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Large pore heavy oil processing catalysts prepared using colloidal particles as templates

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Abstract

Macroporous FCC catalyst and macroporous HDS catalyst were prepared using polystyrene spheres as template. The size of the macropores can be tailored by controlling the size of template. The BET surface area and the pore volume of the macroporous catalysts are larger than those of catalysts prepared without template, and the more template used, the larger the surface area and pore volume obtained. When the same amount of template was used, the smaller diameter template produced a catalyst with larger surface area and pore volume. The increments in surface area and pore volume of the catalysts were greater than those predicted from the geometry of the template, indicating particle template could inhibit the shrinkage of the catalyst during drying. When used as heavy oil FCC catalysts and heavy oil HDS catalyst, the prepared macroporous catalysts are much more active than catalysts prepared without the template.

Keywords: Macropore catalyst; Heavy oil; FCC; Hydrodesulfurization; Particle template

1. Introduction

Converting residue into more transportation fuels is becoming more and more important. Fluid catalytic cracking (FCC) and hydrodesulfurization (HDS) are the most widely used catalytic processes for upgrading residue. However, due to the large molecular size and only partial evaporation of the residue at reaction conditions, the diffusion of the residue molecules inside catalyst is an important factor that limits the catalyst activity and selectivity [1]. The reaction rate no longer depends on catalytic activity of catalysts but on the rate of mass transfer. A new method, the akzo accessibility index (AAI) test, has been developed and patented by akzo nobel to quantify the accessibility of porous materials [2]. As the architecture of catalysts plays a more and more important role in heavy oil processing, much research is aimed at creating large pores inside catalysts [3].

The general method used to synthesize large pore catalysts is based on the self-aggregation of various surfactants [4,5]. However, the pore size of the catalysts prepared through the surfactant template method is usually less than 50 nm [4], and the pore structure is not stable in a moist environment [6]. Heavy oil processing requires catalysts to have pore size >50 nm and to be stable in a moist environment. More recently, the colloidal template method was developed for preparing macroporous materials [7], the pore diameter of which can be tailored by the size of the colloidal particles. Previous investigators have paid more attention to the ordered structure of macroporous materials, and therefore more than 74 vol% of colloidal particles (usually polystyrene) was used to fabricate the ordered macroporous materials (inverse opal). As far as we know, no other research group has reported the use of these catalytic materials to heavy oil processing, probably due to the complexity of the preparation and the low mechanical strength of these materials. In our research work, we developed a method for preparing large pore catalysts using less than 74 vol% polystyrene particles as pore template [8,9]. The synthesis process is simple and the prepared catalysts have higher mechanical strength than inverse opal structure materials. This paper presents the preparation and characterization of the large pore catalysts and their catalytic performance in heavy oil processing.

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2. Experimental

2.1. Preparation of monodisperse polystyrene particles

The uniform polystyrene (PS) particles with diameter larger than 60 nm were synthesized through an emulsion method [10,11]. A specific amount of H_2O, styrene, $NaHCO_3$ and $C_8H_7SO_3Na$ were measured into a reactor, the temperature of which was controlled at 75 ± 0.1 °C. Agitation was achieved by using a magnetic stirrer (~250 rpm). To initiate the reaction, a controlled amount of $K_2S_2O_8$ was introduced into the reactor. After the polymerization reaction was carried out under nitrogen atmosphere for about 10 h, the reaction was stopped and the PS particles solution was deionized with ion exchange resins. The size of the PS particles was measured by dynamic light scattering at 25 °C using a Malvern Zetasizer Nanosizer.

Polystyrene nanosize particles with diameter smaller than 40 nm have been synthesized by a microemulsion polymerization process with a small amount of poly(methyl methacrylate) as seeds. Sodium dodecyl sulfate and ammonium persulfate were used as surfactant and initiator, respectively. The procedures were reported in the literature [12] and are described briefly as follows. A desired amount of de-ionized (DI) water, sodium dodecyl sulfate and ammonium persulfate were put in a reactor, which was kept at 85 °C. A specific amount of methyl methacrylate was added drop-wise to the reactor. After 20 min, a desired amount of styrene monomer was added to the reaction solution. After the reaction was carried out for about 10 h, the reaction was stopped and the PS-PMMA particle solution was deionized with ion exchange resins and the size of PS-PMMA particles was measured by dynamic light scattering at 25 °C using a Malvern Zetasizer Nanosizer.

2.2. Preparation of macropore FCC catalysts

The macropore FCC catalysts were prepared by mixing specific amount of sodium silicate, sodium aluminate, sulfuric acid, REUSY zeolite, DI water and polystyrene particles with stirring. The polystyrene particles were removed from the catalysts through burning in air at 550 °C. The prepared FCC catalysts consisted of 85 wt% amorphous Al_2O_3–SiO_2 and 15 wt% REUSY and the particle size of the catalyst was 0.3–0.45 mm. Before catalytic cracking performance testing, the catalysts were aged in a 750 °C steam for 6 h.

2.3. Preparation of macropore HDS catalysts

The macropore HDS catalysts were synthesized through mixing aluminum sol with polystyrene particles, drying the aluminum sol and then removing the PS particles through burning in air at 550 °C. Thirteen weight percent Mo and 3 wt% Co were supported onto the catalysts. Before hydrodesulfurization performance testing, the macropore Mo–Co/Al_2O_3 was sulfided using of CS_2 at 350 °C and 4.0 H_2 MPa H_2 for 4 h.

2.4. The characterization of the catalyst

The morphology of the catalyst samples was observed by a Hitachi S-4200 SEM. N2 adsorption and desorption isotherms were obtained at −196 °C using a volumetric adsorption apparatus (ASAP 2405N, Micromeritics, USA). The samples were degassed at 300 °C for 4 h under vacuum prior to implementing N_2 adsorption and desorption. The specific surface area was estimated by the Brunauer–Emmett–Teller (BET) method and the static volumetry. The pore size distributions were obtained by the BJH desorption method.

2.5. Testing of catalytic performance of the FCC catalyst

The catalytic performance of the FCC catalysts was tested in a fixed bed tubular reactor, which is made of stainless steel, wherein 3.0 g of catalyst was held centrally within the tube furnace at a temperature of 500 °C. Daqing atmospheric residue was used as feed stock, the characteristics of which are shown in Table 1. The liquid products of the reaction were analyzed with an Agilent & AC GC equipped with a GC capillary column AC40.01.070 and FID detector. The carbon content on the used catalysts was determined by measuring the amount of CO_2 formed during the burning of the carbon-containing catalysts in an O_2 atmosphere at ~800 °C.

2.6. Testing of catalytic performance of the HDS catalyst

The catalytic performance of the HDS catalyst was determined in a high-pressure, tubular, fixed bed reactor made of stainless steel. About 5.0 g of catalyst was packed in the reactor, which was held in a tube furnace. Shengli coke gatch was used as feed and the sulfur content of the feed and of the reaction product was determined by a sulfur and nitrogen element analyzer ANTEK 7000NS. The *S* content of the feed was 10,160 ppm. The HDS measurements were taken after the catalysts were on-stream for more than 10 h.

Table 1
Characteristics of Daqing atmospheric residue

Density (20 °C) (g/cm^3)	0.9069
Dynamic viscosity (100 °C) (mm^2/s)	28.9
Conradson carbon (wt%)	4.3
Average molecular weight	577
Hydrogen element content (wt%)	13.1
Carbon element content (wt%)	86.5
H/C atomic ratio	1.82
The content of aromatic carbon (wt%)	10.9
SARA composition (wt%)	
Saturates	57.1
Aromatics	27.6
Resins and asphaltenes	15.3

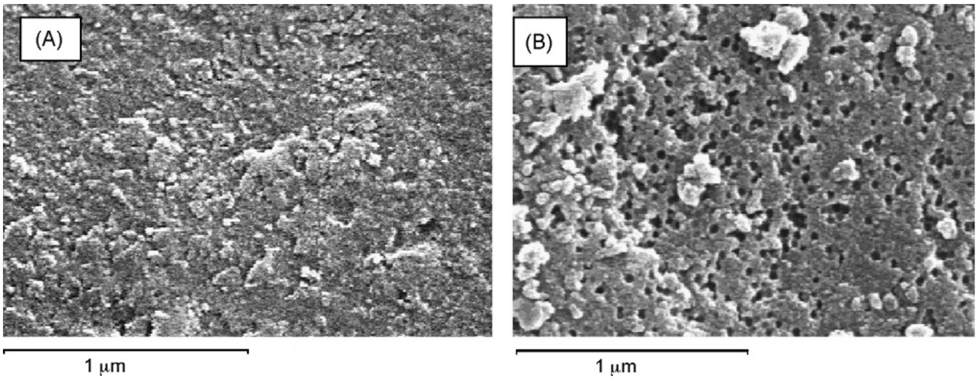

Fig. 1. The SEM of the FCC catalyst. (A) Catalyst prepared without PS template; (B) catalyst prepared with 30 wt% template of 79 nm PS particles.

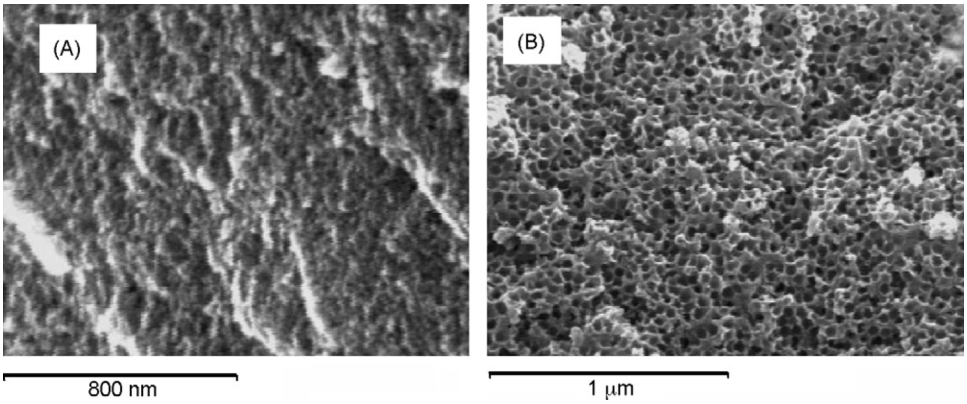

Fig. 2. The SEM of HDS catalysts. (A) Catalyst prepared without PS template; (B) catalyst prepared with 40 wt% template of 351 nm PS particles.

3. Results and discussions

3.1. The pore-structure of the catalyst

SEM images of the FCC catalyst and the HDS catalyst are shown in Figs. 1 and 2, respectively. As shown in Figs. 1 and 2, the catalysts prepared by the use of PS template have much more macro pores than that prepared without use of template. The micro pores are the spaces formed by removing PS particles. The pore size is smaller than the PS particles, indicating that the catalyst shrank during removal of the PS template by calcination.

Fig. 3 shows the pore size distribution of the FCC catalyst. It is obvious that there are two peaks for the catalyst prepared with the template. The peak located in the range of 35–100 nm corresponds to the macro pores, indicating that there were a lot of macro pores of 35–100 nm in the template-made catalyst; another peak located in the range of 2.5–20 nm corresponds to the mesopores. The macro pores were formed by removing PS particles and the size of these pores was equivalent to the size of PS template (79 nm), so that the size of the macropores can be tailored by controlling the template size. On the other hand, only mesopores peak was present in the control catalyst, implying there were few macropores inside the catalyst prepared without template. It is interesting to notice that the mesoporous peak located in the range of 2.5–20 nm for the template-made catalyst was also bigger than that for the controller catalyst. The mesoporous peak shifted to small pore size when the PS template was used. Therefore the PS templates not only create macropores, but also increase the mesoporous volume of the catalyst, especially the volume of 2.5–10 nm pores. The reason for this is that the PS template inhibited, to a certain extent, the shrinkage of the catalyst due to the capillary effect during drying. It is generally accepted that the ideal residue FCC catalyst should have micropores (provided by zeolites), mesopores and macropores simultaneously [13].

The BET surface and pore volume of FCC catalyst prepared with different template diameters sizes are shown in Table 2.

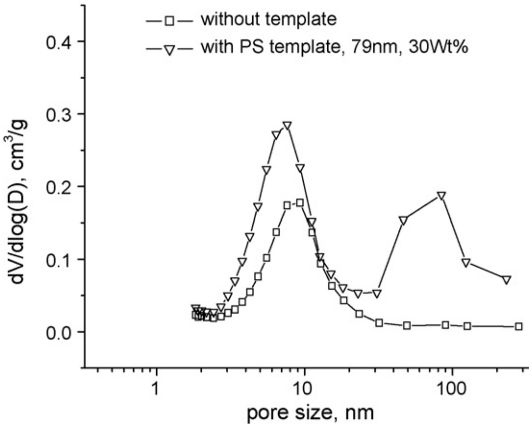

Fig. 3. The pore size distribution of FCC catalysts.

Table 2
BET surface and pore volume of the FCC catalysts prepared with different size of PS template (the amount of PS template used was 23.5 wt% based on the catalyst)

Samples	Diameter of PS (nm)	The number of PS (per g_{cat})	BET surface area (m^2/g)	Increment of BET surface area (m^2/g)		Pore volume (cm^3/g)	Increment of pore volume (cm^3/g)	
				Experimental	Calculated[a]		Experimental	Calculated[b]
C-1	N/A	0.0	103.7	0	0	0.89	0	0
C-2	93	5.32×10^{14}	163.5	59.8	14.4	1.30	0.41	0.224
C-3	118	2.60×10^{14}	146.1	42.4	11.4	1.27	0.38	0.224
C-4	135	1.74×10^{14}	124.8	21.1	9.96	1.25	0.36	0.224

[a] Calculated increment of BET surface: total outside surface area of PS spheres used in 1 g of catalyst.
[b] Calculated increment of pore volume: total volume of PS spheres used in 1 g of catalyst.

Table 3
BET surface and pore volume of the FCC catalysts prepared with different amounts of PS template (the diameter of PS particles used was 118 nm)

No.	Amount of PS wt%	The number of PS (per g_{cat})	BET surface area (m^2/g)	Increment of BET (m^2/g)		Pore volume (cm^3/g)	Increment of pore volume (cm^3/g)	
				Measured	Calculated		Measured	Calculated
C-1	0	0.0	103.7	0.0	0.0	0.89	0.0	0.0
C-5	8.8	9.74×10^{13}	111.3	7.6	4.27	1.09	0.20	0.084
C-3	23.5	2.60×10^{14}	146.1	42.4	11.4	1.27	0.38	0.224
C-6	52.8	5.84×10^{14}	154.9	51.2	25.6	1.52	0.63	0.504

Table 2 shows that, the smaller the template, the larger the BET surface area of the catalyst, while the pore volume decreased slightly with the size of template. When the same weight of PS particles is used, a great number of smaller the particles are present. More particles can inhibit the shrinkage of catalyst more effectively than fewer particles, although their weight is the same. Therefore, the catalysts prepared with smaller templates had larger surface area and pore volume than those with larger templates. The increment in BET surface area and pore volume was a consequence of the out surface area and volume of the PS particles. Table 2 shows that the increment in BET surface area and pore volume of catalysts was larger than that calculated from the morphology of PS spherical particles. This observation further confirms the result that the PS template can inhibit the shrinkage of the catalyst during the drying process.

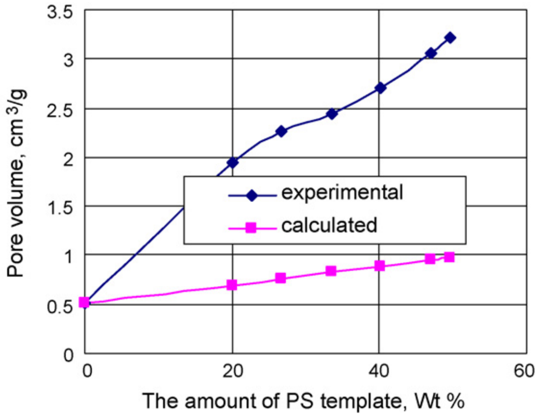

Fig. 4. The pore volume of HDS catalysts prepared using different amount of PS template. Diameter of PS spheres: 274 nm. Calculated pore volume: the pore volume of controlled catalyst added by the total volume of PS spheres used in 1 g of catalyst.

Table 3 shows the BET surface and pore volume of the FCC catalysts prepared with different amounts of PS template. It is obvious that both the BET surface area and the pore volume increase with the amount of PS template. The increments in BET surface area and in pore volume are more than that predicted from the geometrical morphology of the PS spherical particles, and the more PS template used, the larger the increments will be.

Figs. 4 and 5 show the pore volume of the HDS catalyst versus the amount and the size of template respectively. As depicted in Fig. 4, the pore volume of catalyst increases with the amount of template and the experimental value is larger than that calculated from the geometrical morphology of the PS spherical particles. When the same amount of template is used, the smaller the template diameter, the larger the pore volume of the catalyst (see Fig. 5). The relationships between the BET surface area of HDS catalyst and the amount and size of template are shown in Figs. 6 and 7, respectively. The surface area of the catalyst is proportional to the amount of template and greater than that calculated from the geometric morphology

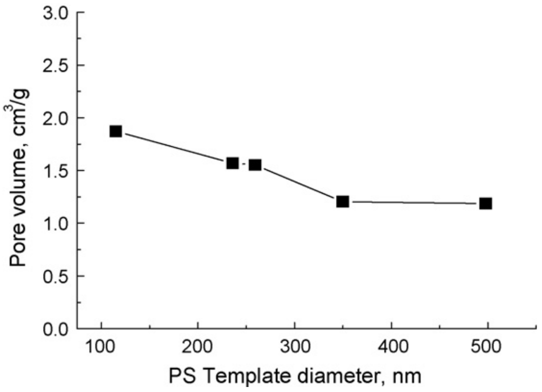

Fig. 5. Effect of PS diameter on pore volume of catalyst. PS: 33.5 wt%.

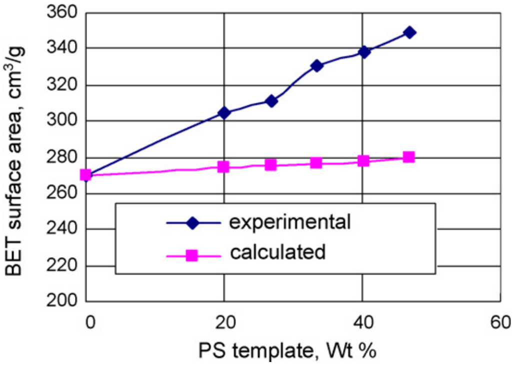

Fig. 6. Relationship of BET surface area of HDS catalyst and the amount of PS template used. PS: 274 nm. Calculated surface area: the surface area of controlled catalyst added by the total outside surface area of PS spheres used in 1 g of catalyst.

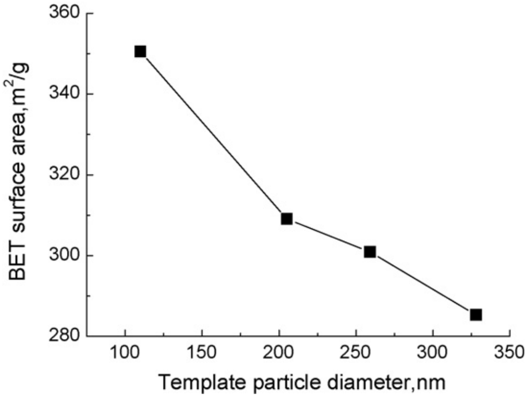

Fig. 7. The effect of template size on BET surface area of HDS catalyst, PS: 33.5 wt%.

of the PS spherical particles. With the same amount of template, the smaller the template diameter, the larger the surface area of the catalyst. The BET surface area and the pore volume of the HDS catalysts vary with the amount and size of template in the same way as those of the FCC catalysts.

3.2. The catalytic performance of the catalysts

The cracking catalytic performance of the FCC catalyst was tested on a fixed bed reactor made of stainless steel using Daqing atmospheric residue as feed. The reaction conditions and test results are shown in Tables 4 and 5. The conversion of the reaction catalyzed by the macropore catalysts, prepared with template, was much larger than that obtained by the control catalyst, and the more the template used, the higher the conversion, as shown in Fig. 4. When the same amount of template was used, the smaller the template diameter, the higher the conversion. The high catalytic activity of the FCC catalysts resulted from the macropore structure, larger surface area and pore volume created by the PS template.

Table 4
The catalytic performance of FCC catalysts prepared with different amounts of PS template[a]

Amount of template (wt%)	N/A	8.8	23.5	52.8
Dry gas (wt%)	0.86	1.12	1.47	1.57
LPG (wt%)	5.39	9.44	13.4	11.6
Gasoline (wt%)	35.5	45.0	44.2	50.7
Diesel (wt%)	24.1	21.9	18.5	17.3
>350 °C liquid (wt%)	26.5	10.9	8.33	4.22
Coke (wt%)	5.89	8.09	9.92	9.69
Conversion (%)	73.5	89.1	91.7	95.8
Mass balance (%)	98.2	96.5	95.8	95.1

[a] PS template: 118 nm; reaction temperature: 500 °C; catalyst to oil weight ratio: 3; WHSV: 20 h^{-1}.

Table 5
The catalytic performance of FCC catalysts prepared with different sizes of PS template[a]

Template size (wt%)	Controller	93 nm	118 nm	135 nm
Dry gas	0.86	1.47	1.47	1.21
LPG	5.39	12.1	13.4	9.64
Gasoline	35.5	49.0	44.2	47.3
Diesel	24.1	19.5	18.5	21.2
>350 °C liquid	26.5	6.3	8.33	8.75
Coke	5.86	8.31	9.92	8.65
Conversion	73.5	93.7	91.7	91.3
Mass balance	98.2	96.5	95.8	96.7

[a] PS template: 23.5 wt%; reaction temperature: 500 °C; catalyst to oil weight ratio: 3; WHSV: 20 h^{-1}.

The hydro-desulfurization reaction was carried out in a tubular fixed bed reactor made of stainless steel using Shengli coke gatch as feed, and the size of the HDS catalysts was 0.45–0.9 mm. As shown in Table 6, under the same reaction condition, the degree of desulfurization of the macropore HDS catalysts was greater than that of the control catalyst, indicating that the activity of the template-made HDS catalyst is higher than that of the control catalyst.

Except for the size and amount of PS template, the preparation procedures and chemical composition of the catalysts prepared with PS template were identical to those of the control catalysts (prepared without PS template). The high FCC and HDS activities of the catalysts prepared with PS template is resulted from the fast mass transfer in template-made catalysts, which have larger pore size and greater pore volume than the controller catalysts. The above result agrees with the generally accepted statement that the catalytic

Table 6
Catalytic performance of the macrospore HDS catalysts[a]

PS particle templates	S content of samples (ppm)	Degree of desulfurization[b]
Controller	4605	54.7
307 nm, 20 vol%	4205	58.6
307 nm, 60 vol%	2031	80.9
307 nm, 40 vol%	3491	65.6
115 nm, 50 vol%	3260	67.9
236 nm, 50 vol%	4031	60.3

[a] Reaction conditions: 360 °C; 6 MPa. LHSV: 1.13 h^{-1}; H_2/oil = 1000; sulfidation conditions: 300 °C; 4 MPa; LHSV:7.54 h^{-1}; H_2/oil = 90; for 4 h, 2 wt% CS2 in cyclohexane. Feed stock: 10,160 ppm S.

[b] Degree of desulfurization = (sulfur content in the feed − sulfur content in the product)/sulfur content in the feed.

processing of heavy oil is controlled by mass transfer inside the catalysts [1,2].

4. Conclusions

1. Macroporous FCC catalyst and macroporous HDS catalyst were prepared using PS spheres as template and the size of the macropores are the same as the size of the template.
2. The BET surface area and pore volume of the catalysts prepared with template were larger than those of catalysts prepared without template, and the more template used, the larger the surface area and the pore volume. When the same amount of the template was used, the smaller the template diameter, the larger the surface area and the pore volume.
3. The increments in surface area and pore volume of the catalysts were larger than those calculated from the geometric morphology of the template. The particle template, therefore, inhibits the shrinkage of the catalyst during drying.
4. When used as heavy oil FCC catalysts and heavy oil HDS catalyst, the prepared macroporous catalysts are much more active than catalysts prepared without the polystyrene particles as template.

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