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Synergetic effect of $FeVO_4$ and α - Fe_2O_3 in Fe–V–O catalysts for liquid phase oxidation of toluene to benzaldehyde

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Abstract

Synergistic effect of FeVO₄ with α -Fe₂O₃ was found in Fe–V–O catalyst, which was responsible for the high apparent formation rate (A.F.R.) of benzaldehyde in liquid phase oxidation of toluene by hydrogen peroxide. The synergistic effect might create VO_x species as active sites; moreover, it improved the reducibility and the reactivity of Fe–V–O catalyst. In order to gain the high A.F.R. of benzaldehyde, the catalyst should have the moderate reducibility.

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Keywords: Liquid oxidation; Synergistic effect; Toluene; Benzaldehyde; FeVO4; a-Fe2O3

Benzaldehyde (BzH) is widely used for producing dyestuffs, perfumery, pharmaceuticals, *etc.* Liquid phase oxidation of toluene to BzH by hydrogen peroxide (H₂O₂) on solid catalyst has attracted great attention, because this process takes some advantages, such as, (1) the high selectivity of BzH, (2) the mild reaction conditions, (3) the easy separation of catalysts from products, (4) the preferable industrial application, *etc.* [1]. Vanadium (V)-based oxide is considered to be one of the promising catalysts for the reaction [1]. For example, 72.8% selectivity of BzH and 13.6% conversion of toluene were obtained at 363 K with bis (acetylacetonato) oxovandium (VO(acac)₂) as catalyst in acetic acid [2]. VO_x/ γ -Al₂O₃ (14 wt.% loading of V₂O₅) catalyst showed 88.4% selectivity of BzH with 29.8% conversion of toluene in the reaction and acetonitrile as solvent at 50 °C [3]. Nevertheless, the reactivity of these catalysts should be further improved for the industrial application. On the other hand, there are some controversies concerning the active sites for V-based catalyst. Some people considered that VO_x species were responsible for the high reactivity of the catalysts; the others thought that V⁴⁺/V⁵⁺ species were possible active sites [2–5]. Without deep understanding the structure–function relationship, it is difficult to develop an effective catalyst by the modification of catalyst composition and preparation.

In this work, the comparatively high apparent formation rate of BzH was achieved on novel Fe–V–O catalyst with Fe/(Fe + V) = 0.5 mol ratio in the liquid oxidation of toluene to BzH by H_2O_2 . Synergetic effect between FeVO₄ and α -Fe₂O₃ in the catalyst was found, and its role on the properties and reactivity of the catalyst were discussed.

Fe–V–O catalysts were prepared by method described as following. The calculated amount of ferric nitrate (Fe(NO₃)₃·9H₂O, Shanghai Chem., A.R.), ammonium metavanadate (NH₄VO₃, Shanghai Chem., A.R.) and citric acid

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Catalytic reactivity and properties of re-v-o catalysis in the inquid-phase oxidation of toluche by hydrogen peroxide.								
Catalysts	$S_{\rm BET}~({\rm m^2/g})$	$V_{\rm pore} \ ({\rm cm}^3/{\rm g})$	Phase composition (mol%) $^{\rm b}$	Apparent formation rate of product ($\times 10^{-2}$, g m ⁻² h ⁻¹)				
				BzH	BzOH	BzA	Phenol	Cresol
Blank	-	-	_	_	_	_	-	_
V_2O_5	3.0	0.20	_	20.5	9.5	12.5	34.5	28.0
$Fe_{0.5}V_{0.5}$	2.8	0.26	$FeVO_4$ (≈ 100)	71.5	12.5	0	6.0	0

FeVO₄ (50.0), α-Fe₂O₃ (50.0)

FeVO₄ (20.0), α-Fe₂O₃ (80.0)

210.0

180.0

35.0

0

0

0

0

0

0

0

Reaction condition: 5 mL toluene, 20 mL H₂O₂ (30 wt.%), 20 mL acetic acid, 0.2 g catalyst, 60 °C, 3 h.

α-Fe₂O₃ (100)

^b The date in the parentheses is the relative content of the phase.

0.26

0.26

0.07

 $(C_6H_8O_7 \cdot H_2O_7 \cdot H_2O_7$ Fe:V:critic acid:H₂O was about x:(1 - x):2:30 (molar ratio, $0 \le x \le 1$). The solution was slowly evaporated at 80 °C for 12 h, and then calcined at 800 °C for 6 h. The as-prepared Fe–V–O catalyst is denoted as Fe_xV_(1 - x), in which x expresses Fe/(Fe + V) molar ratio in the catalyst. α -Fe₂O₃ was prepared by the decomposition of powder ferric nitrate (Fe(NO₃)₃·9H₂O, Shanghai Chem., A.R.) at 600 °C for 8 h, and V₂O₅ was prepared by the pyrolyzation of powder ammonium metavanadate (NH₄VO₃, Shanghai Chem., A.R.) at 600 °C for 8 h.

 N_2 isothermal adsorption-desorption of Fe–V–O catalyst was performed at the temperature of liquid nitrogen by Micromeritics ASAP400 adsorptionmeter. The specific surface area (SBET) was calculated according to BET method, and the volume of pores (V_{pore}) was evaluated by t-plot analysis of adsorption isotherm. As shown in Table 1, the S_{BET} of Fe–V–O catalyst was much low, possibly due to the high calcination temperature of the catalyst. The addition of Fe into the catalyst decreased the S_{BET} and hardly changed the V_{pore} .

XRD patterns of Fe–V–O catalysts were collected by Rogaku Rotflex D/Max-C powder X-ray diffractometer with Cu K α radiation ($\lambda = 0.15046$ nm) operated at 40 kV and 30 mA (Fig. 1). FeVO₄ ($2\theta = 16.5^{\circ}, 24.8^{\circ}, 27.0^{\circ}, 31.2^{\circ}$ and 42.0°) and α -Fe₂O₃ ($2\theta = 24.1^{\circ}$, 33.1°, 35.6°, 40.8°, 49.4°, 54.0°, 62.4° and 63.9°) were detected from Fe_{0.7}V_{0.3} and $Fe_{0.8}V_{0.2}$ catalyst, indicating that these two catalysts were mainly composed of α -Fe₂O₃ and FeVO₄. Fe_{0.5}V_{0.5} was FeVO₄ with trace α -Fe₂O₃ impurity. Relative content of each phase is estimated as the formula $I_i / \Sigma I_i \times 100\%$, where I_i is the strongest diffraction intensity of FeVO₄ ($I_{2\theta = 27.0^{\circ}}$) and α -Fe₂O₃ ($I_{2\theta = 33.1^{\circ}}$). With the increase of Fe/V ratio, the relative content of FeVO₄ decreases while that of α -Fe₂O₃ increases in Fe–V–O catalysts (Table 1).

Raman spectra of Fe-V-O catalysts were recorded by Renishaw Raman system 1000 spectrometer equipped with Ar⁺ laser at $\lambda = 532$ nm and the power of 5 mW (Fig. 2). For Fe_{0.5}V_{0.5} (FeVO₄), Raman bands attributed to stretches of V=O in VO₄ unit (950 cm⁻¹), asymmetric stretches of isolated VO₄ unit (913, 883, 819 and 709 cm⁻¹), asymmetric stretching vibration of V–O–Fe bond (648 cm⁻¹), asymmetric and symmetric bending vibration of VO₄ unit (363 and



Fig. 1. XRD patterns of (a) $Fe_{0.5}V_{0.5}$, (b) $Fe_{0.7}V_{0.3}$, (c) $Fe_{0.8}V_{0.2}$ and (d) α -Fe₂O₃.

Table 1

Fe_{0.7}V_{0.3}

Fe_{0.8}V_{0.2}

a-Fe₂O₃

0.6

0.6

35.2



Fig. 2. Raman spectra of (a) $Fe_{0.5}V_{0.5}$, (b) $Fe_{0.7}V_{0.3}$ and (c) $Fe_{0.8}V_{0.2}$.

327 cm⁻¹) were detected [6,7]. Raman bands at 264 and 212 cm⁻¹ belonging to α -Fe₂O₃ were found in Fe_{0.7}V_{0.3} and Fe_{0.8}V_{0.2}. These results further indicate that Fe_{0.7}V_{0.3} and Fe_{0.8}V_{0.2} contained α -Fe₂O₃ and FeVO₄.

H₂-TPR plot of Fe–V–O was obtained by a home-built fixed bed TPR apparatus (Fig. 3). The onset temperature of reduction (T_o) and the maximal temperature of reduction peak (T_m) were measured to study the reducibility of these catalysts. Three reduction peaks of V₂O₅ occurred at *ca*. 699, 745 and 795 °C, corresponding to the reduction of V₂O₅ \rightarrow V₂O₄ \rightarrow V₆O₁₁ \rightarrow V₂O₃. α -Fe₂O₃ displayed two reduction peaks at 426 and 690 °C for the reduction of Fe₂O₃ \rightarrow FeO \rightarrow Fe. The H₂-TPR plots of Fe–V–O catalysts presented two reduction processes, due to the overlapping reduction stages of V and Fe ions. Fe_{0.7}V_{0.3} and Fe_{0.8}V_{0.2} catalysts showed the different H₂-TPR plots from V₂O₅, α -Fe₂O₃ and Fe_{0.5}V_{0.5} (FeVO₄). T_o decreased as the sequence of V₂O₅ (605 °C) > Fe_{0.5}V_{0.5} (536 °C) > Fe_{0.8}V_{0.2} (529 °C) > Fe_{0.7}V_{0.3} (519 °C) > α -Fe₂O₃ (346 °C). In addition, T_m increased as the order of Fe_{0.7}V_{0.3} (555, 703 °C) < Fe_{0.8}V_{0.2} (615, 718 °C) < Fe_{0.5}V_{0.5} (741, 784 °C). Thus, the interaction of FeVO₄ and α -Fe₂O₃ occurred in Fe_{0.8}V_{0.2} > Fe_{0.5}V_{0.5}.

Liquid phase oxidation of toluene by H_2O_2 on Fe–V–O catalysts was carried out in a three necked round-bottomed flask (250 mL) equipped with a reflux condenser as well as water bath and magnetic stirring. Reactants and products were analyzed by gas chromatography (Beifen Ruili GC-3420) with FID and KB-1 capillary column. In order to evaluate the intrinsic reactivity of Fe–V–O catalysts, the apparent formation rate of product (A.F.R.) on these catalysts was tested (Table 1). A.F.R. of product (g m⁻² h⁻¹) is defined as the mass of product formed on the unit specific-surface-area catalyst and in an hour. BzH did not formed on α -Fe₂O₃ in the reaction. BzH, benzyl alcohol (BzOH), benzoic acid (BzA), phenol and cresol produced on V₂O₅ and Fe–V–O catalysts. A.F.R. of BzH decreased as the order of Fe_{0.7}V_{0.3} > Fe_{0.8}V_{0.2} > Fe_{0.5}V_{0.5} (FeVO₄) > V₂O₅ > α -Fe₂O₃. Fe_{0.7}V_{0.3} showed the higher A.F.R. of BzH than the other reported V-based catalysts [2,3]. These results indicate that vanadium oxygen species were close relative to the reactivity of the catalysts. The synergetic effect of FeVO₄ and α -Fe₂O₃ occurred and significantly improved the A.F.R. of BzH on Fe_{0.7}V_{0.3} and Fe_{0.8}V_{0.2} catalysts. For achieving the high A.F.R. of BzH, Fe–V–O catalyst should possess the proper content of FeVO₄ and α -Fe₂O₃.



Fig. 3. H₂-TPR plots of (a) V_2O_5 , (b) $Fe_{0.5}V_{0.5}$, (c) $Fe_{0.7}V_{0.3}$, (d) $Fe_{0.8}V_{0.2}$ and (e) α -Fe₂O₃.



Fig. 4. Relationship of relative content of FeVO₄ with specific activity of BzH and the reducibility (T_o) of these catalysts.

 α -Fe₂O₃ is trigonal system with six-fold coordination. FeVO₄ has a triclinic structure with eight-fold coordination and consists of three distinct isolated VO₄ units [6,7]. During the preparation of Fe–V–O catalysts, the interaction of α -Fe₂O₃ and FeVO₄ occurred because of their structural difference. The interaction could create lattice defect VO_x species with the weak V–O bond in the interface of FeVO₄ and α -Fe₂O₃. The VO_x species were relative high mobility of V⁵⁺ and the driving force to decrease the surface free energy [6,7]. Hence, Fe–V–O catalyst containing FeVO₄ and α -Fe₂O₃ showed the stronger reducibility than individual V₂O₅ and FeVO₄.

It can be seen in Fig. 4, T_o is close relative to FeVO₄ content in these catalysts, suggesting that FeVO₄ content has great influences on the reducibility of these catalysts. FeVO₄ content might affect the number of VO_x species formed in the interface of FeVO₄ and α -Fe₂O₃. Hence, Fe–V–O catalyst with different FeVO₄ content showed the different reducibility. On the other hand, it is well accepted that the liquid oxidation of toluene by H₂O₂ on oxide catalyst follows Mars–van-Krevelen mechanism [1–5]. Therefore, the reducibility of Fe–V–O catalysts determined their catalytic reactivity. The proper increase in reducibility of the catalyst enhanced the A.R.F. of BzH, but the much high reducibility caused the further oxidation of BzH and the oxidation of phenyl group to phenol and cresol. Fe_{0.7}V_{0.3} exhibited the higher A.F.R. of BzH than any other catalysts, due to its moderate reducibility.

In conclusion, the occurrence of synergetic effect between FeVO₄ and α -Fe₂O₃ led to the formation of VO_x species as active sites and modified the reducibility of Fe–V–O catalyst, which in turn improved the reactivity of the catalyst. It is necessary that the catalyst had the proper reducibility for achieving the high A.F.R. of BzH.

Acknowledgments

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