

Enhancement of catalytic activity by homo-dispersing S₂O₈²⁻-Fe₂O₃ nanoparticles on SBA-15 through ultrasonic adsorption

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1. Introduction

ABSTRACT

Mesoporous superacids $S_2O_8^{2-}$ -Fe₂O₃/SBA-15 (SFS) with active nanoparticles are prepared by ultrasonic adsorption method. This method is adopted to ensure a homo-dispersed nanoparticle active phase, large specific surface area and many acidic sites. Compared with bulk $S_2O_8^{2-}$ -Fe₂O₃, Brönsted acid catalysts and other reported catalysts, SFS with an Fe₂O₃ loading of 30% (SFS-30) exhibits an outstanding activity in the probe reaction of alcoholysis of styrene oxide by methanol with 100% yield. Moreover, SFS-30 also shows a more excellent catalytic performance than bulk $S_2O_8^{2-}$ -Fe₂O₃ towards the alcoholysis of other ROHs (R = C₂H₅-C₄H₉). Lewis and Brönsted acid sites on the SFS-30 surfaces are confirmed by pyridine adsorbed infrared spectra. The highly efficient catalytic activity of SFS-30 may be attributed to the synergistic effect from the nano-effect of $S_2O_8^{2-}$ -Fe₂O₃ nanoparticles and the mesostructure of SBA-15. Finally, SFS-30 shows a good catalytic reusability, providing an 84.1% yield after seven catalytic cycles.

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Acid catalysts play an important role for various chemical reactions of industrial interest. Conventional acids (i.e., H₂SO₄, H₃PO₄ and *p*-toluenesulfonic acid) exhibit a high catalytic activity; however, significant risks are associated with their handling, containment, disposal as well as the issue of equipment corrosion [1,2]. For these reasons, new stringent environmental legislations against the use of these conventional acids in industrial applications have been implemented in many countries. Consequently, in recent years, solid superacids have re-

ceived extensive attention because of their strong acidity, ease of separation, low corrosivity, stability, reusability and environmental friendliness [3–6]. Particularly, $SO_4^{2-}-M_xO_y$ superacids (i.e., $SO_4^{2-}-ZrO_2$, $SO_4^{2-}-TiO_2$ and $SO_4^{2-}-SnO_2$) have been the subject of many investigations because of their good catalytic performance and low waste generation [7,8]. Compared with $SO_4^{2-}-M_xO_y$, $S_2O_8^{2-}-M_xO_y$ with stronger acidities and catalytic activities have begun to attract interest. However, only a few kinds of M_xO_y compounds, such as ZrO_2 and Al_2O_3 , have been studied. Therefore, the exploration of metal oxides is of great value. In addition, Fe-doped superacids are well known for

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their good catalytic activity and stability in several industrial and environmental processes [9,10].

A research focus has been how to overcome the low surface area and porosity of bulk superacids to improve their specific surface area and enhance the catalytic activity of the active phase. Nowadays, with the development of nano-technology, various nanomaterials have been extensively used, including nanoparticles and nanocomposites, and have drawn considerable attention because of their high temperature sensitivity, high ductility, large surface area, high strain resistance, and low electrical resistivity [11,12]. How to turn materials into nanoparticles is a challenging topic. As an efficient and practical technology for the preparation of nano-materials, the ultrasonic technique has the advantages of introducing local stress intensities and ensuring a reproducible state of dispersions [13]. In addition, mesoporous silica materials have been identified as possible catalyst supports, particularly SBA-15, which have ordered hexagonally mesopores, thick channels, big pore diameters, and large surface areas [14-19].

In this context, we have developed homo-dispersed $S_2O_8^{2-}$ -Fe₂O₃ (SF) nanoparticles supported on SBA-15 ($S_2O_8^{2-}$ -Fe₂O₃/SBA-15, SFS) with a large specific surface area by ultrasonic adsorption method. The prepared mesoporous superacid showed better catalytic activities than bulk $S_2O_8^{2-}$ -Fe₂O₃, Brönsted acid catalysts and the other catalysts reported for the probe reaction of alcoholysis of styrene oxide. In addition, the structure, surface acidity, and activity of the superacid catalysts were evaluated.

2. Experimental

2.1. Catalyst preparation

All alcohols were analytical grade and purchased from SINOPHARM Chemical Reagent Co., Ltd. Styrene oxide (99%), (NH₄)₂S₂O₈ (98%) and Fe(NO₃)₃·9H₂O (98%) were supplied from Energy Chemical. SBA-15 was obtained by Nanjing XFNANO Materials Tech Co., Ltd.

The SFS solid superacids were prepared using the UA method (Fig. 1). The $Fe(NO_3)_3$ aqueous solution was slowly added to the SBA-15, then the mixture was evenly dispersed in an ultrasonic bath for 15 min. The $Fe(NO_3)_3$ /SBA-15 was dried at 45 °C for 12 h, and calcined at 550 °C for 6 h to obtain the



Fig. 1. Well-ordered mesoporous $S_2O_8^{2-}$ -Fe₂O₃/SBA-15 prepared by ultrasonic adsorption and dry-calcination.

Fe₂O₃/SBA-15. During calcination, the temperature was increased at a rate of 1 °C/min, starting from 50 °C. A (NH₄)₂S₂O₈ aqueous solution was slowly added to the Fe₂O₃/SBA-15 to afford (NH₄)₂S₂O₈-Fe₂O₃/SBA-15, which was also dried at 45 °C for 12 h and calcined at 500 °C for 4 h after a heating ramp that started at 50 °C with a rate of temperature increase of 2 °C/min to obtain S₂O₈²⁻-Fe₂O₃/SBA-15 (SFS-*x*, *x* = 10, 20, 25, 35, 40, 45). The Fe₂O₃ loading of *x*% was calculated according to Eq. (1). The Fe(NO₃)₃·9H₂O/(NH₄)₂S₂O₈ molar ratio was 1:1.

 $x(\%) = W_{Fe203}/W_{SBA-15} \times 100\%$ (1)

2.2. Catalyst characterization

X-ray fluorescence spectrometry (XRF) was recorded on a ZSX-100e. The surface morphology of the catalyst was observed using a FEI Sirion 200 field-emission scanning electron microscope (SEM) and a JEM-1200EX transmission electron microscope (TEM). The Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 360 FT-IR instrument (KBr discs) in the 4,000-400 cm⁻¹ region. X-ray diffraction (XRD) patterns were collected on the X'Pert Pro Multipurpose diffractometer using a Cu K_{α} radiation source at RT from 0.5° to 5.0° (small angle) and 5° to 50° (wide angle). Measurements were conducted using a voltage of 40 kV, and a current setting of 20 mA for small angle XRD and 40 mA for wide angle XRD. N2 adsorption-desorption isotherms and specific surface areas were measured at -196 °C using a Micromeritics ASAP 2020 surface area and porosity analyzer. The X-ray photoelectron spectroscopy (XPS) measurements were performed on a RBD upgraded PHI-5000C ESCA system (Perkin-Elmer, Norwalk, CT, USA) with Mg K_{α} radiation ($h\nu$ = 1253.6 eV), where binding energies were calibrated by using the containment carbon (C 1s = 284.6 eV). The infrared spectra of adsorbed pyridine (pyridine-IR spectra) were obtained on a PE Frontier FT-IR spectrometer [20].

2.3. Catalytic tests

A comparison of the catalytic performances of superacid catalysts tested in the probe reaction of alcoholysis of styrene oxide with MeOH was performed in a 50-mL flask (Scheme 1). Typically, styrene oxide (1.60 g, 13.3 mmol), MeOH (3.00 g, 93.6 mmol), and the catalyst (10.0 mg) were added to the reactor and stirred at 40 °C. The reaction mixture was sampled periodically, and the samples were analyzed by gas chromatography (Agilent Technologies 7820A GC system, Palo Alto, CA, USA). Under the operating conditions adopted, the product was 2-methoxyl-2-phenylethanol with 100% selectivity, as identified by the analyses of ¹H NMR and ¹³C NMR. The catalyst activity and stability were measured in detail.



Scheme 1. The probe reaction of alcoholysis of styrene oxide.

3. Results and discussion

3.1. Catalyst characterization

The morphology of the solid superacid SF was characterized by SEM and TEM. As shown from the SEM images (Fig. 2(a)), the crystal structure of SF was formed by the coordination of Fe₂O₃ and S₂O₈^{2–} at high temperature (Fig. 2(b)). Moreover, the lattice structures of SF could be clearly seen from the TEM images (Fig. 2(c) and 2(d)). The clear lattice fringes with two interval spacings of 0.405 and 0.30 nm corresponded to the crystallographic planes of monoclinic SF, in accordance with the XRD peaks at 29.7° and 21.5° (Fig. 4(c)). Elemental mappings were taken to gain insights into the distribution of SF (Fig. 2(e)). Furthermore, the XRF analysis showed the element content of SF was 41.8% O, 34.8% Fe, 22.1% S.

The morphology analysis of SFS-30 is shown in Fig. 3. The external structure of SFS-30 (Fig. 3(a) and 3(b)) was similar to that of SBA 15. The TEM images clearly revealed the inner mesoporous channels in which SF nanoparticles of approximately 6 × 8 nm were uniformly distributed (Fig. 3(c)). Moreover, the clear lattice fringe with an interval spacing of 0.44 nm (Fig. 3(d)) corresponded to the crystallographic planes of monoclinic SFS-30, in agreement with the XRD peak at 20.3° (Fig. 4(d)). To gain insights into the distribution of SFS-30, elemental mappings were taken (Fig. 3(e)). It could be seen that the four elements of O, Fe, S and Si were evenly distributed in the prepared catalytic material, which showed that the active components were uniformly dispersed in SBA-15, and no aggregation occurred. Furthermore, the XRF analysis showed the element content of SFS-30 was 42.9% 0, 18.5% Fe, 5% S, and 32.7% Si.

The FT-IR spectra of Fe_2O_3 and SF are shown in Fig. 4(a). Compared with Fe_2O_3 , SF showed the emergence of new bands



Fig. 2. (a) SEM images of SF; (b–d) TEM images of SF; TEM images (e) and elemental mapping (f) of the composite SF.



Fig. 3. (a) SEM images of SFS-30; (b–d) TEM images of SFS-30; TEM images (e) and elemental mapping (f) of the composite SFS-30.

in the range of 900–1300 cm⁻¹, which were attributed to the S =0 or S–0 bonds in the acid structures of the catalysts [21,22]. In this range, the peaks at 995, 1113 and 1127 cm⁻¹ were assigned to the stretching vibration of S–0. Meanwhile, the band at 1227 cm⁻¹ was assigned to the stretching vibration of S=0. The attribution of these characteristic vibration peaks was in accordance with the reported $S_2O_8^{2-}$ ion of solid superacids [2,23–26]. This result indicated a very strong interaction of surface persulfate species with Fe(III) species, which was the significant reason for the formation of the active acid center on the surface of SF [27,28].

The FT-IR spectra characterizing SBA-15 and SFS-30 are shown in Fig. 4(b). The band at 964 cm⁻¹ was related to the characteristic stretching vibration of Si-OH of SBA-15 [29,30]. It was apparent that the absorption band at 964 cm⁻¹ moved to 968 cm⁻¹ and became weaker after loading SF on the pore surface of SBA-15. This effect was attributed to the stretching vibration of Si–OH being perturbed by Fe³⁺ in a neighboring position [28,31]. The special bands in the range of 900–1300 cm⁻¹, attributed to the S=O or S–O bonds, were covered by the band at 1091 cm⁻¹, which was attributed to the asymmetric stretching vibration of Si–O–Si in the SBA-15 [32,33]. However, it was obvious that the band at 1097 cm⁻¹ broadened compared with the band at 1091 cm⁻¹, which indicated the successful loading of SF nanoparticles on the SBA-15.

The XRD patterns of Fe₂O₃ and SF in the wide-angle region of 3°–60° are shown in Fig.4(c). The prepared Fe₂O₃ exhibited all the well-resolved characteristic peaks of the Fe₂O₃ crystallite (JCPDS card No. 33-0664) with the six peaks displayed at 2θ = 24.1°, 33.1°, 35.6°, 40.8°, 49.4° and 54.0°. Six new peaks ap-



Fig. 4. FT-IR spectra of Fe₂O₃, SF (a), SBA-15 and SFS-30 (b); XRD of Fe₂O₃, SF (c), SBA-15 and SFS-30 (d).

peared in the diffraction pattern of SF after $(NH_4)_2S_2O_8$ adsorption and calcination. The six peaks displayed at $2\theta = 14.7^\circ$, 20.2°, 21.5°, 24.7°, 29.7° and 32.5° were well matched with the standard JCPDS card No. 33-0679, and resulted from the interaction of Fe₂O₃ with $(NH_4)_2S_2O_8$.

The XRD patterns of SBA-15 and SFS-30 in the small and wide-angle regions are shown in Fig. 4(d). The small angle ($0.4^{\circ}-10^{\circ}$) XRD patterns were similar for SBA-15 and SFS-30 and showed that $S_2O_8^{2-}$ -Fe₂O₃ was very well dispersed and did not damage the mesoporous structure of SBA-15. However, there were significant differences in the wide-angle XRD pattern ($10^{\circ}-60^{\circ}$). SFS-30 clearly exhibited six new peaks at $2\theta = 14.7^{\circ}$, 20.3°, 21.5°, 24.7°, 29.7° and 32.5° (JCPDS card No. 33-0679), which corresponded to the XRD of SF, and which did not appear in the XRD of SBA-15. Such results indicated the successful loading of SF nanoparticles on SBA-15.

To investigate the chemical states of Fe and S in the samples, XPS measurements were performed. Fig. 5(a) and 5(b) shows the Fe 2p and S 2p XPS spectra of SFS-30. The SFS-30 contained two peaks at 706.75 and 720.07 eV (Fig. 5(a)), which could be assigned to the Fe³⁺ species. The S⁶⁺ species was revealed by the binding energy of 169 eV in Fig. 5(b) [26].

The N_2 adsorption-desorption isotherms of SFS-30 are shown in Fig. 5(c). According to IUPAC classifications [34], the isotherms exhibited a type IV pattern and both showed a clear loop (H1 hysteresis loop) in the relative pressure range of 0.4–0.8. The presence of a hysteresis loop, which arose from capillary condensation, indicated the presence of regular mesoporous channels in the materials. This further confirmed that SFS-30 retained the intact and ordered mesoporous structure of SBA-15 after $S_2O_8^2$ --Fe₂O₃ loading. The parameters describing the textural properties and catalytic activities of bulk SF and SFS-30 are summarized in Table 1. The BET surface area and pore volume of SFS-30 were obviously larger than those of SF. In addition, Fig. 5(c) shows the N₂ adsorption-desorption isotherms of SFS-40, where the BET specific surface area, pore volume, and pore size were 218.09 m²/g, 0.21 cm³/g and 3.50 nm, respectively.

The pyridine-IR spectra were employed to evaluate the type and strength of Brönsted and Lewis acid sites on SFS-30 [35]. The pyridine-IR spectra of SFS-30 (Fig. 5(d)) exhibited bands at 1449 and 1609 cm⁻¹, which demonstrated the existence of Lewis acid sites in the materials. The bands at 1543 and 1639 cm⁻¹ were those characteristic of the pyridinium ion, which showed the presence of Brönsted acid sites. The band at 1490 cm⁻¹ was a combination between two separate bands, namely, those at 1449 and 1543 cm⁻¹, which corresponded to Brönsted and Lewis acid sites, respectively. These indicated that both Brönsted and Lewis acid sites existed in the sample. In addition, the changes of Brönsted acidity and Lewis acidity were observed from the Fig. 5(d), for desorption temperatures of 150, 250, 350, and 450 °C. Compared with Lewis acidity, the



Fig. 5. Fe 2p (a) and S 2p (b) XPS spectra of SF and SFS-30; (c) N₂ adsorption-desorption isotherms of SFS-30 and SFS-40; (d) The pyridine-IR spectra of SFS-30.

Brönsted acidity was significantly reduced with increasing temperature.

3.2. Influence of loading amounts of Fe₂O₃ on SBA-15

To understand the influence of loading Fe_2O_3 on the mesoporous solid superacid, the catalytic performance of SFS-x (x = 10, 20, 25, 30, 35, 40, 45) in the alcoholysis was investigated. As shown in Fig. 6(a), the activity of the catalyst increased as the enhancement of Fe_2O_3 loading amount passed through a maximum at x = 30 and then declined. This implied that when x was below 30, the surface active acid sites increased with the loading of SF. However, when x was above 30, the excessive SF probably caused a partial aggregation of catalyst, and hindered the pore diffusion and decreased the catalytic activity. It indicated that the increasing loading led to a sustained decrease of

Table 1

BET surface area, textural data and catalytic activities for bulk SF, SFS-30 and SBA-15.

Sample	$A_{\text{BET}} a (m^2/g)$	<i>V</i> _p ^b (cm ³ /g)	D°(nm)	Catalytic activity ^d yield (%)	
				reaction time (min)	
Bulk SF	6.57	0.02	11.33	99.5, 45	
SFS-30	263.78	0.38	6.95	100, 30	
SBA-15	605.47	0.86	7.01	-	

^a A_{BET} = BET surface area. ^b V_p = Pore volume. ^c D = Pore size.

^d Reaction conditions were same to Fig. 6(b).

the active surface area and mesopore volume, which had a significant influence on the properties of the acid, as has been previously reported [36].

3.3. Comparison of catalytic activity

A comparison between the catalytic activity of SF and SFS-30 was performed and the results are shown in Fig. 6(b) and (c). When using 10.0 mg of SF catalyst, it was found that the optimal molar ratio of styrene oxide to MeOH (93.6 mmol) was 1:7. As shown in Fig. 6(b), the reaction yield of 99.5% at 40 °C required 45 min for SF. When using the SFS-30 catalyst, the reaction easily achieved a yield of 100% after 30 min. Next, we investigated the alcoholysis of styrene oxide with various other alcohols with SFS-30. As illustrated in Fig. 6(c), it is worth mentioning that the alcoholysis yields of the SFS-30 catalyzed reactions were 99.7% and 99.6% with EtOH and n-PrOH, respectively. However, the yields of the same reactions when catalyzed by SF were only 95.4% and 69.5%. Furthermore, the catalytic activity of SFS-30 was higher than that of SF in the alcoholysis of styrene oxide with n-BuOH, i-PrOH, i-BuOH and s-BuOH. From these results, we can conclude that the catalytic activity of SFS-30 was higher than that of bulk SF, which indicated that the SF nanoparticles loading on the SBA-15 not only enhanced the active surface area of the activity components (Table 1), but also reduced the amounts of effective compo-



Fig. 6. (a) Influence of load amounts of Fe₂O₃ on SBA-15 for alcoholysis of styrene oxide with MeOH, 15 min; (b) Comparison between the catalytic activity of SF and SFS-30, catalyst (10.0 mg), styrene oxide (1.60 g, 13.3 mmol), MeOH (3.00 g, 93.6 mmol), 40 °C; (c) SF and SFS-30 catalyzed alcoholysis of styrene oxide with other alcohols, catalyst (10.0 mg), styrene oxide (1.60 g, 13.3 mmol), alcohols (93.6 mmol), 40 °C, 90 min; (d) Catalytic reusability of SFS-30, catalyst (50.0 mg), styrene oxide (8.00 g, 66.5 mmol), MeOH (15.00 g, 468 mmol), 40 °C, 30 min.

nents. With the synergistic effect from the nano effect of SF nanoparticles and the mesostructure of SBA-15, the reaction time of catalyzed SFS-30 was one-third lower than that required when using bulk SF.

The catalytic performance of SFS-30 and several different Brönsted acids for the alcoholysis is compared in Table 2. Similar to the non-catalyzed system, Fe₂O₃/SBA-15 did not yield any products. Obviously, the styrene-based sulfonic resins presented a lower yield with 12.2% conversion and 89% selectivity. H₂SO₄ and *p*-toluenesulfonic acid exhibited good catalytic properties close to those of SFS-30 with selectivities of 98.9% and 98.8%, respectively. However, the two acids were dissolved in the reaction mixtures and were difficult to isolate and reuse: alkaline materials must be used to neutralize the acids to avoid continuous increase of by-products а (1,2-dimethoxyl-1-phenylethane). As a result, large amounts of salt and wastewater will be produced, which represents an environmental issue. By contrast, SFS-30 exhibited an excellent activity with 100% yield and an ease of separation. However, Fe₂O₃/SBA-15 did not yield any products, which was attributed to more Lewis acidity sites of SFS-30, which originated from the cooperation of $S_2O_8^{2-}$ and Fe₂O₃ [37].

A comparison between the catalytic activity of our SFS-30

and that of other reported catalysts is listed in Table 3. SFS-30 presented the highest catalytic activity, even with the highest substrate/catalyst (S/C) ratio of 160:1 and the lowest MeOH/styrene oxide molar ratio of 7:1. It was also clear that $S_2O_8^2$ --Fe₂O₃ showed a good catalytic performance in the reaction (Fig. 6(b)). [V^{IV}(TPP)(OTf)₂] was the second highest catalytic activity, but the high activity could only be obtained with an S/C of 24:1 and a very high MeOH/styrene oxide molar ratio of 98.8:1. As a result, SFS-30 with the synergistic effect between the nano effect of $S_2O_8^2$ --Fe₂O₃ nanoparticles and the mesostructure of SBA-15 exhibited the more highly efficient

Table 2

Catalytic performances of SFS-30 and several different Brönsted acids for the alcoholysis of styrene oxide with MeOH.

Catalyst	Conversion (%)	Selectivity (%)	
-	0	0	
Fe ₂ O ₃ /SBA-15	0	0	
S ₂ O ₈ ²⁻ -Fe ₂ O ₃ /SBA-15 *	100	100	
H ₂ SO ₄	99.5	98.9	
p-toluenesulfonic acid	99	98.8	
Styrene-based sulfonic resins	12.2	89	
a		11 (1 (0 100	

Reaction conditions: catalyst (10.0 mg), styrene oxide (1.60 g, 13.3 mmol), MeOH (3.00 g, 93.6 mmol), 40 °C, 45 min. *Reaction time was 30 min.

Table 3

Comparison between the catalytic activity of SFS-30 and that of other reported catalysts for the alcoholysis of styrene oxide with MeOH.

	MeOH/Strene Substrate/ oxide Catalyst		Yield	Ref.
Catalyst			(%)	
	molar ratio	(S/C)	(70)	
S ₂ O ₈ ²⁻ -Fe ₂ O ₃ /SBA-15	7:1	160:1	100	This work
[V ^{IV} (TPP)(OTf) ₂]	98.8:1	24:1	100	[37]
MS-SO ₃ H	37:1	6:1	100	[38]
Fe(Cp) ₂ BF ₄	61.8:1	20:1	99	[39]
Fe(Cp) ₂ PF ₆	61.8:1	20:1	99	[39]
ZrCl ₄	61.8:1	20:1	98	[39]
(NH ₄) ₂ Ce(NO ₃) ₆	61.8:1	20:1	91	[39]
FeCl ₃	61.8:1	20:1	99	[39]
InCl ₃	61.8:1	20:1	81	[39]
[Fe(BTC)]	61.8:1	4.8:1	48	[40]
[Cu ₃ (BTC) ₂]	61.8:1	4.8:1	24	[40]
$[Al_2(BDC)_3]$	61.8:1	4.8:1	20	[40]
Iron citrate	61.8:1	4.8:1	24	[40]
Fe ₂ (NO ₃) ₂ •9H ₂ O	61.8:1	2.4:1	97	[40]
Sulfated Zr-doped [TiNbO5]- nanoplates	49.4:1	2.4:1	99	[41]
ZrO(NO ₃) ₂ •nH ₂ O	74:1	5:1	98	[42]

catalytic activity compared with other reported catalysts.

3.4. Catalyst reusability

Since the reusability is an important factor influencing the practical applications of catalysts, we carried out a seven run test over the SFS-30 solid superacid under the optimized reaction conditions to evaluate the recyclability of the catalyst (Fig. 6(d)). The selectivity of alcoholysis remained at 100% in the seven runs test over the SFS-30. Compared with the fresh catalyst, a slow decline in the conversion was observed after seven runs for the SFS-30 catalyzed alcoholysis reaction; however, the yield still remained high at 84.1%. The reason for the decrease of the conversion after reuse was mainly the chemical deactivation of SFS-30 arising from active phase shedding. This result indicated that the SFS-30 exhibited a good stability and can potentially be used in industrial applications.

4. Conclusions

Well-dispersed S₂O₈²⁻-Fe₂O₃/SBA-15 mesostructures with active nanoparticles, prepared by ultrasonic adsorption, present a larger specific surface area and larger mesopore volume with surface acid sites than bulk S₂O₈²⁻-Fe₂O₃. According to our experimental results, S2O82--Fe2O3/SBA-15 with a 30% Fe2O3 loading exhibited the highest activity in the alcoholysis of styrene oxide with MeOH compared with bulk S₂O_{8²⁻}-Fe₂O₃ and other reported Brönsted acids, Lewis acids and other catalysts. Furthermore, this mesoporous superacid also exhibited a more excellent highly efficient catalysis for alcoholysis with other ROHs (R = $C_2H_5-C_4H_9$) than bulk $S_2O_8^{2-}-Fe_2O_3$ and better reusability of the catalyst. Therefore, mesoporous S₂O₈²⁻-Fe₂O₃/SBA-15 possessing highly efficient catalytic activities, good stability and economy shows great promise for in-

dustrial application.

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超声吸附制备均匀分散在SBA-15的 $S_2O_8^{2-}$ -Fe₂O₃纳米粒子: 增强 $S_2O_8^{2-}$ -Fe₂O₃本体催化活性

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摘要: 酸催化剂在化学反应和化工生产中具有重要的作用. 传统无机酸,如H₂SO₄, H₃PO₄和对甲苯磺酸等具有较高的催化 活性,但是存在污染大、设备腐蚀严重以及催化剂不能重复使用等问题. 固体酸具有酸性强、易分离、环境友好以及稳定 性和重复使用性好等特点因而近年来越来越引起人们的关注. 其中,SO₄²⁻-M_xO_y固体超强酸(如SO₄²⁻-ZrO₂, SO₄²⁻-TiO₂和 SO₄²⁻-SnO₂等)因具有很好的催化性能而备受关注. 相比SO₄²⁻-M_xO_y, S₂O₈²⁻-M_xO_y具有更强的酸性和稳定性而成为研究的重 点. 如何克服固体超强酸本体的低比表面积和孔容,增加其比表面积和催化活性是固体超强酸研究的热点. 超声吸附法可 保证所制介孔固体酸活性组分均匀分散,以及大的比表面积和更多的酸性位点. 因此采用超声吸附法制备了一种新型介 孔固体酸S₂O₈²⁻-Fe₂O₃/SBA-15. 相比S₂O₈²⁻-Fe₂O₃本体、B酸和文献报道催化剂,负载30%Fe₂O₃的S₂O₈²⁻-Fe₂O₃/SBA-15在环 氧苯乙烷甲醇醇解的探针反应中显示出很高的催化活性,反应收率为100%. S₂O₈²⁻-Fe₂O₃纳米粒子的纳米效应和SBA-15介 孔结构的协同作用使S₂O₈²⁻-Fe₂O₃/SBA-15具有高催化活性.

相比S2O82-Fe2O3本体,采用超声分散技术制备的S2O82-Fe2O3/SBA-15固体超强酸具有典型的介孔结构、大的比表面积

和孔容,并且表面富含酸性位点.并且吡啶红外分析S₂O₈²⁻-Fe₂O₃/SBA-15表面富含L酸和B酸.环氧苯乙烷甲醇醇解探针反应表明, Fe₂O₃负载量为30%时, S₂O₈²⁻-Fe₂O₃/SBA-15的催化活性最高, 优于S₂O₈²⁻-Fe₂O₃本体和已报道的布朗酸和路易斯酸等催化剂,将醇底物拓展(ROHs, R = C₂H₅-C₄H₉), S₂O₈²⁻-Fe₂O₃/SBA-15的催化活性也优于S₂O₈²⁻-Fe₂O₃本体.同时, S₂O₈²⁻-Fe₂O₃/SBA-15具有很好的重复使用性能,连续使用七次,反应收率在84.1%以上.总之,具有高催化活性、好的稳定性和经济性的S₂O₈²⁻-Fe₂O₃/SBA-15具有广阔的应用前景.

关键词: 介孔固体酸; 纳米粒子; 纳米效应; S₂O₈²⁻-Fe₂O₃/SBA-15; 酸性位; 超声分散; 醇解

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