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Sulfated and persulfated TiO_2/MCM-41 prepared by grafting method and their acid-catalytic activities for cyclization of pseudoionone

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Solid acid catalysts of SO_4^{2-}/TiO_2/MCM-41 and $S_2O_8^{2-}/TiO_2$/MCM-41 were prepared via grafting method and sulfate/persulfate promotion. The catalysts exhibited desirable activity and better selectivity for cyclization reaction of pseudoionone compared to traditional SO_4^{2-}/TiO_2. A combination of XRD, N_2 adsorption–desorption and FTIR spectroscopy indicated that the catalysts possess well-ordered mesostructure, and the grafted TiO_2 are in highly dispersed amorphous form rather than crystalline phase. For $S_2O_8^{2-}/TiO_2$/MCM-41 higher S content and more Brønsted acid sites can be achieved by persulfation, which is favorable for the protons participated cyclization reaction. The similar Si–O–Ti–O–S = O structure of all acid sites on pore surface of the catalysts is attributed to the improvement of selectivity in comparison with SO_4^{2-}/TiO_2.

KEY WORDS: grafted TiO_2; sulfate/persulfate promotion; MCM-41; cyclization of pseudoionone.

1. Introduction

SO_4^{2-}/TiO_2 is a well-known catalyst for many acid-catalyzed reactions, such as isomerization [1], alkylation [2], esterification [3], acylation [4], nitration [5], condensation [6], and oligomerization [7]. However, the relatively small surface area and non-porous structure of SO_4^{2-}/TiO_2 is unfavorable for its catalytic performance. In recent years, chemical grafting method has been applied to introduce highly dispersed TiO_2 onto mesoporous silica to obtain materials with well-ordered mesostructure and large surface area [8–11]. The grafted TiO_2 in the resulting materials are mainly isolated tetrahedrally coordinated species and in amorphous form rather than anatase phase as conventional SO_4^{2-}/TiO_2. Though the Ti content is low, all the active Ti sites in the resulting materials are located on pore surface via Si–O–Ti bonds, thus structurally well defined and easily accessible. It has been shown that this kind of catalysts exhibited good activities for photocatalytic and epoxidation reactions [8–11]. However, there were no reports yet on sulfate treatment of TiO_2 grafted mesoporous silica for acid-catalysis purpose.

The isomeric ionones are of both academic and commercial interest, and have been widely used as fragrance, starting materials or building blocks in synthesis of medicine and many fine chemical products [12]. Ionones are usually produced via cyclization of pseudoionone catalyzed by concentrated liquid acids under rigorous conditions [13–16], and this process essentially results in separation difficulties and environmental problems, to which an efficient solution is the employment of solid acid catalysts. Additionally, there were no reports on cyclization reactions catalyzed with SO_4^{2-}/TiO_2 until now. These reasons drive us to develop a TiO_2 modified catalyst with well-ordered mesostructure for the cyclization of bulky pseudoionone molecule.

In this work, MCM-41 was modified with TiO_2 by grafting method, and promoted with H_2SO_4 and $(NH_4)_2S_2O_8$ aqueous solutions. TiO_2 grafted MCM-41 without sulfation/persulfation and the traditional nanosized SO_4^{2-}/TiO_2 were also prepared for comparison. The structural and acid properties of the catalysts were characterized with XRD, N_2 adsorption–desorption, and FTIR spectroscopy, and their catalytic performances for cyclization of pseudoionone to ionones were examined. The obtained SO_4^{2-}/TiO_2/MCM-41 and $S_2O_8^{2-}/TiO_2$/MCM-41 exhibited desirable acid-catalytic activity and better selectivity for the cyclization reaction in comparison to SO_4^{2-}/TiO_2.

2. Experimental

2.1. Catalyst preparation

Pure siliceous MCM-41 was synthesized following the procedure proposed by Grün et al. [17]. The new solid acid catalysts of SO_4^{2-}/TiO_2/MCM-41 and $S_2O_8^{2-}/TiO_2$/MCM-41 were prepared through grafting reaction of $Ti(OBu^n)_4$ with Si–OH on pore surface of MCM-41 and sulfate/persulfate promotion. Pre-calcined MCM-41 was stirred in mixed solution of excess $Ti(OBu^n)_4$ (C.P.,

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Shanghai Chemical Reagent Co.) and dehydrated *n*-hexane at 70 °C to form surface Si–O–Ti–OBu groups, washed with anhydrous ethanol to remove residual $Ti(OBu^n)_4$ thoroughly, and hydrolyzed in deionized water at room temperature to generate Si–O–Ti–OH on silica wall. The filtered and dried solid was impregnated with 0.5 M H_2SO_4 and $(NH_4)_2S_2O_8$ solution, respectively, followed by drying and calcination at 450 °C for 3 h to get SO_4^{2-}/TiO_2/MCM-41 and $S_2O_8^{2-}/TiO_2$/MCM-41. TiO_2/MCM-41 without sulfation was obtained by calcining the hydrolyzed solid directly.

Nanosized SO_4^{2-}/TiO_2 was prepared through hydrolysis of $TiCl_4$. Pre-cooled $TiCl_4$ (98%, Shanghai Meixing Chemical Co. Ltd.) was added dropwise into dilute HCl solution in ice-bath under vigorous stirring. After stabilization at 0–15 °C for 30 min, aqueous ammonia was added drop by drop at 70 °C under constant stirring until pH = 9. The precipitate was treated with 0.5 M H_2SO_4 solution and calcined at 450 °C to obtain SO_4^{2-}/TiO_2.

2.2. Catalyst characterization

The XRD patterns were collected by Shimadzu XRD-6000 diffractometer using Ni-filtered CuKα radiation operating at 40 kV and 30 mA. N_2 adsorption–desorption isotherms were measured with Quantachrome NOVA 1000 at 77 K. Before measurement the samples were outgassed at 300 °C for 3 h. FTIR spectra were recorded with Nicolet Avartar 360 spectrophotometer. KBr pellets with 1.0 wt.% catalysts containing were used to collect vibration spectra of Si–O–Ti bonds, while self-supporting catalysts wafers were used to characterize the S = O vibration, as well as the presence of Brønsted and Lewis acid sites by pyridine adsorption. The wafers were evacuated at 400 °C for 3 h in an *in situ* cell under vacuum at 6×10^{-2} Pa before scanning. Ti content of the catalysts was analyzed with IRIS ADVANTAGE/1000 ICP-AES, and S content was determined with PE 2400II CHNS/O Analyzer.

2.3. Catalytic testing

The cyclization reaction of pseudoionone to ionones was carried out in a 100 mL flask reactor. The reactant (1.5 g of pseudoionone, >95%, Xinchang Pharmaceutical Factory) and the solvent (20 mL of cyclohexane) were introduced into the reactor. When the temperature was raised to 80 °C, 1.0 g of the catalysts was added under constant stirring. The products were analyzed on Angilent 6890N gas chromatograph with FID detector.

3. Results and discussion

XRD patterns of the catalysts are presented in figure 1. The three peaks at low diffraction angles in figure 1(a) show the long-range ordered hexagonal mesostructure of the pure siliceous MCM-41. For TiO_2/MCM-41, SO_4^{2-}/TiO_2/MCM-41 and $S_2O_8^{2-}/TiO_2$/MCM-41, the intensity of main reflection (100) peak decreased due to the TiO_2 grafting, while the ordered mesoporous structure was generally kept. The intense peaks at 2θ range from 20 to 70 ° in figure 1(e) show the typical anatase phase of SO_4^{2-}/TiO_2, and the average TiO_2 crystallite size was estimated to be 6.8 nm using Sherrer formula on the (101) peak. No peaks corresponding to crystalline TiO_2 can be observed at the same 2θ range in figure 1(b), (c), and (d), indicating that the grafted TiO_2 are in highly dispersed amorphous form without crystalline particles formed within or outside MCM-41 pores.

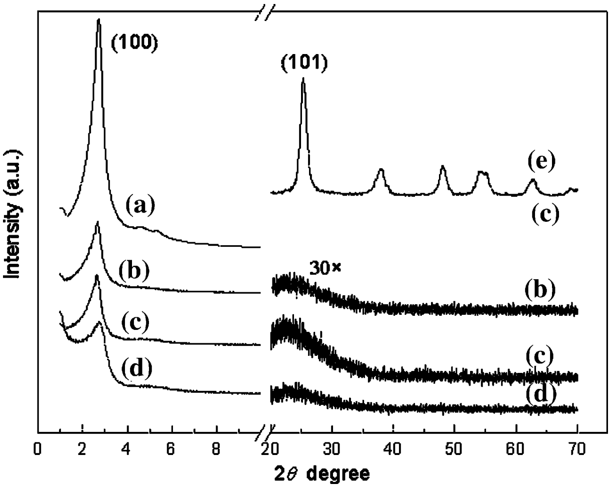


Figure 1. XRD patterns of (a) calcined MCM-41, (b) TiO_2/MCM-41, (c) SO_4^{2-}/TiO_2/MCM-41, (d) $S_2O_8^{2-}/TiO_2$/MCM-41 and (e) SO_4^{2-}/TiO_2.

The BET data, Ti and S contents are listed in table 1. With TiO_2 grafting and sulfation/persulfation, the BET surface area and total pore volume of TiO_2/MCM-41, SO_4^{2-}/TiO_2/MCM-41 and $S_2O_8^{2-}/TiO_2$/MCM-41 decreased in comparison with that of MCM-41, but they are still much higher than those of the nanosized SO_4^{2-}/TiO_2, and the slight shrinkage of their average pore size indicates the incorporation of TiO_2 into MCM-41 mesopores.

Figure 2 shows the FTIR spectra of MCM-41 and its TiO_2 modified samples. For TiO_2/MCM-41, SO_4^{2-}/TiO_2/MCM-41 and $S_2O_8^{2-}/TiO_2$/MCM-41, the band at ca. 966 cm^{-1} corresponding to vibration of Si–O–Ti bonds [18] indicates that TiO_2 have been successfully grafted onto MCM-41 wall. No peaks at 650 cm^{-1} assignable to crystalline anatase were detected using FTIR. The characteristic S = O vibration bands of SO_4^{2-}/TiO_2, SO_4^{2-}/TiO_2/MCM-41 and $S_2O_8^{2-}/TiO_2$/MCM-41 are presented in figure 3. SO_4^{2-}/TiO_2 gave single S = O band at 1379 cm^{-1}, while SO_4^{2-}/TiO_2/MCM-41 showed a band at 1409 cm^{-1} and a shoulder at 1379 cm^{-1}, corresponding to S = O induced from SO_4^{2-}/

Table 1
Physicochemical properties of the catalysts

Samples	BET surface area (m^2/g)	Pore volume (mL/g)	Average pore size (nm)	Ti content (wt.%)	S content (wt.%)
MCM-41	1226	0.74	2.41	–	–
TiO_2/MCM-41	816	0.47	2.31	4.28	–
SO_4^{2-}/TiO_2/MCM-41	823	0.49	2.38	4.24	0.87
$S_2O_8^{2-}/TiO_2$/MCM-41	691	0.39	2.26	4.14	3.18
SO_4^{2-}/TiO_2	167	0.20	4.71	–	4.01

SiO_2 and SO_4^{2-}/TiO_2, respectively. For $S_2O_8^{2-}/TiO_2$/MCM-41, the additional band at 1398 cm^{-1} can be assigned to $S_2O_7^{2-}$ specie on TiO_2 surface according to earlier report [19], and the band at 1379 cm^{-1} results from decomposition of $S_2O_8^{2-}$ into SO_4^{2-} during calcination. According to table 1, $S_2O_8^{2-}/TiO_2$/MCM-41 possesses a much higher S content than SO_4^{2-}/TiO_2/MCM-41, which indicates that $S_2O_8^{2-}$ can be chelated more efficiently on the grafted TiO_2 at a low surface Ti concentration (ca. 0.75 nm^{-2} average by ICP and BET results in table 1) than SO_4^{2-}, because of its favorably larger kinetic diameter compared to SO_4^{2-} (0.31 nm^2) [20].

The pyridine adsorption *in situ* FTIR spectra are present in figure 4. It can be found that SO_4^{2-}/TiO_2, SO_4^{2-}/TiO_2/MCM-41 and $S_2O_8^{2-}/TiO_2$/MCM-41 contain both Brønsted (at 1540 cm^{-1}) and Lewis (at 1445 cm^{-1}) acid sites, while only Lewis acidity can be observed for TiO_2/MCM-41. It is obvious that the peak area at 1540 cm^{-1} was enlarged with the increase of S content list in table 1. For SO_4^{2-}/TiO_2 and $S_2O_8^{2-}/TiO_2$/MCM-41 the Brønsted acidity was predominant, but SO_4^{2-}/TiO_2/MCM-41 showed more Lewis acidity. This result is coincident with the previous report [20] that Brønsted acidity was improved at higher S content.

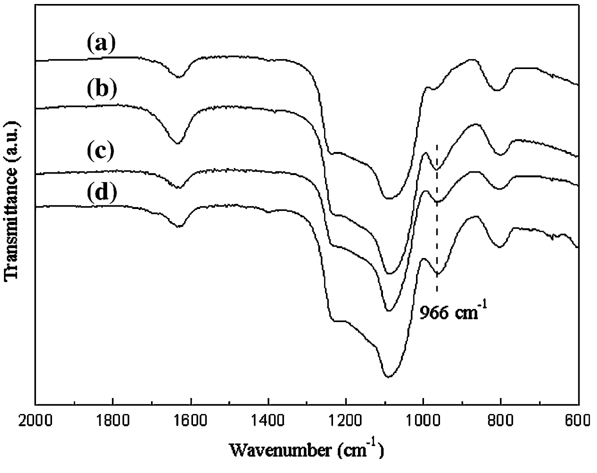
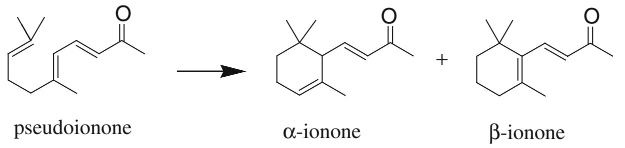


Figure 2. FTIR spectra of (a) calcined MCM-41, (b) TiO_2/MCM-41, (c) SO_4^{2-}/TiO_2/MCM-41 and (d) $S_2O_8^{2-}/TiO_2$/MCM-41.

It has been known that the major product of pseudoionone cyclization is the mixture of α- and β-ionones (equation (1)), and the presence of numerous by-products was difficult to be avoided due to the complexity of the reaction [21]. It was also proposed that protons played a key role in the intra-molecule cyclization reaction [13]. Catalytic performance in this study was evaluated in terms of pseudoionone conversion X (equation (2)) and selectivity S of α- and β-ionones (equation (3)), where a_f is the amount of pseudoionone in reactants, a_p the amount of pseudoionone in products, and a_i the amount of α- and β-ionones in products.



(1)

$$X = 100 \times (a_f - a_p)/a_f \tag{2}$$

$$S = 100 \times a_i/(a_f - a_p) \tag{3}$$

The catalytic behavior of the solid acid catalysts is presented in figure 5 and table 2. It is shown in figure 5 that TiO_2/MCM-41 is almost not active, while activities of the other three catalysts were improved with the increase of S content and Brønsted acidity as illustrated in table 1 and figure 4, and $S_2O_8^{2-}/TiO_2$/MCM-41 possesses a catalytic performance comparable to nanosized SO_4^{2-}/TiO_2. This indicates that higher S content and more Brønsted acid sites are favorable for the proton participated cyclization reaction. Additionally, it can be found in table 2 that $S_2O_8^{2-}/TiO_2$/MCM-41 and SO_4^{2-}/TiO_2/MCM-41 have better selectivity of ionones compared to SO_4^{2-}/TiO_2.

It has been reported that acid activity can hardly be produced on SiO_2 surface promoted with SO_4^{2-}, due to the relatively higher electronegativity and low coordination number of Si^{4+}, while the acidity of conventional SO_4^{2-}/TiO_2 derives from the S = O induction on the edge or corner of anatase surface where the octahedral coordination is unsaturated [22]. For $S_2O_8^{2-}/TiO_2$/MCM-41 and SO_4^{2-}/TiO_2/MCM-41, with the formation

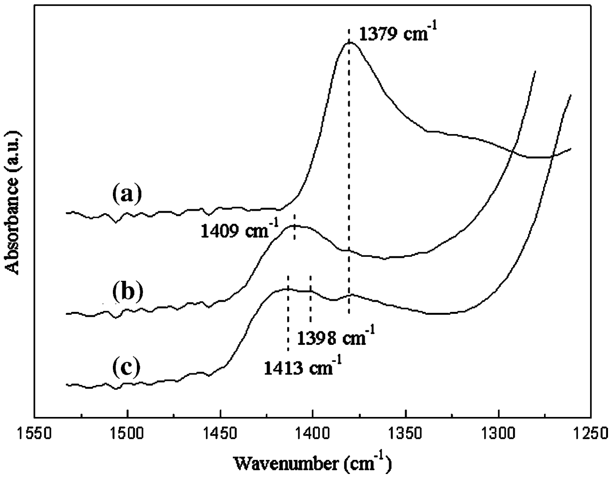


Figure 3. FTIR spectra of (a) SO_4^{2-}/TiO_2, (b) SO_4^{2-}/TiO_2/MCM-41 and (c) $S_2O_8^{2-}/TiO_2$/MCM-41, after evacuation at 400 °C for 3 h.

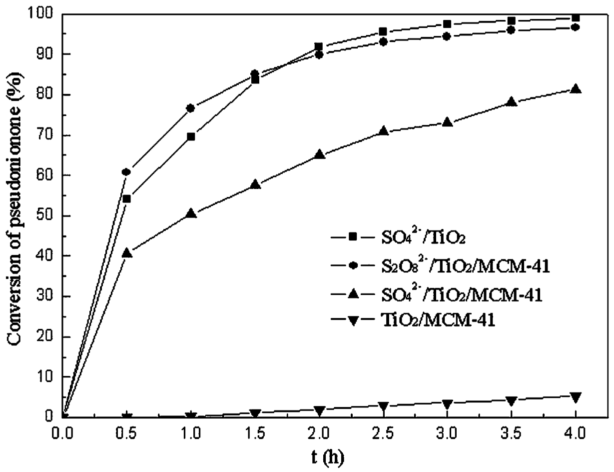


Figure 5. Activity of the catalysts for cyclization of pseudoionone at 80 °C.

Table 2
Selectivity of α- and β-ionones of the catalysts

t (h)	Selectivity (%)		
	SO_4^{2-}/TiO_2	SO_4^{2-}/TiO_2/MCM-41	$S_2O_8^{2-}/TiO_2$/MCM-41
1	21.92	17.24	25.64
2	20.47	21.18	29.33
3	18.90	23.70	29.25
4	18.51	24.86	27.95

of Si–O–Ti–O–S = O bonds on pore surface, both the electronegativity difference of Si from Ti as well as the S = O induction affect on Ti atoms to withdraw electron density to opposite directions, thus to produce desirable acid activity. Since $S_2O_8^{2-}$ can be chelated onto the grafted TiO_2 species more efficiently than SO_4^{2-}, $S_2O_8^{2-}/TiO_2$/MCM-41 exhibited higher activity compared with SO_4^{2-}/TiO_2/MCM-41. On the other hand, all the acid sites on $S_2O_8^{2-}/TiO_2$/MCM-41 and SO_4^{2-}/TiO_2/MCM-41 can be speculated to possess similar structure of Si–O–Ti–O–S = O, which is favorable for improvement of the selectivity.

4. Conclusions

SO_4^{2-}/TiO_2/MCM-41 and $S_2O_8^{2-}/TiO_2$/MCM-41 with well-ordered mesostructure were prepared through grafting reaction of $Ti(OBu^n)_4$ with Si–OH on MCM-41 wall and sulfate/persulfate treatment. Both of the catalysts exhibited desirable catalytic activity and better selectivity for cyclization reaction of pseudoionone compared to conventional SO_4^{2-}/TiO_2, although the grafted TiO_2 are in amorphous form and at a low amount. The acid activity of SO_4^{2-}/TiO_2/MCM-41 and $S_2O_8^{2-}/TiO_2$/MCM-41 derives from the bilateral effect of electronegativity difference of Si from Ti as well as S = O induction on Ti atoms. Higher S content and more Brønsted acid sites are favorable for the protons needed cyclization reaction, and the acid sites with similar structure of Si–O–Ti–O–S = O are responsible for the better selectivity than SO_4^{2-}/TiO_2.

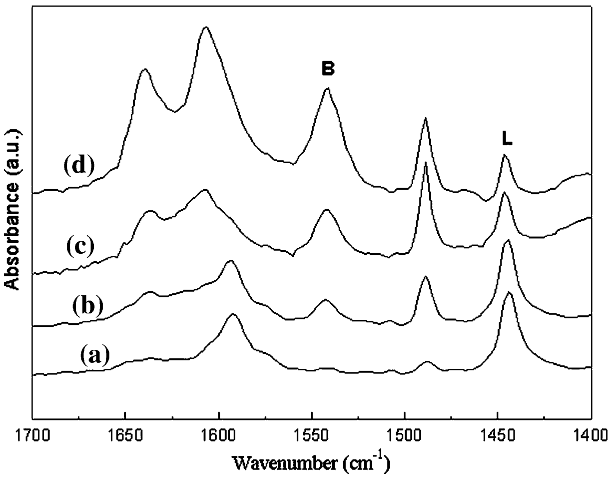


Figure 4. Pyridine adsorption FTIR spectra measured at 200 °C of (a) TiO_2/MCM-41, (b) SO_4^{2-}/TiO_2/MCM-41, (c) $S_2O_8^{2-}/TiO_2$/MCM-41 and (d) SO_4^{2-}/TiO_2.

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