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Article

Preparation of magnetic nanocomposites of solid acid catalysts and their applicability in esterification

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ABSTRACT

Solid acid catalysts are superior to traditional liquid acids because they are noncorrosive, environmentally benign, and recyclable. In addition, nano-magnetic solid acid catalysts are preferable as they exhibit large specific surface areas together with good acidity and are also readily separated from the post-reaction mixture. Three component nano-magnetic solid catalysts $\text{TiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_3\text{O}_4$ and $\text{CeO}_2\text{-Al}_2\text{O}_3\text{-Fe}_3\text{O}_4$ and a four component catalyst $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-CeO}_2\text{-Fe}_3\text{O}_4$ were synthesized by a co-precipitation method and were subsequently characterized by inductively coupled plasma-atomic emission spectroscopy, Brunauer-Emmett-Teller surface area analysis, X-ray diffraction, transmission electron microscopy, and thermal gravimetric analysis. Their catalytic activities were also evaluated in the esterification reaction of acetic acid with *n*-butanol. The results demonstrated that these rare earth-based magnetic nanocomposites exhibited good catalytic activity.

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1. Introduction

Acid catalysts have numerous applications in various industrial organic reactions, and homogenous acids such as H_2SO_4 , HCl , and HF have been widely used in chemical engineering. However, these mineral acids have serious drawbacks in terms of difficulties in post-reaction separation and negative environmental impact, as well as their tendency to contribute to the corrosion of reactors. Over the last few decades, many different solid acid catalysts have been developed as alternatives, including metal oxides, zeolites, metal phosphates, and sulfated metal oxides [1–5], and these are widely used in alkylation [6], esterification [7,8], isomerization [9,10], nitration [11], and other reactions. In addition, it is well known that sulfated solid acids ($\text{SO}_4^{2-}/\text{MO}_x$) are potential candidates for the development of environmentally benign organic syntheses. Unfortunately, the activity of these materials decreases significantly during use because of sulfur reduction and the formation of surface

coke [12–15], hindering their industrial applications. Therefore, there is still a need to develop environmentally benign catalysts with high activity.

Typically, these heterogeneous catalysts are separated by labor-intensive filtration or centrifugation processes. Hence, much research has been devoted to the development of easily separable heterogeneous catalysts. Magnetic nanoparticles (MNPs) have been extensively researched with regard to their applications in disciplines, including magnetic resonance imaging [16], magnetic storage media [17], biotechnology [18], and ferrofluids [19]. Among these magnetic materials, Fe_3O_4 nanoparticles have been used as a versatile support for a variety of heterogeneous catalysts in different types of organic transformations [20].

Based on the above factors and our own previous research results [15], we have designed and synthesized several series of “green” solid acids, $\text{TiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_3\text{O}_4$ (TAF), $\text{CeO}_2\text{-Al}_2\text{O}_3\text{-Fe}_3\text{O}_4$ (CAF), and $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-CeO}_2\text{-Fe}_3\text{O}_4$ (ZACF), each of which

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has been applied to the esterification reaction between a carboxylic acid and an alcohol. We subsequently identified the best catalyst (i.e., that exhibiting the highest activity) by varying the molar ratio of different oxides in the catalyst. Furthermore, we propose a plausible mechanism for the esterification reaction based on characterization of the structures and morphologies of these materials.

2. Experimental

2.1. Preparation of catalysts

ZrOCl₂·8H₂O, AlCl₃·6H₂O, Ce(SO₄)₂·4H₂O, *n*-butanol, acetic acid, tetrabutyl titanate, and toluene were all obtained from commercial sources and used as-received without further purification.

Fe₃O₄ MNPs were generated by dissolving FeCl₃·6H₂O (6.76 g) and FeSO₄·7H₂O (3.80 g) in 100 mL of deionized water to produce a clear solution, following which the pH was adjusted to 10 with NH₄OH acting as a precipitant. After 2 h of vigorous stirring at 60 °C, the precipitate was separated magnetically and then washed with deionized water and ethanol. The resulting black, magnetic solid was dried under vacuum at room temperature (Fig. 1).

TAF-4/4 (4/4 means that the molar ratio of TiO₂/Al₂O₃/Fe₃O₄ is 4:4:1) was obtained by dissolving AlCl₃·6H₂O (4 mmol) and tetrabutyl titanate (4 mmol) in 100 mL of ethanol to produce a clear solution, after which Fe₃O₄ MNPs (0.2314 g) were added with ultrasonic agitation for 30 min. NH₄OH was subsequently added as precipitant while adjusting the pH to 9.2. After 12 h of vigorous stirring at room temperature, the precipitate was filtered, washed with deionized water, and dried overnight at 80 °C in a vacuum oven. The remaining nano-magnetic catalysts were also synthesized using this same method.

2.2. Characterization of catalysts

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) data were collected using an IRIS ER/S emission spectrometer (American TAJ Co.). N₂ adsorption-desorption isotherms were recorded at −195.8 °C on a TriStar II 3020V instrument. The specific surface areas of the materials were calculated using the Brunauer-Emmett-Teller (BET) equation over a range of relative pressure ratios (p/p_0) from 0.06 to 0.3. Powder X-ray diffraction (XRD) patterns were obtained with an X'Pert PRO diffractometer (Holland PANalytical Co.) over the range of $2\theta = 20^\circ$ – 90° at a scan rate of $8^\circ/\text{min}$ using Cu K_α radiation ($\lambda = 0.15406$ nm). Transmission electron microscope

Fig. 1. Preparation of nano-magnetic catalysts.

Scheme 1. Esterification of acetic acid with *n*-butanol.

(TEM) and high resolution TEM (HRTEM) images were obtained using a field emission TEM (Tecnai-G2-F30). Fourier transform infrared (FT-IR) spectra were acquired on a Nicolet NEXUS 670 over the range of 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} . Thermal gravimetric (TG) analyses were performed under N₂ from room temperature to 600 °C at a heating rate of 10 °C/min using a Linseis STA PT 1600 thermoanalyzer.

2.3. Typical procedure for the esterification reaction of acetic acid with *n*-butanol

Acetic acid (0.075 mol), *n*-butanol (0.050 mol), catalyst (0.5 g), and 25 mL toluene were combined in a 50 mL flask along with a magnetic bar and water separator. The flask was then immersed in an oil bath and heated to reflux. During the reaction, produced water was separated by the water separator. After the reaction, the catalyst was detached from the flask with magnets for recycling, and the conversion (yield) was determined by GC with FID (Scheme 1)

3. Results and discussion

3.1. Characterization results

The ICP-AES and BET specific surface areas results are shown in Table 1. When preparing TAF, the pH of the solution was approximately 9.2. At this pH, the reaction mixture contained a significant quantity of $\text{Al}(\text{OH})_4^-$ and $\text{Ti}(\text{OH})_n^-$ ions because these species do not precipitate completely at that pH value. The ICP-AES results show some variations between the actual and theoretical molar ratios due to the loss of Al and Ti through the formation of their same ions, as well as the incomplete precipitation of other metal ions at this pH value [21–23].

The XRD patterns of these catalysts are depicted in Fig. 2. In Fig. 2(a), there are only a few weak peaks from Fe₃O₄, showing

Table 1
ICP-AES data and specific surface areas of the catalysts.

Catalyst	ZrO ₂ (TiO ₂)-Al ₂ O ₃ -CeO ₂ -Fe ₃ O ₄ molar ratio		S_{BET} (m^2/g)
	Theoretical	Measured ^a	
TAF-4/4	4:4:0:1	0.98:0.70:0:1	358.72
TAF-8/8	8:8:0:1	1.69:1.28:0:1	256.50
TAF-12/12	12:12:0:1	2.26:1.79:0:1	54.84
TAF-16/16	16:16:0:1	3.26:2.67:0:1	365.99
CAF-8/8	0:8:8:1	0:2.48:0.99:1	196.24
CAF-12/12	0:12:12:1	0:3.84:0.73:1	192.72
CAF-16/16	0:16:16:1	0:5.05:1.42:1	104.56
ZAF-16/16	16:16:0:1	3.99:3.93:0:1	299.26
ZACF-16/16/2	16:16:2:1	4.33:5.36:0.69:1	268.30
ZACF-16/16/4	16:16:4:1	4.41:2.75:1.48:1	288.60
ZACF-16/16/6	16:16:6:1	5.01:4.29:2.05:1	224.05
ZACF-16/14/2	16:14:2:1	4.08:3.43:0.70:1	271.85

^a Determined by ICP-AES analysis.

Fig. 2. XRD patterns of the magnetic nanocomposite catalysts. (a): (1) TAF-16/16, (2) TAF-12/12, (3) TAF-8/8, (4) TAF-4/4; (b): (1) CAF-16/16, (2) CAF-12/12, (3) CAF-8/8; (c): (1) ZACF-16/14/2, (2) ZACF-16/16/6, (3) ZACF-16/16/4, (4) ZACF-16/16/2, (5) ZACF-16/16/0.

that the TAF catalysts had mainly amorphous structure with low levels of crystallinity. In Fig. 2(b) and (c), there are no sharp peaks, indicating the amorphous structure of the CAF and ZACF catalysts.

TEM and HRTEM images of Fe_3O_4 , CAF-12/12, and ZACF-16/16/4 are presented in Fig. 3. From Fig. 3(a), it is evident that the Fe_3O_4 MNPs were approximately 15 nm in size, while Fig. 3(b) shows that the Fe_3O_4 MNPs exhibited a low degree of crystallinity. In Fig. 3(c) and (e), the CAF-12/12 and ZACF-16/16/4 materials are observed to have particle size of about 25 nm. These particles were therefore approximately 10 nm larger than the Fe_3O_4 MNPs because of their metal oxide coatings. The detailed images of the CAF-12/12 and ZACF-16/16/4 materials in Fig. 3(d) and (f) indicate that they both had amorphous structure. These results are consistent with the XRD data.

Fig. 4 shows the FT-IR spectra of ZACF-16/16/4 both with and without pyridine adsorption (lines (1) and (2), respectively).

ly). In line (1), the band at 3440 cm^{-1} is assigned to water on the particle surfaces [24], the bands at 1384 and 1124 cm^{-1} are characteristic of SO_4^{2-} [25–27], the band at 1631 cm^{-1} is assigned to OH groups on the catalyst surface [14,28,29] and masks the absorption band on the Brönsted acid sites at 1640 cm^{-1} , the band at 603 cm^{-1} is assigned to M–O groups, and the bands at 1541 and 1503 cm^{-1} are attributed to Brönsted and Lewis acid sites, respectively [29]. In line (2), the band at 3441 cm^{-1} is assigned to surface water [24], the bands at 1384 and 1125 cm^{-1} arise from SO_4^{2-} [25–27], the band at 1630 cm^{-1} is assigned to surface OH groups [14,28,29], which again mask the absorption band on the Brönsted acid sites at 1640 cm^{-1} , the band at 636 cm^{-1} is assigned to M–O groups, and the band at 1541 cm^{-1} may be attributed to Brönsted acid sites [30,31].

The thermal properties of the ZACF-16/16/4 and TAF-12/12 catalysts were determined by TG analyses, and the results are illustrated in Fig. 5 (lines (1) and (2), respectively). The mass loss of the catalysts can be attributed to various phe-

Fig. 3. TEM images of (a) Fe_3O_4 , (c) CAF-12/12, and (e) ZACF-16/16/4 and HRTEM images of (b) Fe_3O_4 , (d) CAF-12/12, and (f) ZACF-16/16/4.

Fig. 4. FT-IR spectra of ZACF-16/16/4 (1) with and (2) without pyridine adsorption.

nomena. The gradient at low temperatures below 200 °C is ascribed to the desorption of surface water, whereas the gradient emerging above 200 °C corresponds to the release of crystal water and water chemically bound in $\text{Al}(\text{OH})_3$. The TG curves show that the total mass loss of the TAF-12/12 (35.0%) was higher than that of the ZACF-16/16/4 (23.8%). Above 200 °C, the hydroxyl groups leave although the catalysts themselves do not decompose until 600 °C. Between 200 and 600 °C, the mass loss of the ZACF-16/16/4 is 7.4%, indicating that the hydroxyl group concentration was about 8.7 mmol/g. The mass loss of the ZAF-12/12 was 18.6%, equal to a hydroxyl group concentration of approximately 21.9 mmol/g.

3.2. Activity of catalysts in the esterification reaction

Table 2 shows that the activity of the TAF catalysts was lower than that of ZAF catalysts in our previous work. The ZAF-16/16 showed the highest activity in the series of ZAF catalysts, while the TAF-12/12 exhibited the highest yield among the TAF catalysts.

The activity of various CAF catalysts and the components of the CAF catalysts is summarized in Table 3. The results show that the CAF-12/12 had the highest activity, and that every

Fig. 5. TG profiles of catalysts (1) ZACF-16/16/4 and (2) TAF-12/12.

Table 2

Catalytic activity of TAF in the esterification of acetic acid with *n*-butanol.

Catalyst	TAF-4/4	TAF-8/8	TAF-12/12	TAF-16/16
Yield ^a (%)	39.3	33.8	68.5	40.4

Reaction conditions: catalyst (0.5 g), *n*-butanol (4.6 mL, 0.05 mol), acetic acid (4.3 mL, 0.075 mol), 110 °C, toluene (25 mL), 2 h.

^a Determined by gas chromatography (GC) with a flame ionization detector (FID).

Table 3

Catalytic activity of the CAF catalysts and component metal oxides during the esterification of acetic acid with *n*-butanol.

Catalyst	Yield ^a (%)	Catalyst	Yield ^a (%)
CAF-4/4	66.4	Fe_3O_4	26.8
CAF-8/8	83.2	CeO_2	43.4
CAF-12/12	85.5	Al_2O_3	34.1
CAF-16/16	57.6	CAF-12/0	51.3
CAF-20/20	39.1	CAF-0/12	46.7
		CA-12/12	61.6

Reaction conditions: catalyst (0.5 g), *n*-butanol (4.6 mL, 0.05 mol), acetic acid (4.3 mL, 0.075 mol), 110 °C, toluene (25 mL), 3.5 h.

^a Determined by GC with FID.

Table 4

Catalytic activity of ZACF catalysts in the esterification of acetic acid with *n*-butanol.

Catalyst	Yield ^a (%)	Catalyst	Yield ^a (%)
ZACF-16/16/0	87.2	ZACF-16/10/6	73.7
ZACF-16/16/2	53.2	ZACF-14/16/2	72.0
ZACF-16/16/4	88.2	ZACF-12/16/4	68.4
ZACF-16/16/6	64.2	ZACF-10/16/6	54.5
ZACF-16/16/16	69.2	ZACF-8/16/8	60.0
ZACF-16/14/2	84.6	ZACF-0/16/16	49.5
ZACF-16/12/4	84.0		

Reaction conditions: catalyst (0.5 g), *n*-butanol (4.6 mL, 0.05 mol), acetic acid (4.3 mL, 0.075 mol), 110 °C, toluene (25 mL), 2 h.

^a Determined by GC with FID. The average value of three trials is reported (error $< \pm 0.3$).

component worked cooperatively to contribute to the high activity. This activity was thus the result of combining Al_2O_3 , with numerous Lewis acid sites, and CeO_2 , with many Brönsted acid sites.

The data in Table 4 demonstrate the effects of doping CeO_2 on the ZAF catalysts. The ZAF-16/16 catalyst exhibited the highest activity, which changed through doping CeO_2 with various molar ratios. The esterification catalyzed by the ZACF-16/16/4 catalyst had the highest yield (88.2%), which was superior to that obtained from CAF-12/12. Thus CeO_2 may play an important role in these materials with regard to their catalytic activity.

Based on the data in Tables 1–4, we may conclude that the BET specific surface area of these nano-magnetic catalysts has no effect on their esterification activity.

3.3. Proposed mechanism for the esterification reaction

A proposed cooperative catalysis mechanism for the esterification of acetic acid with *n*-butanol is illustrated in Scheme 2. Our catalysts have both Brönsted and Lewis acid sites that appear to catalyze the esterification in a cooperative manner. We

Scheme 2. Proposed cooperative catalysis mechanism involving Lewis and Brønsted acids.

propose that the Lewis acid sites combine with *n*-butanol to form intermediate **1**, following by the migration of a hydrogen atom to form intermediate **2**. At the same time, the hydroxyl group of the Brønsted acid site combines with acetic acid via hydrogen bonding to form intermediate **3**. The lone electron pair of intermediate **2** attacks the carbonyl carbon of intermediate **3**, leading to the formation of water and *n*-butyl acetate and the regeneration of the Brønsted and Lewis acid sites, completing one catalytic cycle [32].

4. Conclusions

We successfully designed and synthesized three magnetic nanocomposite catalysts (TAF, CAF, and ZACF) that were useable as efficient, green solid acid catalysts in the esterification of *n*-butanol with acetic acid. CAF and ZACF doped with rare earth elements exhibited high catalytic activity. The magnetic nano-metal oxide composites doped with rare earth elements were effective catalysts and were readily recovered from the post-reaction mixture. Furthermore, a cooperative catalysis mechanism for the esterification reaction involving both Lewis and Brønsted acids was proposed.

References

- [1] Reddy B M, Patil M K. *Chem Rev*, 2009, 109: 2185
- [2] Arata K. *Green Chem*, 2009, 11: 1719
- [3] Okuhara T. *Chem Rev*, 2002, 102: 3641
- [4] Clark J H. *Acc Chem Res*, 2002, 35: 791
- [5] Corma A. *Chem Rev*, 1995, 95: 559
- [6] Sheemol V N, Tyagi B, Jasra R V. *J Mol Catal A*, 2004, 215: 201
- [7] Peters T A, Benes N E, Holmen A, Keurentjes J T F. *Appl Catal A*, 2006, 297: 182
- [8] Fernandes D R, Rocha A S, Mai E F, Mota C J A, da Silva V T T. *Appl Catal A*, 2012, 425-426: 199
- [9] Soutanidis N, Zhou W, Psarras A C, Gonzalez A J, Iliopoulou E F, Kiely C J, Wachs I E, Wong M S. *J Am Chem Soc*, 2010, 132: 13462
- [10] Yadav M K, Chudasama C D, Jasra R V. *J Mol Catal A*, 2004, 216: 51
- [11] Katada N, Endo J I, Notsu K I, Yasunobu N, Naito N, Niwa M. *J Phys Chem B*, 2000, 104: 10321
- [12] Chen X R, Chen C L, Xu N P, Mou C Y. *Catal Today*, 2004, 93-95: 129
- [13] Zhang C, Liu T, Wang H J, Wang F, Pan X Y. *Chem Eng J*, 2011, 174: 236
- [14] Liu E M, Locke A J, Frost R L, Martens W N. *J Mol Catal A*, 2012, 353-354: 95
- [15] Wang A Q, Liu X, Su Z X, Jing H W. *Catal Sci Technol*, 2014, 4: 71
- [16] Wan J R, Cai W, Meng X X, Liu E Z. *Chem Commun*, 2007: 5004
- [17] Park J, An K, Hwang Y, Park J G, Noh H J, Kim J Y, Park J H, Hwang N M, Hyeon T. *Nat Mater*, 2004, 3: 891
- [18] Dobson J. *Drug Develop Res*, 2006, 67: 55
- [19] Deng H, Li X L, Peng Q, Wang X, Chen J P, Li Y D. *Angew Chem Int Ed*, 2005, 44: 2782
- [20] Gawande M B, Rath A K, Nogueira I D, Varma R S, Branco P S. *Green Chem*, 2013, 15: 1895
- [21] Holt P K. *Electrocoagulation: Unravelling and Synthesising the Mechanisms behind a Water Treatment Process*. University of Sydney, Chemical Engineering, 2006. 1
- [22] Sugimoto T, Zhou X P. *J Colloid Interface Sci*, 2002, 252: 347
- [23] Sugimoto T, Zhou X P, Muramatsu A. *J Colloid Interface Sci*, 2002, 252: 339
- [24] Cao C Y, Li P, Qu J, Dou Z F, Yan W S, Zhu J F, Wu Z Y, Song W G. *J Mater Chem*, 2012, 22: 19898
- [25] Liu Z, Zhang J D, Wang X D, Pan X H. *Appl Chem Ind* (刘峥, 张京迪, 王小丹, 潘肖宏. 应用化工), 2010, 39: 497

Graphical Abstract

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Preparation of magnetic nanocomposites of solid acid catalysts and their applicability in esterification

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A series of multicomponents nano-magnetic solid catalysts of $\text{TiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_3\text{O}_4$ (TAF), $\text{CeO}_2\text{-Al}_2\text{O}_3\text{-Fe}_3\text{O}_4$ (CAF), and $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-CeO}_2\text{-Fe}_3\text{O}_4$ (ZACF) were synthesized by a co-precipitation method. The obtained nano-magnetic catalysts were fully characterized and demonstrated good catalytic activity in the esterification of acetic acid and *n*-butanol.

- [26] Wang P. [MS Dissertation]. Shanghai: East China Normal University (王平. [硕士学位论文]. 上海: 华东师范大学), 2011
- [27] Mei C S. [MS Dissertation]. Harbin: Harbin Engineering University (梅长松. [硕士学位论文]. 哈尔滨: 哈尔滨工程大学), 2002
- [28] Yan H P, Yang Y, Tong D M, Xiang X, Hu C W. *Catal Commun*, 2009, 10: 1558
- [29] Davis B H, Keogh R A, Alerasool S, Zalewski D J, Day D E, Doolin P K. *J Catal*, 1999, 183: 45
- [30] Babou F, Coudurier G, Vedrine J C. *J Catal*, 1995, 152: 341
- [31] Chen W H, Ko H H, Sakthivel A, Huang S J, Liu S H, Lo A Y, Tsai T C, Liu S B. *Catal Today*, 2006, 116: 111
- [32] El-Sharkawy E A, Al-Shihry S S. *Mater Lett*, 2004, 58: 2122

磁性纳米复合氧化物固体酸催化剂的制备及酯化性能

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摘要: 固体酸催化剂的无腐蚀、环境友好和可循环使用等特点使其成为无机液体酸的最佳替代物。磁性纳米固体酸具有优于常规固体酸催化剂的催化活性及分离简单的特性。用共沉淀法分别合成了一系列三组分 $\text{TiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_3\text{O}_4$ (TAF)和 $\text{CeO}_2\text{-Al}_2\text{O}_3\text{-Fe}_3\text{O}_4$ (CAF)及四组分 $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-CeO}_2\text{-Fe}_3\text{O}_4$ (ZACF)磁性纳米复合氧化物固体酸催化剂, 通过电感耦合等离子体原子发射光谱、比表面积测定、X射线衍射、透射电镜、热重分析和红外光谱等对其进行了表征, 并利用酯化反应作为探针反应评价了其催化性能。结果表明, 合成的磁性纳米固体酸催化剂在酯化反应中表现出很好的催化活性。

关键词: 磁性纳米复合氧化物; 固体酸催化剂; 共沉淀法; 酯化反应

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1. 前言

酸催化有机反应因在化学工业上有大量应用而受到广泛关注, 常用的液体酸有硫酸、盐酸和氢氟酸等。然而, 均相液体酸催化剂用于工业生产的弊端显而易见, 比如催化剂分离回收、环境污染和设备腐蚀等问题。在过去的数十年中, 科研工作者已经研发出多种可替代液体酸的非均相固体酸催化剂, 如 $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$ 、分子筛和杂多酸^[1-5]等。固体酸催化被广泛应用于酰化反应^[6]、酯化反应^[7,8]、异构化反应^[9,10]和硝化反应^[11]等有机反应中。 $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$ 负载型固体酸催化剂因其环境友好无污染而受到大量关注, 但是该催化剂在使用过程中 SO_4^{2-} 的流失和表面结焦积碳使得催化剂活性大幅度降低, 故该催化剂在工业上的应用受到限制^[12-15]。因此, 我们需要制备高活性、可循环使用的新型绿色环保的酸催化剂。

使用抽滤或离心方法分离催化剂过程繁琐, 并难以连续化生产, 因此许多科研工作者致力于研制易分离的非均相催化剂。磁性纳米粒子(NMPs)是目前已经进行了大量研究的磁性材料之一, 在核磁共振成像(MRI)^[16]、磁性存储媒介^[17]、生物技术^[18]和磁流体^[19]等交叉学科都有重要应用。在众多磁性材料中, Fe_3O_4 纳米粒子可用作各种非均相催化剂磁基质, 并催化各种有机反应^[20]。

基于以上分析并结合我们前面的工作^[15], 本文设计了一系列绿色环保的复合金属氧化物型固体酸催化剂, 即三组分 $\text{TiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_3\text{O}_4$ (TAF)和 $\text{CeO}_2\text{-Al}_2\text{O}_3\text{-Fe}_3\text{O}_4$

(CAF)及四组分 $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-CeO}_2\text{-Fe}_3\text{O}_4$ (ZACF)磁性纳米复合氧化物固体酸催化剂, 并将其应用到酯化反应中, 评价了催化剂的活性。通过对比不同掺杂比例和掺杂不同金属氧化物的催化剂的活性, 得到了活性最高的催化剂, 表征了催化剂的形貌结构, 并提出了可能的反应机理。

2. 实验部分

2.1. 催化剂制备

$\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$ 、 $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$ 、 $\text{Ce}(\text{SO}_4)_2\cdot 4\text{H}_2\text{O}$ 、酞酸丁酯、甲苯、正丁醇及其他试剂均为购买后直接使用, 未进行纯化处理。

分别称取6.76 g $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ 和3.80 g $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$, 加50 mL蒸馏水将它们分别溶解, 在搅拌的同时缓慢滴加浓氨水调节溶液的pH为10, 然后加热至60 °C, 恒温搅拌陈化1 h, 待冷却后将其转移到烧杯中, 外加超强磁铁使 Fe_3O_4 分离, 用蒸馏水多次洗涤沉淀以除去杂质离子, 再用无水乙醇洗涤多次, 待其自然干燥后用玛瑙研钵磨细, 所得黑色粉末即为磁性基质 Fe_3O_4 纳米粒子(图1)。

按一定摩尔比分别称取 $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$ 、 $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$ 、 $\text{Ce}(\text{SO}_4)_2\cdot 4\text{H}_2\text{O}$ 和 $[\text{CH}_3(\text{CH}_2)_3\text{O}]_4\text{Ti}$, 加适量水使之完全溶解(在溶解 $\text{Ce}(\text{SO}_4)_2\cdot 4\text{H}_2\text{O}$ 时需加入少量硫酸助溶; $[\text{CH}_3(\text{CH}_2)_3\text{O}]_4\text{Ti}$ 溶解在乙醇溶液中), 然后加入0.2314 g (1 mmol)上述制备的 Fe_3O_4 微粒, 超声30 min使 Fe_3O_4 颗粒尽可能分散, 然后在剧烈搅拌下缓慢滴加浓氨水调节体

系的pH为9.2. 继续常温搅拌陈化12 h, 抽滤, 用蒸馏水反复洗涤所得催化剂, 除去氯离子(用硝酸酸化的0.1 mol/L硝酸银溶液检测), 80 °C真空干燥12 h, 所得沉淀即为复合氧化物磁性纳米固体酸催化剂, 研细后备用. 所制得催化剂TAF-4/4意为催化剂中 $\text{TiO}_2/\text{Al}_2\text{O}_3/\text{Fe}_3\text{O}_4$ 摩尔比为4:4:1. 其他催化剂类似.

2.2. 催化剂表征

用IRIS, ER/S发射光谱(American TJA Company)对催化剂进行ICP-AES元素分析. N_2 吸附-脱附等温线在-195.8 °C下通过TriStar II 3020V型设备记录. 比表面积使用Brunauer-Emmett-Teller (BET) 公式在相对压力0.03–0.6范围内计算得到. XRD谱图通过X'Pert PRO型多晶粉末X射线衍射仪(Holland PAN alypical Company)测定. 磁性纳米基质 Fe_3O_4 以及催化剂CAF-12/12和ZACF-16/16/4的形貌特征通过Tecnai-G2-F30型透射电子显微镜(TEM)获得. 热重分析用Linseis STA PT 1600型热分析仪在 N_2 氛围下, 以10 °C/min的速率从室温升至600 °C测得.

2.3. 催化酯化反应

将0.05 mol (4.6 ml)正丁醇、0.075 mol (4.3 ml)乙酸及一定量催化剂加入到带有分水器和球形冷凝管的三口烧瓶中, 加入25 ml甲苯作为带水剂, 在其回流温度下搅拌反应一定时间, 反应生成的水被分水器分出. 待反应结束后用超强磁铁将催化剂和反应体系分离, 对催化剂进行回收. 用气相色谱(GC)确定正丁醇的转化率即酯化率(图式1).

3. 结果与讨论

3.1. 表征结果

样品的ICP-AES元素分析和BET比表面积测试结果如表1所示. 在制备TAF系列催化剂的过程中, 用100 mL乙醇溶解酞酸丁酯, 并用氨水调节pH, 由于乙醇中羟基氢电离能力的限制, 使得乙醇-氨水混合体系的pH值难以达到9.2以上, 所以本实验中沉淀金属离子的pH为9.2. 在pH为9.2时, 溶液中部分铝以 $\text{Al}(\text{OH})_4^-$ 形式存在, 部分钛以 $\text{Ti}(\text{OH})_n^-$ 形式存在, 由于氨水滴加速率慢, 会部分形成小粒径的胶粒而不是沉淀, 最终沉淀下来的金属离子会小于理论计算值. 同时其他金属氧化物在此pH下也可能未沉淀完全而含量偏低^[21–23].

图2为部分催化剂的XRD谱图. 由图2(a)可以看到, TAF系列催化剂主要为无定形结构, 而且基本只有 Fe_3O_4 有结晶, 且结晶度低, 从TAF-4/4到TAF-16/16,

Fe_3O_4 的峰强减弱, 为所包覆氧化物层增厚所致. 由图2(b)和(c)可以看出CAF和ZACF无尖峰只有宽峰, 为无定形结构.

图3为磁性纳米基质 Fe_3O_4 、催化剂CAF-12/12和ZACF-16/16/4的TEM及HRTEM图片. 由图3(a)可知, Fe_3O_4 纳米离子的粒径在15 nm左右, 为球形形态, 有部分团聚现象; 由图3(b)可以看出, 制备的 Fe_3O_4 纳米离子结晶度低; 由图3(c)和(e)可以看出催化剂CAF-12/12和ZACF-16/16/4的外观形貌均为球形, 粒径在25 nm左右; 由图3(d)和(f)可知, 催化剂CAF-12/12和ZACF-16/16/4均为无定形态的纳米颗粒, 这与XRD分析结果一致.

图4为催化剂的红外光谱. 图4(1)为ZACF-16/16/4催化剂吸附吡啶后的红外光谱, 3440 cm^{-1} 处为催化剂表面吸附水^[24]; 1384和1124 cm^{-1} 为 SO_4^{2-} 特征吸收^[25–27]; 1631 cm^{-1} 处为表面羟基吸收峰^[14,28,29], 在1640 cm^{-1} 处应有Brönsted酸性中心吸收峰, 但被1630 cm^{-1} 大峰包覆, 所以谱图上看不到; 1541 cm^{-1} 处为Brönsted酸性中心吸收峰^[29]; 603 cm^{-1} 处为金属-氧键振动吸收; 1503 cm^{-1} 处为Lewis酸位吸收. 图4(2)为催化剂ZACF-16/16/4未吸附吡啶的红外谱图, 3441 cm^{-1} 处为催化剂表面吸附水^[24]; 1384和1124 cm^{-1} 为 SO_4^{2-} 特征吸收^[25–27]; 1630 cm^{-1} 处为表面羟基吸收峰^[14,28,29], 在1640 cm^{-1} 处应有Brönsted酸性中心吸收峰, 但被1630 cm^{-1} 处大峰包覆; 1541 cm^{-1} 处为Brönsted酸性中心吸收峰^[29]; 636 cm^{-1} 处为金属-氧键振动吸收^[30,31].

图5为催化剂TAF-12/12和ZACF-16/16/4的热重分析图. 催化剂在200 °C以下失去的是催化剂表面的吸附水, 200 °C以上失去的水是催化剂所结合的结晶水. 由图5可知, 催化剂ZACF-16/16/4的总失重量为23.8%, 催化剂TAF-12/12的总失重量为35.0%. 在200 °C之后为表面羟基脱水, 600 °C之前催化剂各组分尚未分解, 200–600 °C之间的失重为羟基脱水失重. 在200–600 °C, 催化剂ZACF-16/16/4失重7.4%, 计算得羟基数量为8.7 mmol/g; 催化剂TAF-12/12失重18.6%, 计算的羟基数量为21.9 mmol/g.

3.2. 催化剂催化酯化反应

TAF系列催化剂催化酯化反应结果见表2. 可以看出, 催化剂TAF-12/12上得到了68.5%的酯化率, 催化活性相对较好.

不同摩尔比的CAF催化剂的催化活性以及磁性纳米复合氧化物固体酸催化剂中所包含的三个金属氧化物对催化活性的影响见表3. 催化剂CAF-12/12表现出最

好的催化活性. 以CAF-12/12为例, 探讨了催化剂中三种金属氧化物对酯化反应催化活性的影响, 从表3可见, 磁性纳米颗粒 Fe_3O_4 不仅为催化剂提供磁性核, 还起到一定的催化作用; 当 Al_2O_3 和 CeO_2 单独作为催化剂或三种氧化物中任意两种相互复合作为催化剂时, 催化活性均比三组分的磁性纳米稀土复合氧化物固体酸催化剂CAF-12/12低, 因而催化剂中的三个组分对催化活性都有贡献, 而且它们具有相互协同作用.

上述结果表明, CAF催化剂在酯化反应中表现出较好的活性. 基于我们以前的工作, 三组分催化剂 $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-Fe}_3\text{O}_4$ (ZAF-16/16)是活性最高的催化剂. 因此, 我们在ZAF-16/16的基础上掺杂稀土氧化物 CeO_2 , 合成了四组分的磁性纳米稀土复合氧化物固体酸催化剂 $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-CeO}_2\text{-Fe}_3\text{O}_4$ (ZACF), 继续以乙酸正丁酯的制备为探针反应, 探究稀土金属氧化物 CeO_2 以不同方式掺入对ZAF-16/16催化剂催化活性的影响. 结果见表4. 当所加原料 $\text{Zr-Al-Ce-Fe}_3\text{O}_4$ 的摩尔比为16:16:4:1时(即ZACF-16/16/4), 催化活性比ZAF-16/16好, 在同等条件下酯化率高出1.0%, 而按其余比例复合得到的催化剂催化活性都不如ZAF-16/16好, 其中将Zr的比例减少所得催化剂的活性下降最多, 出现此现象的原因是 ZrO_2 比 CeO_2

酸性强, 用 CeO_2 代替 ZrO_2 , 导致活性下降.

表1–4结果表明, 催化剂活性与催化剂比表面积之间没有必然联系.

3.3. 反应机理

图式2是磁性纳米固体酸催化剂催化合成乙酸正丁酯的可能机理. 在催化剂中同时存在Lewis酸和Brønsted酸中心, Lewis酸中心与正丁醇结合形成缔合物 $\mathbf{1}$, 经过氢迁移形成中间体 $\mathbf{2}$; 与此同时Brønsted酸的羟基与乙酸以氢键结合形成中间体 $\mathbf{3}$; 中间体 $\mathbf{2}$ 中正丁醇氧的孤对电子进攻中间体 $\mathbf{3}$ 中的羰基碳, 从而脱水形成乙酸正丁酯; 与此同时, Lewis酸和Brønsted酸进行互换并完成一次催化循环^[32].

4. 结论

设计并制备出 $\text{TiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_3\text{O}_4$, $\text{CeO}_2\text{-Al}_2\text{O}_3\text{-Fe}_3\text{O}_4$ 和 $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-CeO}_2\text{-Fe}_3\text{O}_4$ 三种绿色环保、易分离的磁性纳米复合氧化物固体酸催化剂, 其中含稀土的复合氧化物催化剂对乙酸正丁酯的酯化反应有较高的催化活性, 以四组分摩尔比16:16:4:1制备的 $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-CeO}_2\text{-Fe}_3\text{O}_4$ 催化剂(ZACF-16/16/4)可使酯化反应的转化率达到88.2%; 提出了Lewis酸和Brønsted酸协同催化的可能机理.