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Preparation and investigation on a novel nanostructured magnetic base catalyst MgAl–OH-LDH/$CoFe_2O_4$

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ABSTRACT

A novel nanostructured magnetic composite materials for solid base catalyst composed of $CoFe_2O_4$ as the magnetic core and magnesium aluminum layered double hydroxide with OH^- as interlayer anion (abbreviated as MgAl–OH-LDH) providing basic sites has been achieved. The catalyst has been characterized using XRD, IR, TG-DTA, BET, TEM, XPS, VSM and PSD analysis techniques, and evaluated by self-condensation of acetone. The results manifest that a MgAl–OH-LDH Brønsted base catalytic layer coats onto the surface of a magnetic core $CoFe_2O_4$ through Mg–O–Co(Fe) and/or Al–O–Co (Fe) linkage with particle size distribution in the range of 38–126 nm, and the catalyst acts high catalytic activity and selectivity in self-condensation of acetone. The diacetone alcohol conversion reaches 15.3% at 273 K. After easily recovery through an exterior magnetic field, high recovery rate of MgAl–OH-LDH/$CoFe_2O_4$ (98%) is gained, and high activity (14.1% and 13.6%) has still remained in the same two reactions.

1. Introduction

It would be difficult to imagine how the world was without the fruits of heterogeneous catalysis in the 21st century. The replacement of homogenous catalysts with heterogeneous ones is becoming even more important catalytic process in chemical and life science industry due to their advantages such as non-corrosive and environmentally benign, presenting fewer disposal problems, giving higher activity, selectivity and a longer catalyst life [1–3]. Especially nano-materials exhibit unique properties owing to their small particle size and enormous surface area, which are benefit to various high-performance applications [4,5]. However, nanostructured materials simultaneously cause new problems such as difficulties in separation and recovery. The needs for better catalysts will only increase as environmental and economic concerns motivate the development of more efficient catalysts. Magnetic separation technologies can overcome these difficulties due to their magnetism [6–9]. Considering the stability of magnetic materials in higher temperature, spinel $CoFe_2O_4$ has been selected as magnetic core in present work. Various preparation methods have been developed for obtaining nanostructured ferrite particles as follows: precipitation and co-precipitation [10], sol–gel process [11,12], and hydrothermal processing [13]. However, the ultrafine ferrite particle as-synthesized exhibits super-paramagnets at room temperature [13]. It is obvious that super-paramagnets are not fit for the magnetic core of catalysts. Pure ferrite spinels can be prepared according to the layered precursor method [14], so the method has been used to prepare magnetic core in this paper. A novel nanostructured solid base catalyst containing magnetic core was designed in favor of simple separation and recovery through exterior magnetic field.

Layered double hydroxides (LDHs) are generally represented by the formula $[M(II)_{1-x}M(III)_x(OH)_2]^{x+} A^{n-}_{x/n} \cdot mH_2O$, where M(II) and M(III) are the divalent and trivalent cations in the octahedral interstices of the hydroxide layer, and $x = M(III)/(M(II)+M(III))$ $(0.2 \leq x \leq 0.33)$, and A^{n-} is the charge-balancing interlayer anion [15]. LDHs have received interests in the utilization for they can generate strong acid [16–19] or base sites [20,21] for catalytic functionality. Dumitriu et al. [22] have revealed that the MgAl-LDH with ${CO_3}^{2-}$ as charge-balancing interlayer anion and Mg/Al ratio of 3 is of the strongest basicity.

The present work is focused on a novel core–shell structured nano-base catalyst MgAl–OH-LDH/$CoFe_2O_4$ composed of $CoFe_2O_4$ spinel as the magnetic core coated with the nanostructured crystalline MgAl–OH-LDH basic layers using the “calcined and rehydrated” method for the memory property of LDH [23]. To the best of our knowledge, little work has been reported until now on the coating of crystalline material directly onto $CoFe_2O_4$ core for combining usage of solid base catalyst and magnetic material.

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2. Experimental

2.1. Synthesis of magnetic core $CoFe_2O_4$ and nano-scale magnetic solid base catalyst MgAl–OH-LDH/$CoFe_2O_4$ with core–shell structure

2.1.1. Synthesis of magnetic core $CoFe_2O_4$

The layered precursor of magnetic core was prepared as follows: a basic solution of NaOH (1.5 M) was dropwise added into a stirred beaker containing 65 mL aqueous solution of $Co(NO_3)_2·6H_2O$, $FeSO_4·7H_2O$ and $Fe_2(SO_4)_3·7H_2O$ according to Co/Fe(II)/Fe(III) of 3:5:2 (total cation concentration is 0.8 M) till the final pH of 7 at 313 K under N_2 atmosphere. The precipitates were aged in their mother liquor for 4 h at 313 K and then filtered, washed with deionized water resulting in layered precursor Co^{2+}–Fe^{2+}–Fe^{3+}–$SO_4{}^{2-}$-LDH. Then the magnetic core $CoFe_2O_4$ was produced by calcining Co^{2+}–Fe^{2+}–Fe^{3+}–$SO_4{}^{2-}$-LDH sample at 1173 K for 2 h.

2.1.2. Synthesis of the precursor MgAl–CO_3-LDH/$CoFe_2O_4$

The catalyst precursor MgAl–CO_3-LDH/$CoFe_2O_4$ was prepared by a method involving separate nucleation and ageing steps [24]. A suspension of an mixed solution of $Mg(NO_3)_2·6H_2O$ and $Al(NO_3)_3·9H_2O$ in deionized water (Mg/Al ratio of 3) and 1.617 g solid $CoFe_2O_4$ ($Mg(NO_3)_2·6H_2O/CoFe_2O_4 = 24/1$ (w/w)), and another solution of pH = 11 containing NaOH and Na_2CO_3 in deionized water ($[NaOH] = 1.6\{[Mg^{2+} + Al^{3+}]\}$, $[Na_2CO_3] = 2[Al^{3+}]$) were simultaneously added into a custom-designed reactor rotating at 4000 rpm and stirred for 2 min. The resulting slurry was removed to a flask and aged at 373 K for 6 h. The precipitate was filtered, washed thoroughly with deionized water till pH 7 and dried in an open-air oven at 343 K for 24 h, and the catalyst precursor MgAl–CO_3-LDH/$CoFe_2O_4$ was prepared.

2.1.3. Synthesis of nano-sized magnetic solid base catalyst MgAl–OH-LDH/$CoFe_2O_4$

MgAl–CO_3-LDH/$CoFe_2O_4$ was calcined at 773 K for 2 h, and MgAl(O)/$CoFe_2O_4$ was gained. Rehydration of calcined sample MgAl(O)/$CoFe_2O_4$ was performed by dispersing the MgAl(O)/$CoFe_2O_4$ powders in decarbonated water (30 mL H_2O/1 g MgAl(O)/$CoFe_2O_4$) under N_2 atmosphere and vigorously stirring at 298 K for 1 h. The excess of H_2O was removed under vacuum at 323 K [23,25], and the novel catalyst MgAl–OH-LDH/$CoFe_2O_4$ was finally obtained.

2.2. Catalytic evaluation of catalysts

A catalytic reaction self-condensation of acetone aldol condensation of acetone [25] was carried out at 273 K in a well agitated 250 mL round bottom maintained in an ice bath flask under N_2 atmosphere. Typically, 1.42 g of solid was employed and 2 wt% of the catalyst used compare to the weight of acetone. The mixture of products was analyzed by gas chromatography. After one run of reaction, the mixture of reactants, products and magnetic catalyst were transferred into a special beaker equipped with an exterior magnetic field of 0.0427 T. Magnetic catalysts were magnetically attracted to the bottom of beaker. Liquid was easily taken out, and then, the catalysts were reclaimed for the next run.

2.3. Characterization

XRD patterns were obtained on a Shimadzu XRD-6000 diffractometer using Cu Kα radiation (λ=1.54 Å, 40 kV, 30 mA) in range 3–70°. FT-IR spectra were recorded on a Bruker Vector-22 spectro-photometer in the range 4000–400 cm^{-1}. Thermogravimetric differential thermal analysis (TG-DTA) was carried out on a PCT-1A thermal analysis system, from 288 to 873 K in air atmosphere with a temperature ramp rate of 10 K min^{-1}. Low temperature N_2-adsorption measurements were recorded using a Quantachrome Autosorb-1 system. TEM micrographs were recorded on a Hitach-800 instrument. Surface chemical composition of the solid base was measured on a VGESCLAB MKII X-ray photo-emission spectroscopy (XPS) using Mg Kα X-ray source ($h\nu = 1253.6$ eV, 12 kV × 10 mA). The binding energy scale was referenced to the C 1s line of aliphatic carbon contamination set at 284.6 eV. Magnetic curves were obtained at room temperature by a vibrating sample magnetometer (VSM) (model JDM-13), and its measurement range is 0–960,000 A m^{-1} (12,000 Oe). The reaction mixture was analyzed by gas chromatography GC4000 (A) using FID with an SE-30 column. Particle size distribution (PSD) was determined by Malvern Corp. Mastersizer 2000 laser particle size analyzer of which determination range is from 0.02 to 2000 μm.

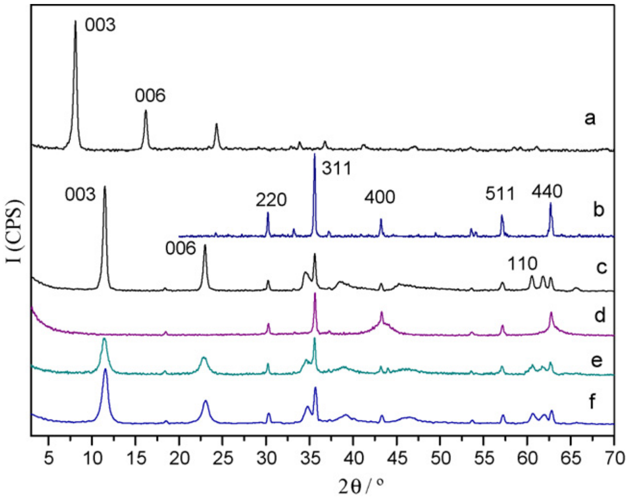

Fig. 1. XRD patterns of $CoFe^{2+}$–Fe^{3+}–$SO_4{}^{2-}$-LDH (a), $CoFe_2O_4$ (b), MgAl–CO_3-LDH/$CoFe_2O_4$ (c), MgAl(O)/$CoFe_2O_4$ (d), MgAl–OH-LDH/$CoFe_2O_4$ fresh (e) and reclaimed (f).

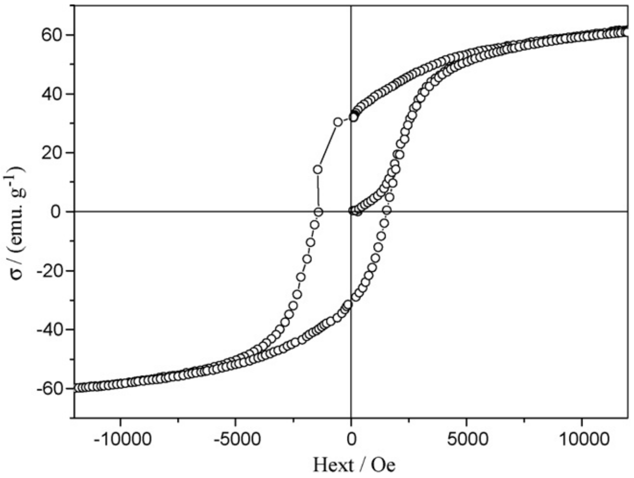

Fig. 2. Hysteresis loop of the $CoFe_2O_4$ sample.

Table 1

XRD parameters of Co^{2+}–Fe^{2+}–Fe^{3+}–$SO_4{}^{2-}$-LDH and $CoFe_2O_4$ spinel.

Samples	[*h k l*]	2*θ* (°)	*d* (nm)	FWHM (°)	*a* (nm)	*c* (nm)	D_a (nm)	D_c (nm)
Co^{2+}–Fe^{2+}–Fe^{3+}–$SO_4{}^{2}$-LDH	[0 0 3]	8.1	1.094	0.39	0.3156	3.28	50.06	20.37
	[0 0 6]	16.2	0.548	0.35				
	[0 0 9]	24.3	0.366	0.31				
	[1 1 0]	58.4	0.158	0.18				
$CoFe_2O_4$	[2 2 0]	30.2	0.296	0.14	0.8370	0.8370	51.03	51.03
	[3 1 1]	35.6	0.252	0.19				
	[2 2 2]	37.2	0.242	0.14				
	[4 0 0]	43.2	0.209	0.16				
	[4 2 2]	53.6	0.171	0.15				
	[5 1 1]	57.1	0.161	0.17				
	[4 4 0]	62.7	0.148	0.16				