

Article

Exclusively catalytic oxidation of toluene to benzaldehyde in an O/W emulsion stabilized by hexadecylphosphate acid terminated mixed-oxide nanoparticles

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ABSTRACT

A series of hexadecylphosphate acid (HDPA) terminated mixed-oxide nanoparticles have been investigated to catalyze the oxidation of toluene exclusive to benzaldehyde under mild conditions in an emulsion of toluene/water with the catalysts as stabilizers. With the HDPA-Fe₂O₃/Al₂O₃ as the basic catalyst, a series of transition metals, such as Mn, Co, Ni, Cu, Cr, Mo, V, and Ti, was respectively doped to the basic catalyst to modify the performance of the catalytic system, in expectation of influencing the mobility of the lattice oxygen species in the oxide catalysts. Under normally working conditions of the catalytic system, the nanoparticles of catalysts located themselves at the interface between the oil and water phases, constituting the Pickering emulsion. Both the doped iron oxide and its surface adsorbed hexadecylphosphate molecules were essential to the catalytic system for excellent performances with high toluene conversions as well as the exclusive selectivity to benzaldehyde. Under optimal conditions, ~83% of toluene conversion and >99% selectivity to benzaldehyde were obtained, using molecular oxygen as oxidant and HDPA-(Fe₂O₃-NiO)/Al₂O₃ as the catalyst. This process is green and low cost to produce high quality benzaldehyde from O₂ oxidation of toluene.

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1. Introduction

The oxidation of toluene to benzaldehyde by O_2 has been one of the reactions highly demanded in industry in the past decades [1–4] and it should be the best route to produce benzaldehyde, a highly useful chemical in many aspects. The reaction seems simple, just an insertion of one oxygen into the C–H bond of benzyl, but very difficult, for the heterogeneous catalytic processes for the reaction have been studied for several decades, of which performance, however, is still far below the demand [3,5]. The present industrial processes have serious environmental and corrosion problems, as shown in Scheme 1, and thus produced benzaldehyde inevitably contained a little amount of halogens [6], which hindered high-end uses of the compound such as in perfumes or foods. Liquid oxidations of toluene by oxygen with noble metals based catalysts including Pd, Au, Pt, Ag, Ru and their alloys have become popular research topics in recent years, owing to their excellent catalytic

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Scheme 1. The main routes used in the current industry for the production of benzaldehyde.

activities [7–14], under solvents or solvent-free conditions [1,3,15–20]. Ag modified mixed-node MOF catalyst has been found highly selective for the oxidation of toluene to benzalde-hyde, but just at very low conversions [8]. Bimetallic PdAu catalysts reported by Hutchings and co-workers for the oxidation of toluene toward benzyl benzoate do get outstanding activity at a relatively mild temperature (160 °C, 1 MPa O₂) [4,21,22]. Generally, high selectivity to benzaldehyde at high toluene conversion has been still not available with these catalytic systems.

For the green oxidation of toluene by O2 exclusively to benzaldehyde, a highly efficient catalytic system was explored in our previous work using a biphasic system with HDPA-FeOx nanoparticles locating themselves at the interface of toluene and water to stabilize the O/W emulsion, i.e, Pickering emulsion [2]. Resasco et al. [23-25] have made the first use of Pickering emulsions for the biphasic hydrodeoxygenation and condensation in biomass refining as well as other reactions. We report here the further investigation on the doping effect of a series of metal oxides such as Mn, Co, Ni, Cu, Cr, Mo, V, and Ti on the catalyst HDPA-FeO_x, anticipating the enhancement of the mobility of lattice oxygen of the catalyst. In addition, we also use a special kind of nano alumina as support for the easy preparation of the modified catalysts and the high stability of the catalysts in application. With the well-defined particle structures, the catalysts show significantly improved and reliably repeated catalytic performance for the title reaction and the NiO co-loaded catalyst exhibits the best performance with ~83% conversion of toluene (a TOF of 0.027 nm⁻²·s⁻¹) and ~100% selectivity to benzaldehyde under mild conditions. This is a very important progress toward the practical use of the catalytic process for production of high quality benzaldehyde.

Fig. 1 schematically shows the composition of the Pickering emulsion with the catalyst nanoparticles positioned at the interface of O/W. The long organic chains of HDPA molecules in a suitable density protect the nanoparticles from gathering and ensure the catalyst particles at the interface of the O/W emulsion, boosting the access of toluene to the nanoparticles. The phosphate head in HDPA adsorbed on the surface is important to tune the catalyst surface as well as to switch off unneeded sites unselective for the toluene oxidation. Considering the solubility of the reactants, the water has a significant effect on the transportation of O_2 from gas phase to the liquid phase as well as the products from the surface of the catalyst to the liquid phase (Figs. 1(a), 1(b), and 1(c)). Fig. 1(d) depicts the real laser confocal fluorescence photograph of the reaction mixture



Fig. 1. (a) Schematic show of the toluene/water Pickering emulsion with HDPA-Fe₂O₃/Al₂O₃ nanoparticles located at the interface of toluene and water. (b) Diagram showing the transfer of toluene, benzalde-hyde and oxygen at the interface. (c) Magnified show of the interface between the Fe₂O₃ (110, as an example) surface and the HDPA layer and the access of reactant molecules to the catalytic sites as well as the seceding of product molecules along the lanes of the HDPA chains. (d) The real laser confocal fluorescence photograph of the emulsion with small amount of rhodamine B as fluorescence dye adsorbed on the catalyst.

with small amount of rhodamine B as fluorescence dye adsorbed on the catalyst, confirming the O/W Pickering emulsion of the reactive system. Under such conditions, the surface-bonded HDPAs boost the access of the nonpolar toluene as well as the seceding of the relatively polar product, i.e., benzaldehyde, from the nonpolar surface to the polar environment, constituting a complete catalytic cycle of high performance.

2. Experimental

2.1. Catalyst preparation

The nano γ -Al₂O₃ used as support in current investigation was obtained according to our previous report [26]. Fe₂O₃/Al₂O₃ sample was prepared by incipient wet impregnation method with corresponding aqueous solution of Fe(NO₃)₃·9H₂O. The 25 wt% loading of Fe₂O₃ was set as the weight ratio of Fe₂O₃/(Fe₂O₃ + Al₂O₃). The impregnating mixture was sealed and aged at room temperature for 24 h. The resulting material was dried at 90 °C overnight and calcined in a tube furnace at 450 °C for 3 h in flowing air. The sample was labeled as 25Fe₂O₃/Al₂O₃. The figure before the metal oxides meant the content in weight percent of the transition metal oxide in the catalyst.

The (Fe₂O₃-MO_x)/Al₂O₃ (M = Mn, Co, Ni, Cu, Cr, Mo, V, Ti) samples were also prepared by incipient wet impregnation method. The precursors of the doped oxides were Mn(NO₃)₂, Co(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O, Cu(NO₃)₂·3H₂O, Cr(NO₃)₃·9H₂O, (NH₄)₂MOO₄·4H₂O, NH₄VO₃, and tetrabutyl titanate, respectively. The mass ratio of Fe₂O₃ to MO_x was 4 : 1, the loadings of (Fe₂O₃-MO_x) in all samples were shown as the weight ratio of (Fe₂O₃-MO_x)/(Fe₂O₃-MO_x + Al₂O₃) and fixed at



Fig. 2. The schematic show of the process of catalyst preparation.

25 wt%. The treatment of these mixtures was similar to Fe_2O_3/Al_2O_3 sample. These sample names were abbreviated as $Fe_{20}Mn_5$, $Fe_{20}Co_5$, $Fe_{20}Ni_5$, $Fe_{20}Cu_5$, $Fe_{20}Cr_5$, $Fe_{20}Mo_5$, $Fe_{20}V_5$ (oxalate was used to help the dissolution of NH4VO₃.), and $Fe_{20}Ti_5$ (HCl was used to inhibit the hydrolysis of tetrabutyl titanate during preparation.), respectively. In addition, a series of $(Fe_2O_3-xNiO)/Al_2O_3$ or $(Fe_2O_3-xCuO)/Al_2O_3$ catalysts was prepared with different doping amount of Ni or Cu and the samples were correspondingly named as $Fe_{20}Ni_5$, $Fe_{15}Ni_{10}$, $Fe_{10}Ni_{15}$, Ni_{25} , $Fe_{20}Cu_5$, $Fe_{15}Cu_{10}$, $Fe_{10}Cu_{15}$, and Cu_{25} .

The decoration of HDPA was performed using a modified preparation hydrothermal method. Taking the of HDPA-25Fe₂O₃/Al₂O₃ as an example, certain amount of HDPA (Sigma-Aldrich) were added into a 100 mL beaker containing 40 mL of deionized water with vigorous stirring at 80 °C until HDPA completely dissolved and then corresponding amount of 25Fe₂O₃/Al₂O₃ powder was added into the above mixture. After stirring for 2 h, the solution was transferred into a Teflon-lined autoclave and heated at 120 °C for 24 h. After that, the mixture was washed with deionized water and absolute ethanol several times and filtered by suction. The achieved solid powders were dried at 80 °C overnight. For convenience, the final catalysts were hereafter denoted as H-Fe25, H-Fe20Mn5, H-Fe20Co5, H-Fe20Ni5, H-Fe20Cu5, H-Fe20Cr5, H-Fe20Mo5, H-Fe20V5, and H-Fe₂₅Ti₅, respectively. For all of the samples, the HDPA loading in the catalysts was expressed as the weight ratio of HDPA/((Fe₂O₃-MO_x)/Al₂O₃) or HDPA/(25Fe₂O₃/Al₂O₃) and fixed at ~5 wt% (the density of surface HPDA was about ~1 HDPA/nm² of the sample). The process of catalyst preparation is schematically shown as Fig. 2. The nano alumina used as support brings about great convenience in catalyst preparation as well as the stability in performance of the catalyst in reac-

Table 1

The abbreviated name of different samples and their corresponding compositions.

Sample name	Composition of the sample	Sample name	Composition of the sample	
FeM	$(Fe_2O_3-MO_x)/Al_2O_3$	H-FeM	HDPA-(Fe ₂ O ₃ -MO _x)/Al ₂ O ₃	
Fe ₂₅	25Fe ₂ O ₃ /Al ₂ O ₃	H-Fe ₂₅	HDPA-25Fe ₂ O ₃ /Al ₂ O ₃	
Fe ₂₀ Mn ₅	(20Fe ₂ O ₃ -5MnO _x)/Al ₂ O ₃	$H-Fe_{20}Mn_5$	HDPA-(20Fe ₂ O ₃ -5MnO _x)/Al ₂ O ₃	
Fe ₂₀ Co ₅	(20Fe ₂ O ₃ -5CoO _x)/Al ₂ O ₃	H-Fe ₂₀ Co ₅	HDPA-(20Fe ₂ O ₃ -5CoO _x)/Al ₂ O ₃	
Fe ₂₀ Ni ₅	(20Fe ₂ O ₃ -5NiO)/Al ₂ O ₃	H-Fe ₂₀ Ni ₅	HDPA-(20Fe ₂ O ₃ -5NiO)/Al ₂ O ₃	
Fe ₁₅ Ni ₁₀	(15Fe ₂ O ₃ -10NiO)/Al ₂ O ₃	H-Fe ₁₅ Ni ₁₀	HDPA-(15Fe ₂ O ₃ -10NiO)/Al ₂ O ₃	
Fe10Ni15	(10Fe ₂ O ₃ -15NiO)/Al ₂ O ₃	H-Fe ₁₀ Ni ₁₅	HDPA-(10Fe ₂ O ₃ -15NiO)/Al ₂ O ₃	
Ni25	25NiO/Al ₂ O ₃	H-Ni ₂₅	HDPA-25NiO/Al ₂ O ₃	
FeNi	$(Fe_2O_3-NiO)/Al_2O_3$	H-FeNi	HDPA-(Fe ₂ O ₃ -NiO)/Al ₂ O ₃	
Fe20Cu5	(20Fe ₂ O ₃ -5CuO)/Al ₂ O ₃	H-Fe ₂₀ Cu ₅	HDPA-(20Fe ₂ O ₃ -5CuO)/Al ₂ O ₃	
Fe15Cu10	(15Fe ₂ O ₃ -10CuO)/Al ₂ O ₃	H-Fe ₁₅ Cu ₁₀	HDPA-(15Fe ₂ O ₃ -10CuO)/Al ₂ O ₃	
Fe10Cu15	(10Fe ₂ O ₃ -15CuO)/Al ₂ O ₃	$H-Fe_{10}Cu_{15}$	HDPA-(10Fe ₂ O ₃ -15CuO)/Al ₂ O ₃	
Cu ₂₅	25CuO/Al ₂ O ₃	H-Cu ₂₅	HDPA-25CuO/Al ₂ O ₃	
FeCu	(Fe ₂ O ₃ -CuO)/Al ₂ O ₃	H-FeCu	HDPA-(Fe ₂ O ₃ -CuO)/Al ₂ O ₃	

tion. The names and compositions of all the catalysts investigated are elucidated in the Table 1 for clarity.

2.2. Catalyst characterization

The X-ray diffraction (XRD) patterns were recorded using a XRD-6000 X-ray diffractometer (Shimadzu, Japan) with Cu $K\alpha$ radiation (0.15418 nm) as X-ray source. The voltage and current were set at 40 kV and 30 mA, respectively. The surface area and textural characteristics of the catalysts were measured by N₂ sorption using a Micrometrics TriStar II 3020 analyzer. Transmission electron microscopy (TEM) images of catalysts were obtained by using a JEOL JEM-2100 at a voltage of 180 kV. Thermogravimetric analysis and derivative thermogravimetry (TG-DTA) analysis was conducted on a STA 449C apparatus (Netzsch) in air from room temperature to 800 °C with a heating rate of 10 °C/min. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was carried out to analyze the leached metal from the catalysts in the solution after the reaction using an instrument of Optima 5300 DV (PerkinElmer).

In-situ Fourier transform infrared (FT-IR) spectra of toluene adsorption on the catalyst H-Fe₂₅ were recorded to analyze the interaction of toluene with the catalyst. The sample was pressed to a self-supported disk in the diameter of 0.5 inch and then was mounted in a quartz cell for evacuation, heat treatment and adsorption of toluene. The transmission FT-IR spectra were recorded through the CaF₂ windows of the quartz cell using a NEXUS870 FT-IR spectrometer.

2.3. Catalytic tests

The liquid oxidation of toluene was performed in a 40-mL of Teflon autoclave with 0.6 mL of toluene and 0.06 g of catalyst in 25 mL of deionized water, which formed biphasic system for catalyst dispersion and transport of reactants and products. The pH of the system was adjusted by H_2SO_4 solution. After purging with O_2 three times, 2.0 MPa of O_2 was fed into the autoclave. Then the autoclave was heated to reaction temperatures under stirring. Qualitative determination and quantitative



Fig. 3. TEM images of γ-Al₂O₃ (a) and H-Fe₂₅ (b) samples.

analysis were conducted by GC-9560 (Shanghai Huaai) gas chromatography equipped with a SE-54 column and FID detector. After reaction, ethylbenzene was added as internal standard to calibrate the conversion of reactant and selectivity of products.

3. Results and discussion

3.1. Characterization of H-FeM nanorods

Fig. 3 depicts the TEM images for observation on the morphology and microstructure of the catalysts. The alumina support and the H-Fe25 show almost the same morphologies of nanorods, implying that Fe₂O₃ mainly exists in a highly dispersed state on the γ -Al₂O₃ surface. According to the specific surface area of the alumina used, 132.7 m²/g, the thickness of iron oxide in amount of 25 wt% can be calculated as ~2-3 atomic layers, which is too thin to be clearly observed by the common TEM. The morphological features of H-FeM (not shown) are also very similar to that of H-Fe25 and the results are consistent with the XRD measurements, which, as shown in Fig. 4, indicate the alumina is γ-Al₂O₃ (JCPDS no.29–0063). After loading with iron oxide, apart from the characteristic peaks of γ -Al₂O₃, some other weak peaks ascribed to Fe₂O₃ are detected. But the extra characteristic peaks ascribed to the other metal oxides are not observed for H-FeM, suggesting that these metal oxides are well dispersed on the corresponding catalysts. For the samples H-Fe20Ni5, H-Fe15Ni10 and H-Fe10Ni15, the diffraction peaks other than those ascribed to y-Al₂O₃ cannot be



Fig. 5. The N₂ adsorption-desorption isotherms and BJH pore size distribution curves (inset) of the typical samples.

observed, indicative of the highly dispersion of the mixture of oxides of iron and nickel in the catalysts (Fig. 4(b)). For the catalyst H-Fe₁₀Cu₁₅, however, the diffraction peaks ascribed to CuO are evident, implying the not so good compatibility or mixing of copper oxide with the iron oxide on the γ -Al₂O₃ support (Fig. 4(c)). For the catalysts H-FeCr, H-FeMo, and H-FeV, further characterizations on their structures have not been performed, because of their complete inertness for the reaction.

The N₂ sorption isotherms of typical samples (Fig. 5) exhibit all the IV-type isotherms with evident H2-type hysteresis loops, which is characteristic of irregular mesostructure and interstice mesoporous structure formed by nanoparticle assembly according to IUPAC [27,28]. After loading metal oxides on the



Fig. 4. XRD patterns of the as prepared samples.

Table 2 Textural parameters of the $\gamma\text{-Al}_2\text{O}_3,$ Fe_25, and FeM samples.

Sampla	$\int (m^2/a)$	Pore volume	Average pore		
Sample	S_{BET} (III ² /g)	(cm ³ /g)	diameter (nm)		
γ-Al ₂ O ₃	132.7	0.48	12.4		
Fe ₂₅	101.9	0.40	14.8		
Fe ₂₀ Mn ₅	107.9	0.32	10.6		
Fe ₂₀ Co ₅	109.6	0.38	13.0		
Fe ₂₀ Ni ₅	114.7	0.40	12.7		
Fe ₂₀ Cu ₅	107.4	0.38	13.1		

 γ -Al₂O₃ surface, the porous textures of the samples seem unchanged much compared with the support alumina. The textural parameters of the samples are summarized in Table 2.

The results of FT-IR and TG measurements, as shown in Fig. 6, confirm the existence of HDPA on the surface of FeM nanorods. The two peaks located at 3000–2800 cm⁻¹ are attributed to the stretching vibration of $-CH_2$ - and they show up with the samples decorated by HDPA adsorption [29]. By the results of TG measurements (Fig. 6(b)), the weight losses from the HDPA adsorbed samples are close to 5 wt%, similar to the amount of hexadecyl in the HDPA added in preparation of the catalyst. According to these results, the density of HDPA on the surface of the catalyst nanoparticles is ~1 HDPA/nm², which should be optimal to the catalytic performance of the catalyst for toluene oxidation and by tuning the active sites on the surface of FeM nanorods and the access of the reactants to the reactive sites, and the full coverage of HDPA on the surface of these samples is about 15 wt% according to our previous works [2].



Fig. 6. FT-IR spectra (a) and TG results (b) of the typical samples.

3.2. Catalytic performance of the catalysts

As shown in Fig. 7(a), the conversion of toluene is \sim 71% and benzaldehyde is the only product with H-Fe₂₅ used as catalyst. A control experiment with Fe₂₅ as catalyst reports a conversion of toluene below 8% with a lower selectivity of benzaldehyde (\sim 40.1%), other byproducts are benzyl alcohol (20.3%) and benzoic acid (39.6%). This means that the modification of HDPA greatly promotes the toluene conversion and ensures an exclusive selectivity in this catalytic system. With the modification of other metal oxides, the benzaldehyde is still the only product and the doping of NiO or CuO to H-Fe₂₅ gives



Fig. 7. (a–c) The catalytic performances of H-FeM nanorods for the toluene oxidation (toluene: 0.6 mL; catalyst: 0.06 g; water: 25 mL; pH: 2.5; p_{02} : 2 MPa; temperature: 180 °C; time: 4 h); (d) XRD patterns of the spent H-FeM catalysts; (e) The TEM image of the spent H-Fe₂₅ catalyst. *The concentration of Fe³⁺ and Ni²⁺ equals respectively to that listed in Table 3 determined by ICP.

promoted catalytic performance. Surprisingly, the catalysts are entirely inactive for the reaction when high valence metal oxides such as Cr, Mo, V, or Ti are used as dopants, even the dope amount is only $1\sim5$ wt%, implying the limitation of the dopants on the mobility of the lattice oxygen of the catalysts.

In order to further investigate the dope effect of NiO or CuO on the property of the catalyst for the reaction, the H-FeM nanorods with different molar ratio of Ni (or Cu) to Fe were prepared and tested for the reaction, as shown in Fig. 7(b) and 7(c). It can be seen from the figures that the catalyst with iron oxide as major active constituent and minor dopant of nickel oxide gives the best catalyst with nickel oxide or copper oxide as major active constituent shows fairly good catalytic performance for the reaction. But the stability of iron oxide catalyst is better than that of the nickel oxide and copper oxide catalysts, as discussed below.

After the use in reaction, the crystal structures (XRD) and morphology (TEM) of the catalysts, as shown in Figs. 7(d) and 7(e) are similar to those before reaction (Fig. 4(a) and Fig. 3(b)), indicating that the inherent structure of this kind of composite catalysts is rather stable. In addition, the concentration of leaching ions from the catalysts is always very low in the aqueous solution after reaction, though the leaching amount to the solution of Mn, Co, Ni, or Cu ions seems a little higher than that of iron (Table 3). As to the functions for the toluene conversion of the metal ions in the solution, control experiment with only Fe3+ and Ni2+ ions in the solution as catalysts, in similar concentrations to those with H-Fe₂₀Ni₅ as catalyst, was carried out and the conversion of toluene is only ~5% with a benzaldehyde selectivity of ~32% (Fig. 7(b)), other byproducts are benzyl alcohol (45.2%) and benzoic acid (22.8%). These facts indicate that the catalytic activity is mainly produced by the metal oxides composite nanoparticles and Fe₂O₃ is very important in this catalytic system. Therefore, it can be concluded that the loading of Fe₂O₃ has an essential influence on toluene conversion and the HDPA appears to ensure the exclusive selectivity of benzaldehyde as well as to promote the conversion of toluene. The moderately doped NiO is beneficial to increase the catalytic performance of the catalyst.

3.3. Effects of pH value and reaction temperature

With the H-Fe₂₀Ni₅ is used as catalyst in the reaction, it is found that, similar to HDPA-FeO_x catalyst, the pH value has a prominent effect on toluene conversion, as shown in Fig. 8(a).

Table 3

The concentrations of metallic ions in aqueous solution after reaction determined by ICP.

Comple	Concentrations (ppm)					
Sample	Fe	Mn	Со	Ni	Cu	
H-Fe ₂₅	7.2	-	-	-	-	
H-Fe ₂₀ Mn ₅	6.7	26.7	-	-	-	
H-Fe ₂₀ Co ₅	7.1	-	12.2	-	-	
H-Fe ₂₀ Ni ₅	9.3	-	-	15.9	-	
H-Fe ₂₀ Cu ₅	6.4	-	-	-	41.5	



Fig. 8. (a) Effect of pH on toluene oxidation (Other reaction conditions are the same); (b) Effect of reaction temperature on toluene oxidation (Other reaction conditions are the same).

The optimal pH value is ~2.5, neither lower nor higher pH value is detrimental to the catalytic activity. According to a previous results [30], the oxidation of toluene proceeded by hydride (H-) transfer from toluene to the catalyst in water, nevertheless, hydride (H-) was replaced by hydrogen atom (H \cdot) in toluene solution. Moreover, the catalyst whose surface is positively charged will benefit to the transfer of hydride (H-) to the catalyst and boost the oxidation of toluene. Therefore, relatively lower pH value in the biphasic catalytic system will lead to the surface of H-Fe₂₀Ni₅ positively charged. More protons in the solution, however, will lead to an unstable surface of the catalyst. Fig. 8(b) shows the influence of temperature on the reaction and the optimal value of temperature is 180 °C with exclusive selectivity. Higher temperatures used would result in the homogeneous oxidation initiated by O2 diradicals and generate byproducts. The turnover frequencies (TOF, in unit of nm⁻² s⁻¹) based on the surface area of the catalysts are listed in Table 4.

3.4. In-situ FT-IR study to explore the surface species during the toluene oxidation

In order to explore the interaction of toluene with the catalysts, in-situ FT-IR spectra of the catalyst H-Fe₂₅ were recorded with the surface adsorbed toluene. The sample was pressed into a self-supported disk of 0.5 inch in diameter and then was mounted in a quartz cell for evacuation, heat treatment and adsorption of toluene. The transmission FT-IR spectra were recorded through the CaF₂ windows of the quartz cell using a NEXUS870 FT-IR spectrometer. The results are shown in Fig. 9. The bands at ~2912 and ~2847 cm⁻¹ are attributed to the vi-

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The turnover	frequency	(TOF)	of the	catalysts	for to	luene	conversion.
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Samula	TOF	Comple	TOF	
Sample	$(nm^{-2} s^{-1} \times 10^{-2})$	Sample	(nm ⁻² s ⁻¹ × 10 ⁻²)	
H-Fe ₂₅	2.34	H-Fe ₁₀ Ni ₁₅	1.88	
H-Fe ₂₀ Mn ₅	0.86	H-Ni ₂₅	1.61	
H-Fe ₂₀ Co ₅	1.62	H-Fe ₁₅ Cu ₁₀	1.53	
H-Fe ₂₀ Ni ₅	2.74	H-Fe ₁₀ Cu ₁₅	1.41	
H-Fe ₂₀ Cu ₅	2.07	H-Cu ₂₅	2.27	
H-Fe ₁₅ Ni ₁₀	2.05	*Fe ³⁺ , Ni ²⁺	0.16 s ⁻¹	

* The concentrations of $Fe^{3\ast}$ and $Ni^{2\ast}$ equal to those listed in Table 3 determined by ICP.



Fig. 9. Spectra of the samples. (a) toluene; (b) benzaldehyde; (c) $H-Fe_{25}$ evacuated at room temperature; (d) $H-Fe_{25}$ evacuated and followed by adsorption of gaseous toluene at room temperature for 30 min; (e) $H-Fe_{25}$ evacuated at room temperature and followed by toluene adsorption at 180 °C for 30 min. The spectrum was recorded at room temperature after the sample disk cooling down to room temperature and the gaseous toluene in the quartz cell was pumped out.

brations of C-H bonds in the methyl or methylene groups of the toluene (curve a) or the HDPA in H-Fe25 (curves c, d and e) [29, 31]. The absorptions at \sim 3079 and \sim 3027 cm⁻¹ should be referred to the vibration of C-H bond connected to the aromatic ring of toluene. It appears that the toluene has hardly adsorbed at room temperature but strongly adsorbed on the catalyst at 180 °C (curve e), by the intensities of the peaks at \sim 3079 and \sim 3027 cm⁻¹. More importantly, the absorption at \sim 1219 cm⁻¹ shows up by the chemical adsorption of toluene at 180 °C which can be assigned to the formation of R-C-O-Fe by the insertion of the lattice oxygen of Fe₂O₃ into the C-H bond of benzyl [32,33]. Coincidently, the shoulder peaks near 3079 and 3027 cm⁻¹ (i.e., 3091 and 3044 cm⁻¹) are also observed, which are reasonably attributed to the vibrations of aromatic C-H bonds in the adsorbed C₆H₅-C-O-Fe, which are also influenced by the narrow HDPA lanes. Summing up the results, we speculate that the lattice oxygen species are involved in the conversion of toluene to benzaldehyde with the assistance of HDPA at the catalyst surface.

3.5. Possible mechanism for the oxidation of toluene

With the results presented above, the mechanism of the catalytic system seems clear (Fig. 1). The HDPA-functionalized oxides nanorods locate themselves at the interface of toluene and water in the biphasic system as observed by laser confocal fluorescence microscope (Fig. 1(d)), and their hydrophilic/hydrophobic characteristics play an important role to stabilize the O/W emulsion (Fig. 1(a)). The surface HDPA molecules in a suitable density protect the nanorods from gathering and endow the catalyst amphipathic property. The HDPA in a surface density of ~1 molecule per nm² boosts the access of toluene toward the catalyst surface and, more important, it seems that HDPA molecules can align the toluene molecules touching the catalyst surface. The phosphate head in HDPA adsorbed on the surface may tune the catalyst surface to switch off unneeded sites unselective for the toluene oxidation. The hole dispersion system forms a Pickering emulsion under the stirring conditions, preventing the aggregation of droplets [34].

In addition, the water is helpful for the transfers of O_2 from gaseous as well as the products from the surface of the catalyst to the liquid phase (Figs. 1(b) and 1(c)), considering their relatively better solubility in water. In the process, the HDPA plays a role indispensable. As the consequence of synergistic interactions in the catalytic system, high-quality benzaldehyde is produced in exclusive selectivity at high conversions of toluene under mild conditions with gaseous O_2 as oxidant.

4. Conclusions

In summary, we have demonstrated a reliable strategy to prepare hexadecylphosphate acid (HDPA)-functionalized $(Fe_2O_3-MO_x)/Al_2O_3$ catalysts for the oxidation of toluene to benzaldehyde in toluene/water biphasic system with exclusive selectivity of benzaldehyde under mild conditions. The use of Al₂O₃ nanorods as support is greatly beneficial to the preparation and modification of the catalyst, with which the catalyst is more stable and easily tuned by deposition of HDPA and the dope of other metals. In the catalytic system, the HDPA-functionalized (Fe₂O₃-MO_x)/Al₂O₃ nanoparticles locate at the interface between oil and water phases to stabilize the Pickering emulsion. The loading of Fe₂O₃ and the HDPA are essential to ensure the exclusive selectivity of benzaldehyde and the catalytic activity for toluene conversion. Among the metal oxides of Mn, Co, Ni, Cu, Cr, Mo, V and Ti used as modifiers, the moderately doped nickel oxide enhances the catalytic performance of the system. Under optimal conditions, ~83% of toluene conversion and ~100% selectivity to benzaldehyde are obtained with molecular oxygen used as oxidant. This work displays an effective process, green and low cost, to produce high-quality (halogen-free) benzaldehyde from toluene oxidation using O_2 as oxidant and it should also be useful for other similar reactions to produce important chemicals in high quality.

Notes

The authors declare no competing financial interest.

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Graphical Abstract

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Exclusively catalytic oxidation of toluene to benzaldehyde in an O/W emulsion stabilized by hexadecylphosphate acid terminated mixed-oxide nanoparticles

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A hexadecylphosphate acid-functionalized ($Fe_2O_3-MO_x$)/ Al_2O_3 nanorods as the catalyst was used for the oxidation of toluene to benzaldehyde in toluene/water biphasic system under mild conditions. Both the doped iron oxide and the surface adsorbed hexadecylphosphate molecules were essential to provide the excellent catalytic performance for high toluene conversion and the exclusive selectivity to benzaldehyde.

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十六烷基膦酸配合的复合氧化物纳米催化剂稳定的O/W乳液中 甲苯单一氧化为苯甲醛

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摘要:苯甲醛是一种用途广泛的重要化学品,通过O₂氧化甲苯制取苯甲醛是最佳生产途径,也是近几十年来工业界迫切 需要的反应之一.虽然该反应在苄基上结合一个氧再脱除两个氢即可,对该反应的多相催化过程也已经研究了几十年, 但其性能仍远远低于工业要求.当前的工业过程主要有甲苯氯化水解法和甲苯均相氧化法两种,但都存在严重的环境污 染和腐蚀问题,且产品中含有少量卤素,阻碍了其在诸如香水或食品中的高端应用.近年来,以O₂作为氧化剂及Pd,Au, Pt,Ag,Ru等贵金属或它们间的合金为催化剂的甲苯液相氧化反应研究取得了一些很好的进展,但仍然不能在高甲苯转化 率下高选择性地得到苯甲醛.本课题组曾报道了一种高效的混相催化体系,以O₂作为氧化剂将甲苯专一地催化氧化为苯 甲醛,其中十六烷基膦酸-氧化铁(HDPA-FeO_x)纳米颗粒处在甲苯和水的界面上,稳定了该O/W类皮克林乳液(Pickering). 为了进一步提高催化剂晶格氧的移动性以提升催化活性,本文采用Mn,Co,Ni,Cu,Cr,Mo,V和Ti等一系列金属氧化物对催 化剂HDPA-FeO_x进行掺杂,同时使用一种特殊的纳米Al₂O₃作为载体,大大地增加了催化剂制备的便捷性和保证了催化剂 在实际应用中的稳定性.

TEM和XRD结果表明, Al₂O₃负载了金属氧化物后, 其形貌仍为纳米棒状结构, 并只能观察到Al₂O₃的晶相衍射峰, 表明金属氧化物均匀地负载在其表面. BET结果表明, 负载后的催化剂的孔结构与载体Al₂O₃类似. FT-IR结果表明, HDPA很好地吸附在了催化剂表面. TG结果表明, 催化剂中HDPA含量与加入量相符, 质量分数为~5%. 结合前期工作可知, HDPA能够调整FeM纳米棒表面催化性质, 且以1 HDPA/nm²的密度为最佳, 此时, 甲苯液相氧化为苯甲醛的催化性能最佳.

催化性能测试结果表明,催化剂吸附了HDPA后,甲苯的转化率显著增加,且只生成苯甲醛.在所考察的第二种掺杂 金属中,以Ni的效果为最好.该催化剂在最佳反应条件下,甲苯转化率为83% (TOF = 0.027 nm⁻²·s⁻¹),苯甲醛选择性为 ~100%.而Cr,Mo,V和Ti等高价金属则抑制了该反应,这也说明通过掺杂第二种金属调变晶格氧的活动性可影响反应性 能.经过优化后,最佳反应条件为:pH值为2.5,反应温度为180 ℃.原位FT-IR结果表明,180 ℃下,甲苯在吸附有HDPA的 催化剂表面能够发生化学吸附,苄基C-H键解离并与晶格氧产生结合,形成了C₆H₅--CH₂-O-Fe中间物种,该物种脱附即得 苯甲醛.该温度下,表面HDPA对甲苯的化学吸附不可缺.

关键词: 甲苯氧化; 苯甲醛; 十六烷基膦酸; 分子氧; 皮克林

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