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Article

A novel method for enhancing the stability of ZSM-5 zeolites used for catalytic cracking of LPG: Catalyst modification by dealumination and subsequent silicon loading

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ABSTRACT

Composite structures of ZSM-5 zeolites were prepared by the synthesis of mesopores and micropores using carbon nanotubes as a template. Dealumination of mesopores was performed selectively using trichloroacetic acid, which could only diffuse into the mesopores and not the micropores owing to the size of the trichloroacetic acid molecules. Empty spaces are created in the catalyst as a result of removal of the Al atoms from the zeolite structure. If Si atoms fill the empty space, then the structure of the mesopores becomes similar to silicates, which do not have any catalytic properties. Silicon containing solution was used to fill the empty spaces, and in doing so, a unique method was developed, by which silicon atoms can directly replace the extracted Al atoms from the mesopore structure. Therefore, by changing the geometry and properties of the mesopores and micropores, the amount of coke reduced from 14% for HZSM-5 to 3% for the modified zeolite.

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1. Introduction

Light olefins, particularly ethylene and propylene, are valuable materials in the oil industry. The production of these materials by the process of catalytic cracking is of special importance. The most important catalyst used for this purpose is ZSM-5 zeolite [1–4]. This catalyst consists of micropores as active sites for reactions, whereby each one is considered a nanoreactor. However, the major problem in the application of nanoreactors is their small size (≈ 0.56 nm) [5], which makes them difficult to access and perhaps the majority of them remain intact during the reaction, as only the catalyst surface is involved in the reaction. By the formation of mesopores, the penetration resistance of the micropores becomes minimal. Mesopores can be formed in several ways, including: (1) using a variety of templates, especially carbon [6–9]; (2) using mate-

rials as surfactants [10–16] and (3) alkali treatment [17–24]. Among the methods for the formation of mesopores in zeolites, using a carbon template is the most suitable. Surfactants are expensive, the alkali treatment method destroys the zeolite structure and with increasing concentration of NaOH the catalyst structure is destroyed. Therefore, the use of carbon templates, and carbon nanotubes in particular, preserves the structure of the catalyst and results in mesopores with specified regularity. Although the access to micropores becomes easier by construction of mesopores, the formation of coke increases in the mesopore channels, which is not mentioned in most articles [25–27]. The catalyst structure of the mesopores can be changed to a non-catalyst structure in a selectable way through dealumination and filling of the resulting free space with Si atoms; this modification minimizes the formation of coke in the mesopores. Various methods for dealumination

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have been used but not the approach used in this study [28–31].

Silicon tetra chloride (SiCl_4) is a material that has dealumination properties and a molecule size of about 0.632 nm [32]. It has been used for the dealumination of zeolites in numerous studies. Because the molecule size of this material is larger than the ZSM-5 zeolite micropores, they do not penetrate them; hence, only the mesopores get dealuminated. The fundamental problem of using SiCl_4 is that it is dangerous. Dealumination is performed at 400 °C, which is very difficult and completely unsafe. Trichloroacetic acid (TCA) is a material with a molecular size of approximately 0.7 nm. It dealuminates zeolites because of its acidic properties and is regarded as safe and very easy to use. Thus, the catalytic properties of the mesopores are reduced by TCA owing to the removal of aluminum. As a result of the removal of Al from the zeolite structure, an empty space is created in the catalyst. If Si atoms fill the empty spaces the structure of the mesopores becomes similar to silicate, which does not have any catalytic properties. But what material can be used as a silicon source? The structure of silicates is very strong and not easily damaged so that its Si atoms are not free and replaced. Silicon compounds such as tetraethyl orthosilicate, which are used as a source of silicon for synthesis of zeolites, are very expensive. In addition to these two problems, silicates are insoluble in water, so their ions are not mobile. The method used for the first time in this study solves these three existing problems. If an alkaline solution such as a NaOH solution is combined with zeolite at 80 °C, silicon atoms are removed from the zeolite structure. In many cases, this method has been used for the production of mesopores in zeolites because the empty space is created in the catalyst by the removal of Si atoms. Si atoms are released from the zeolite structures and are soluble in water. This is the best material to replace the aluminum in the previous step. High Si/Al ratios in the zeolite and high NaOH solution concentrations increase the amount of Si atoms extracted. For this reason, ZSM-5 zeolite with a ratio of Si/Al = 200 was treated with 2 mol/L NaOH solution. After 2 h, the silicon containing solution was separated from the catalyst with a syringe filter and combined with dealuminated zeolite from the previous step. The Si atoms fill the empty space left by the Al atoms and mesopores with a structure similar to silicates are produced and are inactive for the production of coke.

In this study, mesopores and micropores were formed using carbon nanotube templates during the synthesis of ZSM-5 zeolite. Both the micro and meso structures were created in the catalyst. The micropores are the active sites for the reaction, and each is considered to be a nanoreactor. Different catalytic properties were created in the mesopores and micropores by changing the mesopore properties through dealumination of the micropores and replacement of the aluminum atoms with silicon atoms, which are obtained by desilication of a separate zeolite. The mesopores are disabled for the production of coke and the micropores are activated for catalytic cracking reactions. Therefore, by reforming the ZSM-5 zeolite structure, the stability of the catalyst was increased dramatically. The synthesized ZSM-5 catalysts were used for the production of light olefins through LPG catalytic cracking. The cracking products

were analyzed by gas chromatography (GC).

2. Experimental

2.1. Materials

Ludox® silica sol AS-30 colloidal silica, 30 wt% suspension in water (Sigma-Aldrich), $\text{Al}(\text{OH})_3$ (Riedel-de Haën), NaOH (Panreac Quimica SAU), and deionized water were used for the synthesis of ZSM-5. H-form zeolite was obtained using NH_4NO_3 (Sigma-Aldrich). Carbon nanotubes (Pars Carbon Black) were used as a carbonic template to produce mesopores in zeolite. TCA (Sigma-Aldrich), ZSM-5 with Si/Al = 200 (Ali baba) and HCl (Sigma-Aldrich) were used for modification of zeolite.

2.2. Catalyst preparation

The molecular structure of zeolites is $a\text{SiO}_2:b\text{Al}_2\text{O}_3:c\text{Na}_2\text{O}:d\text{H}_2\text{O}$, in which the value of the variables is $a = 40$, $b = 1$, $c = 4.5$, and $d = 1500$ to produce pure ZSM-5 [33,34]. ZSM-5 was synthesized as follows. Solution A: 0.72 g NaOH and 0.312 g $\text{Al}(\text{OH})_3$ were dissolved in 28.2 mL deionized water. Solution B: 16 g silica sol was diluted with 14.6 mL deionized water. Solution A was slowly added to Solution B under vigorous stirring. The formed gel was stirred for 45 min until perfectly homogeneous. The gel mixture was mixed with carbon nanotubes at a weight ratio of SiO_2 in silica sol (30 wt%). The mixture was stirred for 3 h to obtain fully dispersed carbon particles. The mixture was transferred into a Teflon-lined, 500-mL stainless steel autoclave to perform the hydrothermal reaction at 197 °C for 42 h (optimized temperature and time, results have not been shown). The products were filtered on a Buchner funnel under vacuum, washed with deionized water, and then dried at 110 °C for 5 h. After drying, the catalysts were calcined in a furnace at 600 °C for 12 h to remove the carbon nanotubes deposited among the ZSM-5 crystals to create mesopores. The synthesized Na-form ZSM-5 zeolites were converted into H-form ZSM-5 by ion-exchange treatment three times in 100 mL of 1 mol/L NH_4NO_3 solution at 80 °C for 3 h. The product was then filtered, washed with deionized water, dried at 110 °C for 12 h, and calcined in a furnace at 550 °C for 5 h. The obtained ZSM-5 zeolites were labeled as HZSM-5 CNT(30) [34].

TCA with a molecular size of approximately 0.7 nm, good solubility in water, and appropriate acidic power is suitable for dealumination of mesopores. Samples of HZSM-5 CNT(30) were mixed at 80 °C with different concentrations of TCA (0.1–2 mol/L) for different durations (2–8 h). The silicon atoms filled the empty space left by the extracted aluminum atoms. Silicon compounds are usually insoluble in water and are not released easily from their molecule compounds. To solve this problem, desilication of a zeolite was with a high Si/Al ratio (Si/Al = 200) was performed using a 2 mol/L NaOH solution at 80 °C for 2 h. After 2 h, the solution was removed from the catalyst by a syringe filter. The pH of the obtained solution changed from 14 to 11.4, indicating that there was still some NaOH in the solution containing the silicon. If this solution was not neutralized, desilication of the synthesized zeolite occurred.

Therefore, it was neutralized with 0.1 mol/L HCl to pH = 7. The obtained solution was mixed with the dealuminated HZSM-5 CNT(30) zeolite at 80 °C for 3 h. The catalyst was then filtered and washed several times with deionized water and dried at 110 °C for 12 h. The modified ZSM-5 zeolite was denoted as “HZSM-5 CNT(30):acid(TCA) Si”.

2.3. Characterization

The synthesized catalysts were characterized by X-ray diffraction (XRD) using Cu $K\alpha$ radiation (40 kV, 40 mA, λ = 0.178897 nm) in the 2θ range of 5°–50°, with a step size of 0.02. For scanning electron microscopy (SEM) imaging, the powdered sample was dispersed on a carbon tape support with metal coating and analyzed under a Hitachi S-4800 SEM with a field-emission gun. Transmission electron microscopy (TEM) was performed using a JEOL 1011 microscope operated at 100 kV. Samples were suspended in methanol and supported on a carbon-coated copper grid. Nitrogen adsorption-desorption isotherms were measured at –196 °C by using the Quantachrome Instruments Autosorb-1 system. Prior to the adsorption measurements, the samples were degassed for 15 h at 120 °C. The Brunauer-Emmett-Teller (BET) method was used to estimate the specific surface areas. The micropore volume was calculated by a t -plot and the mesopore volume by subtracting the micropore volume from the total pore volume measured at a p/p_0 = 0.984. Temperature-programmed desorption of ammonia (NH₃-TPD) was performed to detect the surface acidity of the synthesized catalysts. The acid properties of the synthesized and modified HZSM-5 catalysts were measured using the NH₃-TPD method on a mass spectrometer (M-200GA-DM, Canon Anelva) as a detector of desorbed ammonia. ²⁷Al MAS NMR spectra were recorded by a Bruker DRX-400 spectrometer using 4-mm ZrO₂ rotors at room temperature, with a pulse width of 0.5 μ s, a radio frequency field strength of 50 G, a pulse delay of 0.5 s, a spinning rate of 4 kHz, and 85000 scans. The chemical shifts were referenced to 1% aqueous [Al(H₂O)₆]³⁺. High-resolution solid state ²⁹Si MAS NMR spectra were obtained using a Bruker MSL-400 spectrometer at 79.49 MHz with a pulse width of 12 μ s, a pulse delay of 100 s, a spinning rate of 4 kHz, and 2000 scans.

2.4. Catalytic tests

About 0.12 g of synthesized catalyst diluted with 0.6 g of sil-

ica was inserted in the reactor between quartz wool. The catalyst in the reactor was pre-treated by passing 40 mL/min of air for 1 h, followed by 25 mL/min of N₂ for 1 h at 650 °C. LPG at a rate of 27 mL/min (propane 48%, *n*-butane and isobutene 52%) diluted in N₂ as a carrier gas was flowed through an atmospheric, fixed-bed quartz reactor with a length of 60 cm and a diameter 1 cm and passed over the synthesized HZSM-5 at a controlled temperature of 650 °C. The obtained products were analyzed by on-line Agilent refinery gas analyzer with a capillary aluminum column (100 m $\times$ 0.50 mm), a flame ionization detector (FID), and two thermal conductivity detectors (TCDs).

3. Results and discussion

3.1. Catalyst properties

The physicochemical properties of the synthesized catalysts were measured with N₂ adsorption-desorption isotherms and shown in Table 1. The results show that the mesopores have been formed in the HZSM-5 CNT(30) catalyst and the crystallinity of the structure did not change much.

N₂ adsorption-desorption isotherms and BJH pore size distributions for HZSM-5 and HZSM-5 CNT(30) zeolites are shown in Fig. 1. A type-IV isotherm without any clear hysteresis loop was obtained for ZSM-5 zeolite (Fig. 1(a)), because of the existence of micropores and a type-H4 hysteresis loop for ZSM-5 CNT(30) owing to both micro and mesoporosity characteristics (Fig. 1(c)). The BJH models show the pore size distribution of the synthesized ZSM-5 zeolites. The ZSM-5 CNT(30) zeolite has mesopores with a pore size of 20–40 nm (Fig. 1(d)).

Fig. 2 shows SEM images of HZSM-5 and HZSM-5 CNT(30) zeolites and confirms that mesoporous channels are formed in the synthesized zeolite.

The TEM images of HZSM-5 and HZSM-5 CNT(30) in Fig. 3 show that mesopores were formed in the ZSM-5 zeolite by carbon nanotubes, which confirms the SEM and BET results.

There were no changes to the XRD graphs after dealumination and filling with silicon atoms to form HZSM-5 CNT(30) zeolite. Fig. 4 shows the XRD patterns for HZSM-5 CNT(30) zeolite, HZSM-5 CNT(30):acid(TCA) and HZSM-5 CNT(30):acid(TCA) Si. The observed peaks in 2θ = 7°–9° and 23°–25° are related to the ZSM-5 zeolite. No change to the peaks was observed after modification of the zeolite, indicating that the crystal structure of the catalyst was preserved.

NH₃-TPD profiles of the modified HZSM-5 zeolites are

Table 1

Textural and chemical properties of the synthesized HZSM-5 zeolites.

Catalyst	SiO ₂ /Al ₂ O ₃ ratio ^a	S_{BET} ^b (m ² /g)	S_{meso} ^c (m ² /g)	V_{total} ^d (cm ³ /g)	V_{micro} ^e (cm ³ /g)	V_{meso} ^f (cm ³ /g)	Crystallinity ^g (%)
HZSM-5	40	340	180	0.12	0.10	0.02	98
HZSM-5 CNT(30)	37	379	226	0.14	0.05	0.09	96

^a Measured by XRF analysis.

^b Surface areas were calculated by the BET method using adsorption data in p/p_0 = 0.05 to 0.5.

^c Measured by t -plot method.

^d Total pore volumes were estimated from the adsorbed amount at p/p_0 = 0.984.

^e Measured by t -plot method.

^f V_{meso} = V_{total} – V_{micro} .

^g (Sum of peak area owing to ZSM-5/Sum of the total area) $\times$ 100, obtained from XRD patterns.

Fig. 1. N_2 adsorption-desorption isotherms (a, c) and BJH pore size distributions (b, d) for the synthesized ZSM-5 zeolites. (a, b) HZSM-5; (c, d) HZSM-5 CNT(30).

shown in Fig. 5. Two NH_3 desorption peaks are present. The peak at the higher temperature (≈ 500 °C) is assigned as the desorption peak of ammonia adsorbed on the strong Brønsted acid sites, whereas the peak at the low temperature (≈ 260 °C)

Fig. 2. SEM images of the synthesized HZSM-5 zeolites.

Fig. 3. TEM images of ZSM-5 and mesoporous ZSM-5. (a, c) HZSM-5; (b, d) HZSM-5 CNT(30).

may exhibit weak Lewis acidity [24,35]. The result of the NH_3 -TPD analysis suggests that the strong acid sites of HZSM-5 CNT(30):acid(TCA) decrease after acid leaching as a result of the extraction of aluminum from the zeolite framework because aluminum is a strong Brønsted acid site. However, the weak Lewis acid sites are almost unchanged. After silicon treatment of the HZSM-5 CNT(30):acid(TCA) Si zeolite, the strong Brønsted acid sites are unchanged but the weak Lewis acid sites increase. This may be owing to the formation of silanol groups, which are Lewis acid sites.

3.2. Dealumination and silicon treatment processes

^{27}Al solid state MAS NMR spectroscopy can be used to determine the framework Al (FAI) and extra-framework Al (EFAl) [36,37]. In the present study, samples of ZSM-5 zeolite with 30% carbon nanotube having a mesopore and micropore

Fig. 4. XRD patterns of the modified HZSM-5 and HZSM-5 zeolites.

Fig. 5. NH_3 -TPD profiles of the modified ZSM-5 zeolites.

structure were dealuminated with TCA selectively. The large size of these acid molecules (≈ 0.7 nm) causes only the mesopores to be dealuminated. The properties of the mesopores change after dealumination and they become inactive for the production of coke, whereas the micropores maintain their activity for the reaction. The acidic power and solubility of TCA in water has had a positive impact on the dealumination process of mesopores. Dealumination of HZSM-5 CNT(30) zeolite using TCA was done at different concentrations and durations. The optimal conditions were obtained at an acid concentration of 2 mol/L and a mixing time of 5 h (according to XRD results and amount of coke). Fig. 6 shows the ^{27}Al MAS NMR spectra of the HZSM-5 zeolite samples before (HZSM-5 CNT(30)) and after (HZSM-5 CNT(30):acid(TCA)) dealumination. A strong peak at ≈ 52 ppm is assigned to tetrahedrally coordinated FAI and a very weak peak at ≈ 0 ppm owing to octahedrally coordinated EFAl [36,37]. According to Fig. 6, in the case of the dealuminated zeolite, the peak intensities of FAI reduced and that of EFAl increased, which indicates that a number of framework aluminum atoms were removed from the structure of mesopores and became non-framework aluminum. The small peak observed at 0 ppm for HZSM-5 CNT(30) zeolite is related to the removal of aluminum from the zeolite channels during calcination.

The empty space resulting from the extraction of aluminum atoms from the mesopores was filled with silicon atoms. This

Fig. 6. ^{27}Al MAS NMR spectra of HZSM-5 CNT(30) and HZSM-5 CNT(30):acid(TCA).

results in the formation of less coke. The ^{29}Si MAS NMR spectra of the HZSM-5 CNT(30):acid(TCA) and HZSM-5 CNT(30):acid(TCA) Si samples are shown in Fig. 7. The ^{29}Si MAS NMR spectrums of the zeolites shows the presence of five components, corresponding to Si(0Al), Si(1Al), Si(2Al), Si(3Al), and Si(4Si) species at -108 , -103 , -98 , -93 , and -113 ppm, respectively [38].

After mixing dealuminated zeolite with a solution of silicon at 80°C for 3 h, the modified zeolite obtained had an increased peak intensity of Si(2Al) and Si(3Al). Although the number of aluminum atoms attached to Si is higher, the structure of the internal network increases. Therefore, by comparing the graphs in Fig. 7, it can be concluded that the existing Si in the silicon containing solution has entered the network structure of the zeolite.

Table 2 shows the physicochemical properties of the modified ZSM-5 zeolites (HZSM-5 CNT(30):acid(TCA) and HZSM-5 CNT(30):acid(TCA) Si) that were obtained by N_2 adsorption-desorption isotherms. As indicated in Table 2, no parameters were changed except the Si/Al ratio, which is the result of processes of dealumination and filling of the resulting empty spaces in the ZSM-5 structure with silicon atoms.

3.3. Catalyst testing

Catalytic cracking reactions of LPG were conducted to determine the effect of the modification in the catalysts on the yield and selectivity of light olefins and coke content. The conversion of feed, yield, and selectivity for light olefins (ethylene and propylene) were calculated on the basis of Eqs. (1)–(3):

$$\text{Conversion of LPG (\%)} = \frac{\text{weight of LPG reacted}}{\text{weight of LPG supplied}} \times 100\% \quad (1)$$

$$\text{Yield of light olefins (ethylene and propylene)} = \frac{\text{The total wt\% of ethylene \& propylene}}{\text{Conversion of LPG}} \quad (2)$$

$$\text{Selectivity of light olefins (ethylene and propylene)} = \frac{\text{Yield of light olefin}}{\text{Conversion of LPG}} \times 100\% \quad (3)$$

The amount of formed coke is measured using a very accu-

Fig. 7. ^{29}Si MAS NMR spectra of HZSM-5 CNT(30):acid(TCA) (1) and HZSM-5 CNT(30):acid(TCA) Si (2).

Table 2

Physicochemical properties of the modified HZSM-5 zeolites.

Catalyst	SiO ₂ /Al ₂ O ₃ ratio ^a	S _{BET} ^b (m ² /g)	S _{meso} ^c (m ² /g)	V _{total} ^d (cm ³ /g)	V _{micro} ^e (cm ³ /g)	V _{meso} ^f (cm ³ /g)	Crystallinity ^g (%)
HZSM-5 CNT(30):acid (TCA)	65	385	245	0.15	0.05	0.10	98
HZSM-5 CNT(30):acid (TCA) Si	77	380	230	0.13	0.04	0.09	98

^a Measured by XRF analysis.^b Surface areas were calculated by the BET method using adsorption data in $p/p_0 = 0.05$ to 0.5.^c Measured by t -plot method.^d Total pore volumes were estimated from the adsorbed amount at $p/p_0 = 0.984$.^e Measured by t -plot method.^f $V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}}$.^g (Sum of peak area owing to ZSM-5/Sum of the total area) $\times 100$, obtained from XRD patterns.

rate gravimeter on the basis of the ratio of produced carbon weight (2 h after reaction) to used zeolite weight in a fixed-bed reactor.

Fig. 8 shows the results of GC analysis of LPG catalytic cracking over the synthesized HZSM-5 and mesoporous HZSM-5. As shown in Fig. 8, HZSM-5 CNT(30):acid(TCA) Si zeolite produced greater olefin yield and selectivity than other zeolites and the amount of the formed coke was very low. Because less coke is formed in the synthesized and modified mesopores, more active sites are available for the reactions, which results in increased olefins yield and a selectivity increase from 54% in HZSM-5 to 62% for HZSM-5 CNT(30):acid(TCA) Si. Fig. 8(b) shows the stability of the catalyst after 2 h of reaction based on olefins yield. According to Fig. 8(b), during the reaction, the activity of the catalyst for HZSM-5 CNT(30):acid(TCA) Si zeolite is much more than the other zeolites. Increased stability of this zeolite is related to the structural modification, whereby less coke formation protects the catalyst active sites from closure by coke. For the HZSM-5 CNT(30) zeolite, because of the production of large meso channels, more space is created for the formation of coke. Therefore, coke formation increases and the catalytic activity of this type of zeolite is reduced. No attention has been paid to this in past research; mesopores were created to increase access to materials without considering the extra room created for the formation of coke.

4. Conclusions

A ZSM-5 zeolite with a unique structure and properties was synthesized. Mesopores and micropores were formed during the synthesis of the ZSM-5 zeolite containing 30 wt% carbon nanotubes. Selective dealumination with TCA was performed in the mesopores to form large channels of mesopores that are inactive for the formation of coke. Finally, the empty space left by aluminum was replaced with silicon atoms. The structure of the mesopores was prepared using a unique procedure and is similar to silicates structures that do not have any catalytic activity. The synthesized catalysts were used for LPG catalytic cracking. The amount of coke produced with the modified catalyst dropped to 3% and the efficiency and selectivity of light olefins remained high.

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Fig. 8. (a) Yield and selectivity of olefins and the amount of coke produced by catalytic cracking of LPG over HZSM-5, HZSM-5 CNT(30), and HZSM-5 CNT(30):acid(TCA) Si. (b) Stability of zeolite samples during the LPG catalytic cracking.

Graphical Abstract

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A novel method for enhancing the stability of ZSM-5 zeolites used for catalytic cracking of LPG: Catalyst modification by dealumination and subsequent silicon loading

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We have reported the synthesis of mesopores and micropores in ZSM-5 zeolites by changing the geometry and properties of the mesopores using a new method. Selective dealumination of the mesopores by trichloroacetic acid and filling of the empty space with Silicon atoms resulted in inactive mesopore channels with lower production of coke and enhanced catalytic activity for catalytic cracking.

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增强LPG催化裂化催化剂ZSM-5稳定性的新方法：脱铝和负载硅

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摘要: 以碳纳米管为模板合成的带有介孔和微孔的ZSM-5分子筛具有不同的复合结构. 用三氯乙酸(TCA)可选择性地将中孔的铝脱除. 基于TCA分子大小, 它可能只扩散到中孔中, 因而使得微孔部分不脱铝. 从分子筛结构中脱除铝原子导致催化剂中出现中空的空间. 若将硅原子填充到空位中, 那么介孔部分的结构会变得与硅酸盐类似, 不具有催化性能. 本文使用含硅的溶液来填充空位, 将硅原子直接取代中孔结构中的铝原子. 通过此特殊方法改变微孔和介孔的几何形状和性质, 从而使改性HZSM-5上的积碳量从14%降低至3%.

关键词: 介孔; 碳纳米管; ZSM-5分子筛; 脱铝; 三氯乙酸

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