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ordered mesoporous composite Ti-FDU-12 and its application in the hydrodesulfurization of DBT and 4,6-DMDBT⁺ Zhengkai Cao,^a Aijun Duan,^{*a} Zhen Zhao,^{*a} Jianmei Li,^b Yuechang Wei,^a

A simple two-step method to synthesize the well-

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Mesoporous FDU-12 silicas with different morphologies have been synthesized under static and stirring conditions in a water bath. Furthermore, a series of mesoporous FDU-12 silicas modified by different amounts of titania have been synthesized, through a two-step method of prehydrolysis of TEOS followed by addition of titanium butoxide as a titanium precursor. Their respective NiMo supported catalysts were also prepared and characterized to elucidate the effects of titania, on the characteristics of the Mo surface species and their hydrodesulfurization (HDS) activities on dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT). The composites were characterized by various techniques (XRD, SEM, TEM, FT-IR, UV-vis, ²⁹Si NMR, Raman, XPS and N₂ adsorption-desorption); meanwhile, the catalysts were also tested in a higher pressure HDS reactor at T = 340 °C and P = 4 MPa with different liquid hourly space velocity (LHSV) values. The results show that the two-step synthetic route can prepare well-ordered mesoporous composites with high surface areas and large pore sizes and volumes. Obvious differences in the Mo species can be observed on the sulfided NiMo/Ti-FDU-12 catalysts. This showed that appropriate Ti loading could facilitate the dispersion of molybdena and the formation of the MoS₂ and NiMoS phases, which are the important factors for the HDS reaction. All of the catalysts presented high HDS activity, and when the Si : Ti molar ratio was increased to 5, the HDS activities on DBT and 4,6-DMDBT could reach as high as 97% and 65% respectively.

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1. Introduction

Recently, much attention has been paid to the environmental problems caused by petroleum products with high sulfur contents. Accordingly, the development of catalysts with higher activities becomes important. Among different supports and their combinations with catalysts, Mo catalysts supported on TiO₂ displayed a higher intrinsic hydrodesulfurization (HDS) activity.^{1,2} This high HDS activity was attributed to the well dispersed molybdena species and the support of titania made the formation of MoS₂ easier. However, the TiO₂ supports have an important disadvantage: they generally have low surface area and small pore size, which is caused by the agglomeration of TiO₂ particles.³ TiO₂-incorporated mesoporous silica with appropriate physicochemical properties can solve this problem.^{4,5} Mesoporous silica materials with large surface areas

^bCollege of Science, China University of Petroleum, Beijing 102249, P. R. China † Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ta03691c and pore volumes and uniform pore size distributions can provide a favourable platform for TiO₂ loading. Since the first ordered mesoporous silica MCM-41S was synthesized,⁶ different kinds of titanium-containing mesoporous silica composites have been reported, including Ti-MCM-41,^{7,8} Ti-MCM-48,⁹ Ti-SBA-15 (ref. 10 and 11) and Ti-SBA-16.¹²

There are two main methods for the synthesis of titaniumcontaining mesoporous silica composites: the direct incorporation method^{13,14} and the post-synthetic method,¹⁵ both of which have pros and cons. For the direct incorporation method, the composites may maintain high surface areas and large pore volumes and pore sizes, but the structure may collapse upon addition of excess amounts of titanium.¹² For the post-synthetic method, the structures of the composites can maintain integrity, but a decrease in surface areas and pore diameters occurs.16 Klimova and coworkers¹⁷ prepared Ti/MCM-41 samples by the post-synthetic method using titanium butoxide as a titanium source, and showed that the characteristic MCM-41 structure remained almost intact after Ti incorporation. It was found that a better dispersion of Mo was obtained by this method, but that it would also cause a decrease in pore diameter. Shen and coworkers12 successfully synthesized Ti-SBA-16 mesoporous

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silica through a simple two-step prehydrolysis method, using TEOS and TiCl₄ as silica and titanium sources, respectively. It showed that the approach of prehydrolysis of precursor TEOS was effective to synthesize the $TiO_2/silica$ mesoporous composites. The composites maintained large pore volumes, pore sizes and surface areas.

TiCl₄ is generally used as a titanium source; however, its property of easy hydrolysis make it difficult to add to the mixture. Because of this problem, titanium butoxide is used as a titanium precursor instead. Since the hydrolytic rate of the titanium precursor is faster than that of silicon, a method of two-step prehydrolysis of TEOS followed by the addition of titanium butoxide was used, which can facilitate the titanium species to be effectively incorporated into the silica framework and protect the mesoporous structure from being destroyed, to some extent.¹² Furthermore, *n*-butanol is added to the solution to decrease its hydrolytic rate, which can also serve as the expansion agent to increase the pore diameter and reduce the wall thickness of the pores.

FDU-12 is a type of 3-dimensional material with a face-centred cubic (Fm-3m) structure. The entrance size can be continuously tailored (4–9 nm),¹⁸ indicating that FDU-12 is favourable for the mass transfer and diffusions of guest molecules. However, few works have been carried out on metal-incorporated FDU-12, which is probably due to the difficulties encountered with the conditions of the composites synthesis, such as a strongly acidic environment. To the best of our knowledge, the synthesis and characterization of well-ordered Ti-FDU-12 materials with high titanium loading and their application in the HDS reaction have not been reported in the literature so far.

In this work, firstly, different morphologies of FDU-12 were synthesized under static or stirring conditions in a water bath. Secondly, face-centred cubic structured (Fm-3m) Ti-FDU-12 composites with different amounts of titanium were prepared through a two-step method. The composites possessed wellordered mesoporous structures, and the molar ratio of Si: Ti could be as high as 5. Finally, Ti-FDU-12 supported NiMo catalysts were also prepared by a two-step incipient wetness method. The sulfided catalysts were also studied, and it was found that the incorporation of titanium could enhance the dispersion of molybdena and make the formation of MoS₂ and NiMoS phase easier. This was favourable for efficient hydrodesulfurization. The NiMo/Ti-FDU-12 catalysts were tested in the HDS of DBT and 4,6-DMDBT, and all the samples presented high HDS activities. The catalyst with the Si: Ti ratio of 5 exhibited the highest activities for DBT and 4,6-DMDBT HDS, of 97% and 65% respectively (the concentration of DBT was about 500 ppm).

2. Experimental

2.1. Preparation of FDU-12 and Ti-FDU-12

Mesoporous structured pure FDU-12 silica was synthesized according to the literature¹⁸ using nonionic block copolymer $EO_{106}PO_{70}EO_{106}$ (F127) as the template, and 1,3,5-trime-thylbenzene (TMB) together with inorganic salts (KCl) as

additives. The FDU-12 sample was synthesized in the following steps: 2.0 g of triblock copolymer $EO_{106}PO_{70}EO_{106}$ F127, 2.0 g of TMB and 5.0 g of KCl were dissolved in 120 mL of 2 M HCl, then kept under stirring at 313 K for 24 h. 8.3 g of TEOS was added in the mixture which was then kept under stirring in a water bath for 24 h. The mixture was then transferred to an autoclave at 373 K for 24 h, and the solid was filtrated with deionized water and dried at 353 K for 6 h. Finally, the powder was calcined at 773 K for 6 h, and the product was named as FDU-12 stirring. The sample synthesized without stirring after adding TEOS was denoted FDU-12 static. In this research, the sample of FDU-12 static served as a contrast to the other composites referred to as FDU-12 stirring.

The Ti-FDU-12 composite was prepared by a two-step method using different amounts of titanium in an acidic solution. Typically, the synthetic procedure for ST-20 (Si : Ti initial molar ratio = 20) was as follows: 2.0 g of F127, 2.0 g of TMB and 5.0 g of KCl were dissolved in 120 mL of 1.5 M HCl and stirred at 313 K for 24 h. 6 g of *n*-butanol was added two hours earlier than TEOS (8.3 g). After three hours, 0.68 g of titanium butoxide was dropped slowly into the resulting reaction mixture, which was kept understirring for a further 24 h at 313 K and then transferred to an autoclave and heated at the desired temperature for 24 h. The solid was isolated by filtration with deionized water and dried at 353 K for 6 hours. The resulting silica surfactant composite powder was calcined at 773 K for 6 h to obtain the composite, denoted ST-20.

Ti-FDU-12 with different Si : Ti initial molar ratios (x = 40, 20, 10, 5, 2.5) were also prepared in a similar manner taking appropriate amounts of the Si and Ti sources, and were denoted ST-x.

2.2. Catalyst preparation

A series of NiMo/Ti-FDU-12 catalysts with different Si : Ti ratios, denoted NiMo/ST-*x* (*x* was from 40 to 2.5) were prepared by impregnation *via* a two-step incipient wetness method with aqueous solutions of heptamolybdate tetrahydrate $((NH_4)_6Mo_7O_{24} \cdot 4H_2O)$ and nickel nitrate hexahydrate $(Ni(NO_3)_2 \cdot 6H_2O)$, stepwise. After each impregnation, the catalysts were dried at 80 °C for 12 h and then calcined at 500 °C for 6 h. The composition of the catalysts was 12 wt% of MoO₃ and 3 wt% of NiO.

2.3. Catalytic activity

The DBT HDS activity tests were performed in a continuous fixedbed reactor with 0.5 g catalyst. Before the catalytic activity testing, the catalysts were sulfided *in situ* with a mixture of 2 mol% CS_2 -cyclohexane at 340 °C for 4 h under 4 MPa H₂ pressure. After sulfidation, the DBT reactant, with a concentration of 500 ppm (cyclohexane was used as solvent), was fed to the reactor under the conditions of the same volume ratio of H₂ : oil (200 : 1), the same temperature of 340 °C and different LHSV values from 20–150 h⁻¹. Finally, the products were analyzed by a sulfur and nitrogen analyzer (RPP-2000SN, Taizhou Central Analytical Instruments Company, China). The 4,6-DMDBT HDS activity tests were also performed with the above procedure. The HDS activities (η) are calculated by the following formula:

$$\eta = \frac{S_{\rm f} - S_{\rm p}}{S_{\rm f}} \times 100\% \tag{1}$$

where $S_{\rm f}$ refers to the content of sulfur in the feed, and $S_{\rm p}$ refers to the content of sulfur in the products.

2.4. Characterization

The supports and catalysts were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), FT-IR, UV-vis, 29 Si NMR, Raman spectroscopy, N₂ adsorption–desorption and X-ray photoelectron spectroscopy (XPS).

Low angle and wide angle XRD patterns were taken between $0.5-5^{\circ}$ and $10-80^{\circ}$ with an instrument (Shimadzu X-6000) at 40 kV using Cu K α (k = 0.154 nm, step size 0.02° , 0.5 s) radiation.

SEM images were obtained on a Cambridge S-360 apparatus operating at 20 kV. The samples were coated with gold before the SEM measurement.

TEM was carried out using a JEOL JEM 2100 electron microscope equipped with a field emission source at an accelerating voltage of 200 kV.

Fourier transform infrared (FT-IR) absorbance spectra were recorded at wave numbers ranging from 4000 to 400 cm⁻¹ using a FTS-3000 spectrophotometer. The measured wafer was prepared with a weight ratio of sample to KBr of 1 : 100. The resolution was set at 2 cm⁻¹ during the measurements.

The UV-visible diffuse reflectance spectra of the supports and catalysts were recorded in a 200–800 nm range at room temperature using a UV-visible spectrophotometer (Hitachi U-4100) with the integration sphere diffuse reflectance attachment.

 ^{29}Si MAS NMR was carried out on a Bruker AVANCE III 600 spectrometer at a resonance frequency of 119.2 MHz using a 4 mm HX double-resonance MAS probe at a sample spinning rate of 12 kHz. Single-pulse ^{29}Si MAS NMR experiments with 1H decoupling were performed with a $\pi/4$ pulse width of 2.6 μs , an 80 s recycle delay, a 1H decoupling strength of 60 kHz and for 400 scans. The chemical shifts of ^{29}Si were referenced to TMS.

Raman spectra were recorded with a Renishaw Micro-Raman System 2000 spectrometer with a spectral resolution of 2 cm⁻¹. The laser line at 532 nm of a He/Cd laser was used as the excitation source with an output of 20 mW. The spectra were recorded at room temperature in conditions of 50 s integral time at a 1 cm⁻¹ resolution.

The pore sizes and surface areas of different samples were measured at -196 °C using N₂ adsorption-desorption with a Micromeritics TriStar II 2020 porosimetry analyzer. The samples were degassed at 300 °C for 8 h prior to the measurements. The specific surface area was calculated *via* the Brunauer-Emmett-Teller (BET) method. The total volumes of micropores and mesopores were calculated from the amounts of nitrogen adsorbed at a relative pressure of approximately $P/P_0 = 0.99$.

X-ray photoelectron spectroscopy (XPS) was performed on a PerkinElmer PHI-1600 ESCA spectrometer using a Mg K α

(hv = 1253.6 eV) X-ray source. The binding energies were calibrated using the C 1s peak of contaminant carbon (BE = 284.6 eV) as an internal standard.

The XPS data of the promotion rate (PR) and the promoter ratio (Ni : Mo)_{slabs}, which are presented in Table 3, are calculated as follows: 19

$$PR = \frac{[NiMoS]}{[Ni]total} \times 100$$
(2)

$$(Ni:Mo)_{slabs} = \frac{[NiMoS]}{[MoS_2]}$$
(3)

3. Results and discussion

3.1. X-ray diffraction analysis

The low angle powder X-ray diffraction (XRD) pattern of the pure FDU-12 silica is shown in Fig. 1A. It exhibits five characteristic peaks, which should be assigned to the (111), (220), (311), (331), (442) reflections of a face-centred cubic structure, indicating that the mesoporous FDU-12 silica was successfully synthesized. Low angle XRD patterns of different samples with various Si : Ti molar ratios are shown in Fig. 1B. It is clear that the typical peak (111) weakens and broadens and its intensity reduces, which suggests that the order degree of mesoporous structure decreases with the increasing Si : Ti molar ratio. The mesostructure collapses with the Si: Ti molar ratio up to 2.5 (Fig. 1B curve f), which is identified by the weak characteristic peak. The Si : Ti molar ratio can reach 5, at which a well-ordered face-centred cubic structure is obtained. In addition, XRF analysis of the ST-5 sample shows that the ratio of Si : Ti in the final product is 7.9:1, so the two-step method is effective for the synthesis of the well-ordered mesoporous composite Ti-FDU-12.

To confirm the type of TiO_2 present in the samples, the powder wide angle XRD patterns are shown in Fig. 1C. A diffraction peak at 23° in all composites indicates the presence of amorphous silica.²⁰ There are no diffraction peaks of TiO_2 in the materials with no or less titanium content (FDU-12, ST-40, and ST-20), suggesting that the titania crystal phase is absent. The peaks at 36.2°, 48.1° and 54.0° appearing in the samples of ST-5 and ST-2.5 correspond to anatase (JCPDS 21-1272). A weak peak belonging to anatase at 25.2° appears in the sample of

Table 1 Physicochemical properties of pure FDU-12 silica and ST-x (x = 40, 20, 10, 5, 2.5)

Samples	Si : Ti molar ratio	$S_{\rm BET} ({ m m}^2 { m g}^{-1})$	Pore volume BJH ($cm^3 g^{-1}$)	Pore diameter BJH (nm)
FDU-12	8	539.4	0.46	5.13
ST-40	40	631.7	0.63	7.97
ST-20	20	854.5	0.75	7.50
ST-10	10	646.2	0.61	8.54
ST-5	5	611.7	0.36	4.16
ST-2.5	2.5	530.4	0.38	4.03

Table 2The distribution of Mo species over various Ti-modifiedNiMo/FDU-12catalysts, as determined by XPS analysis a

Catalysts	Mo ⁴⁺ /Mo _{total}	Mo ⁵⁺ /Mo _{total}	Mo ⁶⁺ /Mo _{total}	$S: Mo^b$
NiMo/FDU-12	0.49	0.19	0.32	1.28
NiMo/ST-10	0.50	0.18	0.32	1.30
NiMo/ST-5	0.58	0.15	0.27	1.78
NiMo/ST-2.5	0.38	0.21	0.41	1.32

^{*a*} Mo_{total} (total molybdenum) = $Mo^{4+} + Mo^{5+} + Mo^{6+}$. ^{*b*} Atomic ratios of S : Mo determined by XPS analysis.

Table 3The distribution of Ni species over different catalysts and theirsulphidity, as determined by XPS analysis

Catalysts	NiS/Ni _T	NiO/Ni _T	Ni _{sulphidity}	PR	(Ni : Mo) _{slabs}
NiMo/FDU-12	0.28	0.36	64	32	0.22
NiMo/ST-10	0.32	0.30	70	42	0.23
NiMo/ST-5	0.37	0.16	84	47	0.30
NiMo/ST-2.5	0.31	0.30	70	39	0.28

^{*a*} Ni_T = NiS + NiMoS + NiO. Ni_{sulphidity} = (NiS + NiMoS)/Ni_T × 100. PR (promotion rate) = (NiMoS/Ni_T) × 100. (Ni : Mo)_{slabs} = promoter ratio = NiMoS : Mo⁴⁺.

ST-10. Furthermore, there are some peaks appearing at 27.3° and 41.2° in the samples of ST-5 and ST-2.5, which are assigned to rutile (JCPDS 29-1360); meanwhile, the characteristic peak of brookite at 30.8° is presented in the ST-2.5 sample, but the intensity is very weak.

3.2. The results of BET

Normal N₂ adsorption-desorption isotherms of different samples are shown in Fig. 2. Mesoporous pure FDU-12 silica shows a larger H2 hysteresis loop.¹⁸ The pore sizes and BET of FDU-12 and the series of ST-*x* materials are listed in Table 1. It is noteworthy that the pore sizes of Ti-modified composites become larger than the pure FDU-12 silica while the ratios of Si : Ti are low (40, 20 and 10), which is caused by adding the expansion agent *n*-butanol. The sample ST-10 possesses the largest pore diameter, of 8.54 nm, and the ST-20 material has the largest surface area (854.5 m² g⁻¹) and pore volume



Fig. 2 N₂ adsorption-desorption isotherms of different samples: (a) FDU-12, (b) ST-40, (c) ST-20, (d) ST-10, (e) ST-5, and (f) ST-2.5. All isotherms are set vertically in order to observe them clearly.



Fig. 3 FTIR spectra of different samples: (a) FDU-12 and (b) ST-20.

 $(0.75 \text{ cm}^3 \text{ g}^{-1})$. The pore size of ST-5 decreases to some extent but the surface area is well maintained. Meanwhile the same physical parameters of ST-2.5 drastically decrease, which may be due to the collapse of the mesoporous structure. This will result in ST-2.5 having poor mass transfer and diffusion abilities, and more so in it having fewer catalytic active sites.



Fig. 1 (A) Low angle XRD pattern of FDU-12 (B) and (C) low angle and wide angle XRD patterns of different samples: (a) FDU-12, (b) ST-40, (c) ST-20, (d) S T-10, (e) ST-5, and (f) ST-2.5.



Fig. 4 Raman spectra of supports with different Si : Ti ratios (A–C); (D) Raman spectra of different catalysts: (a) NiMo/FDU-12, (b) NiMo/ST-40, (c) NiMo/ST-20, (d) NiMo/ST-10, (e) NiMo/ST-5, and (f) NiMo/ST-2.5.



3.3. FTIR spectroscopy

The FTIR spectra of FDU-12 and the ST-20 composites are shown in Fig. 3. For the two samples, the clear adsorption peak at 1068 cm⁻¹ is attributed to the asymmetric stretching vibrations of the Si–O–Si band, while the bands at 457 and 808 cm⁻¹ are caused by the symmetric stretching vibration of the Si–O–Si band. The peak at 1640 cm⁻¹ is observed in two of the samples, which indicates the existence of a surface silanol group.²¹ Importantly, a peak at 948 cm⁻¹ can be observed from the spectra after modification with titanium butoxide; this is attributed to the combination of the stretching modes of the Si–O–Ti⁴⁺ sequences

involving tetrahedrally coordinated Ti⁴⁺ ions.²² Finally, these results confirm that titanium ions successfully enter the silicon skeleton.

3.4. Raman spectroscopy

The Raman spectra of FDU-12 and ST-x (x = 40, 20, 10) are shown in Fig. 4A. The bands at 430, 491, 604, 800 and 977 cm⁻¹ should be ascribed to pure silica.²³ Two bands at 491 and 604 cm⁻¹ are assigned to the tri- and tetracyclosiloxane rings produced by condensation of surface hydroxyls. The peak appearing at 977 cm⁻¹ is caused by the surface Si-OH stretching mode. The band at 430 cm^{-1} is attributed to Si–O–Si bending mode, and the band at 800 cm⁻¹ is ascribed to the symmetrical Si-O-Si stretching mode.24,25 When the amount of titanium species is relatively less (ST-40, ST-20), the characteristic peaks of titanium are not present; this indicates that there is no bulk crystalline titania present in the cubic Ti-FDU-12 mesoporous silica composites and that the titanium ions are successfully incorporated into the framework of the FDU-12. As for ST-10, the band at 144 cm^{-1} belonging to anatase is very weak, which is consistent with the results of wide angle XRD and UV-vis DRS. Raman spectra of ST 5 and ST 2.5 are shown in Fig. 4B and C. For the samples of ST-5 and ST-2.5 with comparatively high titanium contents, the intense absorbance of anatase at 144 cm⁻¹ can be observed. Furthermore, as the atomic ratios of Si and Ti reach 5, two peaks assigned to anatase at 395 and 515 $\rm cm^{-1}$ can be observed. Meanwhile the two broad bands attributed to rutile at 445 and 607 cm⁻¹ become prominent, since the



Fig. 6 (A) UV-vis DRS spectra of different samples: (a) ST-40, (b) ST-20, (c) ST-10, (d) ST-5, and (e) ST-2.5; (B) and (C) UV-vis DRS spectra and plots of $\alpha^{1/2}$ versus photon energy ($h\nu$) of different catalysts: (a) NiMo/FDU-12, (b) NiMo/ST-40, (c) NiMo/ST-20, (d) NiMo/ST-10, (e) NiMo/ST-5, and (f) NiMo/ST-2.5.



Scheme 1 Proposed schematic representation of a two-step method to synthesise Ti-FDU-12 (OH = surface silanol group, Si = silyl group, Ti = titanium complex).

rutile phase is easily formed in strongly acid environments.²⁶ The highest titanium loading composite, ST-2.5, exhibits a complex spectrum. Four typical anatase bands at 144, 399, 515 and 634 cm⁻¹ are observed. It should also be noted that the Raman spectrum of ST-2.5 sample shows one typical rutile band at 445 cm⁻¹ and brookite bands at 249, 323, 366 cm⁻¹.²⁷ These results indicate that the rutile and brookite phases with low specific surface areas and pore diameters will reduce the physicochemical properties of the sample ST-2.5, which is consistent with the low angle XRD analysis. Fig. 4D shows the Raman spectra of the catalysts containing different amounts of titanium in terms of the atomic ratio of Si and Ti, from ∞ to 2.5. The peaks appearing from 750–1000 cm⁻¹ are assigned to Mo species.²⁸ A band at 958 cm⁻¹ is observed in all samples; the peak centred at 958 cm⁻¹ should be ascribed to large clusters of MoO_x species, such as Mo₈O₂₆⁻⁴.²⁹ However, the peak at 943 cm⁻¹ belonging to ${\rm Mo_7O_{24}}^{-6}$ species is not clearly observed, which suggests that the amount of the $Mo_8O_{26}^{-4}$ species is larger than that of $Mo_7O_{24}^{-6}$. Meanwhile, there are no peaks appearing in the 990-1000 cm⁻¹ region, demonstrating that the large polymeric MoO_x species must not be present.³⁰ The characteristic peaks of TiO₂ can also be observed in the samples of NiMo/ST-5 and NiMo/ST-2.5.

3.5. ²⁹Si NMR spectroscopy

²⁹Si NMR spectroscopy is a well-established method for characterizing the heteroatoms incorporated in the framework of crystalline silicate minerals, which should also be suitable for mesoporous silicas.³¹ The ²⁹Si NMR spectra of FDU-12 and ST-20 are shown in Fig. 5. The peak appearing at about -110 ppm (Q_4) is attributed to Si(-O-)₄ units but does not include silanol (SiOH).³² The shoulder at -102 ppm (Q₃) is ascribed to the silicon nuclei with a single silanol group, Si(OH)(-O-)₃. A signal peak at -91 ppm (Q₂) assigned to Si(OH)₂(-O-)₂ is very weak in the FDU-12 and ST-20 samples. In comparison with FDU-12, a peak region narrowing and characteristic intensity weakening are observed for the Ti-containing sample ST-20. In particular, the shoulders at -102 ppm and -91 ppm that are assigned to silicon-oxygen bond containing silanol groups become weak, which is probably caused by the titanium ions replacing the hydrogen in silanol groups, meaning that the Ti⁴⁺ ions are incorporated into the FDU-12 silica framework. Meanwhile, the intensity of Q_4 (Si(-O-)₄) decreases more than Q_2 and Q_3 , which suggests that Ti⁴⁺ ions replace the silicon and form Si-O-Ti bonds.

3.6. UV-vis DRS spectra of the supports and catalysts

Fig. 6A shows the UV-vis DRS spectra of Ti-FDU-12 with different Si : Ti ratios. All the absorption ranges are associated with the ligand-to-metal charge transfer from the O²⁻ to Ti⁴⁺ which forms its charge-transfer excited state, (Ti³⁺-O⁻).³³ Meanwhile, the absorption ranges become wider with an increasing amount of Ti incorporation. The band appearing at about 200–210 $\rm cm^{-1}$ in all samples can be assigned to the charge-transfer transitions of oxygen to tetrahedrally coordinated Ti⁴⁺ ions within the framework site of Ti(OSi)4,34,35 confirming that Ti4+ ions are successfully incorporated into the framework of the silica. A band at 220-230 nm can be observed when the Si: Ti ratio reaches 20, which can be assigned to the framework site of Ti(OH)-(OSi)₃.^{36,37} Furthermore, when the Si : Ti ratios are low (ST-40, ST-20), the bands of TiO₂ cannot be observed. However, a weak absorption of the composite ST-10 appearing at 390 nm should be assigned to anatase. The ST-5 and ST-2.5 samples present an absorption edge in the visible region around 405 nm,



Fig. 7 SEM images and particle size distribution of different samples: (a) FDU-12 static (b) FDU-12 stirring and (c) ST-20. The image in the same column represents the same sample.

demonstrating that the rutile phase appears in these two composites. Other lower-energy absorption regions at about 250 and 300–330 nm are apparent in the samples with higher titanium contents (ST-5 and ST-2.5), which are assigned to Ti–O–Ti bonds and the presence of high coordination number titanium sites. The band at 250 nm is generally attributed to isolated penta-coordinated titanium sites or TiO₂ oligomers.^{38,39} In addition, it should be noted that the adsorption of ST-2.5 shows a red-shifted displacement compared with the ST-5 sample. The ST-2.5 sample also presents a broader visible-light region, which may caused by the appearance of brookite.⁴⁰

From the above results, the form of titanium in the composites can be deduced. Firstly, when the amount of titanium incorporation is low (ST-20), the titanium atoms substitute the silicon atoms and form the internal framework sites of

Ti(OSi)₄. Secondly, as the Si : Ti ratio reaches 20, the framework sites of Ti(OH)–(OSi)₃ in the surface coexist with the former site of Ti(OSi)₄. Finally, with the increase in Ti content (ST-10, ST-5 and ST-2.5), the TiO₂ phases (Ti–O–Ti bonds) are formed out of the FDU-12 framework. In addition, the above two framework sites also exist in these three samples as well. Accordingly, there are three main forms of Ti atoms: Ti(OSi)₄, Ti(OH)–(OSi)₃ and titania phases (anatase, rutile and brookite), which change with the various amounts of titanium incorporated.

In conclusion, the Ti-FDU-12 synthesis route is shown in Scheme 1. Firstly, the silicate species interact with randomly arranged micellar units through Coulomb force, then SiO_2 is formed on the surface of the micellar units. Secondly, the units pile up together and spontaneously form a well-ordered cagelike structure. Finally, after the addition of a titanium source



Fig. 8 (A) XPS spectra (O 1s) of different samples: (a) Pure silica FDU-12 and (b) ST-5; (B) Ti 2p XPS scan of ST-5.



Fig. 9 XPS envelope of the Mo 3d region of the sulfided Ti-modified NiMo/FDU-12 catalysts loaded with different amounts of titanium.



Fig. 10 Ni 2p scan of sulfided Ti-modified NiMo/FDU-12 catalysts prepared with different amounts of titanium.

and calcinations, the template F127 is removed and wellordered mesoporous Ti-FDU-12 composites are successfully synthesized. Si–O–Ti bonds are also formed through titania atoms replacing the hydrogen atoms in the silanol groups and

Table 4Product distribution of the HDS of DBT over NiMo/FDU-12,NiMo/ST-10, NiMo/ST-5 and NiMo/ST-2.5

		HYD route			
Catalysts	DDS route BP (%)	CHB (%)	THDBT (%)	HYD : DDS ^a ratio	
NiMo/FDU-12	96.4	2.4	1.2	0.04	
NiMo/ST-10	82.9	15.6	1.5	0.21	
NiMo/ST-5	74.0	22.5	3.5	0.35	
NiMo/ST-2.5	90.7	7.3	2.0	0.10	

 a The HYD : DDS ratio of the DBT reaction is determined by (CHB + THDBT)/BP under the conditions that the DBT conversion was fixed at about 50%.



Scheme 2 Reaction scheme for the DBT HDS routes over the NiMo/FDU-12 and NiMo/Ti-FDU-12 catalysts: hydrogenation (HYD), direct desulfurization (DDS), tetrahydrodibenzothiophene (THDBT), biphenyl (BP), and cyclohexylbenzene (CHB).

silicon. Furthermore, based on the FTIR and ²⁹Si NMR results, a peak attributed to Si–OH bonds is observed, indicating that titanium doesn't replace the hydrogen in silanol groups completely. Moreover, the groups of Si(–O–)₄, Si(OH)(–O–)₃ and Si(OH)₂(–O–)₂ coexist in the Ti-FDU-12 structure. In addition, there are three main forms of titanium as deduced from the UV-vis spectra analysis, including Ti(OSi)₄, Ti(OH)–(OSi)₃ and titania phases, which change with an increase in the titanium contents. More importantly, in this two-step process, the



Fig. 11 DBT and 4,6-DMDBT HDS activities of the catalysts modified with different amounts of titanium at various LHSV values.

characteristic cage-like structure units are protected from destruction due to titanium incorporation of some degree.

UV-vis DRS spectroscopy was also used to study the species of molybdenum oxide in the NiMo supported catalysts modified by different amounts of titanium. In Fig. 6B, the absorption bands in the 200-400 nm region are attributed to the ligand-tometal charge transfer from (LMCT)O²⁻ to Mo⁶⁺. The characteristic band at about 250 nm is assigned to the isolated molybdate in tetrahedral coordination, Mo(Td). The polymolybdate species in octahedral coordination Mo(Oh) are observed in a wider region between 260 and 330 nm.41 The spectra clearly show that the bands of Mo oxide species change with different amounts of titanium in the catalysts. The characteristic region of Mo(Oh) (between 260 and 330 nm) widens with an increasing titanium contents, which indicates that the incorporation of titania is conducive to the formation of Mo(Oh). Band gap energy can be estimated by a plot of $(\alpha)^{1/2}$ *versus* photon energy (hv); the position of the absorption edge can then be determined by extrapolating the linear part of the rising curve to zero. The average domain size of the oxide nanoparticles increases along with a decrease in the energy gap.^{42,43} In Fig. 6C, the energy band gap of molybdenum oxides in the catalysts becomes larger with an increase in the amount of titanium loading, indicating a decrease in the average domain size of molybdenum, which will result in a decrease in aggregation and an improvement in the dispersion of molybdena. These results clearly propose that the addition of titanium species has a great influence on the oxidic molybdenum species and domain size.

3.7. SEM and TEM observations

The SEM image of the pure mesoporous FDU-12 silica under stirring conditions is shown in Fig. 7a. It can clearly be seen that these particles have an inerratic polyhedral morphology and a uniform particle size distribution. The SEM image of FDU-12 under static conditions is given in Fig. 7b. It was found that these particles have a spherical morphology, but that the particle size distribution is non-uniform. The image in Fig. 7c shows that ST-20 exhibits polyhedral but uniform particle morphology, and aggregation is also observed. These results suggest that the conditions, either stirring or static, in the water bath have a great influence on the morphology and particle size distribution of pure FDU-12 silica. Furthermore, the incorporation of titanium also affects the morphology of the composite.

The particle-size distributions are also shown in Fig. 7. The average particle size of sample 1 (FDU-12 static) is about 2.5 μ m, that of sample 2 (FDU-12 stirring) is about 5 μ m and that of sample 3 (ST-20) is about 7 μ m. It can be observed that the composite synthesized under stirring conditions has a narrow particle size distribution and a small average particle size. Moreover, the average particle size of the composite ST-20 is larger than the pure FDU-12 silica, which is probably caused by titanium incorporation.

TEM images of different samples are presented in Fig. S1.[†] The image of FDU-12 is consistent with the literature.¹⁸ The highly ordered lattice array over large domains seen under TEM observation suggests that the FDU-12 product has a uniform, well ordered face-centred cubic (Fm-3m) structure without intergrowth, indicating that FDU-12 was successfully synthesized. Moreover, in the images of ST-40, ST-20 and ST-10, the Ti-FDU-12 composites also have well-ordered mesoporous structures, but the order degree of the composites decreases slightly with an increase in titanium content. The TiO₂ phase is presented in the ST-5 and ST-2.5 samples. Meanwhile, (111) reflection still exists in ST-5, indicating that the composite has a relatively ordered mesoporous structure. The image of ST-2.5 exhibits a disordered structure, which suggests that the structure has already been destroyed by the addition of excess titanium.

3.8. XPS results

The O 1s XPS analysis performed on the FDU-12 and ST-5 samples is presented in Fig. 8A. The peak at 532 eV should be assigned to the Si–O–Si unit. The spectrum of ST-5 (Fig. 8A, curve b) shows an extra peak at 530 eV that may be attributed to the Ti–O–Ti or Si–O–Ti units that do not appear in the FDU-12 sample (Fig. 8A, curve a). A weak shoulder appearing at about 531 eV is assigned to the Ti–OH unit,^{44–46} which is consistent with the UV-vis DRS spectra. In addition, the Ti 2p XPS scan of ST-5 is shown in Fig. 8B. The Ti 2p peaks at 458.2 eV and 464.1 eV can be assigned to Ti⁴⁺ 2p3/2 and Ti⁴⁺ 2p1/2. This confirms that TiO₂ is present at the surface of the ST-5 composite. The analysis results demonstrate the appearance of TiO₂ in the ST-5 sample, which is consistent with the Raman spectroscopy observations.

Fig. 9 shows the XPS profiles of the Mo 3d region of various sulfided Ti-modified NiMo/FDU-12 catalysts. The data of peak deconvolution for various Mo species are summarized in Table 2. Beccat et al. proposed that Mo 3d signals included Mo4+ (corresponding to MoS_2), Mo^{5+} (oxysulfide species) and Mo^{6+} (oxidic molybdenum).47 Different types of Mo species have doublet binding energies (BEs) (Mo 3d5/2 and 3d3/2). Peak deconvolution is in accordance with the BE values (Mo 3d5/2) for Mo^{4+} , Mo^{5+} and Mo^{6+} , which are about 228.6 eV, 230.7 eV, 232.3 eV respectively. The BE values of Mo 3d3/2 are fixed at 3.1 eV more than those of Mo 3d5/2, and the intensity ratio of Mo 3d5/2 and Mo 3d3/2 is approximately fixed at 3 : 2. Furthermore, a peak at about 226.0 eV is assigned to the S2s line and is shown in the spectrum of Mo 3d. Sulphidity can be observed by the ratio of Mo^{4+} : $Mo_{total} (Mo_{total} = Mo^{4+} + Mo^{5+} + Mo^{6+})$ in Table 2. It is apparent that TiO_2 affects the Mo species distribution. As the amount of titanium addition is relatively low (Si : Ti = 10), the change in Mo species distribution is small. Meanwhile, the Mo⁴⁺: Mo_{total} and S: Mo ratios increase much more when the titanium loading is high (Si: Ti = 5), whereas the ratios decrease when the Si : Ti ratio is as high as 2.5. From the Raman spectrum (Fig. 4C) and BET analysis (Table 1) of the NiMo/ST-2.5 catalyst, the brookite phase appears and the surface area decreases in comparison with the NiMo/ST-5 catalyst. Therefore, the decreases int he Mo⁴⁺ : Mo_{total} and S : Mo ratios should be due to the appearance of the brookite phase and the decrease of the surface area is adverse to the formation of Mo⁴⁺. These

The Ni 2p XPS spectra of the sulfided Ti-modified NiMo/FDU-12 catalysts are presented in Fig. 10. The Ni 2p envelope is composed of three contributing compounds (NiS, NiO and NiMoS).48 The binding energies of NiS (2p3/2 and 2p1/2) for each of the catalysts are 852.6 and 873 eV. The peak appearing at 862 eV is assigned to NiO.49 The binding energy of the NiMoS phase appeared between 854.6 and 855.0 eV.19 Two parameters of promotion rate (PR) and promoter ratio (see the corresponding formulas in the footnote in Table 3) are closely related to the formation of NiMoS active phases over the sulfided NiMo catalysts. The PR value represents the total percentage of nickel in the NiMoS phase. The promoter ratio signifies the active species.^{19,50} It is clear that the PR, (Ni : Mo)_{slabs} and Ni_{sulphidity} (shown in Table 3) of NiMo/ST-5 are higher than NiMo/FDU-12 and NiMo/ST-10, which is probably caused by the appearances of anatase and rutile. However the above three values of the NiMo/ST-2.5 catalyst decrease in comparison with the NiMo/ST-5 catalyst, which could be also attributed to the appearance of brookite and the decrease in the surface area, which makes the formation of the active phase more difficult. In conclusion, an appropriate amount of Ti loading can facilitate the formation of more activity sites and lead to a high efficiency of desulfurization.

3.9. HDS performance on DBT and 4,6-DMDBT

The pore properties of the support play an important role in the HDS reaction. The composites with large surface areas and pore sizes can facilitate the diffusion of reactant molecules and form abundant active sites. In addition, an appropriate amount of Ti incorporation is conducive to the formation of MoS2 and NiMoS (XPS test), which can also improve the HDS activity of the catalysts. The hydrodesulfurization performances on DBT and 4,6-DMDBT at different LHSV values (150 h^{-1} , 120 h^{-1} , 80 h^{-1} , 50 h^{-1} and 20 h^{-1}) of NiMo/ST-x are shown in Fig. 11. It is obvious that the DBT and 4,6-DMDBT HDS activities become better with a decreasing LHSV value. The DBT and 4,6-DMDBT HDS activities of NiMo/FDU-12 are lower than the other Tiincorporated samples, confirming that the incorporation of titanium can increase the HDS efficiency. Furthermore, when the amount of titanium added is relatively low (NiMo/ST-40, 20, 10 and 5), the catalysts show higher activity with an increasing titanium content at the same LHSV value. It should also be noted that the 4,6-DMDBT HDS conversion rates over all the catalysts are lower than those for DBT, since the steric hindrance of the methyl groups in the 4,6-DMDBT molecule resulted in a lower HDS.2 The NiMo/ST-5 catalyst exhibited the highest HDS activity; the DBT and 4,6-DMDBT HDS conversions could reach 97% and 65%, respectively, at the low LHSV value of 20 h^{-1} . This is probably because the ST-5 support keeps a relatively ordered structure and an appropriate amount of titanium incorporation helps to increase the HDS activity. Meanwhile the NiMo/ST-2.5 catalyst presented a poorer HDS activity. There are three main factors to consider when explaining the reasons for this. Firstly, according to low angle XRD analysis,

the excess addition of titanium (sample ST-2.5) causes a collapse of the well-ordered mesoporous structure. Secondly, as can be seen using the BET measurement, the pore volume and surface area of ST-2.5 have drastically decreased. The above two results indicate a high diffusion resistance of the reactants and fewer catalytic active sites, which are not favourable for the HDS reaction. Finally, as the amount of titanium incorporation is excessive, the appearance of the brookite phase and the decrease in the surface area will decrease the percentages of $Mo^{4+}: Mo_{total}, Ni_{sulphidity}, S: Mo NiMoS$ (PR value) and (Ni : Mo)_{slabs}, which are the important factors for a high HDS efficiency.

3.10. The selectivity of DBT HDS

The selectivity of the DBT HDS reaction is also studied. The product distributions of the HDS of DBT over the catalysts detected by GC-MS are shown in Table 4. There are two major routes in the HDS of DBT, as shown in Scheme 2. These are: the direct desulfurization (DDS) route, which involves the hydrogenolysis of C-S bonds without hydrogenation of the aromatic ring; and the hydrogenation (HYD) route, which requires ring saturation prior to the desulfurization step.⁵¹ In this research, the main products of the DBT HDS are biphenyl (BP), cyclohexylbeneze (CHB) and traces of tetrahydrodibenzothiophene (THDBT). It has been reported that selectivity is related to the mode of DBT adsorption. BP is the main product when using all of the catalysts, which indicates that DBT adsorbs on the active phase perpendicularly according to a vertical geometry.52 For all the catalysts, the amount that the HYD route produced is less than the DDS route, This is because the adsorption of π -electrons of the DBT molecule, which facilitates the HYD route, appears more difficult than direct C-S bond cleavage.53 The HYD: DDS ratios in the supported NiMo catalysts follow the order: NiMo/FDU-12 < NiMo/ST-2.5 < NiMo/ST-10 < NiMo/ST-5. The HYD : DDS ratios of the Ti-incorporated catalysts are higher than that of the NiMo/FDU-12 catalyst, indicating that the desulfurization of DBT over the Ti-modified supported catalysts promotes the HYD route more than the pure silica supported catalyst; this is consistent with the literature.54-57 The effect of Ti incorporation can be attributed to the structure and specific electronic properties of the active phases formed on the Tiloaded support.54,56 It has also been reported that the acceleration of the HYD pathway must be associated with a good dispersion of the active phase.⁵⁸ From the above analysis results (Fig. 6C), it appears that the titania incorporation can lead to a decrease in the aggregation and an improvement in the dispersion of molybdena. Hence, the Ti-incorporated catalysts present relatively higher HYD selectivities than the NiMo/FDU-12 sample. The NiMo/ST-5 sample presents the highest HYD : DDS ratio, while the ratio decreases in the ST-2.5 sample. This may be explained by the fact that the excess titania coated on the surface inhibits the adsorption of DBT molecules on the active sites.53,58 Indeed, the excess titania loading causes a decrease in surface area and the appearance of brookite, which will lead to a decrease in amount of active phases (MoS₂ and

NiMoS), resulting in the adsorption of the DBT molecules

4. Conclusion

becoming more difficult.

In summary, pure FDU-12 silicas with spherical and inerratic polyhedral morphologies were synthesized under static and stirring conditions. Highly ordered mesoporous Ti-modified FDU-12 composites with an Fm-3m structure were synthesized through a simple two-step method of prehydrolysis of TEOS followed by the addition of titanium butoxide as a titanium source. Low angle XRD spectra and TEM results showed that even when the Si: Ti ratio of the composites reaches 5, a relatively ordered structure can still be obtained. N2-adsorption and desorption measurement indicated their high surface areas, and large pore volumes and sizes. XPS analysis of the sulfided catalysts showed that titanium incorporation facilitates the dispersion of molybdena, and an appropriate Ti incorporation make the formation of MoS₂ and NiMoS phases easier. These are very important for the HDS reaction. HDS tests of DBT and 4,6-DMDBT showed that all catalysts present high activities, with the NiMo/ST-5 catalyst exhibiting the highest HDS efficiency due to its relatively ordered structure, high surface area and the incorporation of TiO₂.

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