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Titanium-Doped Mesoporous Silica with High Hydrothermal Stability for Catalytic Cracking Performance of Heavy Oil

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Abstract: With the increasing attention to light oil, the catalytic cracking process of heavy oil is being vigorously developed. The silicon hydroxyl groups on the surface of mesoporous silica materials can be used as weak acid centers to preliminarily crack heavy oil macromolecules. Herein, a strategy of introducing titanium into a silica skeleton for modification is proposed to increase active sites, as well as improve the hydrothermal stability. After titanium modification, the mesoporous silica material has more weak acid sites, and shows better ability in deep cracking heavy oil. Notably, when the content of titanium doping is 2%, the CT(2) catalyst exhibited the best high-temperature hydrothermal stability, which can be used as a suitable heavy oil catalytic cracking catalyst. This kind of titanium-modified mesoporous silica material shows great application prospects in heavy oil catalytic cracking, which may provide a novel idea for subsequent development.

Keywords: titanium-doped mesoporous silica; hydrothermal stability; catalytic cracking; heavy oil



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1. Introduction

With the rapid growth of global energy consumption and the decline of conventional oil reserves, the huge reserves of heavy oil will become the main source of oil supply in the future. Due to the characteristics of high viscosity, high density, high carbon residue, high sulfur nitrogen, and heavy metal content, heavy oil is facing a series of challenges in the deep processing of raw oil [1–3]. Among them, the catalytic cracking technology of heavy oil is increasingly becoming an important means of petroleum processing. Therefore, the preparation of heavy oil catalytic cracking catalysts with high activity stability, high heavy oil conversion efficiency, and strong metal pollution resistance is the key to lightening heavy oil. However, the development of catalytic cracking catalysts still faces challenges, mainly in the following two aspects: (1) the high impurity content in the oil causes a lot of coking for the cracking catalyst during the reaction process, which seriously affects the heat conduction efficiency of the equipment, shortens the service life of the equipment, and is difficult to reproduce; (2) the more complex the composition in the oil product, the higher the requirements of the mass transfer ability of the catalyst.

Recently, it is the case that acidic solid materials, such as molecular sieves [4–8] and mesoporous heteroatom molecular sieves [9,10], are widely used in the catalytic cracking of heavy oil. The abundant acid sites can effectively catalyze the breaking of the carbon chain of larger heavy oil molecules into light oil molecules and reduce the viscosity of oil products, thus, the improvement and modification of catalyst acidity in catalytic cracking reactions is a research hotspot in this field [11]. Meanwhile, the large specific surface area and abundant pore structure of the catalyst significantly improves the effective contact efficiency of the heavy oil reactant macromolecules and acid sites, which is beneficial to the efficient progress of the cracking reaction [12]. In addition, the more complex composition of heavy oil is very likely to cause the catalyst to form coke and plug the pores, thereby limiting the diffusion of macromolecular reactants. Therefore, the development of catalysts with abundant pore structures and a large number of acidic sites is a long-standing goal.

The heavy oil catalytic cracking catalyst needs frequent regeneration due to the problem of carbon deposition, in that case, high hydrothermal stability is urgently required to ensure that its structure and active sites will not change greatly during the regeneration process. Common mesoporous materials, such as mesoporous molecular sieves, exhibit well catalytic activity in the catalytic cracking reaction of macromolecular oils [13], but their pore structure is basically destroyed after hydrothermal treatment, and the catalyst is completely deactivated. In other words, the regeneration stability required for heavy oil catalysts cannot be met. Therefore, the preparation of a mesoporous catalytic material with high hydrothermal stability is the core of overcoming the catalytic cracking technology of heavy oil.

Herein, the titanium-doped mesoporous silica catalyst was obtained by introducing titanium into the silica framework for modification. Compared with mesoporous silica, the titanium-modified catalyst showed higher catalytic activity in the cracking of relatively inferior high-carbon residual vacuum residue after the hydrothermal simulated regeneration process, and the conversion rate of heavy oil was higher than 90%. The yields of high value-added products, liquefied gas and triene, are over 15% and 10%, respectively. The introduction of titanium not only increases the number of active centers of the catalyst and improves the reaction activity, but also makes the silicon species more inclined to form a highly polymerized stable structure during the polymerization process, improving its hydrothermal stability. This titanium-modified mesoporous silica material shows great application prospects in the process of heavy oil catalytic cracking and provides a new approach for the subsequent development of heavy oil catalytic cracking catalysts.

2. Experimental Section

2.1. Chemicals

All the chemical agents were used without further purification. Sulfuric acid (AR, 95–98%), titanium sulfate and silica sol (40%) were supplied from Macklin. Water glass (~95%) and kaolin were provided by Tianjin Guangfu Co., Ltd., Tianjin, China.

2.2. Synthesis of Catalysts

First, the water glass was completely dissolved in distilled water at room temperature. Sulfuric acid was added to adjust the pH value to 9 in order to generate a silica suspension. Then the mixture was aged for 3 h at 80 °C. After cooling down to 30 °C, a titanium sulfate dilute sulfuric acid was added dropwise and heated to 80 °C and kept for another 1 h. After centrifugation, washing, drying, and calcination at 823 K for 6 h, the silica catalysts with different titanium contents (calculated as TiO_2) were obtained. According to the amount of TiO_2 introduced, the samples were marked as TiSi(0), TiSi(1), TiSi(2), and TiSi(3), and the sample numbers after hydrothermal treatment were marked as TiSi(0)H, TiSi(1)H, TiSi(2)H, and TiSi(3)H.

2.3. Formation of the Catalyst

The titanium-containing mesoporous silica catalyst, kaolin, and silica sol obtained above were uniformly mixed in a ratio of 4:4:2 in terms of dry mass ratio, and then an appropriate amount of deionized water was added to form a slurry in which the solid content is 21%, then it is crushed by a sand mill with the particle size of $D_{90} < 10 \mu\text{m}$, and finally, spray-dried to prepare a microsphere catalyst with at the size of 40–130 μm . According to the amount of TiO_2 introduced, the obtained sample is marked as Ct(0), Ct(1), Ct(2), and Ct(3).

2.4. Characterization

The morphological characteristics of titanium-containing mesoporous silica materials were measured by S-4800 high-resolution field emission scanning electron microscope (SEM) from Hitachi, Japan; the acceleration voltage was 30 KV, and the test was carried out under vacuum conditions. The particle size distribution of the catalyst after spray

molding was measured by a Mastersizer2000 particle analyzer. The silicon–titanium ratio was measured by a SRS 3400 X-ray fluorescence spectrometer (XRF). The pore structure and pore size of the samples were measured by a Micromeritics ASAP 3020 adsorption instrument at $-196\text{ }^{\circ}\text{C}$ in liquid nitrogen. Before the test, the samples were pretreated under N_2 atmosphere at $350\text{ }^{\circ}\text{C}$ for 6 h. The ultraviolet visible absorption spectrum (UV-Vis) of the sample was recorded on a V-750 UV-Vis spectrophotometer, with a scanning range of 190–800 nm and a scanning speed of 200 nm/min. The acid content was measured by an AutoChemII2920 automatic temperature-programmed chemisorption instrument, using the temperature-programmed ammonia adsorption method (NH_3 -TPD). The samples were pretreated at $500\text{ }^{\circ}\text{C}$ for 1 h under He atmosphere, and then cooled to $50\text{ }^{\circ}\text{C}$ for NH_3 adsorption. Finally, desorption was carried out under He atmosphere, and the desorption temperature was increased from $50\text{ }^{\circ}\text{C}$ to $500\text{ }^{\circ}\text{C}$, and the spectrum was recorded.

2.5. Evaluation of Catalysts

2.5.1. Hydrothermal Stability Performance Test

A sample size of 40 g was placed in a crucible, and then it was transferred in a hydrothermal device, with compressed air passing through. The temperature was first heated up from $25\text{ }^{\circ}\text{C}$ to $450\text{ }^{\circ}\text{C}$ at a heating rate of $5\text{ }^{\circ}\text{C}/\text{min}$, and then raised to $800\text{ }^{\circ}\text{C}$ at a heating rate of $3.5\text{ }^{\circ}\text{C}/\text{min}$. At this time, the compressed air valve was closed, the water vapor valve was opened, and water vapor started to be introduced. Under 100% water vapor, the temperature was maintained at $800\text{ }^{\circ}\text{C}$ for 17 h, then the valve was switched to the air valve and lowered to room temperature.

2.5.2. Strength Test

Next, 10 g of the spray-molded sample was weighed and then transferred into the test tube of the abrasion tester. The air pump was turned on and the flow rate was controlled to 20 mL min^{-1} so that the sample could flow stably in the test tube. After purging for one hour, the dust removal cloth bag was recorded as W1. After another four hours of purging with other conditions unchanged, the dust removal cloth bag was taken as W2. The remaining sample was removed from the test tube and weighed as M. The wear calculation formula is shown in Formula (1).

$$\text{Wear} = \frac{W2 - W1}{W2 - W1 + M} * 25 * 100\% \quad (1)$$

2.5.3. Evaluation of Catalyst

An 800 g sample of catalyst was loaded into the reactor; the catalyst in the reactor was treated by air fluidization, heated to a certain temperature, and then changed to a steam fluidized state. The reaction conditions were as follows: the reaction temperature was $530\text{ }^{\circ}\text{C}$, the water–oil ratio was 8%, and the agent–oil ratio was 6. After the reaction was completed, the reaction product was stripped out with water vapor, and the reacted product and its stripped water vapor entered the cooling system to be condensed and collected in a liquid collection bottle. After the stripping was completed, the temperature of the reactor was automatically raised to the regeneration temperature, and oxygen was introduced to scorch the carbon deposits on the catalyst. After the regeneration was completed, the reactor was automatically cooled to the reaction temperature to prepare for the next reaction–regeneration cycle. The reaction–regeneration cycles are always alternated in the same stationary reactor, where the catalyst is always in a fluidized state.

3. Results and Discussion

3.1. Synthesis and Characterization of Mesoporous Silica with Different Titanium Content

The actual silicon content and titanium content in the different catalysts were determined by XRF analysis, and the results are listed in Table 1. Among them, the $\text{TiSi}(0)$ contains almost no titanium element, and the titanium content of titanium-modified meso-

porous silica TiSi(1), TiSi(2), and TiSi(3) are 0.96 wt%, 2.01 wt% and 2.98 wt%, respectively. The actual titanium content in the samples is very close to the feeding amount during preparation, indicating that most titanium elements successfully entered into the silicon oxide during the synthesis process, and the utilization rate of titanium is close to 100%. Since we used industrial water glass as the silicon source in the experiment process, which contained residual aluminum, the final titanium modified mesoporous silica we obtained contained a small amount of aluminum oxide.

Table 1. Elemental composition of mesoporous silica catalysts with different titanium contents.

Catalysts	SiO ₂	Al ₂ O ₃	TiO ₂	Na ₂ O	Others
TiSi(0)	99.37	0.21	0.01	0.12	0.29
TiSi(1)	98.50	0.21	0.96	0.13	0.20
TiSi(2)	97.38	0.28	2.01	0.14	0.19
TiSi(3)	96.39	0.23	2.98	0.15	0.25

The nitrogen adsorption–desorption isotherms and pore size distribution curves of the mesoporous silica samples with different titanium contents before and after hydrothermal treatment are shown in Figure 1a–d, respectively, and all samples showed an adsorption step in the range of relative pressure p/p_0 of 0.6–0.8, corresponding to the larger pore size distribution peak at 2–10 nm in the pore size distribution curve. The corresponding physical and structural properties are listed in Table 2. Both mesoporous silica and titanium-modified mesoporous silica have higher specific surface area ($627.9\text{--}683.9\text{ m}^2\text{ g}^{-1}$) and pore volume ($0.87\text{--}1.16\text{ cm}^3\text{ g}^{-1}$), with an average pore diameter of 5.37–6.94 nm, which has the potential as a catalyst for the catalytic cracking of heavy oil. The specific surface of TiSi(3) is slightly lower than that of TiSi(2). This may be due to the introduction of more of the Ti species, which has a relative larger atomic mass than Si atom. The pore size of titanium-modified mesoporous oxidation increased slightly, which may be due to the increase in the polymerization degree of silica, the formation of larger particles, and the increase in pore size.

Because the heavy oil catalytic cracking reaction is usually carried out at a relatively high temperature, the high-temperature hydrothermal stability of the material is required. Therefore, the silica catalysts with different titanium contents were hydrothermally treated at 800 °C for 17 h to investigate the high-temperature hydrothermal stability of the catalysts. The results are shown in Table 2. After hydrothermal treatment, the mesoporous structure of Ti-containing silica was partially collapsed, and Ti species removed from the framework blocked the pore structure. Meanwhile, after hydrothermal treatment, the silica framework was condensed, the micropores of the Ti-silica were totally collapsed, and the micropores disappeared. All the above factors resulted in a decrease in the surface area after hydrothermal treatment.

After hydrothermal treatment, the specific surface area of TiSi(0) decreases from $667.1\text{ m}^2\text{ g}^{-1}$ to $232.8\text{ m}^2\text{ g}^{-1}$, while the titanium-modified mesoporous silica shows excellent high-temperature hydrothermal stability. After high-temperature hydrothermal treatment at 800 °C for 17 h, the specific surface area remains above $300\text{ m}^2\text{ g}^{-1}$, and the specific surface retention of TiSi(2) is highest at $384.6\text{ m}^2\text{ g}^{-1}$, indicating that the skeleton strength of mesoporous silica is significantly improved after titanium doping, which makes it have better hydrothermal stability, and thus, better catalytic cracking potential of heavy oil.

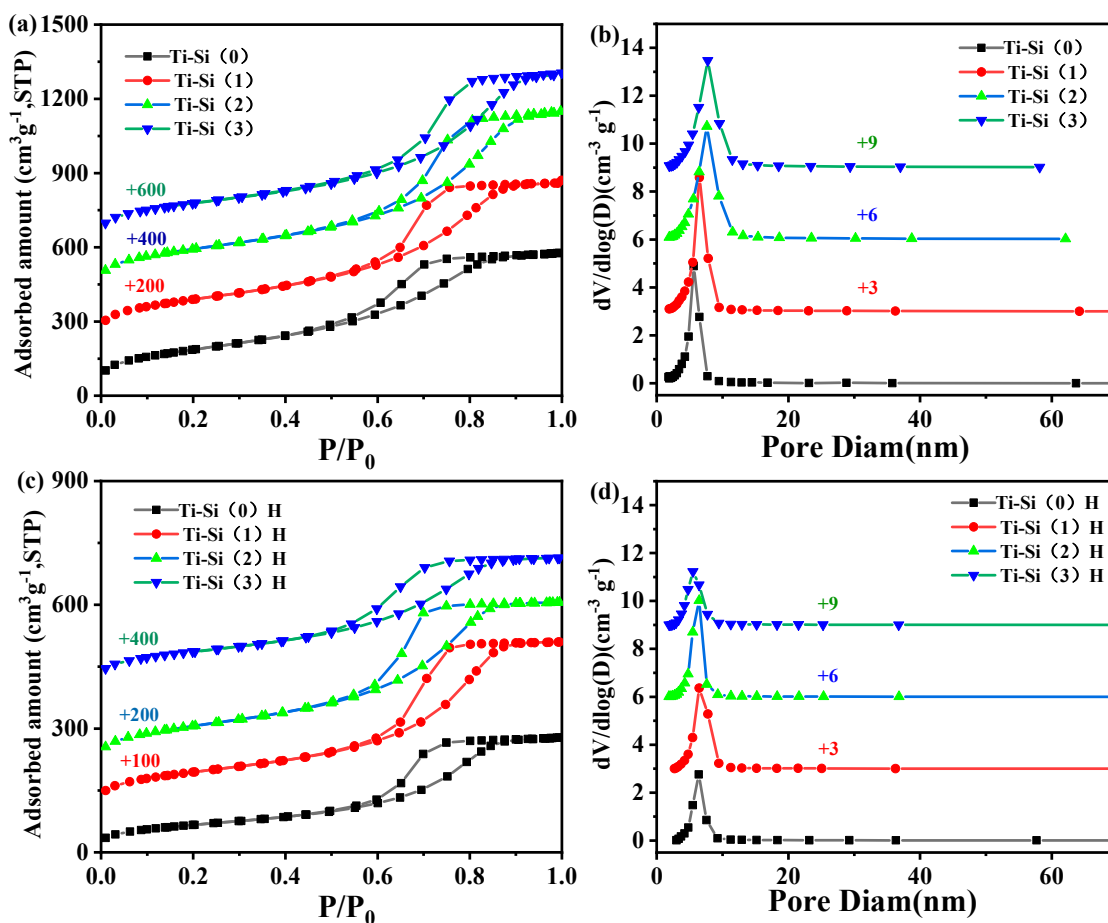


Figure 1. Nitrogen adsorption–desorption isotherms and pore size distribution curves of mesoporous silica catalysts with different titanium contents: (a,b) before hydrothermal treatment, (c,d) after hydrothermal treatment.

Table 2. Physical and structural properties of mesoporous silica with different contents.

Catalysts	Specific Surface Area ($\text{m}^2 \text{g}^{-1}$)	Micropore Specific Surface Area ($\text{m}^2 \text{g}^{-1}$)	Pore Volume ($\text{m}^3 \text{g}^{-1}$)	Average Pore Size (nm)
Before Hydrothermal Treatment				
TiSi(0)	667.1	11.2	0.87	5.24
TiSi(1)	673.4	36.8	1.04	6.16
TiSi(2)	683.9	40.0	1.16	6.78
TiSi(3)	627.9	38.8	1.09	6.94
After Hydrothermal Treatment				
TiSi(0)H	238.7	-	0.43	7.22
TiSi(1)H	340.6	-	0.63	7.44
TiSi(2)H	384.6	-	0.63	6.53
TiSi(3)H	312.3	-	0.49	6.21

The acid strength and acid content of the mesoporous silica catalysts with different titanium contents were characterized by NH_3 -TPD. As shown in Table 3 and Figure 2, the silica-based catalysts have desorption peaks at about 120°C , which are classified as weak acid desorption. However, the amount of weak acid in titanium-modified mesoporous silica TiSi(1) is significantly higher than that in TiSi(0) [14], from 0.22 mmol g^{-1} to 0.46 mmol g^{-1} . With the increase in titanium doping, the amount of weak acid increases gradually. The acid amounts of TiSi(2) and TiSi(3) are 0.55 mmol g^{-1} and 0.63 mmol g^{-1} , respectively. With

the increase in Ti content, the specific surface area of mesoporous silica is similar, and the acidity gradually increases, because the doped Ti species are the main source of the acidity of the material, without direct relationship with the specific surface area. According to the literature reports, large Ti ions enter the skeleton, causing local structural deformation. The skeleton titanium ions near the silicon hydroxyl group can change the charge density around Si, making the strength of Si–OH weaker, and making it easier to provide protons, and thus showing strong acidity. The NH₃-TPD acid content test was carried out on the catalyst after high-temperature hydrothermal treatment. The results show that the acid strength and acid content of the catalyst decreased significantly after high-temperature hydrothermal treatment. However, the titanium-modified mesoporous silica retained more weak acid content, indicating that the doping of titanium can effectively enhance the structural stability of mesoporous silica [15].

Table 3. NH₃-TPD characterization results of mesoporous silica catalysts with different titanium contents (a) before hydrothermal treatment, (b) after hydrothermal treatment.

Samples	Acid Strength (°C)	Acidity (mmol g ^{−1})
(a) Before Hydrothermal Treatment		
TiSi(0)	114.2	0.22
TiSi(1)	120.9	0.46
TiSi(2)	122.6	0.55
TiSi(3)	123.9	0.63
(b) After Hydrothermal Treatment		
TiSi(0)H	110.0	0.07
TiSi(1)H	112.6	0.21
TiSi(2)H	122.7	0.30
TiSi(3)H	124.1	0.32

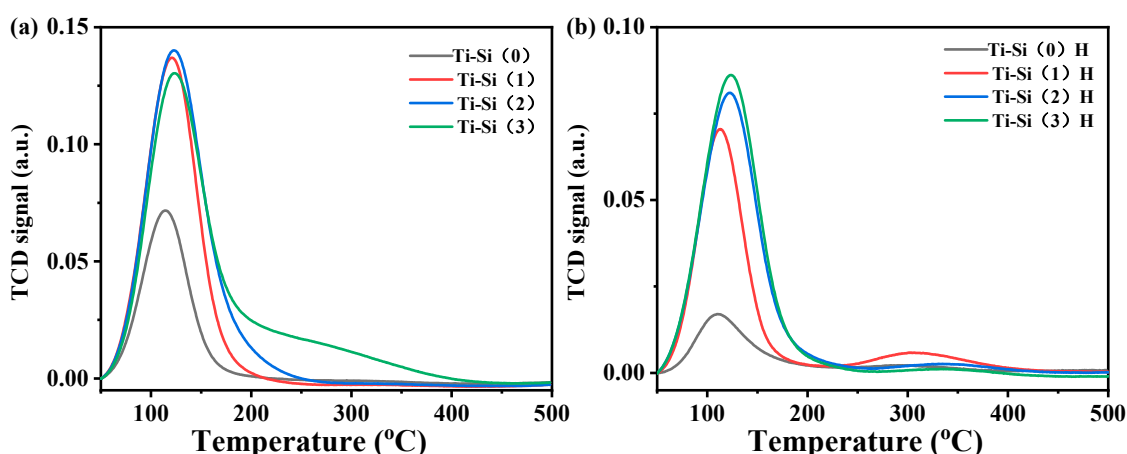


Figure 2. NH₃-TPD curves of mesoporous silica catalysts with different Ti contents: (a) before hydrothermal treatment, (b) after hydrothermal treatment.

UV-Vis spectroscopy was performed on titanium-modified mesoporous silica materials to analyze the coordination states of titanium species. The strong absorption peak at ~210 nm indicates that titanium mainly exists in the four-coordinated form [16,17]. The absorption peaks at ~260 nm and 300 nm were assigned to six-coordinated titanium species and anatase species, respectively [18–21]. The titanium species in the TiSi(1) and TiSi(2) samples mainly exist in the form of four-coordination, as shown in Figure 3a. No anatase phase is produced basically, indicating that the titanium species in the lower titanium content and incorporated into the mesoporous silica framework is in a four-coordinated form. Continuing to increase the addition of titanium, TiSi(3) not only contains four-coordinated titanium species, but also has six-coordinated titanium species and anatase

phase, which indicates that when the addition amount of titanium is 3 wt%, some titanium species exist in the state of non-skeleton titanium (anatase phase). Therefore, the optimal doping amount of titanium is determined to be 2 wt%. As shown in Figure 3b, after the high-temperature hydrothermal treatment of mesoporous silica samples with different titanium contents, the coordination state of the titanium species in the samples changed significantly, and part of the framework titanium was transformed into non-framework titanium species. With the increase in titanium content, this phenomenon is more obvious. The titanium species in the TiSi(1) sample mainly exist in a four-coordinate state, and only a small part is converted into extra-framework titanium. The TiSi(2) samples have more six coordination and anatase phases, and the TiSi(3) samples have more titanium species outside the framework.

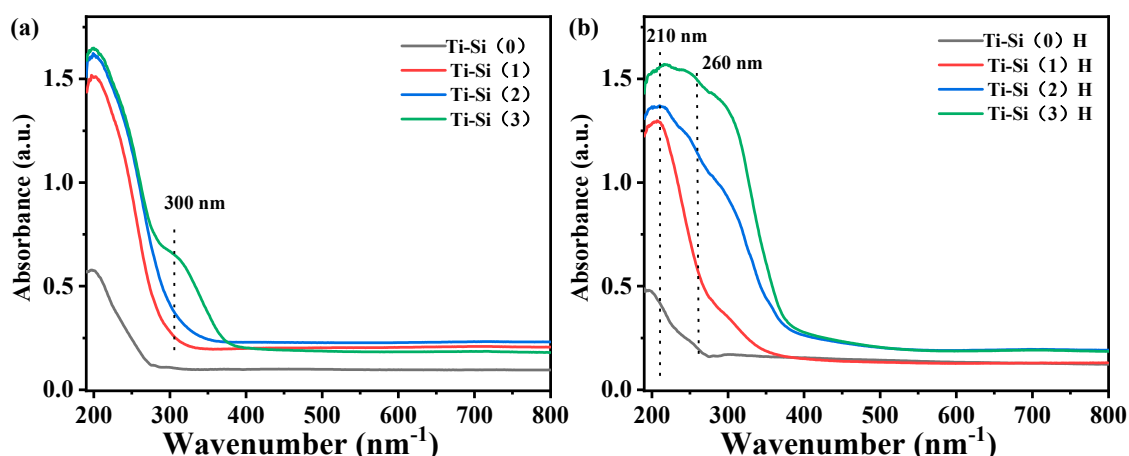


Figure 3. UV-Vis spectra of mesoporous silica catalysts with different Ti contents: (a) before hydrothermal treatment, (b) after hydrothermal treatment.

The coordination state of silicon in the titanium-modified mesoporous silica material was analyzed by silicon nuclear magnetic resonance (^{29}Si NMR), as shown in Figure 4. There are three signal peaks in the ^{29}Si NMR spectrum, which correspond to the three existing states of silicon, which are $\text{Q4}[(\text{Si}-\text{O}-\text{Si})_4]$, $\text{Q3}[(\text{Si}-\text{O}-\text{Si})_3-\text{OH}]$, and $\text{Q2}[(\text{Si}-\text{O}-\text{Si})_2-(\text{OH})_2]$ [22]. The corresponding ^{29}Si NMR spectra were subjected to peak fitting to determine the proportion of various silicon species in the sample, as listed in Table 4. The titanium-modified mesoporous silica is compared with TiSi(0), and the content of Q4 increased, indicating that the incorporation of titanium improves the framework connectivity of silicon oxide, and the degree of polymerization of silicon species is higher. The catalysts after high-temperature hydrothermal treatment were analyzed by ^{29}Si NMR. The content of Q4 was increased, and the content of Q3 and Q2 was decreased in all samples, indicating that the improvement of the connectivity of the titanium-modified mesoporous silica framework made it have high hydrothermal stability, which is consistent with the specific surface area data after high-temperature hydrothermal.

To make the catalyst have appropriate shape, size, and mechanical strength, so as to be suitable for catalytic reaction, it is necessary to shape the catalyst to make it have a certain shape and particle size that is conducive to the solid-liquid separation of the catalyst, reduce the operation cost, and promote its industrial application range. At the same time, the shaped catalyst has certain catalytic activity, selectivity, and long service life. Herein, the particle size distribution of the titanium-containing mesoporous silica catalyst after spray molding is shown in Table 5. The particle size is mainly concentrated in the range of 40–130 μm , and the distribution is relatively uniform. There is no obvious difference in the particle size of samples with different titanium content after molding, and they all have similar fluidization capacity in the process of catalytic reaction evaluation. The SEM image of the titanium-containing mesoporous silica catalyst after spray forming is shown in Figure 5. The formed catalyst is spherical in shape, with good sphericity, and

the particle surface is relatively smooth without dents or cracks. The dispersion is between 40 and 130 μm , which is consistent with the particle size distribution detected by the laser particle size analyzer.

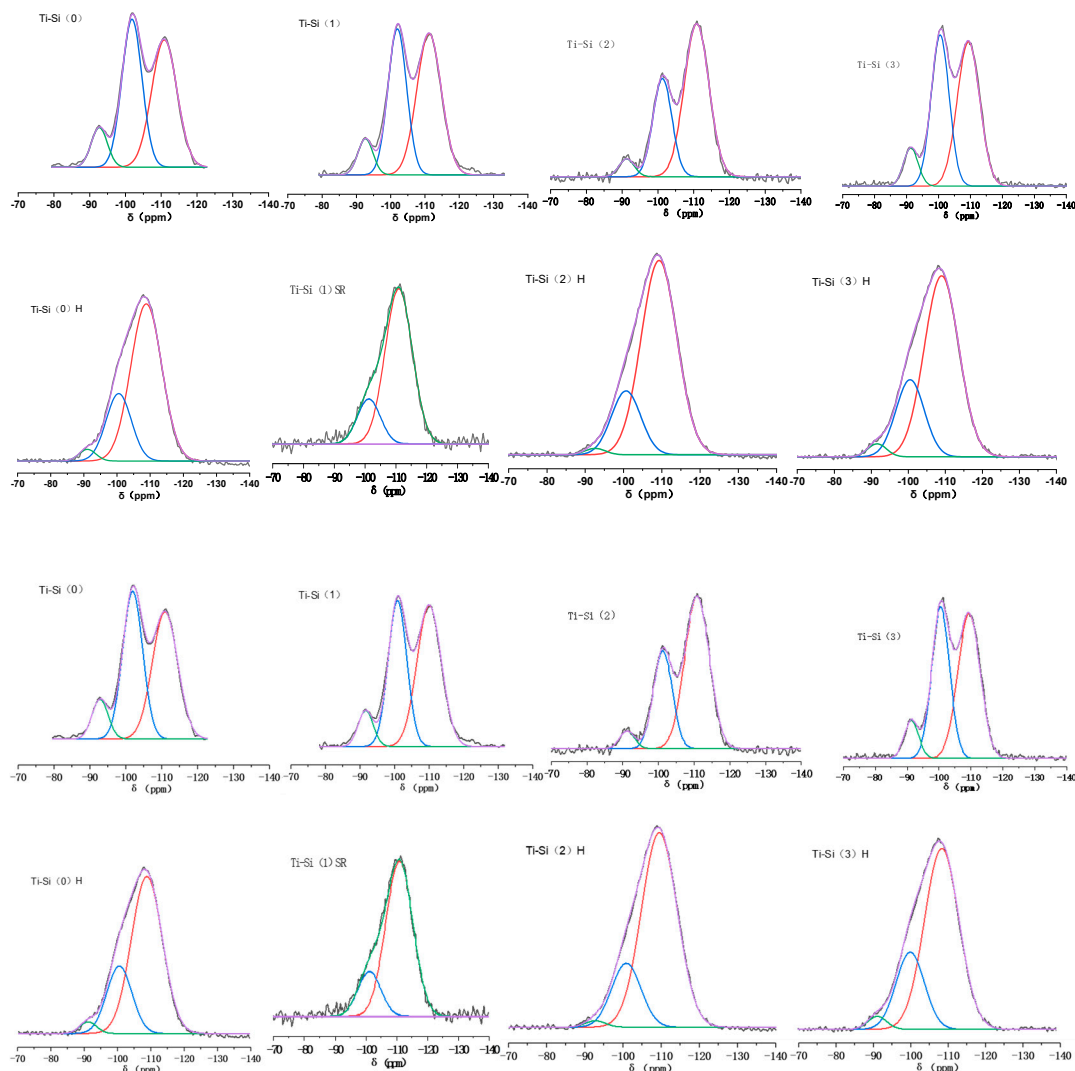


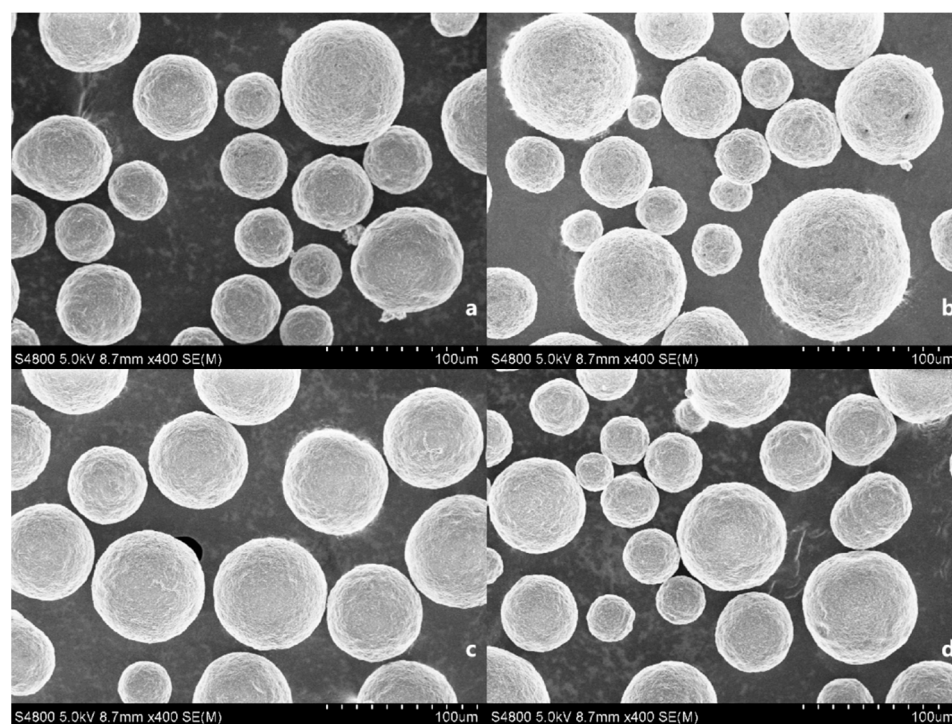
Figure 4. ^{29}Si NMR images of samples before and after hydrothermal treatment of mesoporous silica with different titanium contents.

Table 4. ^{29}Si NMR characterization results of samples before and after hydrothermal treatment of mesoporous silica with different titanium contents.

Catalysts	Q2/%	Q3/%	Q4/%
Before Hydrothermal Treatment			
TiSi(0)	9	45	46
TiSi(1)	8	40	52
TiSi(2)	9	33	58
TiSi(3)	6	37	57
After Hydrothermal Treatment			
TiSi(0)H	3	25	72
TiSi(1)H	0	28	72
TiSi(2)H	1	21	78
TiSi(3)H	3	25	72

Table 5. Particle size distribution of titanium-containing mesoporous silica catalysts.

Catalysts	D10/ μm	D50/ μm	D90/ μm
Ct(0)	49.9	78.4	121.7
Ct(1)	42.2	74.3	126.5
Ct(2)	50.1	79.2	122.7
Ct(3)	46.8	77.6	125.4

**Figure 5.** SEM images of the as-formed titanium-containing mesoporous silica catalysts (a) Ct(0); (b) Ct(2); (c) Ct(3); and (d) Ct(4).

The NH_3 -TPD data before and after hydrothermal treatment of the titanium-containing mesoporous silica catalyst after molding are listed in Table 6. The formed catalyst has an obvious weak acid desorption peak at about 120 °C, but the acid amount decreases significantly after being mixed with kaolin and silica sol. On the one hand, kaolin and silica sol do not have acid centers, on the other hand, the introduction of these two substances will reduce the proportion of silica-based materials. The acid content of the spray-formed catalyst also decreased after hydrothermal treatment, and the weak acid content of the titanium-containing sample decreased less, which indicates that the introduction of titanium enhances the skeleton structure of the silica material, improves its hydrothermal stability, and maintains the acid properties of the catalyst.

The mechanical strength of the catalyst is an important factor to determine its service life, and it is also one of the bases for the overall reliable operation of a catalytic reaction system. Therefore, the wear resistance of the titanium-containing mesoporous silica catalyst was evaluated after spray molding. As listed in Table 7, the wear index of the spray-formed catalyst samples prepared by the method described in this study is less than 3%, and the particle size distribution, morphology, and strength differences produced by the forming process are small, eliminating the interference of catalyst particle size, morphology and strength characteristics.

Table 6. Characterization results of NH₃-TPD before and after hydrothermal treatment of mesoporous silica catalysts with different titanium contents after molding.

Catalysts	Acid Strength (°C)	Acidity (mmol g ⁻¹)
Ct(0)	114.2	0.12
Ct(1)	118.4	0.29
Ct(2)	120.5	0.35
Ct(3)	122.2	0.44
Ct(0)H	112.1	0.06
Ct(1)H	115.6	0.18
Ct(2)H	117.3	0.24
Ct(3)H	119.1	0.26

Table 7. Abrasion test results of molded titanium-containing mesoporous silica catalysts.

Item	Ct(0)	Ct(1)	Ct(2)	Ct(3)
Wear /%	1.31	1.15	1.25	1.37

3.2. The Catalytic Cracking Performance of Titanium-Containing Mesoporous Silica Catalyst for Heavy Oil

In this study of heavy oil catalytic cracking, the feed oil used is high residual carbon vacuum residue, and the specific composition information is listed in Table 8. The oil has high viscosity, low hydrogen content and saturated hydrocarbon content, and high aromatics, resin, and residual carbon content. From the perspective of element composition, the content of alkaline nitrogen and sulfur is high, so it is a relatively inferior raw oil.

Table 8. Compositional analysis of feedstock oils.

Item		Vacuum Residue
Density (80 °C), g/cm ³		0.9437
Viscosity (100 °C), mm ² /s		645.33
carbon residue, w%		15.24
Basic nitrogen, µg/g		957.5
total sulfur, µg/g		6410
elements analysis, w%	C	85.45
	H	11.25
	S	0.84
	N	0.41
Four-component analysis, w%	Saturated hydrocarbons	26.00
	Aromatic hydrocarbons	33.95
	Petroleum gum	37.39
	Asphaltene	1.99

The catalytic cracking performance of the above oil products was tested with the formed titanium-containing mesoporous silica material as the catalyst. As shown in Table 9, the mesoporous silica CT(0) without titanium species can catalyze the conversion of 60.2% of the heavy oil, and the lower conversion ability comes from the less weak acid sites in the silicon oxide structure. Among them, dry gas, liquefied gas, gasoline, diesel, and heavy oil accounted for 2.3%, 11.1%, 18.7%, 26.3%, and 39.8%, respectively. However, due to the weak acidity and abundant mesoporous structure in Ct(0), it has a low coke yield of only 1.8% during heavy oil conversion. Compared with the Ct(0) sample, the introduction of titanium effectively increased the acid content of the catalyst, especially the residual

acid content after hydrothermal treatment, and the conversion rate of heavy oil was also significantly improved. At the same time, the yield of liquefied gas and gasoline gradually increased, and the yield of heavy oil gradually decreased. Due to more acid sites in the catalyst, the oil undergoes a deeper cracking reaction, and the coke and triene yields both increase (Table 10). Therefore, in comparison, CT(2) shows a higher heavy oil conversion (80.7%) while retaining a lower coke yield (3.2%).

Table 9. Conversion and product distribution of formed catalyst in heavy oil catalytic cracking (the averaged conversion and product distribution of three measurements were recorded, and the experimental error was approximately 3%).

Product, m%	Ct(0)	Ct(1)	Ct(2)	Ct(3)
Dry gas	2.3	2.8	2.8	2.7
Liquefied gas	11.1	19.7	18.8	17.2
Gasoline	18.7	25.4	28.8	31.7
Diesel oil	26.3	26.1	27.1	27.4
Heavy oil	39.8	23.1	19.3	16.3
Coke	1.8	2.9	3.2	4.7
Heavy oil conversion rate, %	60.2	76.9	80.7	83.7

Table 10. Yield of light olefin.

Item, m%	Ct(0)	Ct(1)	Ct(2)	Ct(3)
Ethylene	0.6	0.9	0.9	0.8
Propylene	3.8	6.3	6.5	5.7
Butene	5.6	8.1	8.1	7.0
Triolefins	10.0	15.3	15.5	13.5

4. Conclusions

The surface of mesoporous silica shows a weak acid center, which has the ability of cracking heavy oil macromolecules. The titanium-modified mesoporous silica material has more weak acid centers and higher hydrothermal stability, showing a better ability for deep cracking heavy oil. The conversion rate of heavy oil is significantly improved, and the yields of liquefied gas and gasoline in the product are significantly improved. However, due to abundant acid sites, heavy oil molecules are deeply cracked, and the yields of coke and triolefins are increased. With the increase in Ti content, the conversion rate of heavy oil gradually increased, and sample CT(3) exhibited 83.7% conversion of heavy oil. However, due to the strong acidity of the CT(3), the coke yield increased and the triolefin yield decreased. Among them, the sample CT(2) catalyst with 2% titanium doping (TiO₂) showed the best high-temperature hydrothermal stability. Considering the heavy oil conversion, coke yield, and triolefin yield, CT(2) is a more suitable heavy oil catalytic cracking catalyst.

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References

1. Zhao, F.; Liu, Y.; Lu, N.; Xu, T.; Zhu, G.; Wang, K. A review on upgrading and viscosity reduction of heavy oil and bitumen by underground catalytic cracking. *Energy Rep.* **2021**, *7*, 4249–4272. [\[CrossRef\]](#)
2. Fujimoto, K.; Chang, J.; Tsubaki, N. Hydrothermal Cracking of Residual Oil. *J. Jpn. Pet. Inst.* **2000**, *43*, 25–36. [\[CrossRef\]](#)
3. Lyadov, A.S.; Petrukhina, N.N. Extraction and Refining of Heavy Crude Oils: Problems and Prospects. *Russ. J. Appl. Chem.* **2018**, *91*, 1912–1921. [\[CrossRef\]](#)
4. Le Van Mao, R.; Al-Yassir, N.; Nguyen, D. Experimental evidence for the pore continuum in hybrid catalysts used in the selective deep catalytic cracking of n-hexane and petroleum naphthas. *Microporous Mesoporous Mater.* **2005**, *85*, 176–182. [\[CrossRef\]](#)
5. Safari, S.; Khoshbin, R.; Karimzadeh, R. Catalytic upgrading of heavy oil over mesoporous HZSM-5 zeolite in the presence of atmospheric oxygen flow. *React. Kinet. Mech. Catal.* **2020**, *129*, 941–962. [\[CrossRef\]](#)
6. Pan, M.; Zheng, J.; Liu, Y.; Ning, W.; Tian, H.; Li, R. Construction and practical application of a novel zeolite catalyst for hierarchically cracking of heavy oil. *J. Catal.* **2018**, *369*, 72–85. [\[CrossRef\]](#)
7. Liu, Y.; Qin, B.; Gao, H.; Ning, W.; Zhang, L.; Zheng, J.; Du, Y.; Wang, Y.; Li, W.; Li, R. A core-shell Y zeolite with a mono-crystalline core and a loosely aggregated polycrystalline shell: A hierarchical cracking catalyst for large reactants. *Catal. Sci. Technol.* **2020**, *10*, 2303–2312. [\[CrossRef\]](#)
8. AfsharEbrahimi, A.; Tarighi, S. The Influence of Temperature and Catalyst Additives on Catalytic Cracking of a Heavy Fuel Oil. *Pet. Sci. Technol.* **2015**, *33*, 415–421. [\[CrossRef\]](#)
9. Liu, H.; Wang, J.J.; Feng, W.; Xu, C.Y. Synthesis of La-substituted aluminosilicates with hierarchical pores by pH-adjusting method. *J. Alloys Compd.* **2013**, *557*, 223–227. [\[CrossRef\]](#)
10. Zhang, X.; Zhang, F.; Yan, X.; Zhang, Z.; Sun, F.; Wang, Z.; Zhao, D. Hydrocracking of heavy oil using zeolites Y/Al-SBA-15 composites as catalyst supports. *J. Porous Mater.* **2007**, *15*, 145–150. [\[CrossRef\]](#)
11. Su, L.; Guan, Z.; Li, Q.; Li, C.; Wang, X.; Li, X.; Yang, J.; Zhang, Z. Synthesis of SO_4^{2-} /Zr-silicalite-1 zeolite catalysts for upgrading and visbreaking of heavy oil. *J. Nanoparticle Res.* **2017**, *19*, 305. [\[CrossRef\]](#)
12. Han, D.; Chen, Y.; Li, C. The hydrothermal stability of the alkali-treated ZSM-5 and its catalytic performance in catalytic cracking of VGO. *Chem. Pap.* **2018**, *73*, 215–220. [\[CrossRef\]](#)
13. Tan, Q.; Fan, Y.; Liu, H.; Song, T.; Shi, G.; Shen, B.; Bao, X. Bimodal micro-mesoporous aluminosilicates for heavy oil cracking: Porosity tuning and catalytic properties. *AIChE J.* **2008**, *54*, 1850–1859. [\[CrossRef\]](#)
14. Perez-Beltran, S.; Balbuena, P.B.; Ramírez-Caballero, G.E. Surface Structure and Acidity Properties of Mesoporous Silica SBA-15 Modified with Aluminum and Titanium: First-Principles Calculations. *J. Phys. Chem. C* **2016**, *120*, 18105–18114. [\[CrossRef\]](#)
15. Shang, H.J.; Wang, L.W.; Li, X.H.; Wu, H.H.; He, M.Y.; Wu, P. Intermolecular condensation of monoethanolamine to 1, 4-diazabicyclo [2, 2, 2] octane over TS-1 catalysts. *Xian Dai Hua Gong* **2014**, *34*, 110–112.
16. Bhaumik, A.; Tatsumi, T. Organically Modified Titanium-Rich Ti-MCM-41, Efficient Catalysts for Epoxidation Reactions. *J. Catal.* **2000**, *189*, 31–39. [\[CrossRef\]](#)
17. Zhuang, J.; Ma, D.; Yan, Z.; Liu, X.; Han, X.; Bao, X.; Zhang, Y.; Guo, X.; Wang, X. Effect of acidity in TS-1 zeolites on product distribution of the styrene oxidation reaction. *Appl. Catal. A Gen.* **2004**, *258*, 1–6. [\[CrossRef\]](#)
18. Capel-Sanchez, M.C.; Campos-Martin, J.M.; Fierro, J.L.G. Removal of refractory organosulfur compounds via oxidation with hydrogen peroxide on amorphous Ti/SiO₂ catalysts. *Energy Environ. Sci.* **2010**, *3*, 328–333. [\[CrossRef\]](#)
19. O'Shea, V.A.D.L.P.; Capel-Sanchez, M.; Blanco-Brieva, G.; Campos-Martin, J.M.; Fierro, J.L.G. The Usefulness of Time-Dependent Density Functional Theory to Describe the Electronic Spectra of Ti-Containing Catalysts. *Angew. Chem. Int. Ed.* **2003**, *42*, 5851–5854. [\[CrossRef\]](#)
20. Zhang, T.; Chen, X.; Chen, G.; Chen, M.; Bai, R.; Jia, M.; Yu, J. Synthesis of anatase-free nano-sized hierarchical TS-1 zeolites and their excellent catalytic performance in alkene epoxidation. *J. Mater. Chem. A* **2018**, *6*, 9473–9479. [\[CrossRef\]](#)
21. Song, Y.; Bai, R.; Zou, Y.; Feng, Z.; Yu, J. Temperature-regulated construction of hierarchical titanasilicate zeolites. *Inorg. Chem. Front.* **2020**, *7*, 1872–1879. [\[CrossRef\]](#)
22. Zhao, E.W.; Ganesh, R.V.M.; Mentink-Vigier, F.; Zhao, T.Y.; Du, Y.; Pei, Y.; Huang, W.; Bowers, C.R. Atomic-Scale Structure of Mesoporous Silica-Encapsulated Pt and PtSn Nanoparticles Revealed by Dynamic Nuclear Polarization-Enhanced ²⁹Si MAS NMR Spectroscopy. *J. Phys. Chem. C* **2019**, *123*, 7299–7307. [\[CrossRef\]](#) [\[PubMed\]](#)