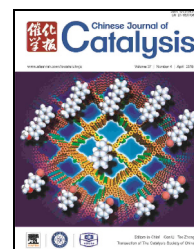


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## Article

# 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 ( $\approx 0.56$  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 ( $\text{SiCl}_4$ ) 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  $\text{SiCl}_4$  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  $\text{NH}_4\text{NO}_3$  (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  $\text{SiO}_2$  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  $\text{NH}_4\text{NO}_3$  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.

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