

# Possibility of Using Sepiolite as the Matrix of FCC Catalysts

KUI – 21/2009  
Received April 14, 2009  
Accepted October 5, 2009

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The effect of acid concentration, time and temperature of modification on the magnesium removal from sepiolite modified by hydrochloric acid, sulfuric acid and nitric acid and on its effectiveness as an active matrix for FCC catalysts, were investigated. The modified sepiolite was characterized by XRD, SEM and N<sub>2</sub> adsorption. The results show that the removal of magnesium, specific surface area, and pore specific volume of modified sepiolite are improved with increasing acid concentration, treating time and treating temperature. Hydrochloric acid appears preferable to the modification of sepiolite. The suitable acid modification conditions of sepiolite for FCC catalysts are 80 for 2.5 h with 1 mol L<sup>-1</sup> HCl acid, under which the removal of magnesium in sepiolite is 27 %. With the modified sepiolite as an active matrix for FCC catalysts, the specific surface area, pore specific volume and mesopore pore specific volume of the catalysts can increase effectively, the catalysts exhibit excellent heavy-metal resisting performance and better cracking properties as a result of the introduction of magnesium oxide from the modified sepiolite.

Key words: *Sepiolite, acid modification, FCC catalyst, matrix*

## Introduction

Sepiolite is a fibrous hydrated magnesium phyllosilicate resulting from the molecular organization of an ideal unit Si<sub>12</sub>O<sub>30</sub>Mg<sub>8</sub>(OH)<sub>4</sub>(OH<sub>2</sub>)<sub>4</sub> · 8 H<sub>2</sub>O.<sup>1–2</sup> It contains a continuous two-dimensional tetrahedral silicate sheet. 2 : 1 lamellar structural unit is formed by a layer of magnesia octahedral between two layers of continuous silica tetrahedral inverting apical direction every six silica tetrahedral units. Sepiolite as a porous material characterized by 0.37 × 1.06 nm channels parallel to the x-axis between opposing 2 : 1 ribbons. This results in a fibrous morphology with the channels parallel to the fiber length. The size of individual fibers is determined by the length in the range 100–5000 nm, the width in the range 100–300 nm and thickness in the range 50–100 nm. H<sub>2</sub>O and exchangeable cations lie in channels extending in the x-axis direction.<sup>3–4</sup> This special structure gives sepiolite a large specific surface area and high capacity of ion exchange. Therefore, sepiolite has been used widely in adsorbent<sup>5</sup> and catalyst fields<sup>6</sup>. The application of modified sepiolite as an adsorbent has been investigated by addition of compounds of Pt, Fe, Co and Ni<sup>7</sup>. The application of modified sepiolite as a catalyst has also been investigated with addition of V<sup>8</sup>, Pd<sup>9</sup>, Ni<sup>10</sup>, and Pt<sup>11</sup>. In general, sepiolite as catalytic material is used for cracking of hydrocarbon.<sup>12–13</sup> Because of its specific chemical composition, pore structure and high strength, sepiolite has been attracting considerable attention in petrochemical industry.<sup>14–15</sup>

The fluid catalytic cracking unit (FCC) is still a main conversion unit in many refineries. It is able to process very large amounts of heavy oil fraction, and it is flexible enough to direct production preferentially to gases (propylene, butenes), gasoline or diesel, with minor modifications of the unit or operating conditions. The FCC catalyst is a complex mixture containing an active zeolite, a matrix that can participate in the overall cracking process at different levels, a binder, and different additives for specific functions. Whereas the zeolite properties will affect more the composition of gases and gasoline, the matrix will have a direct influence on the properties of the heavier LCO fraction. It is known that their chemical composition and pore structure properties play an important role in the final selectivity of the catalyst. When the matrix of the catalyst has large pore specific volume and more medium-sized pores, during the cracking processing, the catalyst particle's architecture is engineered to provide the porosity needed for sufficient access to the active matrix sites, and subsequently to allow these primary cracking products to diffuse to the crystalline zeolite and continue cracking to give the desired gasoline and LPG products. Catalysts possessing more medium pores are more effective for entry of large molecules in the petroleum feedstock and for egress of products.

The surface acidity of natural sepiolite is so weak that it cannot make NH<sub>3</sub> protonated, its catalytic activity and heat stability is too low.<sup>16</sup> Examples of the direct application of natural sepiolite as catalyst are rare. Acid modification of sepiolite can improve heat stability, catalytic activity and surface reaction ability.<sup>17–20</sup> In acid treatment process, the

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size of internal channel of sepiolite is developed from microporous to mesoporous, so that the ratio of mesoporous increases,<sup>21–22</sup> in favor of heavy oil catalytic cracking reaction. Jiang Wenbin et al.<sup>23</sup> reported that the vanadium resisting property had been improved using acid modified sepiolite. Therefore, in order to make the sepiolite in favor of cracking reaction, it is best carried out on sepiolite acid modification to enhance its surface acidity, and at the same time modified sepiolite having special structure. The presence of magnesium in modified sepiolite was beneficial to enhance heavy metal resisting capacity.

At present, kaolin is frequently used as support of FCC catalysts. Compared with kaolin, sepiolite has higher specific surface area and pore specific volume, but contains more impurity and magnesium unfit for FCC catalyst matrix. Therefore, modification must be carried out. Modified sepiolite possesses little impurity and appropriate magnesium. With modified sepiolite as an active matrix for FCC catalysts, the catalysts exhibit excellent heavy-metal resistance and better cracking properties.

## Experimental

### Materials

Sepiolite ( $w(\text{SiO}_2) = 54.36\%$ ,  $w(\text{MgO}) = 16.68\%$ ,  $w(\text{Al}_2\text{O}_3) = 0.42\%$ ,  $w(\text{CaO}) = 1.53\%$ ,  $w(\text{Fe}_2\text{O}_3) = 0.69\%$ ,  $w(\text{Na}_2\text{O}) = 0.25\%$ ,  $w(\text{K}_2\text{O}) = 0.13\%$ ,  $w = 25.94\%$ , others.) was purchased from Hunan Xiangtan Hongyan Sepiolite Co. Ltd.

Kaolin ( $w(\text{SiO}_2) = 46.35\%$ ,  $w(\text{Al}_2\text{O}_3) = 37.98\%$ ,  $w(\text{Fe}_2\text{O}_3) = 0.63\%$ ,  $w(\text{Na}_2\text{O}) = 0.21\%$ ,  $w(\text{K}_2\text{O}) = 0.33\%$ ,  $w(\text{MgO}) = 0.18\%$ ,  $w(\text{CaO}) = 0.53\%$ ,  $w = 13.79\%$ , loss on ignition.) was purchased from Suzhou Kaolin Co. Ltd.

Alumina gel ( $w(\text{Al}_2\text{O}_3) = 23.16\%$ ) was purchased from Yueyang Jucheng Chemical Co. Ltd.

Pseudoboehmite ( $w(\text{Al}_2\text{O}_3) = 65.76\%$ ) was purchased from China Shandong Aluminum Co. Ltd.

Hydrochloric acid, sulfuric acid and nitric acid were supplied from the Beijing chemical company.

REUSY zeolite was kindly provided by the Catalyst producing factory of the Changlian petrochemical company.

### Acid modification of sepiolite

5.0 g sepiolite (see SEM of raw Hongyan sepiolite in Fig. 1) were modified by hydrochloric acid, sulfuric acid and nitric acid, respectively, and treated with  $1\sim 6\text{ mol L}^{-1}$  acid solution at ratio of liquid to solid 10 : 1 and  $20\sim 80\text{ }^\circ\text{C}$  for  $0\sim 2.5\text{ h}$ , at a pH of about  $2.5\sim 3.0$ . Deionized water, sepiolite and acid were added to a 250 ml beaker, in order, and the ingredients were stirred at a rate sufficient to suspend the solids. The reactant slurry was separated from their mother liquor by vacuum filtration on Buchner funnels, washed with warm deionized water, and dried at  $100\text{ }^\circ\text{C}$  in oven.

### Model catalyst preparation

Model catalyst A is the base catalyst with kaolin as matrix, model catalyst B is prepared by modified sepiolite replacing kaolin as matrix, model catalyst C is prepared by modified

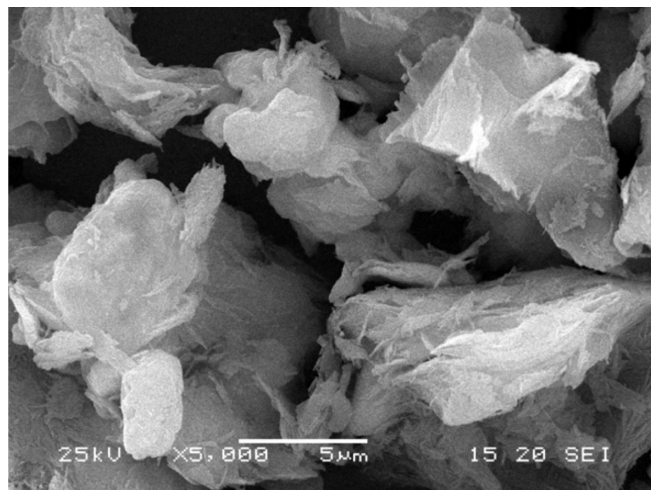


Fig. 1 – SEM of sepiolite from Hongyan, scale bar =  $5\text{ }\mu\text{m}$

Slika 1 – Pretražne elektronske mikrofotografije uzoraka sepiolita iz Hongyana, podjela =  $5\text{ }\mu\text{m}$

sepiolite and kaolin as matrix. The amounts of ingredients used in model catalysts are shown in Table 1.

Deionized water, kaolin (or sepiolite / or sepiolite and kaolin) were added to a 1000 ml beaker and stirred at a rate sufficient to form a uniform slurry. After blending enough, alumina sol and zeolite were subsequently added in order, the mixture was stirred at temperature for  $1\sim 2\text{ h}$ . The reactant slurry was oven-dried at  $100\text{ }^\circ\text{C}$ . The sample was broken and sieved to get  $20\sim 40$  mesh size catalyst sample.

### Catalyst preparation

The amounts of ingredients used in catalysts were same as shown in Table 1.

Table 1 – Fractions of ingredients used in model catalysts w/%

Tablica 1 – Udjeli sastojaka upotrijebljenih u odgovarajućim katalizatorima, w/%

Catalyst Katalizator	Alumina gel $\text{Al}_2\text{O}_3$ -gel	Kaolin Kaolin	Modified sepiolite Modificirani sepiolit	Pseud- boehmite Pseudo- bemit	Zeolite Zeolit
Catalyst A Katalizator A	13	25		22	40
Catalyst B Katalizator B	13		25	22	40
Catalyst C Katalizator C	13	12.5	12.5	22	40

Deionized water, kaolin (or sepiolite/or sepiolite and kaolin) were added to a 10 000 ml liter stainless steel kettle reactor and stirred at a rate sufficient to form a uniform slurry. After blending enough, alumina sol and zeolite were subsequently added in order, the mixture was stirred at temperature for  $1\sim 2\text{ h}$ . The reactant slurry was produced by spray drying the subsequent ion exchange was conducted by different methods. Finally, the catalyst was obtained by flash drying.

## Impregnation of the catalyst

The catalyst was impregnated with a nickel-vanadium mixture ( $w = 0.8\%$ ) as follows:<sup>24</sup> a dried catalyst sample is impregnated with ammonium metavanadate dissolved in oxalic acid solution ( $w(V) = 0.5\%$ ) and nickel nitrate ( $w = 0.3\%$  Ni). The amount of the solution used is sufficient for impregnating the catalyst to its puddle point, that is, the point when additional drops will result in the formation of a solvent puddle. The solvent is then evaporated at room temperature, carbonized at  $540\text{ }^\circ\text{C}$  and the organic burned off at  $800\text{ }^\circ\text{C}$  leaving the bare metal deposited on the catalyst.

## Characterization

### Removal of magnesium

Concentration of magnesium in the liquid samples obtained was determined by atomic absorption spectroscopy. AASD-400 atomic absorption spectrometer (Perkin-Elmer) was used for this purpose.

Sepiolite was modified by acid, and treated with  $1\sim 6\text{ mol L}^{-1}$  acid solution at ratio of liquid to solid  $10 : 1$  and  $20\sim 80\text{ }^\circ\text{C}$  for  $0\sim 2.5\text{ h}$ , at a pH of about  $2.5\sim 3.0$ . After reaction, the slurry was immediately carried out in centrifuge, sepiolite and the solution were separated, and the solution part was determined by atomic absorption spectroscopy.

The mass fraction of magnesium in the liquid samples ( $w(\text{Mg})$ ) was obtained by the following equation:

$$w(\text{Mg}) = \frac{w(\text{Mg}_1) - w(\text{Mg}_2)}{w(\text{Mg}_1)} \cdot 100\%$$

Where:  $w(\text{Mg}_1)$  is the fraction of magnesium in natural sepiolite;  $w(\text{Mg}_2)$  is the fraction of magnesium in modified sepiolite; and  $w(\text{Mg}_1) - w(\text{Mg}_2)$  is the fraction of magnesium in the liquid samples determined by atomic absorption spectroscopy.

### XRD characterization

Phase composition of samples and crystallinity of catalysts were identified with powder X-ray diffraction (XRD) taken on a Rigaku-D-Max rA 12 kW Diffractometer with  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.54056\text{ nm}$ ), at an operation voltage and current of  $40\text{ kV}$  and  $300\text{ mA}$ , respectively. The reference sample was standard NaY. The crystallinity of zeolite Y was estimated according to the following equation:

$$\text{crystallinity (\%)} = \frac{\text{peak height at } 22\text{--}24.5^\circ 2\theta \text{ (product)}}{\text{peak height at } 22\text{--}24.5^\circ 2\theta \text{ (reference)}} \cdot 100$$

### SEM characterization

SEM was obtained by a JEOL JSM-6360 microscope and Pt coated samples, at an operating voltage of  $U = 25\text{ kV}$ .

### BET specific surface area and pore structure

The Brunauer–Emmett–Teller (BET) specific surface area, pore diameter distribution and pore specific volume of the sample were recorded on USA Micromeritics Instrument Corp, TriStar3000 using adsorption and desorption isotherm plots at  $77\text{ K}$ . Prior to adsorption tests, the samples were degassed under vacuum for  $24\text{ h}$  at  $423\text{ K}$ .

## Catalytic performance testing

The performances of the catalysts were tested in a FFB reactor. The experiment was performed under the conditions of  $500\text{ }^\circ\text{C}$  and weight hourly space velocity (WHSV) of  $19\text{ h}^{-1}$ . The mass ratio of catalyst to oil was  $\zeta = 1 : 6$ . Prior to the FFB test, the catalysts were steam-deactivated at  $800\text{ }^\circ\text{C}$  for  $10\text{ h}$  in a fluid bed in  $100\%$  steam.

## Results and discussion

### Acid modification of sepiolite

#### Modification of sepiolite with different mineral acids

Removal of magnesium takes place by its substitution with  $\text{H}^+$  ions from used acids, as it is schematically represented in Fig. 2, 3 shows the results of fraction of removed magnesium. For all used acids, the extent of removed magnesium increases approximately linearly with acid concentration, the best effect is achieved with sulfuric acid and the worst with nitric acid, and the acid modification causes a gradual destroying of sepiolite structure, the degree of destruction increases with the extent of removed magnesium.

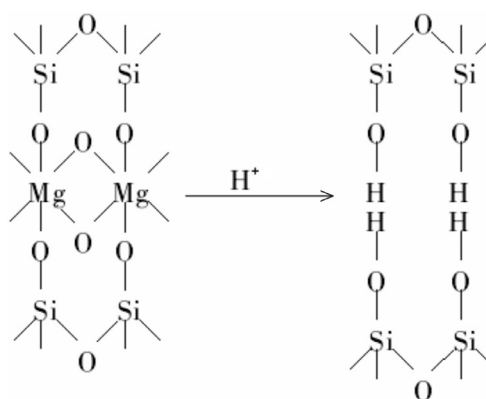


Fig. 2 – Mechanism of acid treatment for sepiolite  
Slika 2 – Mehanizam obrade sepiolita kiselinom

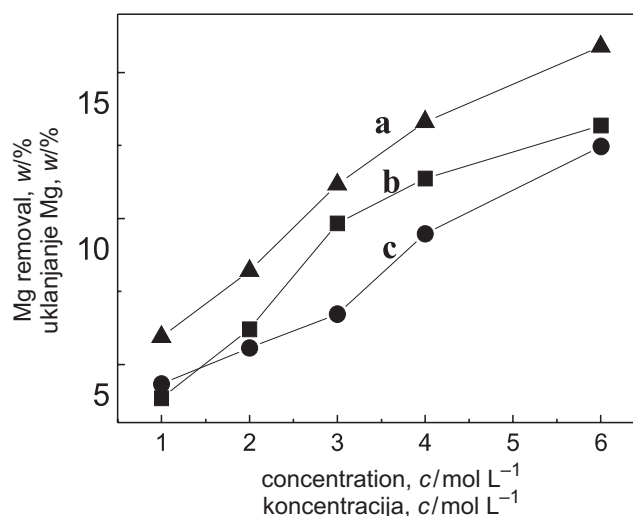


Fig. 3 – Relationship between concentration of three acids and removal of magnesium

Slika 3 – Povezanost između koncentracije upotrijebljenih kiselina i uklanjanja magnezija



### Reaction temperature

Hydrochloric acid used, its concentration is 1 mol L<sup>-1</sup>, 20 solid-liquid ratio and 2.5 h, relationship between reaction temperature and fraction of removed magnesium is shown in Fig. 4. The results show that the fraction of removed magnesium increases with temperature. This may be due to increasing temperature, the rate of magnesium oxide dissolved in sepiolite accelerated.

### Reaction time

Hydrochloric acid was used, its concentration was 1 mol L<sup>-1</sup>, 20 solid-liquid ratio and 80 °C, extent of removed magnesium with time is shown in Fig. 5. The results show that the increase of the removed magnesium with reaction time was expected.

### Modification conditions

Based on the above results, and combining the technique for preparing FCC catalysts, the optimum modification conditions are as follows: hydrochloric acid, concentration of 1 mol L<sup>-1</sup>, 80 °C, 2.5 h. Under these conditions, the removal of magnesium in sepiolite is about 27 %.

### Specific surface area and pore structure of modified sepiolite

Table 2 shows that both natural and modified sepiolite has about two times higher specific surface area and about 10 times higher total specific pore specific volume than kaolin, frequently used as support of FCC catalysts. The natural sepiolite is mainly mesoporous material, about 70 % of pore specific volume is yielded by the >9.94 nm pores, pore specific volume of >9.94 nm pores is 0.2272 cm<sup>3</sup> g<sup>-1</sup>. Acid modification increases the total pore specific volume (its increase for about 7 %) by increase of the volume yielded by >9.94 nm pores and simultaneous decrease of the volume yielded by >9.94 nm pores. Pore specific volume of >9.94 nm pores is 0.2554 cm<sup>3</sup> g<sup>-1</sup>.

### XRD characterization

Fig. 6 shows the X-ray powder diffraction pattern of samples showing the reflections up to 70° 2θ. Curve a, b and c followed by Sep-0 (nature sepiolite), Sep-16 (16 % removal of magnesium) and Sep-26 (26 % removal of magnesium). The diffraction peak of sepiolite at 2θ = 7.20°, talc at 2q = 9.46°, quartz at 2θ = 26.64°. The XRD patterns can be seen with increase in the removal of magnesium, the diffraction peak of sepiolite at 2θ = 7.20° and the diffraction peak of talc at 2θ = 9.46° have no change, the diffraction peak of quartz at 2θ = 26.64° obvious increase, the diffraction peak of calcium oxide decrease. This illuminates that at moderate modification conditions, the sepiolite transformation to talc is not obvious, but with the increase in removal of magnesium, a decrease in the intensity of the diffraction peaks of sepiolite, indicates that crystal structure in sepiolite was gradually destroyed.

### Catalysts properties

#### The chemical composition of the catalyst

The chemical properties of the catalysts A, B and C, prepared as described in Experimental by ingredients listed in Table 1 are shown in Table 3.

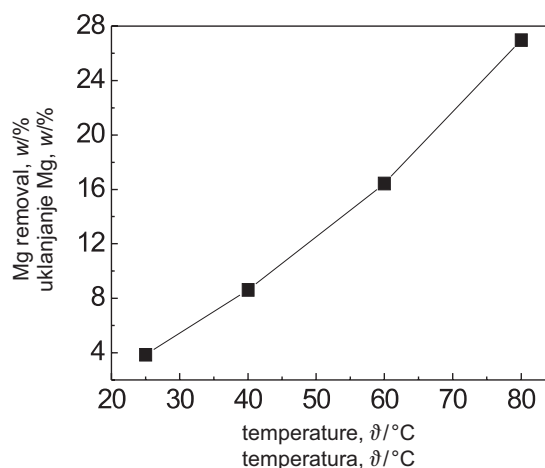


Fig. 4 – Relationship between reaction temperature and removal of magnesium

Slika 4 – Povezanost između temperature reakcije i uklanjanja magnezija

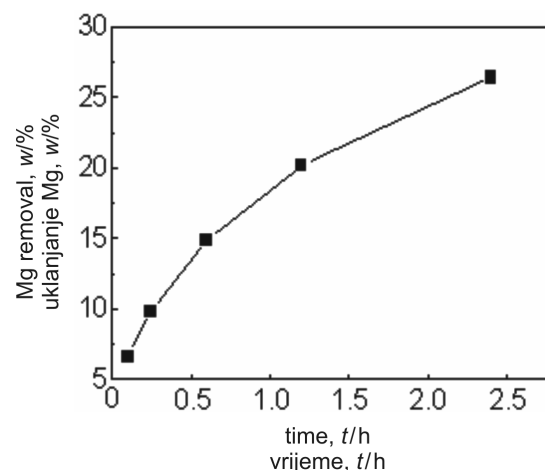


Fig. 5 – Relationship between reaction time and removal of magnesium

Slika 5 – Povezanost između vremena reakcije i uklanjanja magnezija

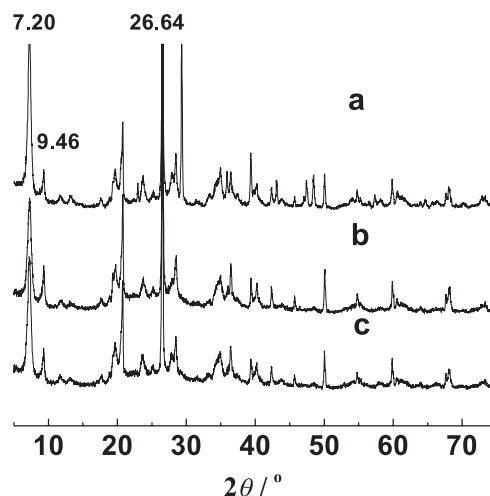


Fig. 6 – XRD patterns of natural sepiolite and modified sepiolite

Slika 6 – Rendgenski difraktogram prirodnog i modificiranog sepiolita

Table 2 – Specific surface area and pore specific volume of sepiolite and kaolin

Tablica 2 – Specifična površina i volumen pora sepiolita i kaolina

Items Stavke	Modified sepiolite Modificirani sepiolit	Sepiolite Sepiolit	Kaolin Kaolin
Specific surface area, $\text{m}^2 \text{g}^{-1}$ specifična površina, $\text{m}^2 \text{g}^{-1}$	110.318	106.988	46.012
Total pore specific volume, $\text{cm}^3 \text{g}^{-1}$ ukupni volumen pora, $\text{cm}^3 \text{g}^{-1}$	0.3183	0.2941	0.0654
0~3.02 nm pore specific volume, $\text{cm}^3 \text{g}^{-1}$ 0~3.02 nm specifični volumen pora, $\text{cm}^3 \text{g}^{-1}$	0.0159	0.0189	0.0093
3.02~9.94 nm pore specific volume, $\text{cm}^3 \text{g}^{-1}$ 3.02~9.94 nm specifični volumen pora, $\text{cm}^3 \text{g}^{-1}$	0.0469	0.0480	0.0276
> 9.94 nm pore specific volume, $\text{cm}^3 \text{g}^{-1}$ > 9.94 nm specifični volumen pora, $\text{cm}^3 \text{g}^{-1}$	0.2554	0.2272	0.0285

Table 3 – Chemical composition of catalysts w, %

Tablica 3 – Kemijski sastav katalizatora, w/%

Catalyst Katalizator	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{Fe}_2\text{O}_3$	$\text{Na}_2\text{O}$	$\text{MgO}$
Catalyst A Katalizator A	32.12	47.14	0.60	0.22	—
Catalyst B Katalizator B	23.06	53.49	0.29	0.21	2.41
Catalyst C Katalizator C	27.36	48.23	0.45	0.23	1.17

Catalyst A is the base catalyst with kaolin as matrix, catalyst B is prepared by modified sepiolite replacing kaolin as matrix, catalyst C is prepared by modified sepiolite and kaolin as matrix. As shown in Table 3,  $\text{Na}_2\text{O}$  content of three catalysts is rather similar, the silica content of catalyst B is the highest, alumina and iron oxide content is the lowest. At the same time, catalyst B and catalyst C have certain magnesium oxide content due to the modified sepiolite added to the catalyst, magnesium oxide is an ideal component for heavy metal resistance.

#### Surface area and pore distribution of catalyst

Solid catalysts are porous, and their surface area and pore structure not only affect the catalytic activity and selectivity, but also the mechanical strength, life, and so on. Clay is the important composition in the semi-synthetic catalyst, in theory, the pore structure of the clay affecting the performance of the catalyst is inevitable and direct. The surface area and pore size distribution of three catalysts are shown in Table 4. Fig. 7–9 show the pore size distribution of catalysts.

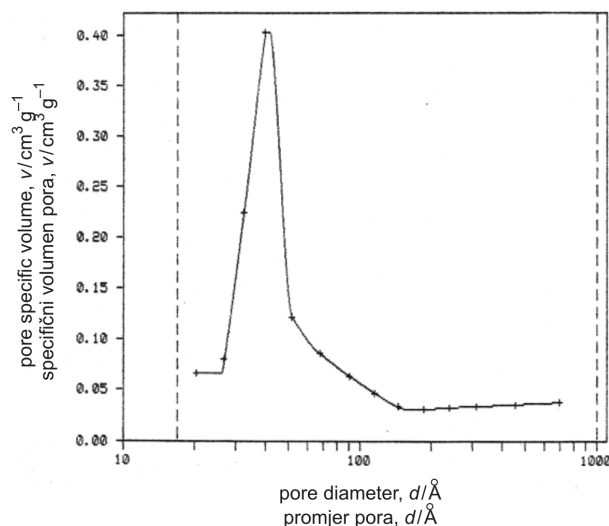


Fig. 7 – Pore size distribution of catalyst A

Slika 7 – Raspodjela volumena pora katalizatora A

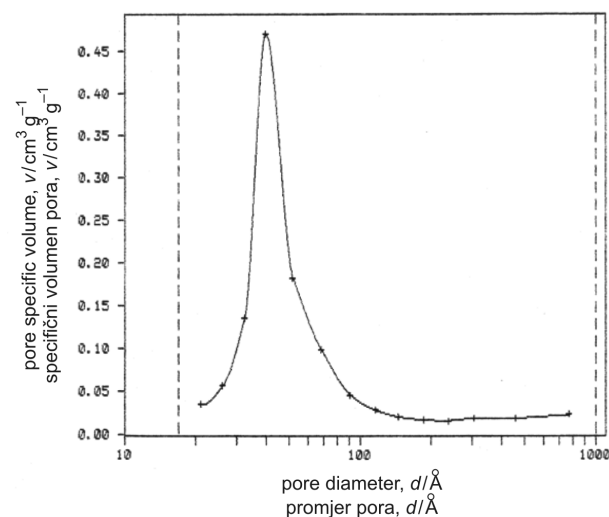


Fig. 8 – Pore size distribution of catalyst B

Slika 8 – Raspodjela volumena pora katalizatora B

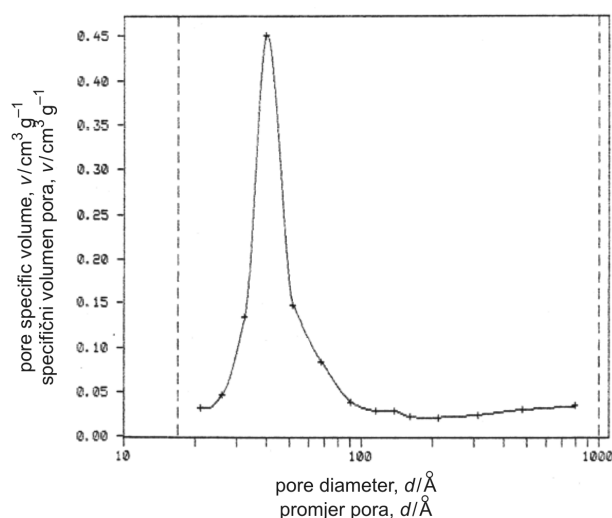


Fig. 9 – Pore size distribution of catalyst C

Slika 9 – Raspodjela volumena pora katalizatora C

Table 4 – Specific surface area and pore specific volume of catalysts

Tabela 4 – Specifična površina i volumen pora katalizatora

Items Stavke	Catalyst A Katalizator A	Catalyst B Katalizator B	Catalyst C Katalizator C
Specific surface area, $\text{m}^2 \text{g}^{-1}$ Specifična površina, $\text{m}^2 \text{g}^{-1}$	242.53	270.02	262.21
Total pore specific volume, $\text{cm}^3 \text{g}^{-1}$ Ukupni specifični volumen pora, $\text{cm}^3 \text{g}^{-1}$	0.15	0.22	0.17
0~2.99 nm pore specific volume, $\text{cm}^3 \text{g}^{-1}$ 0~2.99 nm specifični volumen pora, $\text{cm}^3 \text{g}^{-1}$	0.0075	0.0087	0.0152
2.99~10.6 nm pore specific volume, $\text{cm}^3 \text{g}^{-1}$ 2.99~10.6 nm specifični volumen pora, $\text{cm}^3 \text{g}^{-1}$	0.1121	0.1880	0.1189
>10.6 nm pore specific volume, $\text{cm}^3 \text{g}^{-1}$ >10.6 nm specifični volumen pora, $\text{cm}^3 \text{g}^{-1}$		0.0230	0.0358

As can be seen from Table 4, compared with the base catalyst A, the specific surface area of catalyst B increases  $s = 28 \text{ m}^2 \text{g}^{-1}$ , pore specific volume increases  $s = 0.07 \text{ mL g}^{-1}$ ; the specific surface area of C catalyst increases  $s = 20 \text{ m}^2 \text{g}^{-1}$ , pore specific volume increases  $0.02 \text{ mL g}^{-1}$ . These results show that modified sepiolite as matrix of FCC catalyst could improve the special surface area and pore specific volume of catalysts. From pore size distribution of the results, pore specific volume of 2.99 ~ 10.6 nm range of aperture size of the catalyst B is the biggest, indicating that modified sepiolite as a matrix could improve the pore specific volume of mesopores of catalyst and improve the diffusivity of intermediate products, particularly suitable for preparation of heavy oil cracking FCC catalyst.

#### Prevention of poisoning by heavy metals

Because of the different behavior of nickel and vanadium, strategies for their passivation can differ significantly. The oxide form of nickel is more likely to remain immobile and embed itself in an oxide structure such as alumina forming solid state compounds such as spinel. Vanadium on the other hand is best passivated by adding metal oxides which will readily form metal vanadate. Metal vanadate formation reduces metal mobility while at the same time prevents the vanadium from catalyzing dehydrogenation reactions. Alkaline earth compound can perform this task.<sup>25–26</sup>

Sepiolite contains the magnesium oxide components, and through the appropriate acid modification, it contains the

appropriate amount of magnesium oxide to reduce the heavy metal concentration.

The catalysts were artificially impregnated with  $w = 0.3 \%$  nickel and  $w = 0.5 \%$  vanadium, and then steamed at  $800 \text{ C}^\circ$  for 17 h in 100 % steam. The crystallinity retention of catalysts is separately summarized in Table 5.

From Table 5, it is worthy to note that under high levels of contaminant metals, compared with the base catalyst A, the crystallinity of catalyst B has increased 4.4 units, and the crystallinity of catalyst C has increased 2.1 units. This indicates that modified sepiolite as a matrix of FCC catalyst can observably enhance anti-heavy metal performance.

#### Catalytic test

The performances of the catalysts were tested in a FFB reactor. The cracking selectivity results are summarized in Table 6.

Table 5 – Crystallinity of fresh catalysts and contaminated catalysts

Tabela 5 – Kristaliničnost čistih i kontaminiranih katalizatora

Catalyst Katalizator	Crystallinity of fresh catalyst, % Kristaliničnost svježeg katalizatora, %	Crystallinity of contaminated catalyst, % Kristaliničnost kontaminiranog katalizatora, %
Catalyst A Katalizator A	27.23	17.12
Catalyst B Katalizator B	28.19	21.59
Catalyst C Katalizator C	27.45	19.26

Table 6 – Evaluation results in small-scale fixed fluidized bed reactor

Tabela 6 – Rezultati evaluacije reaktora umanjene mjerila u fluidiziranom sloju

Catalyst Katalizator	Catalyst A Katalizator A	Catalyst B Katalizator B	Catalyst C Katalizator C
Product yield (%) Prinos produkta (%)			
Dry gas suhi plin	2.18	2.03	2.11
LPG	16.62	15.32	15.87
$\text{C}^5$ +gasoline $\text{C}^5$ +benzin	47.66	47.97	47.33
LCO	17.29	19.76	18.79
HCO	7.73	6.97	7.57
Coke Koks	8.52	7.95	8.34
Conversion (%) Konverzija (%)	74.98	73.27	73.65
Light oil, w/% Lako ulje, w/%	64.95	67.73	66.01

From Table 6, it is worthy to note that under high levels of contaminant metals, light oil and LCO of catalyst B and catalyst C increase; dry gas, coke and HCO decrease. In addition, catalytic properties of catalyst B are the best.

In summary, the catalyst that modified sepiolite as matrix has a good advantage in bottoms conversion and higher performance of nickel and vanadium passivation.

## Conclusions

(1) In the process of acid modification of sepiolite, the removal of magnesium, specific surface area, and pore specific volume of sepiolite are improved with increasing acid concentration, treating time and treating temperature.

(2) The suitable acid modification conditions of sepiolite for FCC catalysts are 80 °C for 2.5 h with 1 mol L<sup>-1</sup> HCl acid, under which the rate of magnesium removal is 27 %.

(3) With the modified sepiolite as active matrix of FCC catalysts, the specific surface area, pore specific volume and mesopore pore specific volume of the catalysts can increase effectively, and the catalysts exhibit excellent heavy-metal resistance and better cracking properties as a result of the introduction of magnesium oxide from the modified sepiolite.

## ACKNOWLEDGEMENTS

Financial support was provided by the item of National Natural Science Foundation of China (No.20871045), and the major item of Scientific Research of Hunan Province Education Department (No. 08A027)

## List of symbols

### Popis simbola

$c$	– concentration, mol l <sup>-1</sup> – koncentracija, mol l <sup>-1</sup>
$d$	– diameter, Å (1 Å = 0.1 nm) – promjer, Å (1 Å = 0,1 nm)
$s$	– specific surface area, m <sup>2</sup> g <sup>-1</sup> – specifična površina, m <sup>2</sup> g <sup>-1</sup>
$t$	– time, h – vrijeme, h
$U$	– voltage, kV – napon, kV
$V$	– pore specific volume, cm <sup>3</sup> g <sup>-1</sup> – specifični volumen pora, cm <sup>3</sup> g <sup>-1</sup>
$w$	– mass fraction, % – maseni udjel, %
$\zeta$	– mass ratio, $m_1 m_2^{-1}$ – maseni omjer, $m_1 m_2^{-1}$
$\theta$	– Bragg angle, ° – Braggov kut, °

$\vartheta$	– Celsius temperature, °C – Celsiusova temperatura, °C
$\lambda$	– wavelength, nm – valna duljina, nm

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## SAŽETAK

## Mogućnost korištenja sepiolita kao matrice katalizatora FCC

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U radu je istraživano djelovanje koncentracije kiseline, vremena i temperature modificiranja na uklanjanje magnezija iz sepiolita, kao i na djelotvornost aktivne matrice FCC-katalizatora pripremljenog korištenjem solne, sumporne i dušične kiseline. Modificirani sepiolit je bio karakteriziran rendgenskom difrakcijom praškastih uzoraka, pretražnom elektronskom mikroskopijom te adsorpcijom N<sub>2</sub>. Dobiveni rezultati ukazuju na povećanje uklanjanja magnezija, specifične površine i volumena pora modificiranog sepiolita s povišenjem koncentracije kiseline, vremena i temperature reakcije. Uvjeti pogodni za kiselinsko modificiranje sepiolita jesu 80 °C tijekom 2,5 sata te  $c(\text{HCl}) = 1,0 \text{ mol dm}^{-3}$ , pri čemu se postiže 27-postotno uklanjanje magnezija. Korištenjem modificiranog sepiolita kao aktivne matrice FCC katalizatora, povećana je specifična površina, volumen pora te volumen mezopora katalizatora. Također, tako pripremljeni katalizatori iskazuju odličnu otpornost na kontaminaciju teškim kovinama te bolja kreirajuća svojstva kao posljedicu uklanjanja magnezijeva oksida iz sepiolita.

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Prispjelo 14. travnja 2009.  
Prihvaćeno 5. listopada 2009.