Synergetic effect of FeVO$_4$ and α-Fe$_2$O$_3$ in Fe–V–O catalysts for liquid phase oxidation of toluene to benzaldehyde

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Abstract

Synergistic effect of FeVO$_4$ with α-Fe$_2$O$_3$ 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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Benzaldehyde (BzH) is widely used for producing dyestuffs, perfumery, pharmaceuticals, *etc.* Liquid phase oxidation of toluene to BzH by hydrogen peroxide (H$_2$O$_2$) 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-Al$_2$O$_3$ (14 wt.% loading of V$_2$O$_5$) 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 V^{4+}/V^{5+} 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$_2$O$_2$. Synergetic effect between FeVO$_4$ and α-Fe$_2$O$_3$ 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(NO$_3$)$_3$·9H$_2$O, Shanghai Chem., A.R.), ammonium metavanadate (NH$_4$VO$_3$, Shanghai Chem., A.R.) and citric acid

Table 1
Catalytic reactivity and properties of Fe–V–O catalysts in the liquid-phase oxidation of toluene by hydrogen peroxide.[a]

| Catalysts	S_{BET} (m²/g)	V_{pore} (cm³/g)	Phase composition (mol%) [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	$FeVO_4$ ($\approx$100)	71.5	12.5	0	6.0	0
$Fe_{0.7}V_{0.3}$	0.6	0.26	$FeVO_4$ (50.0), α-Fe_2O_3 (50.0)	210.0	35.0	0	0	0
$Fe_{0.8}V_{0.2}$	0.6	0.26	$FeVO_4$ (20.0), α-Fe_2O_3 (80.0)	180.0	0	0	0	0
α-Fe_2O_3	35.2	0.07	α-Fe_2O_3 (100)	–	–	–	–	–

[a] Reaction condition: 5 mL toluene, 20 mL H_2O_2 (30 wt.%), 20 mL acetic acid, 0.2 g catalyst, 60 °C, 3 h.
[b] The date in the parentheses is the relative content of the phase.

($C_6H_8O_7 \cdot H_2O$, Tianjin Chem. A.R.) were solved thoroughly by deionized water to form solution. In this solution, Fe:V:critic acid:H_2O was about x:(1 − x):2:30 (molar ratio, $0 \leq x \leq 1$). 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-Fe_2O_3 was prepared by the decomposition of powder ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, Shanghai Chem., A.R.) at 600 °C for 8 h, and V_2O_5 was prepared by the pyrolyzation of powder ammonium metavanadate (NH_4VO_3, 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 (S_{BET}) 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 $K\alpha$ radiation (λ = 0.15046 nm) operated at 40 kV and 30 mA (Fig. 1). $FeVO_4$ (2θ = 16.5°, 24.8°, 27.0°, 31.2° and 42.0°) and α-Fe_2O_3 (2θ = 24.1°, 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-Fe_2O_3 and $FeVO_4$. $Fe_{0.5}V_{0.5}$ was $FeVO_4$ with trace α-Fe_2O_3 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 $FeVO_4$ ($I_{2\theta = 27.0°}$) and α-Fe_2O_3 ($I_{2\theta = 33.1°}$). With the increase of Fe/V ratio, the relative content of $FeVO_4$ decreases while that of α-Fe_2O_3 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 λ = 532 nm and the power of 5 mW (Fig. 2). For $Fe_{0.5}V_{0.5}$ ($FeVO_4$), Raman bands attributed to stretches of V=O in VO_4 unit (950 cm^{-1}), asymmetric stretches of isolated VO_4 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 VO_4 unit (363 and
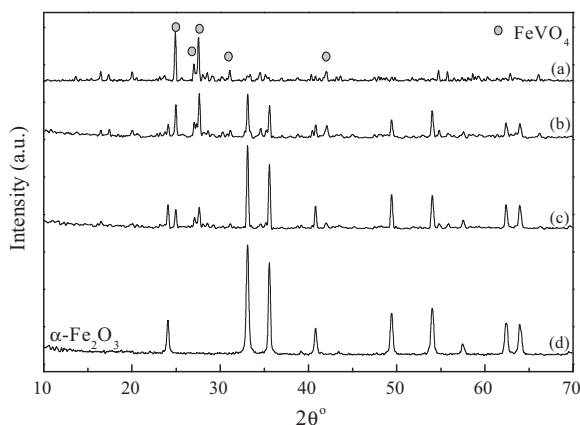
Fig. 1. XRD patterns of (a) $Fe_{0.5}V_{0.5}$, (b) $Fe_{0.7}V_{0.3}$, (c) $Fe_{0.8}V_{0.2}$ and (d) α-Fe_2O_3.