



Preparation of silica-supported sulfate and its application as a stable and highly active solid acid catalyst

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ABSTRACT

Silica sulfate was prepared by a simple procedure, and proved to be an efficient and recyclable solid acid catalyst. SO₃H groups were successfully introduced to silica surface while keeping its structure intact, as proved by XRD patterns and SEM images of the catalyst. With the catalysis of the supported sulfate materials, many of the ketones are efficiently transformed into the corresponding lactones with 30% hydrogen peroxide. In addition, the high performance of silica sulfate as a heterogeneous catalyst was further demonstrated for the esterification of varieties of carboxylic acid with ethanol.

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1. Introduction

Solid acids are mineral oxides such as sulfated zirconia [1], Cs-exchanged heteropoly acids [2], acidic polymers [3,4] and zeolites [5] that contain both Lewis and Brønsted acid sites. However, traditionally inorganic-oxide solid acids have low densities of effective acid sites and thus cannot achieve adequate performance in some acid-catalyzed reactions [6]. Although strong acidic cation-exchangeable resins (such as nafion and amberlyst) have abundant sulfonic acid groups, such materials have extremely low surface area (0.02 m²/g) that typically requires the use of polar reactants or solvents [7–9]. At the same time, sulfuric acid, methane sulfonic acid, *p*-toluene sulfonic acid and dried hydrogen chloride are also the most conventional and essential homogeneous catalysts [10–12], but the liquid–acid catalysts cannot be recycled and require special process of neutralization after the reaction, which will produce large amounts of waste [13,14]. All of the limitations mentioned above have restricted the practical utility of these catalysts. Therefore, there has been considerable interest in the development of more stable, reusable, and highly active solid acid catalysts currently.

Supported solid acid catalysts, often have advantages of strong acid site, large surface area, easily to be separated and recycled, are the good replacements for their homogeneous counterparts. Over the last decades, a large number of such SO₃H-functionalized solid acid catalysts are reported, such as sulfonated saccharides [15], sulfonated carbons [16–19], cellulose supported sulfuric acid [20] and organo-

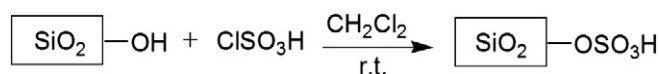
sulfonic acid functionalized mesoporous silica [21,22]. SO₃H was usually chosen as functional group, because it is not only known for efficient proton acid catalyst but also can be easily incorporated to many different materials.

Generally, chlorosulfuric acid is a typical strong acid, but it is very corrosive and will strongly decompose to hydrochloride and sulfate acid when encountered water. The use of silica-supported sulfate acid will not only an alternative to overcome these problems but also can exploit the strong acidic advantages of chlorosulfuric acid. Typically silica sulfate acid was used to catalyze Beckmann rearrangement of oximes [23]. In this paper, we report a direct-synthesis method for the incorporation of sulfate acid onto mesoporous silica structures giving high sulfur content. A series of silica-supported sulfate catalysts with different sulfate acid loadings were prepared. The prepared silica-supported sulfate acid acted as efficient and recyclable heterogeneous solid acid catalyst for Baeyer–Villiger oxidation of ketones and esterification of carboxylic acids with ethanol.

2. Experiments

2.1. Materials and Instrumentations

Silica (200 mesh) was purchased from Tianjin Guangfu Chemical Factory. Chlorosulfuric acid was obtained from Alfa Aesar (Tianjin)



Scheme 1. Typical synthesis mechanism for silica-supported sulfate catalyst.

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Table 1
The textural properties of the silica and silica-supported sulfate materials.

Material	Silica	SS-0.005	SS-0.010	SS-0.015
Specific surface area (m ² /g) ^a	121.7	95.34	77.17	45.05
Pore diameter (Å) ^b	117	255	256	320
Pore volume (cc/g) ^b	0.253	0.268	0.279	0.303

^a The specific surface area of the catalysts was obtained from nitrogen adsorption experiment and calculated by BET analysis.

^b Pore size and pore volume were calculated by BJH analysis.

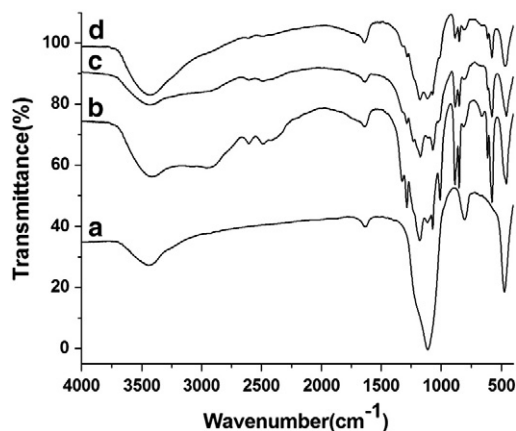


Fig. 1. FT-IR spectra for (a) silica, (b) SS-0.005, (c) SS-0.010, and (d) SS-0.015.

Chemical Co. Ltd. 2-Andamantanone, cyclopentanone, cyclohexanone, acetophenone, 2-methylcyclohexanone, 4-methylcyclohexanone, 2-*tert*-butylcyclohexanone, 4-*tert*-butylcyclohexanone, DL-menthone and 4-methyl-2-pentanone were obtained from Meryer (Shenzhen) Chemical Co. Ltd. Carboxylic acids and other reagents are of analytic grade and used as received without further purification.

GC analysis was carried out on a Shimadzu GC-2010 gas chromatographic instrument equipped with a 15 m × 0.53 mm × 1.50 μm RTX-1 capillary column. ¹H NMR and ¹³C NMR spectra were recorded on a Varian Mercury 400 plus instrument in CDCl₃ using TMS as an internal standard. Sulfur elements analysis was carried out on an Elementar Vario EL system. FT-IR spectra were recorded on a Nicolet Nexus 670 Fourier transform infrared spectrometer using KBr tableting technique. X-ray diffraction (XRD) was collected on a Bruker D8 Advance instrument using CuKα radiation ($k = 1.5406 \text{ \AA}$). SEM images were taken on a Hitachi S-4800 scanning electron microscope. BET specific surface areas of different catalyst were measured by using N₂ adsorption isotherms at 77 K with a Quantachrome Autosorb-1

automated nitrogen sorption system. TG-DTA analysis was carried out using Pyris Diamond (Perkin Elmer) equipment and with the heating rate of 10 K/min under a flow of dry air.

2.2. Catalyst Preparation

Silica sulfate was prepared according to literature procedure [23,24]. One typical synthesis process was as follows (Scheme 1): silica (2.0 g) was dispersed in CH₂Cl₂ (10 mL) in a flask. Different amount of chlorosulfonic acid ("x", $x = 0.005, 0.010, 0.015 \text{ mol}$) was added to the mixture through a constant-pressure dropping funnel under stirring over a period of 30 min at room temperature. After the addition was completed, the mixture was stirred for another 30 min at room temperature. The white solid was collected by evaporation of the solvent. The obtained solid was then dried at room temperature and kept in desiccators. A series of silica-supported sulfate catalysts with different sulfate loading ($x \text{ mol}$), denoted as SS- x , were prepared according the above methods.

2.3. General Procedures for Catalytic Reactions

A typical procedure for oxidation of ketones is: ketone (0.1 mmol), 30% H₂O₂ (2.0 eq.), silica sulfate (6.0 mg) and acetonitrile (3 mL) were added to a 10 mL flask. The mixture was stirred at 75 °C for 3–24 h. Esterification of carboxylic acid was carried out by stirring the mixture of 10.0 mg of catalyst, 50 mmol mol of ethanol and 2.50 mmol of acetic acid at 100 °C for 4–12 h. The products in the resulting mixture were determined by GC analysis. Some of the lactones were purified by a silica gel column chromatography with hexane/ethyl acetate as eluent.

3. Results and Discussion

3.1. FT-IR Spectra of the Catalyst

The IR spectra of pure silica and SS- x were shown in Fig. 1. The absorption at 3443 cm⁻¹ was attributed to the hydroxyl groups. As to the SS-0.010 material, the band near 1111 cm⁻¹ was the asymmetric stretching modes of Si-O-Si bond. Compared to pure silica, the peaks of silica sulfate at 883 and 851 cm⁻¹ were attributed to the S-O stretching modes, and the peaks that lie in 1286 and 1231 cm⁻¹ correspond to the asymmetric stretching and symmetric stretching of S=O bond, respectively [23]. These signals suggested the existence of sulfate group in silica structure. The FT-IR spectra of SS-0.005 and SS-0.015 are similar to SS-0.010.

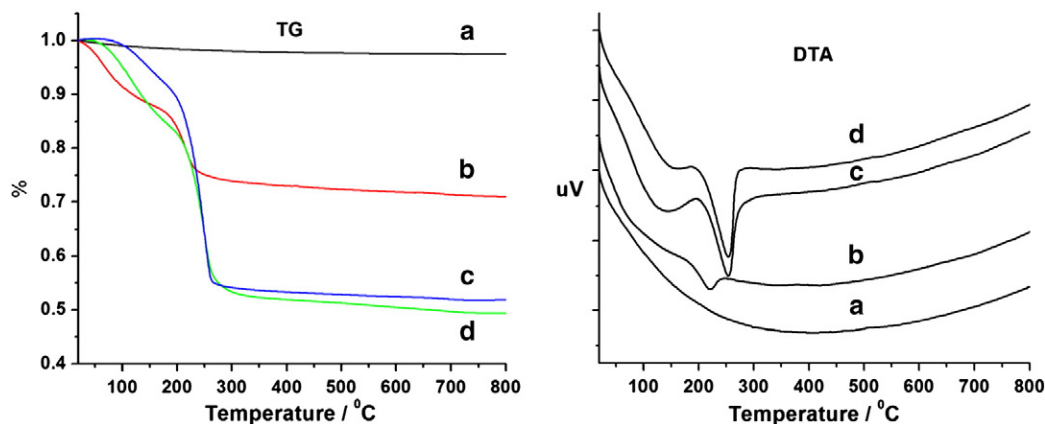


Fig. 2. TG-DTA analysis for (a) silica, (b) SS-0.005, (c) SS-0.010, and (d) SS-0.015.

3.2. Textural Properties of the Materials

The textural properties of the catalysts were obtained from nitrogen adsorption experiment and were listed as below (Table 1).

We can find that with the increasing of sulfate acid loadings, the specific surface area of the three supported catalyst gradually decreased and the pore diameter and the pore volume appeared increasing tendency when compared to pure silica. These results support that the sulfate group was successfully entered the channel of the silica gel.

3.3. The Thermal Gravimetric Analysis of the Catalysts

The TG-DTA analysis was applied to characterize the thermal stability of the prepared catalyst (Fig. 2). As shown in Fig. 2, the raw silica shows no weight loss and no endothermic peak in the TG-DTA curve. However, for three supported catalysts, the TG curve all showed a two-stage weight loss which considered to be the removal of physical adsorbed water (80–110 °C) and the elimination of SO₂ (120–280 °C), respectively. DTA analysis further demonstrates the presence of the various species, the endothermic peak at lower temperature represents the removal of water from the material, while the endothermic peak at higher temperature represents solely the decomposition of the silica sulfuric acid and the elimination of SO₂ [25,26]. These results also suggested the presence of target group (SO₃H) in the catalysts.

3.4. XRD Patterns and SEM Images of the Catalyst

Fig. 3 shows the X-ray diffraction patterns of silica and silica-supported sulfate catalyst. It was observed for all of four patterns a shoulder around $2\theta = 23^\circ$ characteristic of materials with low crystallinity [27]. As seen from SEM images (Fig. 4), the surface of the supported catalyst becomes denser when compared with pure silica. This result agreed well with the XRD patterns indicated that SO₃H groups were successfully introduced to silica surface while keeping its structure intact.

3.5. Catalytic Properties of the SS-0.010 Catalyst

3.5.1. Baeyer–Villiger Oxidation of Ketones Catalyzed by SS-0.010

Here we report new method to realize the classical Baeyer–Villiger oxidation catalyzed by silica-supported sulfate acid. Results show that the oxidation reaction did not proceed in the absence of the silica sulfate, or in the presence of silica. This indicates that supported sulfate group helps to catalyze the Baeyer–Villiger oxidation of ketones.

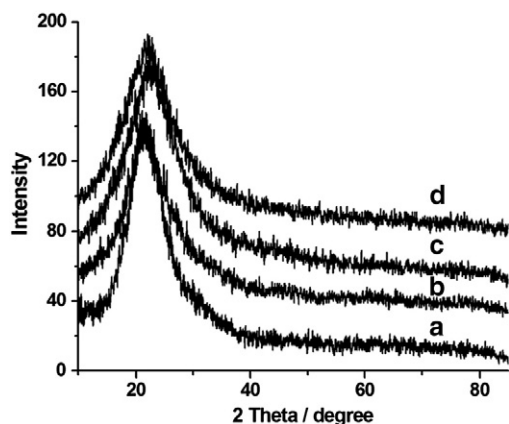


Fig. 3. XRD patterns for (a) silica, (b) SS-0.005, (c) SS-0.010, and (d) SS-0.015.

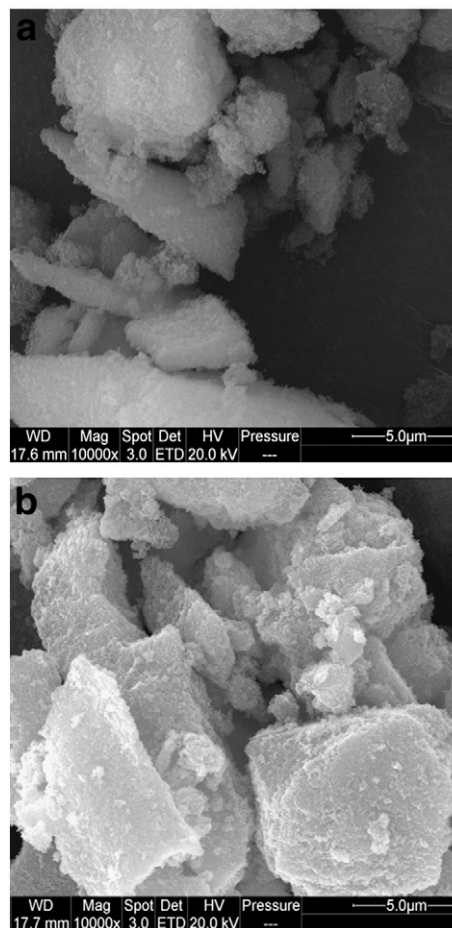


Fig. 4. SEM images for (a) silica and (b) SS-0.010.

Oxidation of ketones was carried out in its optimize condition (see Supplementary data) as follows: ketones (0.1 mmol), 30% H₂O₂ (2.0 eq.), and SS-0.010 (6.0 mg) were dissolved in acetonitrile (3 mL) and stirred at 75 °C for 12 h. As shown in Table 2, silica sulfate performs excellent catalytic activity for Baeyer–Villiger oxidation of many ketones. The results also suggest that the relative reactivity of ketones depend on the ring size and the migratory ability of the substituent group. For example, 2-adamantanone and cyclopentanone are converted to ketones with high conversion and selectivity

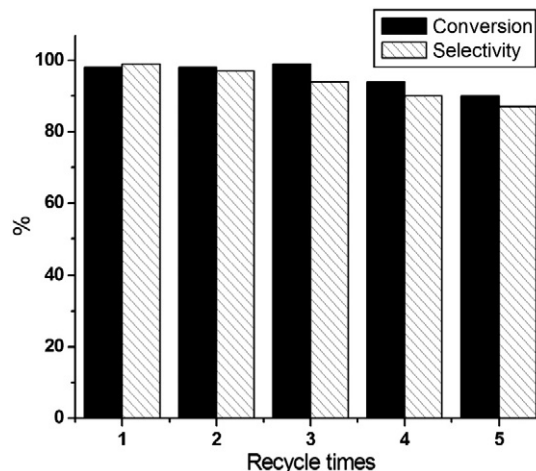






















Fig. 5. Recycling properties of SS-0.010 in the Baeyer–Villiger oxidation of 2-adamantanone.

Table 2
Baeyer–Villiger oxidation of ketones catalyzed by SS-0.010.

Entry	Substrate	Conversion (%) ^a	Selectivity (%) ^a	Product	TOF ^b (mmol/g·h)
1		100	98		1.36
2		65	100		0.90
3		97	100		1.35
4		85	97		1.15
5		88	100		1.22
6		94	70		0.91
7		86	84		1.00
8		37	86		0.44
9		11	100		0.15
10		45	100		0.63

Reaction condition: substrate 0.1 mmol, catalyst 6.0 mg, 30% H₂O₂ 2.0 eq., acetonitrile 3 mL, 12 h, 75 °C.

^a Conversion and selectivity were determined by GC analysis.

^b TOF = (ketone amount (mmol) * substrate conversion * product selectivity) / (catalyst amount (g) * reaction time (h)).

due to the strong ring strain of the molecular structure (entries 1, 2). In contrast, for the oxidation of cyclohexanone, 2-methylcyclohexanone, 4-methylcyclohexanone and 4-*tert*-butylcyclohexanones (entries 3, 4, 5, 7), as shielding role of the substituent groups is weak, the active site of the catalyst can be easily coordinated with carbonyl oxygen atom and activate the substrate, and the conversion of substrate is relatively higher. For the oxidation of DL-menthone (entry 6), due to the presence of methyl or *tert*-butyl which can fully

disperse positive charge in the formation of Criegee intermediate, good reaction activity was achieved. However, as for 2-*tert*-butylcyclohexanone (entry 8), the large steric hindrance from the *tert*-butyl group near the carbonyl group caused the difficulty in the coordination of the catalyst to the carbonyl oxygen, which leads to lower reaction activity. The lowest conversion was obtained in the oxidation of acetophenone due to the conjugation effect in the molecular structure, and to our surprise no lactone was found in the acetophenone oxidation (entry 9). Besides, it is noteworthy that the catalyst also shows promising activity in the oxidation of chain ketones, such as 4-methyl-2-pentanone was oxidized to the corresponding lactone with middle conversion (entry 10).

3.5.2. Esterification of Carboxylic Acid Catalyzed by SS-0.010

As we know, conventional esterifications do not proceed to completion but reach equilibrium. Although the equilibrium can be shifted towards higher conversion by using one reactant in excess or by selective removal of one of the products, the excess substrate will generally increase processing costs and contributes to pollution. In contrast, catalytic direct condensation will solve these problems. Here, the high performance of SS-0.010 as a heterogeneous catalyst was demonstrated for the esterification of varieties of carboxylic acid with ethanol.

As shown in Table 3, variety of carboxylic acid was converted into the corresponding esters in high to excellent yields in the presence of SS-0.010. No competitive side reactions such as etherification of alcohol, decomposition of acid sensitive substrates, or decarboxylation of the carboxylic acids were observed.

We can also see from Table 3 that steric and diffusional effects play an important role in the esterification of carboxylic acid over silica-supported catalysts. For example, the reaction was completed within 4 h for acetic acid and propanoic acid (entries 1, 2). Similarly, the relatively high conversion was achieved for lactic acid and phenylacetic acid (entries 3, 5). However, only 14.6 mmol/g·h of TOF was obtained for saethyl (entries 4). This is maybe due to high steric-hindered substitute group on carboxylic acid influences in the nucleophilic attack to the polarized of carbonyl centre and thus reduces the extent of esterification [28]. On the other hand, relatively low reaction activity was performed for dicarboxylic acids compared to these monocarboxylic acids (entries 6, 7). In a word, we can draw a conclusion that SS-0.010 is a potential heterogeneous catalyst for the esterification of varieties of carboxylic acid with ethanol.

3.6. The Recycling Property of the Catalyst

To investigate the recycling properties of the catalyst, SS-0.010 was removed from the reaction mixture after 12 h by filtration, washed with acetonitrile, dried and subjected to another catalytic reaction with 2-andamantanone as substrate (Fig. 5). As a result, we can find that the silica sulfate can be recycled at least five times without significant decline in catalytic activity.

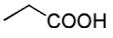
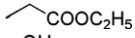
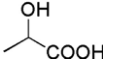
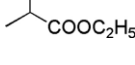
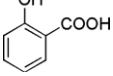
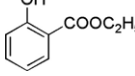
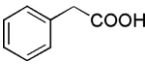
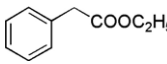

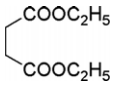
3.7. Products Separation and Identification

Some of the lactones were purified by a silica gel column chromatography with hexane/ethyl acetate (10:1, V/V) as eluent. The spectral (¹H NMR and ¹³C NMR) data of the product are given below.

Product 1b: ¹H NMR (CDCl₃, 400 MHz): δ 4.489 (1H), 3.076 (1H), 2.114 (2H), 2.004 (2H), 1.957 (1H), 1.921 (2H), 1.856 (2H), 1.739 (2H), 1.280 (1H). ¹³C NMR (CDCl₃, 100 MHz): δ 178.960, 73.136, 41.151, 35.862, 35.679, 33.713, 30.863, 29.628, 25.856, 25.650.

Product 2b: ¹H NMR (CDCl₃, 400 MHz): δ 4.282 (2H), 2.49 (2H), 1.798 (2H). ¹³C NMR (CDCl₃, 100 MHz): δ 171.339, 69.331, 29.636, 22.091, 18.875.

Table 3
Esterification of carboxylic acid with ethanol catalyzed by SS-0.010.

Entry	Substrate	Reaction time (h)	Conversion (%) ^a	Selectivity (%) ^a	Product	TOF ^b (mmol/g·h)
1	CH ₃ COOH	4	99	99	CH ₃ COOC ₂ H ₅	61.1
2		4	99	99		61.1
3		5	96	98		47.0
4		12	71	99		14.6
5		5.5	99	98		44.1
6	HOOC–COOH	7	94	99	C ₂ H ₅ OOC–COOC ₂ H ₅	33.2
7		6.5	99	94		35.8

Reaction condition: ethanol (2.3 g, 50 mmol), carboxylic acid (2.50 mmol), catalyst SS-0.010 (10.0 mg), 100 °C.

^a Conversion and selectivity were determined by GC analysis.

^b TOF = (carboxylic acid amount (mmol) * substrate conversion * product selectivity) / (catalyst amount (g) * reaction time (h)).

Product **3b**: ¹H NMR (CDCl₃, 400 MHz): δ 4.235 (2H), 2.643 (2H), 1.867 (2H), 1.795 (4H). ¹³C NMR (CDCl₃, 100 MHz): δ 171.339, 69.331, 29.636, 22.091, 18.875.

Product **4b**: ¹H NMR (CDCl₃, 400 MHz): δ 4.449 (1H), 2.653 (2H), 1.930 (4H), 1.627 (2H), 1.352 (3H). ¹³C NMR (CDCl₃, 100 MHz): δ 175.60, 76.80, 36.21, 35.00, 28.28, 22.88, 22.57.

Product **5b**: ¹H NMR (CDCl₃, 400 MHz): δ 4.188 (2H), 2.630 (2H), 1.912 (2H), 1.862 (1H), 1.498 (1H), 1.343 (1H), 1.002 (3H). ¹³C NMR (CDCl₃, 100 MHz): δ 175.995, 67.984, 37.097, 35.116, 33.081, 30.634, 22.008.

Product **6b**: ¹H NMR (CDCl₃, 400 MHz): δ 4.054 (1H), 2.518 (2H), 1.857 (4H), 1.611 (1H), 1.310 (1H), 1.051 (3H), 0.975 (6H). ¹³C NMR (CDCl₃, 100 MHz): δ 174.951, 84.659, 420493, 37.379, 33.248, 30.848, 30.330, 23.905, 18.319, 17.039.

Product **7b**: ¹H NMR (CDCl₃, 400 MHz): δ 4.335 (1H), 4.158 (1H), 2.585 (1H), 2.569 (1H), 2.085 (2H), 1.527 (1H), 1.369 (2H), 0.898 (3H). ¹³C NMR (CDCl₃, 100 MHz): δ 176.285, 68.579, 50.667, 33.386, 32.936, 30.261, 27.472, 27.373, 27.304, 23.669.

Product **9b**: ¹H NMR (CDCl₃, 400 MHz): δ 11.548 (1H), 8.129 (2H), 7.641 (1H), 7.473 (2H). ¹³C NMR (CDCl₃, 100 MHz): δ 172.307, 133.821, 130.202, 129.264, 128.479.

4. Conclusions

The prepared silica sulfate, especially SS-0.010, was acted as an efficient and recyclable solid acid catalyst for Baeyer–Villiger oxidation of ketones and esterification of carboxylic acid under mild conditions. The catalyst exhibits the advantages of high conversion, high selectivity, recyclability, and multifunction. The results also showed that SO₃H groups were successfully introduced to silica surface while keeping its structure intact, which suggested that the immobilizing method described here can be extended for attachment of other functional groups on the surface of silica to generate diverse functionalized silica for different applications.

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Appendix A. Supplementary Data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2011.01.028.

References

- [1] Y.X. Rao, J.J. Kang, D. Antonelli, *J. Am. Chem. Soc.* 130 (2008) 394–395.
- [2] T. Okuhara, *Chem. Rev.* 102 (2002) 3641–3666.
- [3] a). M.A. Harmer, Q. Sun, *Appl. Catal., A* 221 (2001) 45–62.
- [4] R. Xing, N. Liu, Y.M. Liu, H.H. Wu, Y.W. Jiang, L. Chen, M.Y. He, P. Wu, *Adv. Funct. Mater.* 17 (2007) 2455–2461.
- [5] A. Corma, *Adv. Mater.* 7 (1995) 137–144.
- [6] M.A. Harmer, W.E. Farneth, Q. Sun, *Adv. Mater.* 10 (1998) 1255–1257.
- [7] a). T. Okuhara, *Chem. Rev.* 102 (2002) 3641–3666.
- [8] S. Inagaki, S. Guan, T. Ohsuna, O. Terasaki, *Nature* 416 (2002) 304–307.
- [9] A.A. Kiss, A.C. Dimian, G. Rothenberg, *Adv. Synth. Catal.* 348 (2006) 75–81.
- [10] a). C.F.H. Allen, F.W. Spangler, *Org. Synth.* 3 (1955) 203–204.
- [11] E.H. Huntress, T. Lesslie, E. Bornstein, *J. Org. Synth.* 4 (1963) 329–330.
- [12] J. Munch-Peterson, *Org. Synth.* 5 (1973) 762–765.
- [13] J.M. DeSimone, *Science* 297 (2002) 781–799.
- [14] B. Harton, *Nature* 400 (1999) 797–799.
- [15] X. Mo, D.E. Lopez, K. Suwannakarn, Y. Liu, E. Lotero, J.G. Goodwin Jr., C. Lu, *J. Catal.* 254 (2008) 332–338.
- [16] M. Toda, A. Takagaki, M. Okamura, J.N. Kondo, S. Hayashi, K. Domen, M. Hara, *Nature* 438 (2005) 178–179.
- [17] X.Q. Wang, R. Liu, M.M. Waje, Z.W. Chen, Y.S. Yan, K.N. Bozhilov, P.Y. Feng, *Chem. Mater.* 19 (2007) 2395–2397.
- [18] V.L. Budarin, J.H. Clark, R. Luque, D.J. Macquarrie, *Chem. Commun.* 6 (2007) 634–636.
- [19] M. Kitano, D. Yamaguchi, S. Suganuma, K. Nakajima, H. Kato, S. Hayashi, M. Hara, *Langmuir* 25 (2009) 5068–5075.
- [20] A. Shaabani, A. Maleki, *Appl. Catal., A* 331 (2007) 149–151.
- [21] I.K. Mbaraka, D.R. Radu, V.S.Y. Lin, B.H. Shanks, *J. Catal.* 219 (2003) 329–336.
- [22] L. Peng, A. Philippaerts, X.X. Ke, J.V. Noyen, F.D. Clippel, G.V. Tendeloo, P.A. Jacobs, B.F. Sels, *Catal. Today* 150 (2010) 140–146.
- [23] Z. Li, R.B. Ding, Z. Lu, S.X. Xiao, X.L. Ma, *J. Mol. Catal. A Chem.* 250 (2006) 100–103.
- [24] M.A. Zolfigol, *Tetrahedron* 57 (2001) 9509–9511.
- [25] H.R. Shaterian, M. Ghashang, M. Feyzi, *Appl. Catal., A* 345 (2008) 128–133.
- [26] M. Hara, T. Yoshida, A. Takagaki, T.i. Takata, J.N. Kondo, S. Hayashi, K. Domen, *Angew. Chem. Int. Ed.* 43 (2004) 2955–2958.
- [27] A. Loaiza-Gil, M. Villarreal, J.F. Balbuena, M.A. Lacruz, S. Gonzalez-Cortes, *J. Mol. Catal. A: Chem.* 281 (2008) 207–213.
- [28] A.L. Cardoso, S.C.G. Neves, M.J. da Silva, *Energy Fuels* 23 (2009) 1718–1722.