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Gas Phase Selective Catalytic Oxidation of Toluene to Benzaldehyde on V_2O_5-Ag_2O/η-Al_2O_3 Catalyst

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Abstract: Gas phase selective catalytic oxidation of toluene to benzaldehyde was studied on V_2O_5-Ag_2O/η-Al_2O_3 catalyst prepared by impregnation. The catalyst was characterized by XRD, XPS, TEM, and FT-IR. The catalytic results showed that toluene conversion and selectivity for benzaldehyde on catalyst sample No.4 (V/(V+Ag)=0.68) was higher than other catalysts with different V/Ag ratios. This was attributed to the higher surface area, larger pore volume and pore diameter of the catalyst sample No. 4 than the other catalysts. The XRD patterns recorded from the catalyst before and after the oxidation reaction revealed that the new phases were developed, and this suggested that silver had entered the vanadium lattice. XPS results showed that the vanadium on the surface of No.4 and No.5 sample was more than that in the bulk, thus forming a vanadium rich layer on the surface. It was noted that when the catalyst was doped by potassium promoter, the toluene conversion and selectivity for benzaldehyde were higher than those on the undoped catalyst. This was attributed to the disordered structure of V_2O_5 lattice of the K-doped catalyst and a better interfacial contact between the particles.

Key words: V_2O_5-AgO, gas phase, selective catalytic oxidation, toluene, benzaldehyde

1. Introduction

The selective catalytic oxidation of toluene on V_2O_5-Ag_2O catalysts is known to give a valuable product, benzaldehyde. The products of deep oxidation, CO_2 and CO, are also formed in accordance to a parallel-consecutive scheme. Different types of oxygen species are known to be present on the oxide surface. Besides structural (lattice) nucleophilic oxygen species (O^{2-}), electrophilic anion radical oxygen species (O^-, O_2^-) with high reactivity were detected [1]. According to [1,2] (O^{2-}) species is mainly responsible for partial oxidation of hydrocarbons, while (O^-, O_2^-) species are suggested to be involved in deep oxidation, leading to CO_x product formation. The hindrance of the electrophilic species formation and facilitating of the formation of the nucleophilic O^{2-} species promoted by K has been reported in the literature [3] and found in our experimental results.

2. Experimental

2.1. Catalyst preparation

Catalysts were prepared by impregnation from aqueous solution of ammonium metavanadate (Beijing Liulidian Chemical Plant, A.R., ≥99.0%) and silver nitrate (Beijing Chemical Plant, A.R., ≥99.8%). The catalyst doped by potassium was prepared by impregnation from aqueous solution of ammonium metavanadate containing potassium carbonate (Beijing Chemical Plant, A.R., ≥99.8%). Concentration of potassium in catalyst was 2%. The catalysts were dried at room temperature, and then calcined in air at 773 K for 5 h before use. XPS analysis showed that

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the atomic V:Ag ratio on the surface of the K-doped catalyst was the same as the undoped catalyst.

2.2. Set-up and procedure

Toluene (Beijing Chemical Plant, ≥99.5%) was introduced into a heated evaporator by a syringe-pump (LB-10). Products were analyzed by gas chromatography. Measurements of the catalytic activity were carried out in a plug-flow reactor. The tip of a thermocouple was inserted into the middle of the catalyst bed. The loading of the catalyst throughout the study was 0.5 g. The catalyst was diluted with quartz powder in a 1:3 ratio. All lines and valves were heated to 453 K in order to avoid the condensation of products and toluene. Experimental set-up has been described in Reference [4].

All catalysts were pre-treated in air at 773 K for 1 h before the reaction. The temperature was subsequently decreased to 753 K and the flow was switched. During reaction the temperature was increased stepwise by SHIMADEN PROG controller.

2.3. Catalyst characterization

The XRD data were acquired by using a D/max-IIIA X-ray instrument, with graphite monochromatized Cu K_α, XPS measurements were performed by VG ESCALAB MARKII, ASAP-2400 was used to measure the specific surface area of the catalysts.

3. Results and discussion

3.1. Catalyst performance

The data on the activity and selectivity in toluene oxidation for the V_2O_5-Ag_2O/η-Al_2O_3 catalyst are presented in Table 1.

Table 1. Catalyst performance of different composition [4]

Sample number	V/(V+Ag) (atomic ratio)	V_2O_5 (%)	Ag_2O (%)	Toluene conversion (%)	Selectivity for benzaldehyde (%)	Selectivity for CO_x (%)	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
1	1.00	20.00	0.00	39.44	25.08	36.81	115.96	0.211	7.28
2	0.90	17.52	1.26	41.99	18.64	38.09	21.27	0.066	12.34
3	0.75	14.03	3.18	44.05	18.19	37.45	56.03	0.134	9.53
4	0.68	12.50	4.00	49.58	29.22	43.27	57.10	0.149	10.44
5	0.60	10.81	4.91	44.56	30.50	41.83	39.38	0.117	11.90
6	0.50	8.80	5.99	37.10	22.69	34.56	75.08	0.181	9.65
7	0.30	5.05	8.02	36.80	23.42	33.29	146.07	0.316	8.66

Reaction conditions: temperature 663 K; SV 467.6 h^{-1}; air/toluene (molar ratio)=2.66.

It can be seen from Table 1 that when Ag was added to V_2O_5, toluene conversion first increases to a maximum of 49.58% at the V/(V+Ag) atomic ratio of 0.68, and then decreases. With the increase in Ag content, the surface area of catalyst decreases gradually, and the yield of benzaldehyde reaches a maximum. This is closely related to the change of usable surface area and pore distribution. This results in the increase in the volume of reactant molecules in the pore. These results improved the utilization efficiency of interior surface of the catalyst and diffusion of the molecule and catalytic performance greatly. When pore diameters become smaller, the obstruction to benzaldehyde was relatively severe, and benzaldehyde would stay longer in the pore. This causes deep oxidation reaction and produces CO_2. The bigger the pore, the bigger the catalyst effective factor, and therefore the catalyst demonstrates better activity. When Ag content is too high, too much Ag covers the catalyst active center, this would decrease the surface area and volume of the pore, therefore the activity drops instead. So the activity and selectivity of the catalyst is related to the pore with certain diameter range of the catalyst. For gas phase selective catalytic oxidation of toluene to benzaldehyde, the catalyst with a pore diameter of 10.44–11.90 nm shows the best selectivity to benzaldehyde, while the catalyst with too big or too small pore diameter will decrease the yield of benzaldehyde.

3.2. XRD studies

XRD results of phase composition for catalysts with different V/Ag ratios are listed in Table 2.

The result shows that the vanadium in the catalyst prepared by impregnation from aqueous solution of ammonium metavanadate was mainly present as V^{5+} ion before the reaction, and new phases of V_4O_9

and VO_2 were formed after the reaction. This indicates that a redox reaction between the V^{5+} and V^{4+} had taken place. It can be seen for the catalyst of No.2 (V/(V+Ag)=0.9), besides V_2O_5, new phase of $Ag_{0.35}V_2O_5\beta$ and AgV_7O_{18} were detected, this shows that the fresh catalyst contained a certain amount V^{4+} vacancy, transforming into $Ag_{0.80}V_2O_5$, V_2O_4 and VO_2 after the reaction, and Ag was separated out from the catalyst. In the sample of No.3 (V/(V+Ag)=0.7), new phase of $Ag_2V_4O_{10.84}$, $Ag_{1.2}V_3O_8$ were detected, but the phase of V_2O_5 was not found, this indicates that Ag entered the bulk. Besides the phases of V_2O_4 and VO_2 produced, $Ag_{0.80}V_2O_5$ and $Ag_{0.68}V_2O_5$ also were formed after the reaction with the appearance of Ag. For the No.4 catalyst (V/(V+Ag)=0.5), the main phase was $AgVO_3$, a small amount of $Ag_2V_4O_{10.84}$ as well as a minimum amount of Ag were found to exist before the reaction, and $Ag_{0.80}V_2O_5$, $Ag_{0.68}V_2O_5$, V_2O_4 and VO_2 were formed after the reaction, accompanied by the appearance of Ag. It is Ag that the sample of No.5 catalyst makes up; there is no change before and after the reaction for the catalyst. Addition of Ag is useful for the redox reaction of V^{5+} and V^{4+}, making it easy to form oxygen vacancy and beneficial to the oxidation of toluene to benzaldehyde. It is worth noticing that new phases of $Ag_{0.80}V_2O_5$, V_2O_4 and VO_2 products were formed after the reaction.

Table 2. The phase composition of catalysts with different V/Ag ratios

No	V/(V+Ag)	Phase compositions	
		Fresh catalyst	After the reaction
1	1.0	V_2O_5	V_2O_5 (little), V_4O_9, VO_2
2	0.9	$Ag_{0.35}V_2O_5\beta$, AgV_7O_{18}, V_2O_5 (little)	$Ag_{0.80}V_2O_5$, V_2O_4, VO_2, Ag
3	0.7	$Ag_2V_4O_{10.84}$, $Ag_{1.2}V_3O_8$	$Ag_{0.80}V_2O_5$, $Ag_{0.68}V_2O_5$, V_2O_4, VO_2, Ag
4	0.5	$AgVO_3$, $Ag_2V_4O_{10.84}$, Ag (minim)	$Ag_{0.80}V_2O_5$, $Ag_{0.68}V_2O_5$, V_2O_4, VO_2, Ag
5	0.0	Ag	Ag

3.3. XPS results

The binding energy values of V_2O_5-Ag_2O/η-Al_2O_3 catalyst before and after the reaction are shown in Table 3. The XPS spectra for V of the catalyst are presented in Figures 1 and 2.

Table 3. Binding energy values of V_2O_5-Ag_2O/η-Al_2O_3 catalyst before and after the reaction

Catalyst	V/(V+Ag)in bulk	V/(V+Ag) on surface	O 1*s*	Al 2*p*	V $2p_{1/2}$	V $2p_{3/2}$	Ag $3d_{3/2}$	Ag $3d_{5/2}$
No.4 (fresh)	0.68	0.72	530.8	74.3	522.5	517.3	373.8	367.8
No.4 (after reaction)	0.68	0.48	531.2	74.5	522.5	517.3	374.1	368.1
No.5 (fresh)	0.60	0.45	531.2	74.5	522.5	517.4	374.0	368.0
No.5 (after reaction)	0.60	0.44	531.5	74.7	522.8	517.6	374.3	368.3

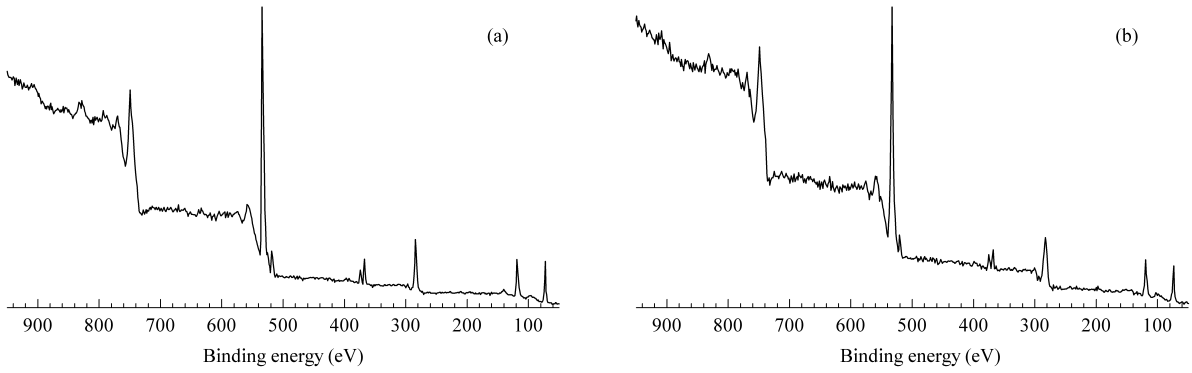

Figure 1. XPS spectra of sample No.4 (V/(V+Ag)=0.68) in V_2O_5-Ag_2O catalyst
(a) Fresh, (b) After reaction

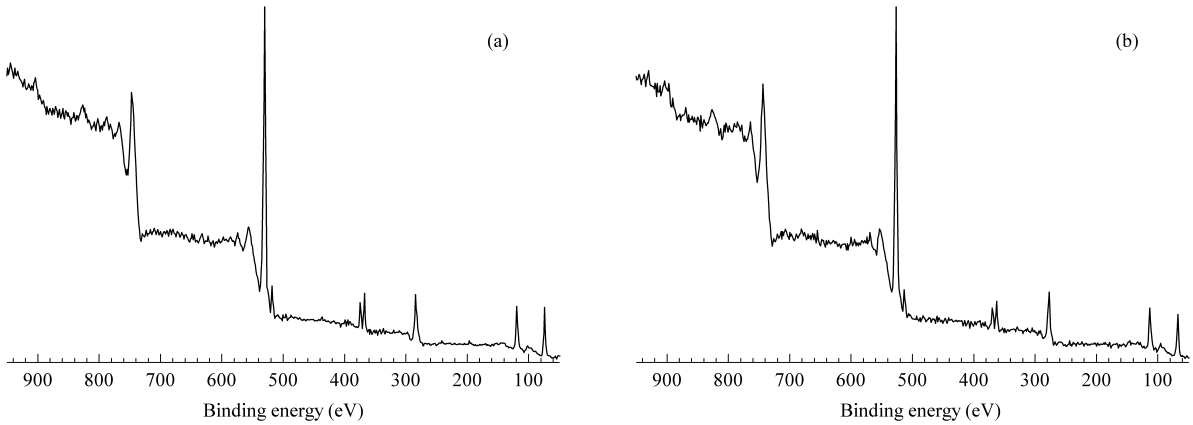

Figure 2. XPS spectra of sample No.5 (V/(V+Ag)=0.60) in V_2O_5-Ag_2O catalyst

(a) Fresh, (b) After reaction

From Figures 1 and 2, it can be shown that the $3d_{3/2}$ signal peak at 367.8 eV and the $3d_{5/2}$ signal peak at 373.8 eV of element Ag are two sharp independent peaks respectively, its position is a characteristic peak of Ag^+ ion. The weak $3d_{3/2}$ signal peak at 377.1 eV and the $3d_{5/2}$ signal peak at 377.6 eV of element Ag are attributed to metallic silver, and it indicates that metallic silver enriches on the surface of the sample. The $3p_{1/2}$ signal peak at 517.3 eV and the $3p_{3/2}$ signal peak at 522.5 eV of element V are characteristic peaks respectively, showing that vanadium in the sample has two different chemical environment, that is, vanadium in or on the surface. These results are in agreement with the result given above by XRD studies. Thus XPS result suggests that V is richer on the surface than in the bulk. In addition, the vanadium rich layer on the surface, might be the main reason for the high catalytic performance and selectivity to benzaldehyde for No.4 and No.5 samples.

3.4. SEM studies

The SEM images of No.4 and No.5 samples before and after the reaction are shown in Figures 3 and 4 .

From SEM image of the sample, it is seen that active components were distributed evenly on the surface of the catalyst before the reaction, and clusters were formed by the assemblage of particles after the reaction. It can be inferred that micro-pores are very few and the channel of the pore is short as the result of the the assemblage of particles. This would help to improve the selectivity of the catalyst.

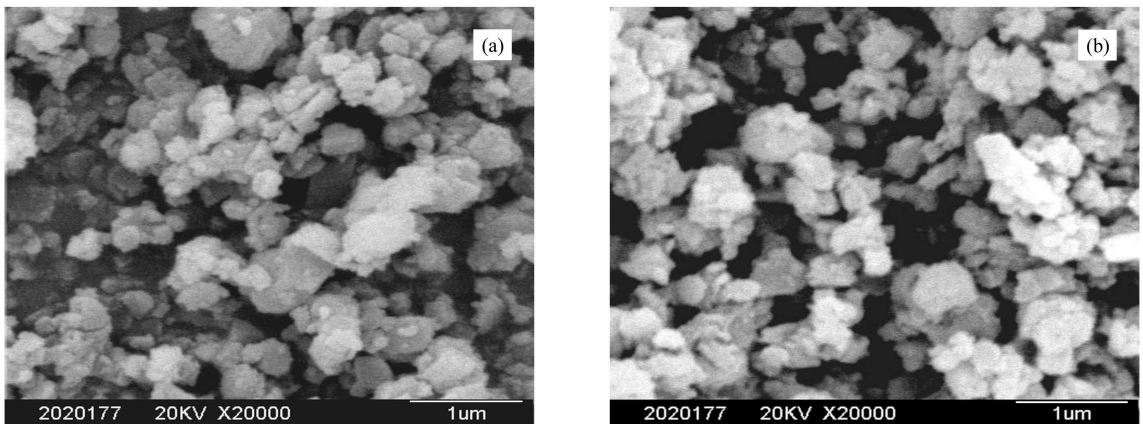

Figure 3. SEM image of sample No.4 (V/(V+Ag)=0.68)

(a) Before reaction; (b) After reaction

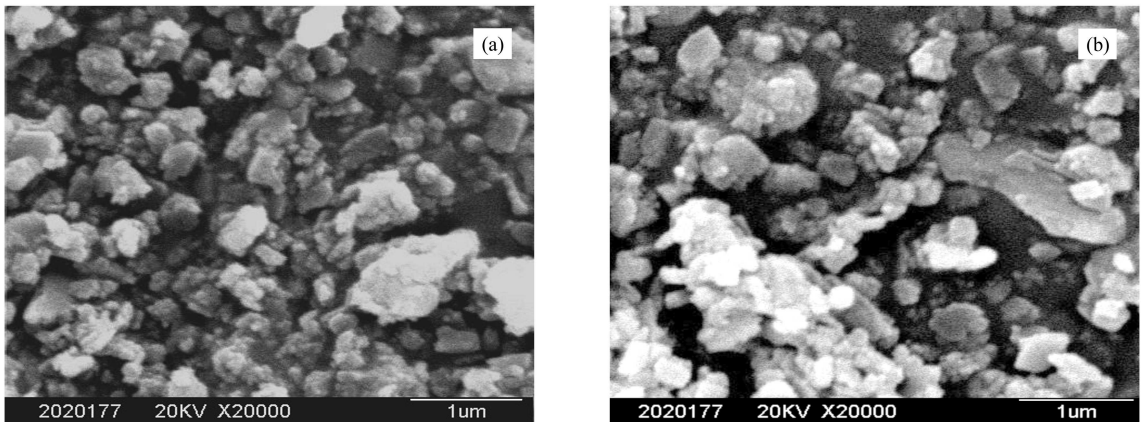

Figure 4. SEM image of sample No.5 (V/(V+Ag)=0.60)
(a) Before reaction; (b) After reaction

3.5. Effect of potassium on the catalyst

The catalyst doped with promoter potassium can improve the selectivity to benzaldehyde. The catalyst doped remarkably improved the toluene conversion and selectivity to benzaldehyde. This maybe understood by the following consideration. Potassium, being an electron-donating additive to vanadia, facilitates the process of electron transfer to the electrophilic species accompanied by the formation of the nucleophilic species. Thus, the concentration of $(V^{5+}(O_n^-))$ sites, active in the deep oxidation, decreases as the result of doping. This agrees with the change of the catalytic selectivity due to K-doping in the presence of gaseous oxygen (Table 4). Furthermore, the K-doping introduces disorder in the structure of the V_2O_5 particles. The particles would have a better interfacial contact to each other. This would cause a positive effect in the partial oxidation [5]. Catalytic property of doped K and undoped K catalyst of V_2O_5-Ag_2O is shown in Table 4. The FT-IR spectra for the catalyst are shown in Figure 5. The broad bands at 1050 cm^{-1} are attributed to the vibrations of V=O. The broad band at 1630 cm^{-1} is due to the water of crystallization of support Al_2O_3. The broad band at 3000 cm^{-1} is due to absorption of the K—O bond.

Table 4. Catalytic property of V_2O_5-Ag_2O/η-Al_2O_3 catalyst with or without the promoter potassium

Catalysts	Toluene conversion (%)	Selectivity for benzaldehyde (%)
V_2O_5-Ag_2O/η-Al_2O_3	29.35	11.27
V_2O_5-Ag_2O-K_2O/η-Al_2O_3	42.16	20.86

Reaction conditions: temperature 763 K, SV 500 h^{-1}, air/toluene (molar ratio)=5.00.

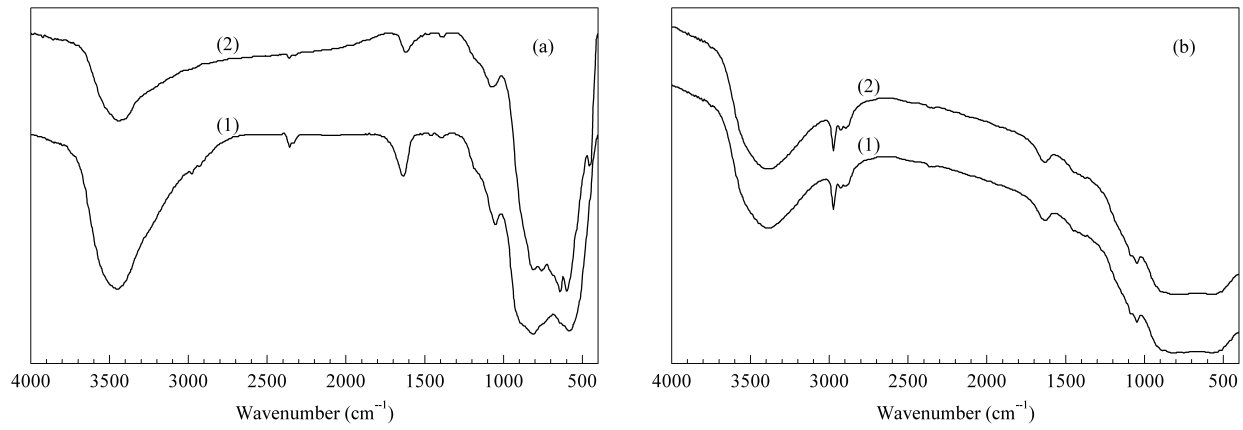

Figure 5. FT-IR spectra of the sample catalyst
(a) V_2O_5-Ag_2O, (b) V_2O_5-Ag_2O-K_2O; (1) Before reaction, (2) After reaction

3.6. Reaction mechanism

In the fixed bed reactors, gas-solid reactions take place on the catalyst surface. The main reactions for the gaseous phase selective catalytic oxidation of toluene are [6].

$$C_7H_8(\text{toluene}) + O_2 \rightarrow C_7H_6O(\text{benzaldehyde}) + H_2O \quad (1)$$

$$C_7H_6O + \frac{1}{2}O_2 \rightarrow C_7H_6O_2(\text{benzoic acid}) \quad (2)$$

$$C_7H_6O_2 + \frac{15}{2}O_2 \rightarrow 7CO_2 + 3H_2O \quad (3)$$

$$C_7H_8 + \frac{3}{2}O_2 \rightarrow C_6H_6(\text{benzene}) + CO_2 + H_2O \quad (4)$$

$$C_6H_6 + \frac{15}{2}O_2 \rightarrow 6CO_2 + 3H_2O \quad (5)$$

Among them, reactions (4) and (5) are free radical reactions caused by gaseous phase decomposition and oxidation, and the reaction rate is related to the density of oxygen. Reaction (3) is the catalytic oxidation, and reactions (1) and (2) are catalytic reaction of partial oxidation. The redox mechanism for the selective catalytic oxidation, according to the model of Mars and VanKrevelen, consists of two steps. First, hydrocarbon compounds are adsorbed on the catalyst surface and react to turn into the product with oxygen atom of the catalyst, at the same time the catalyst is reduced. The second step is that the reduced catalyst is changed back to the original catalyst with the participation of oxygen. The model is shown in Figure 6 [7].

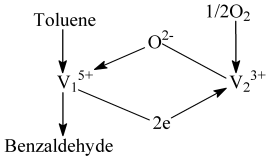

Figure 6. The model of Mars and VanKrevelen on catalytic oxidation

It has been confirmed that oxygen has the following adsorbing forms, O^-, O_2^-, O_3^-, O_2^{2-}, and O^{2-}. O^{2-} in fact has changed into lattice oxygen of the catalyst surface [8]. Because sliver has very strong ability to give electrons, the adsorbed oxygen of the catalyst surface would be impelled to turn into O_2^- and O^-, and finally O^{2-}. The course of oxygen adsorption on silver surface as follows: $O_2(g) \xrightarrow{e^-} (O_2^-) \xrightarrow{e^-} 2O^- \xrightarrow{2e^-} 2O^{2-}$ (lattice). This shows that oxygen adsorbed has entered to the catalyst bulks. The adsorbed species of oxygen stayed on the catalyst surface, participated in the oxidation, and enabled the redox reaction to keep on going.

V_2O_5 is *n*-semiconductor with O^{2-} vacancy, generally contains some V^{4+}, so it is apparently paramagnetic. V^{4+} is well dispersed and so the V_2O_5 crystal remains steady.

4. Conclusions

The incorporation of Ag_2O to the V_2O_5 catalyst improved the toluene conversion and selectivity for benzaldehyde in the catalytic oxidation of toluene. This is ascribed to the appearance of a V-rich layer on the catalyst surface and a better pore structure of the catalyst as the result of Ag addition. On the K-doped catalyst, the catalytic performance was further improved, this is attributed to the formation of a disorder structure of the V_2O_5 lattice and so, leads to the suppression of the deep oxidation of toluene.

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