HAD method exhibited much higher activity than its counterpart prepared by the co-precipitation for the conversion of isopropanol and the selective oxidation of toluene to benzaldehyde and benzoic acid in air.
- (3) In the series of catalysts prepared by the HAD method, the addition of Ag into VO_x significantly increased the conversion of toluene and selectivity to benzaldehyde and benzoic acid, due to the decreased surface acidity and enhanced redox ability. Addition of more silver seemed to lead to the production of more benzaldehyde. Excellent performance of selective oxidation of toluene to benzaldehyde and benzoic acid could be obtained over the V-Ag-O catalysts prepared by the HAD method. For example, the conversion of toluene reached 14% with 93% selectivity to benzaldehyde (58%) and benzoic acid (35%) over the V-Ag-O with V/Ag = 1.5 at 593 K.

Acknowledgements

Financial supports from NSFC (20233040 and 20673055) and MSTC (2005CB221400) are acknowledged.

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