Ti-modified hierarchical mordenite as highly active catalyst for oxidative desulfurization of dibenzothiophene

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ARTICLE INFO

ABSTRACT

Ti-modified hierarchical mordenites (Ti/MM) were prepared using tetrabutyl orthotitanate (TBOT) as the precursor of Ti species by incipient wetness impregnation technique. The introduced Ti species were located outside the micropores in mordenite due to the large molecular size of TBOT. As a result, the active Ti species over hierarchical mordenites are easily accessible. The catalytic results indicated that Ti/MM were highly active ODS catalysts in the oxidative desulfurization (ODS) of dibenzothiophene due to rich mesoporosity. The sulfur removal content over a Ti-modified hierarchical mordenite (Ti/MM-0.5) with relatively large mesopore volume reached 98.6% after a reaction time of 120 min at 333 K by using H_2O_2 as oxidant, which is nearly four times as that over Ti-modified conventional mordenite. Accordingly, the sulfur content in model fuel was reduced from 1000 ppmw to 14 ppmw. These results indicated that Ti-modified hierarchical mordenite with rich accessible Ti sites and low cost has potential applications for ODS of transportation fuels.

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1. Introduction

Deep desulfurization of transportation fuels have received much attention in recent years. Due to the stringent demand of the environmental regulations, the sulfur level in fuels must be reduced below 10 ppmw in many countries [1]. That means that the refractory sulfur-containing molecules like dibenzothiophene (DBT) and its derivatives such as 4,6-dimethyldibenzothiophene (4,6-DMDBT) have to be desulfurized. However, it is difficult to remove these sulfur-containing molecules by industrial hydrodesulfurization (HDS) process [2,3]. Therefore, there have been lots of attempts to develop non-HDS methods for producing ultra-low sulfur fuels.

Currently, several alternative technologies such as catalytic oxidative desulfurization [4], selective adsorption [5], bio-desulfurization [6] and extraction [7] have been widely investigated. Among them, catalytic oxidative desulfurization (ODS) is considered to be one of most promising processes [8]. Based on this reason, various types of heterogeneous catalysts have been exploited [9–17]. Thereinto, Ti-modified microporous zeolites including TS-1 [14–16], Ti-MWW [17] and Ti-Beta [18] have been attempted as the ODS catalysts. The results indicated that these

catalysts were active in the ODS reaction of thiophene. However, the catalysts like TS-1 almost had no catalytic reactivity in the ODS reactions of sulfur compounds with relatively large molecular size like DBT or 4,6-DMDBT mainly due to the inaccessibility of active sites located in micropores.

To remedy the disadvantage of Ti-modified microporous zeolites, Ti-containing mesoporous materials such as Ti-MCM-41 [19] and Ti-HMS [20] have been studied. The results indicated that the introduction of mesopores may improve the catalytic performance in the bulky ODS reactions. However, due to their amorphous nature of mesopore wall, it has been of great interest to prepare Ti-modified hierarchical zeolites by the creation of additional mesopores or/and macropores. Up to now, there are few reports about the preparation of Ti-modified hierarchical zeolites for ODS of fuel oil [21–26]. These works were only focused on hierarchical Ti-ZSM-5 (TS-1). However, the issue is that some active Ti species in hierarchical TS-1 were inaccessible to the reactants in the ODS reaction of the bulky sulfur-containing molecules such as DBT or 4,6-DMDBT because they may be located in the framework of micropores. Additionally, the number of available active sites is low because the content of Ti species that can be incorporated into zeolite framework is limited. Also, the preparation cost of hierarchical TS-1 is high due to the use of expensive template. Therefore, the synthesis of Ti-modified hierarchical zeolites with rich accessible Ti species and low cost is highly desired.

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In this work, we developed Ti-modified hierarchical mordenite with rich accessible Ti species and low cost using tetrabutyl orthotitanate (TBOT) with large molecular size as the precursor of Ti species by incipient wetness impregnation technique. The catalytic performance of the obtained catalysts was evaluated mainly by the ODS reaction of DBT. Considering that H_2O_2 is an eco-sustainable and cheap reagent [27,28], it was utilized as the oxidant in the catalytic evaluation.

2. Experimental

2.1. Materials

Commercial mordenite was purchased by the Catalyst Plant of Nankai University. DBT and 4,6-DMDBT were purchased by Aldrich. Tetrabutyl orthotitanate (TBOT), HNO_3, NaOH, NH_4NO_3, hydrogen peroxide (30 wt.%), octane and acetonitrile (MeCN) were purchased from Sinopharm Chemical Reagent Co. All reagents are analytical purity and used without further purification.

2.2. Preparation of catalysts

The commercial mordenite was ion-exchanged with a solution of 1 M NH_4NO_3 at 353 K for 1 h, followed by calcination at 823 K for 5 h according to Ref. [29]. The obtained sample was labeled as HM.

Synthesis of hierarchical mordenites: The preparation procedure is followed as reported in our previous work [29]. Typically, HM was re-fluxed with a solution of 2 M HNO_3 at 373 K for 2 h with a liquid-to-solid ratio of 20 mL/g. Then, the solid sample was filtered, washed, dried, calcined at 823 K for 5 h. The resultant sample was treated with a solution of 0.2 M or 0.5 M NaOH with a liquid-to-solid ratio of 20 mL/g at 343 K for 0.5 h. Finally, the sample was treated with a solution of 0.2 M HNO_3 at 323 K for 1.5 h. The final product was ion-exchanged again, followed by calcination at 823 K for 5 h to obtain hierarchical mordenite HMM-0.2 or HMM-0.5 based on the molar concentration of NaOH solution, respectively. The yield of HMM-0.2 and HMM-0.5 is around 75%.

Synthesis of Ti-modified hierarchical mordenites: Ti-modified hierarchical mordenites were prepared by incipient wetness impregnation technique. HM, HMM-0.2 or HMM-0.5 (0.3 mg) was added into an methanol solution of TBOT (112 μL, a calculated Ti content of 5 wt.%). The solution was shaken for 1.5 h under ultrasound condition, dried at 333 K for 12 h. Finally, the sample was calcined at 823 K for 5 h. The obtained products were named as Ti/M, Ti/MM-0.2 and Ti/MM-0.5, respectively.

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max-2550 diffractometer equipped with a SolX detector – Cu Kα radiation with wavelength of λ = 1.5418 Å. Nitrogen sorption isotherms were obtained at 77 K on a Micromeritics TriStar II 3020 Gas Sorption and Porosimetry system. Samples were normally prepared for measurement after degassing at 423 K under vacuum until a final pressure of 1×10^{-3} Torr was reached. Scanning electron microscopy (SEM) images and Energy dispersive X-ray spectroscopy (EDX) elemental mapping were recorded on SUPRA 55 operated with an acceleration voltage of 200 kV. Ti content was determined by inductively coupled plasma emission spectrometry (ICP) on a PerkinElmer Optima 5300DV atomic emission spectrometer. UV–vis spectra were recorded with a U-4100 UV–vis–NIR spectrometer. The measurement parameters were scan speed 300 nm/min, slit width (UV–vis) 2.0 nm. Raman spectra were recorded on an inVia Reflex Raman spectrograph.

The 325 nm line of a He–Cd laser were used as the excitation sources. Fourier Transform infrared (FT-IR) spectra were recorded on a NicoLET iS10 spectrometer.

2.4. Catalytic tests

The ODS reaction was carried out in a three-phase S–L–L reaction system: catalyst (S), octane phase (L) and acetonitrile phase (L). A certain amount of DBT or 4,6-DMDBT was dissolved in *n*-octane to act as model fuel, and the concentration of sulfur in model fuel was about 1000 ppmw for DBT reaction or 300 ppmw for 4,6-DMDBT reaction. The reaction was performed in a 100 mL three-neck glass flask heated by an oil-bath under vigorous stirring (1000 r/min). In a standard run, 10 g of model fuel, isometric acetonitrile (14.3 mL), and 50 mg (DBT reaction) or 100 mg (4.6-DMDBT reaction) of catalyst (powder form) were added to the reactor. H_2O_2 (30 wt.%, 195 μL) was used as oxidant with a H_2O_2/S molar ratio of 6:1. The reaction was carried out at 333 K. This moment of adding H_2O_2 was regarded as the initial reaction time. The agitation of reaction solution was stopped every 30 min until the liquids layered. Then, 0.5 mL of liquid in each phase was taken and analyzed by gas chromatography on an Agilent 7890A GC with an FID detector using a 30 m packed HP5 column. The products were also identified by GC–MS (5975C-7890A) analysis. The removal content of DBT (R) is defined based on the amount of DBT removed from model oil that included the removal by the extraction and oxidative processes. The data were obtained according to the equation $R = (C_0 - C_t)/C_0 \times 100\%$. C_0 and C_t stand for the initial and practical concentration of DBT in n-octane, respectively. The yield of dibenzothiophene sulfones (DBTO) is calculated by the mole number of DBTO divided by the initial mole number of DBT in model fuel. The occurrence of a partial removal of DBT by acetonitrile extraction didn't influence the interpretation of the reaction results because the final calculation about the removal content of DBT was not disturbed by acetonitrile extraction. Moreover, the effect about the adsorption of DBT on few amount of catalyst (50 mg) may be neglected after checking.

3. Results and discussion

3.1. Characterization of catalyst

Fig. 1 showed the powder XRD patterns of Ti/M, Ti/MM-0.2 and Ti/MM-0.5. As seen, they exhibited well-resolved diffraction peaks at 2 theta of 19.6°, 22.2°, 25.6°, 26.2° and 27.7°, which are characteristic of the mordenite framework structure [29]. Notably, a weak
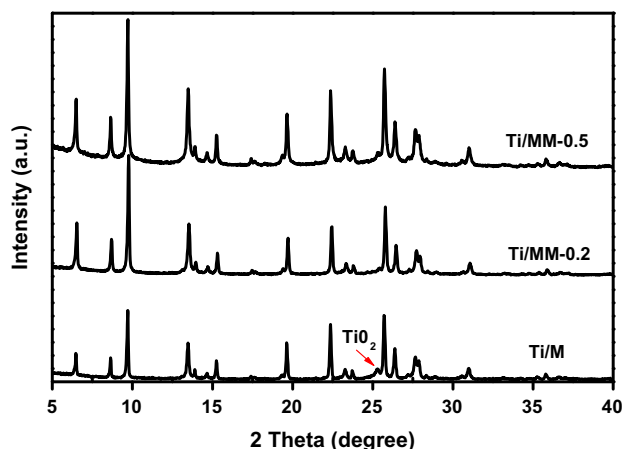

Fig. 1. XRD patterns of various samples.

diffraction peak at 25.3° for Ti/M was observed, which should be assigned to the anatase structure of TiO$_2$. Comparatively, it is difficult to recognize this peak in the XRD patterns of Ti/MM-0.2 and Ti/MM-0.5, suggesting that most of Ti species in Ti/MM-0.2 and Ti/MM-0.5 were possibly incorporated into the framework of mordenite or formed into TiO$_2$ nanoclusters. This means that the dispersion degree of Ti species in Ti/MM-0.2 and Ti/MM-0.5 should be higher than that in Ti/M.

Fig. 2 exhibited N$_2$ sorption isotherms of various samples. Obviously, all the samples gave a type I isotherm at low relative pressure and a type IV isotherm with a hysteresis loop at high relative pressure, indicating the existence of hierarchical pores. As previously reported [29], the mesopores in HM should be from inter-crystalline pores formed by the aggregates of particles. However, the extent of mesoporosity is low. The mesopore volume of HM is 0.1 cm^3/g, which is much lower than that of HMM-0.2 (0.28 cm^3/g) and HMM-0.5 (0.40 cm^3/g). The detailed sorption data are listed in Table 1. Apparently, after introducing Ti species, the BET surface area and mesoporous surface area were decreased. However, the micropore volume almost had no change if the effect of the introduced Ti species mass was deducted, suggesting the introduced Ti species should be located outside the micropores in mordenite. Moreover, the mesopore volume of HMM-0.2 and HMM-0.5 after the addition of Ti species was decreased, indicating that these Ti species should be mainly located in mesopores although the change on the distribution of average pore diameter was not obviously observed. Specially, Ti/M showed slightly higher mesopore volume than HM. To explain this result, the fact that the mesopores in HM is from inter-crystalline pores and the extent of mesoporosity is low need be considered. Compared with Ti/MM-0.2 and Ti/MM-0.5, Ti species in Ti/M easily aggregated each other due to poor mesoporosity, which can be proved by the results from XRD and the following UV–vis spectroscopy. Such aggregates possibly resulted in the formation of additional mesopores from inter-particles to some extent. As a result, this helped more or less improve the mesopore volume of HM after the introduction of Ti species.

SEM images of Ti/M, Ti/MM-0.2 and Ti/MM-0.5 are shown in Fig. 3. It can be seen that Ti/M has a morphology of prismatic shape and most of particle size is around 400 nm (Fig. 3a), which are similar to those of parent mordenite. Comparatively, the crystal shape of mordenite in Ti/MM-0.2 and Ti/MM-0.5 is irregular and crystal size is relatively small (Fig. 3b and c), which are also similar to those in HMM-0.2 and HMM-0.5 mainly because the process of post treatment destroyed the morphology and changed particle size of parent mordenite [29]. To verify the existence of Ti species
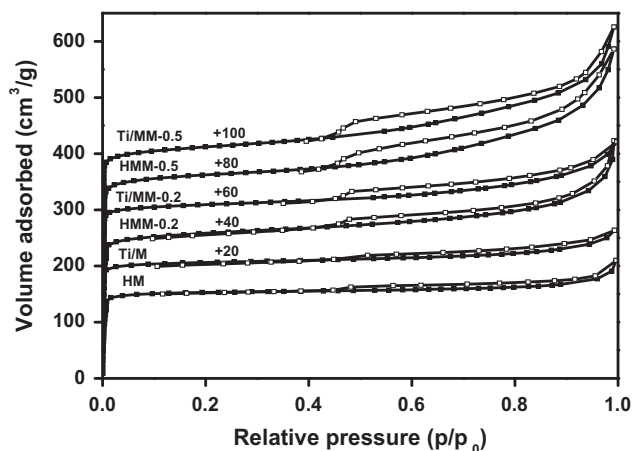
in the Ti-modified catalysts and observe their distribution, EDX mapping images of Ti element and EDX patterns in the region of whole SEM images were taken (Fig. 3d–f). It can be clearly seen that Ti species existed in these catalysts and their distribution was homogeneous. Moreover, Ti content in these catalysts is similar, which is 3.49 wt.% in Ti/M, 3.26 wt.% in Ti/MM-0.2, and 3.58 wt.% in Ti/MM-0.5, respectively (Fig. 3g–j). These data were in accordance with the results from ICP analysis (Table 1).

To detect the coordination state of Ti species, UV–vis spectra of Ti/M, Ti/MM-0.2 and Ti/MM-0.5 were given in Fig. 4A. It is well known that the absorption band between 210 and 230 nm corresponds to isolated tetra-coordinated Ti species, the peak between 260 and 300 nm should be assigned to the penta- and hexa-coordinated non-framework Ti species [26] and the band around 330 nm was ascribed to the anatase phase [30]. Notably, both Ti/MM-0.2 and Ti/MM-0.5 displayed a strong absorption band centered around 270 nm and a shoulder peak around 230 nm. This result suggested that the Ti species in Ti/MM-0.2 and Ti/MM-0.5 are similar and should mainly be the penta-, and hexa-coordinated non-framework Ti with small amount of tetra-coordinated Ti [26]. Differently, Ti/M displayed a strong peak centered around 315 nm and even had absorption signal in visible region, suggesting the presence of bulky TiO$_2$. These results are in good agreement with the XRD results. Additionally, on FT-IR spectra these Ti-containing catalysts didn't show a strong adsorption peak at 960 cm^{-1} assigned to Ti species in the framework of zeolites (Fig. 4B). This indicated that the most of Ti species in these samples should be non-framework Ti [26,28]. Further, they displayed strong absorption peaks at 144 cm^{-1}, 390 cm^{-1}, 516 cm^{-1} and 637 cm^{-1} on Raman spectra [28,31], which confirmed that these Ti species were mainly TiO$_2$ with anatase phase (Fig. 4C).

3.2. Catalytic evaluation

The catalytic performance of these Ti-modified catalysts was evaluated by the ODS reaction of DBT as a probe reaction. The reaction pathway was shown in Scheme 1. As known, DBT is first oxidized into sulfoxide and further into dibenzothiophene sulfones (DBTO).

Fig. 5 showed the removal content of DBT with reaction time over various catalysts. In the absence of catalyst, 55% DBT may be removed by the extraction of acetonitrile. However, in the presence of Ti/M catalyst, the removal content of DBT reached 64.5% and 70.1% after 30 min and 120 min, respectively. Comparatively, Ti/MM-0.2 exhibited better catalytic activity than Ti/M. The removal content of DBT was 83.7% after a reaction time of 120 min, which was nearly 1.2 times as that over Ti/M. Further, Ti/MM-0.5 displayed best catalytic activity among these catalysts. The removal content of DBT reached 98.6% after 120 min, which was nearly twice as that over Ti/M. Accordingly, the sulfur content in model fuel was reduced from 1000 ppmw to 14 ppmw.

Considering that partial DBT was removed by the extraction of acetonitrile, the removal content of DBT cannot indeed reflect the ODS ability of the catalysts. Therefore, to know exactly how much DBT was oxidized into DBTO, the components in model fuel and extraction phase before and after reaction were analyzed by GC–MS. As seen, 67.6% DBT existed actually in acetonitrile phase for Ti/M catalyst after a reaction time of 120 min, indicating that most of DBT was not oxidized into DBTO (Fig. 6A). In comparison, Ti/MM-0.2 displayed better ODS ability than Ti/M. There was 27.3% DBT in acetonitrile phase. Further, only a small amount of DBT (2.5%) could be detected in acetonitrile phase when Ti/MM-0.5 was used as a catalyst, indicating that most of DBT was indeed oxidized into DBTO (Fig. 6B). Based on these data, the calculated yield of DBTO was shown in Fig. 7. The yield of DBTO for Ti/MM-0.5 is

Fig. 2. N$_2$ isotherms of various samples.

Table 1
Textural properties of various samples.

Samples	BET surface area (m^2/g)	Mesopore surface area (m^2/g)	Micropore volume (cm^3/g)[a]	Mesopore volume (cm^3/g)[b]	Ti content (wt.%)[c]	Ti content (wt.%)[d]
HM	398	60	0.19	0.10	–	–
HMM-0.2	473	151	0.19	0.28	–	–
HMM-0.5	440	230	0.14	0.40	–	–
Ti/M	368	56	0.17	0.12	3.49	4.15
Ti/MM-0.2	441	135	0.18	0.22	3.26	4.30
Ti/MM-0.5	388	216	0.13	0.33	3.58	3.91

[a] t-plot method.
[b] BJH method (adsorption branch).
[c] EDX.
[d] ICP.
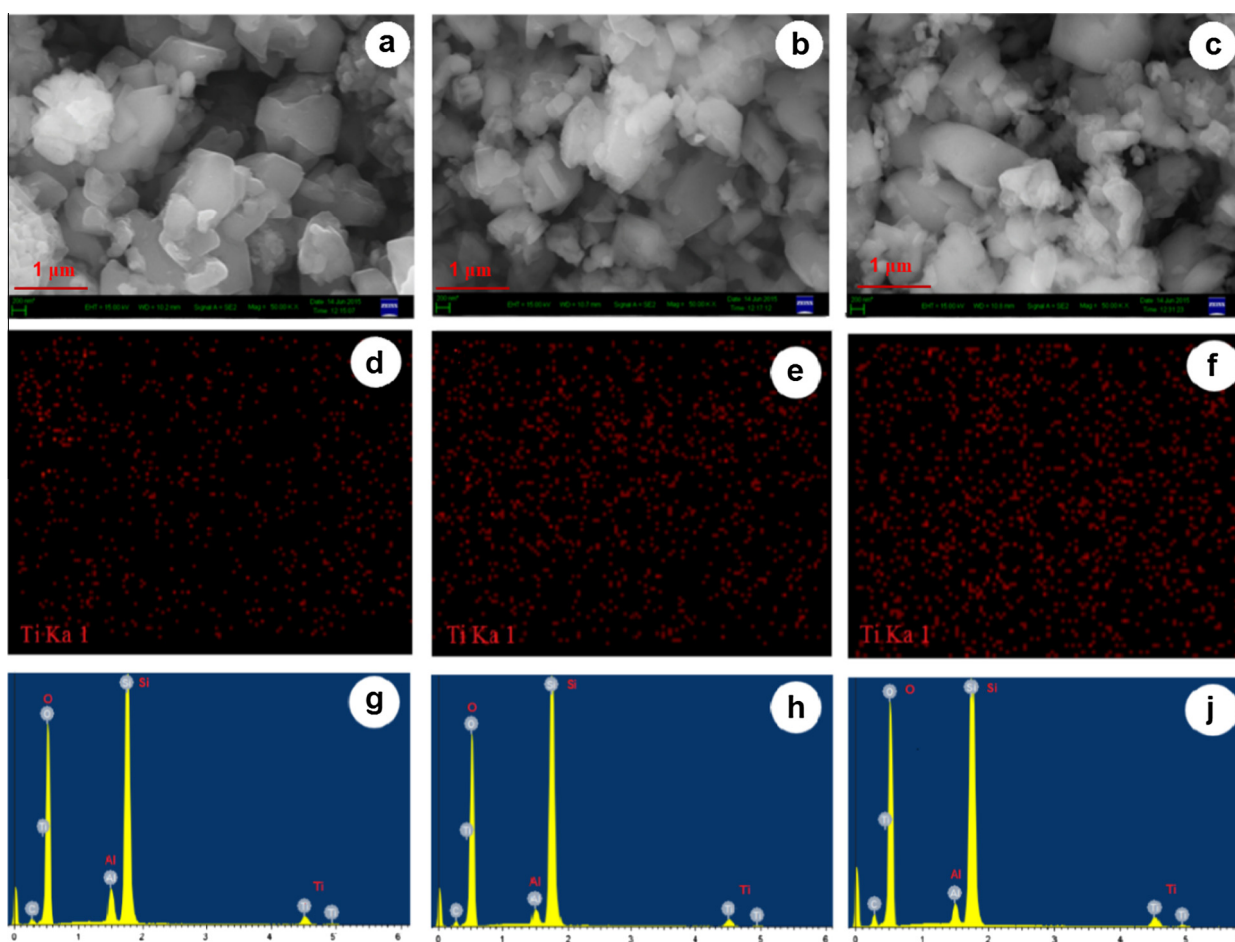
Fig. 3. SEM, EDX elemental mapping images, and EDX patterns of various samples Ti/M (a, d, g), Ti/MM-0.2 (b, e, h), and Ti/MM-0.5 (c, f, j).

97.4%, which is nearly twice as that for Ti/MM-0.2 (56.5%) and four times as that for Ti/M (27.3%).

To explain the above catalytic results, an imaginative diagram about Ti species and their location in Ti/M and Ti/MM was drawn (Scheme 2). As shown, because the molecular size (around 0.9 nm) of TBOT (the precursor of Ti species) is bigger than micropore size (below 0.7 nm) in mordenite, it is difficult for TBOT to enter the micropores. This means that the introduced Ti species had to be located outside the micropores in mordenite. Actually, the data from N_2 adsorption (micropore volume almost had no change after the addition of Ti species) can support the supposition. In this case, it is no doubt that large mesopore volume would be beneficial for improving the dispersion of Ti species. It may be

imagined that the aggregation of Ti species in Ti/M is easy to occur during the preparation and form into bulky TiO_2 due to the small mesopore volume. Comparatively, the aggregation degree of Ti species in Ti/MM with relatively large mesopore volume could be greatly relieved. Thus, the dispersion of Ti species in Ti/MM should be much better than that in Ti/M, which can be proved by the results from XRD and UV–vis spectroscopy (bulky TiO_2 in Ti/MM was not detected). This means that the number of exposed active sites in Ti/MM should be more than that in Ti/M. Based on the above analysis, the dispersion degree of Ti species and the number of exposed active sites in Ti/MM-0.5 should be highest because HMM-0.5 had largest mesopore volume among these studied samples. In addition, it is well known that rich mesoporosity should be
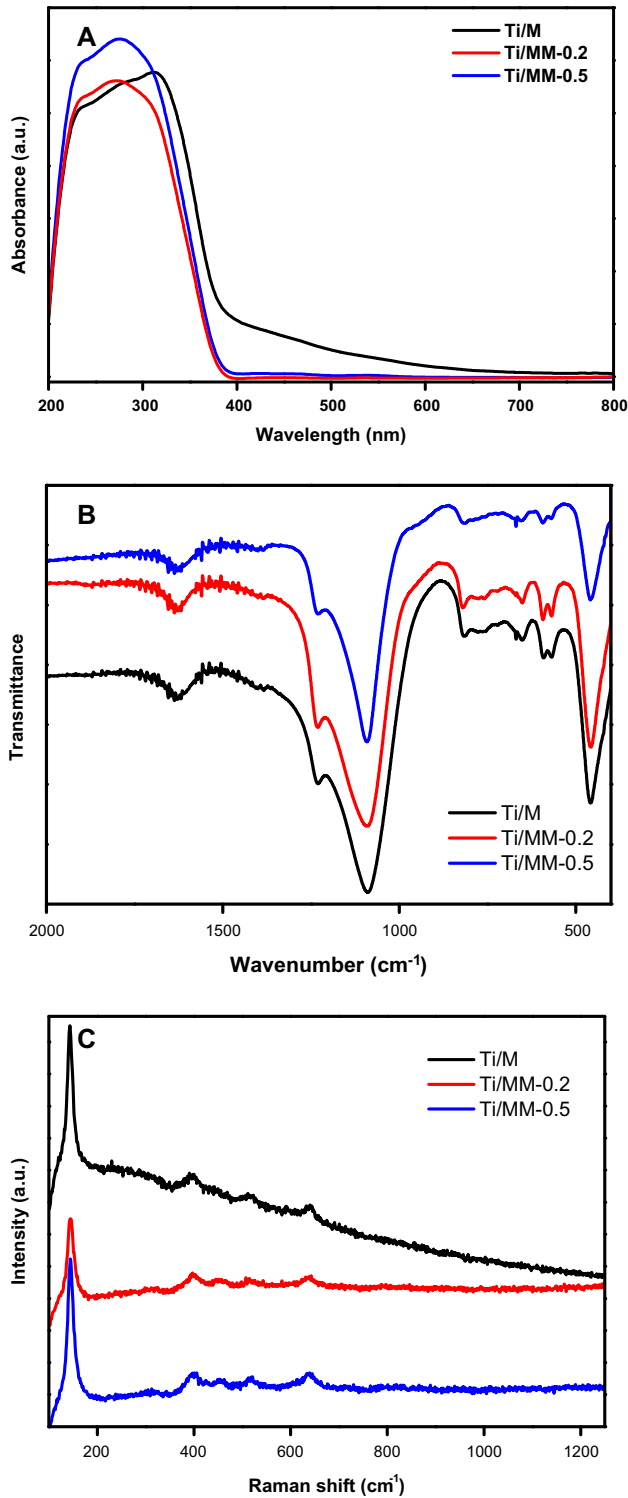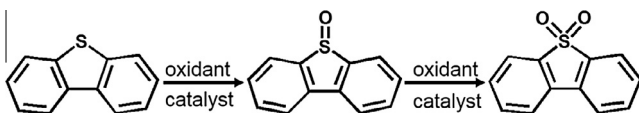
Fig. 5. Removal content of DBT with reaction time over various catalysts.

Fig. 4. UV–vis (A), FT-IR (B) and Raman spectra (C) of various catalysts.
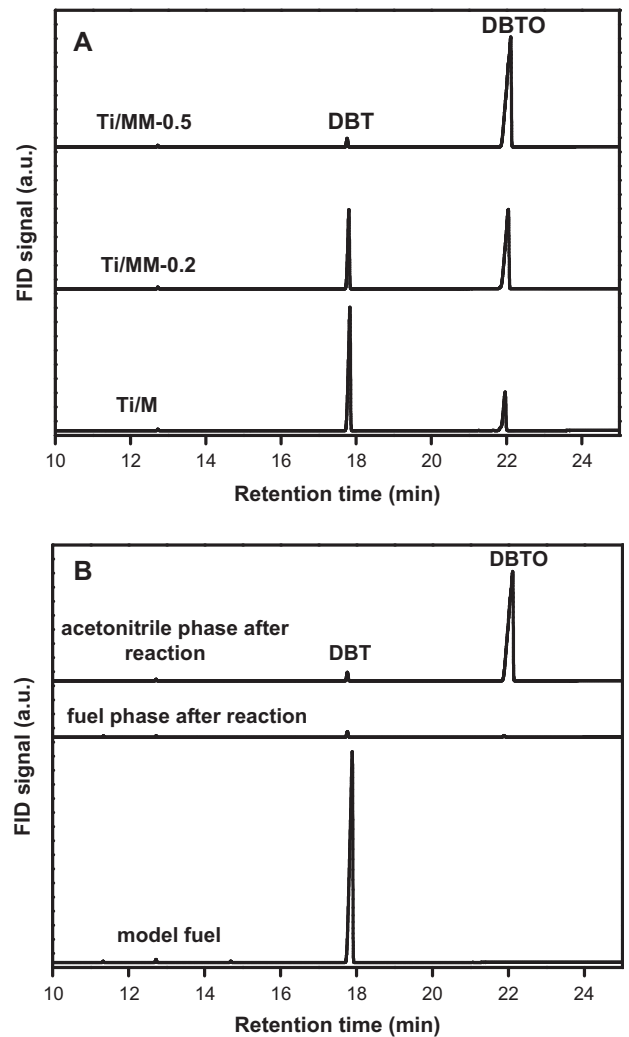

Fig. 6. GC-FID chromatograms of components in acetonitrile phase over various catalysts (A) and of model fuel and components in different phases after reaction over Ti/MM-0.5 (B).

helpful for improving diffusion ability of catalyst. Therefore, Ti/MM-0.5 with richer mesoporosity exhibited better catalytic performance than Ti/MM-0.2 and Ti/M.
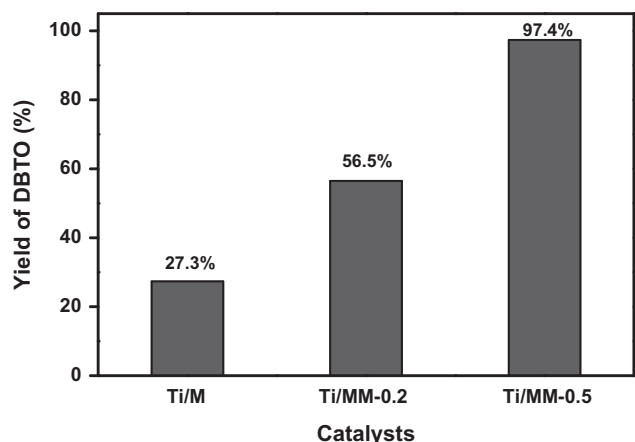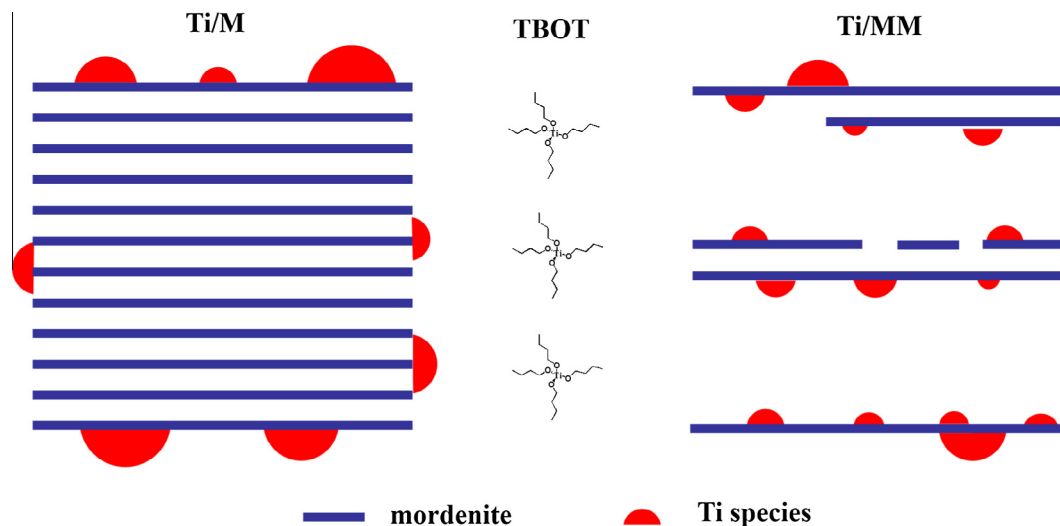

Scheme 1. Reaction pathway in the ODS reaction of DBT.

Fig. 7. Yield of DBTO over various catalysts in the ODS reaction of DBT.

Ti-containing catalysts with relatively large pore size displayed better catalytic activity than TS-1. For examples, the TOF number of DBT removal over Ti-MWW, Ti-HMS and Ti-MCM-41 is 2.3 h^{-1} (345 K), 0.6 h^{-1} (333 K) and 0.7 h^{-1} (343 K), respectively. Notably, the introduction of mesopores greatly improved the catalytic performance of TS-1. HTS-1 gave a TOF number of 1.4 h^{-1} at 333 K and Meso-TS-1 showed a TOF value of 3.7 h^{-1} at 333 K. Comparatively, the catalyst Ti/MM-0.5 gave a TOF number of 4.3 h^{-1} at 333 K. These results demonstrated again that mesoporosity is helpful for the oxidative removal of DBT. Ti/MM-0.5 can be one of highly active ODS catalysts.

The reusability of heterogeneous catalysts is one of their main advantages. To test the reusability of Ti/MM-0.5, ODS reaction of DBT was carried out at 333 K. After each cycle, the catalyst was separated and calcined at 823 K. The catalytic results were shown in Fig. 8. It can be seen that the removal content of DBT over Ti/MM-0.5 almost remained no change after three cycles, indicating that Ti/MM-0.5 is a heterogeneous catalyst and can be reused.

In addition, to evaluate catalytic performance of these Ti-modified mordenite catalysts in the ODS reaction of alkylated-DBT with large molecular size, the ODS reaction of 4,6-DMDBT is carried out under the similar reaction conditions to that of DBT. The catalytic results were shown in Fig. 9. It can be seen that Ti/MM-0.5 still exhibited higher catalytic activity than Ti/M and Ti/MM-0.2, indicating that Ti/MM-0.5 could be an active ODS

To make further comparison, the catalytic performance of several representative Ti-containing catalysts under similar reaction conditions (DBT or 4,6-DMDBT as single sulfur compound in model oil, H$_2$O$_2$ as oxidant) was listed in Table 2. As seen, TS-1 (a well-known catalyst used in oxidation reactions) almost had no catalytic activity due to the limitation of pore size [21].

Scheme 2. Imaginative diagram of Ti species and their location in Ti/M and Ti/MM.

Table 2
Comparison of catalytic performance over some representative Ti-containing catalysts in ODS of DBT or 4,6-DMDBT by H$_2$O$_2$ as oxidant.

Catalysts	Ti content (wt.%)	S content (ppmw)	Catalyst amount (g/L)	Temperature (K)	Reaction time (min)	Removal of DBT or 4,6-DMDBT (%)	TOF (h^{-1})	Ref.
TS-1	1.80[a]	240	10	333	120	0	0	[20]
						0[b]	0[b]	
TS-1	0.98[a]	174	5	333	60	0	0	[22]
Ti–MWW	2.20[a]	1000	10	343	180	95	2.3	[17]
Ti/HMS	4.10[a]	500	20	333	120	81	0.6	[21]
Ti–MCM-41	1.80[a]	240	10	333	120	>99	0.7	[19]
						55[b]	0.4[b]	
HTS-1	1.80[a]	240	10	333	60	>99	1.4	[19]
					120[b]	65[b]	0.5[b]	
Meso-TS-1	0.98[a]	174	5	333	60	>99	3.7	[20]
Ti–MM-0.5	3.58	1000	3.4	333	120	99	4.3	This work
		300[b]				61.0[b]	0.8[b]	

[a] Ti content was calculated according to the reported Si/Ti molar ratio.
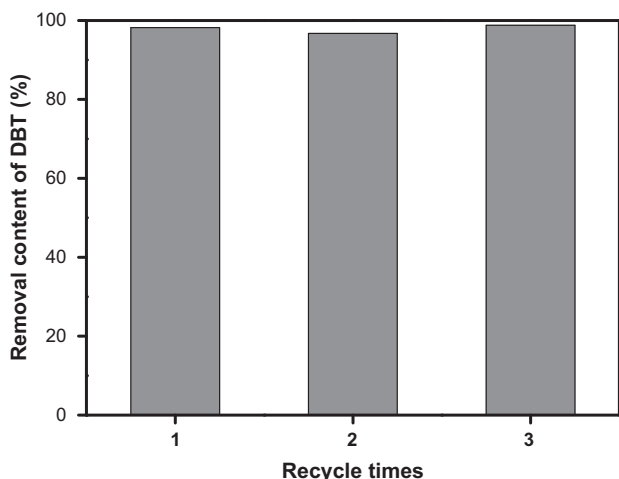[b] For 4,6-DMDBT.

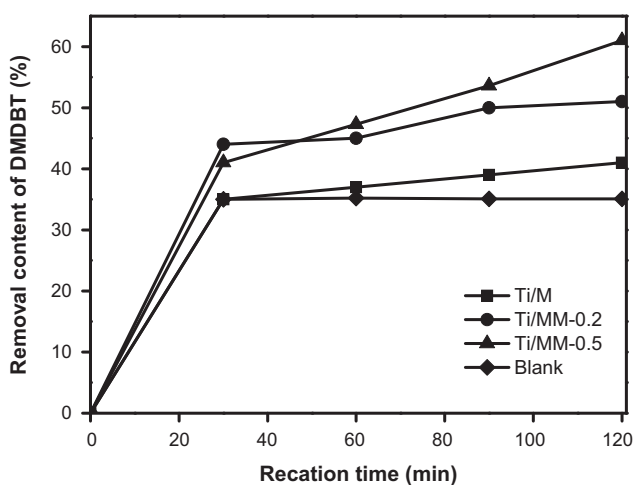**Fig. 8.** Reusability of Ti–MM-0.5 in the ODS reaction of DBT.

Fig. 9. Removal content of 4,6-DMDBT with reaction time over various catalysts.

catalyst for the removal of alkylated-DBT (Table 2). This result suggested that Ti/MM might have potential application as ODS catalysts for deep desulfurization of fuel oil.

It need be noted that the catalytic performance over Ti-modified hierarchical mordenite may be further enhanced because the mesoporosity of hierarchical mordenite and the content of introduced Ti species can be tuned. Also, this synthetic method that TBOT was chosen as the precursor of Ti species to make richly accessible Ti species may be extended to prepare Ti-modified hierarchical zeolites with other framework types, especially toward hierarchical zeolites with rich mesoporosity.

4. Conclusions

Ti-modified hierarchical mordenites were prepared using TBOT with large molecular size as the precursor of Ti species by incipient wetness impregnation technique for ODS of DBT. By this synthetic method, the introduced Ti species were easily accessible to the reactant because they had to be located outside the micropores in mordenite. As a result, rich mesoporosity is helpful for improving the dispersion of Ti species and the diffusion ability of catalyst. Therefore, a Ti-modified hierarchical mordenite (Ti/MM-0.5) with relatively large mesopore volume exhibited superior catalytic performance. The removal content of DBT over this catalyst reached 98.6% after a reaction time of 120 min at 333 K by using H_2O_2 as oxidant, which was nearly twice as that over Ti/M. Accordingly, the sulfur content in model fuel was reduced from 1000 ppmw to 14 ppmw.

Additionally, the catalytic performance over Ti-modified hierarchical mordenite may be further enhanced because the mesoporosity of hierarchical mordenite and the content of introduced Ti species can be tuned. Such catalyst has potential applications for not only ODS of transportation fuels but also other oxidation reactions due to richly accessible active sites and low preparation cost.

Acknowledgments

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