

Microwave-Assisted Adsorptive Desulfurization of Model Diesel Fuel Using Synthesized Microporous Rare Earth Metal-Doped Zeolite Y

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Abstract: The microwave-assisted adsorptive desulfurization of model fuel (thiophene in n-heptane) was investigated using a synthesized rare earth metal-doped zeolite Y (RE Y). Crystallinity of the synthesized zeolite was 89.5%, the silicon/aluminium (Si/Al) molar ratio was 5.2, the Brunauer-Emmett-Teller (BET) surface area was 980.9 m²/g, and the pore volume and diameter was 0.3494 cm³/g and 1.425 nm, respectively. The results showed that the microwave reactor could be used to enhance the adsorptive desulfurization process with best efficiency of 75% at reaction conditions of 100 °C and 15 minutes. The high desulfurization effect was likely due to the higher efficiency impact of microwave energy in the interaction between sulfur in thiophene and HO-La(OSiAl).

Keywords: Desulfurization; Thiophene; Microwave; Diesel; Zeolite RE Y.

إزالة الكبريت بالامتزاز من نموذج وقود الديزل عن طريق توليف المسام الصغيرة للزيوليت RE Y بمساعدة الميكروويف

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ملخص: تم فحص إزالة الكبريت بالامتزاز لنموذج وقود (ثيوفين في ن- هيبتان) باستخدام توليف الزيوليت RE Y (معادن الأرض النادرة المطعمة بالزيوليت Y). التبلور للزيوليت المولف كان 89.5%. نسبة المولارية في Si/Al كانت 5.2. وكان مساحة BET 980.9 متر مربع لكل جرام وكان حجم المسام 0.3494 سنتيمتر مكعب لكل جرام وبقطر 1.425 نانو متر. أظهرت النتائج أن تفاعل الميكروويف يمكن استخدامه لتحسين عملية الامتزاز لإزالة الكبريت بأفضل كفاءة 75% عند شروط تفاعل 100 درجة مئوية و 15 دقيقة. تأثير إزالة الكبريت الكبير كان غالباً بسبب تأثير الكفاءة العالية لطاقة الميكروويف في التفاعل بين الكبريت في الثيوفين و HO-La(OSiAl).

كلمات مفتاحية: إزالة الكبريت، ثيوفين، الميكروويف، الديزل، الزيوليت RE Y.

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1. Introduction

Diesel fuel has become one of the most popular energy sources for driving industrial, domestic, and transportation engines due to its high efficiency (Dasgupta *et al.* 2013). The exponentially growing demand for diesel has increasingly heightened the environmental concerns arising from environmental pollution caused by diesel engine exhaust (Hans *et al.* 1989; Lin *et al.* 2009; Zhang *et al.* 2001). Diesel engine exhaust contains high levels of sulfur-containing gasses in the form of sulphur oxides (SO_x), which have been identified as detrimental to human health and the environment. These detrimental effects include adverse reactions in the human respiratory system, contributions to the greenhouse effect, and acid rain. Most developed countries in the world such as the USA, Canada, and Japan, and various countries in Europe have enacted environmental regulatory policies to control sulphur levels in the diesel used by highway vehicles and restrict emissions to a bare minimum. In the USA, for instance, the Environmental Protection Agency (USEPA) has mandated a maximum sulphur content of 15 ppm in highway diesel since 2006 and, in Europe, a maximum sulphur content of 10 ppm was instituted as the EU-wide limit for diesel used in road transportation (Dasgupta *et al.* 2013).

Due to these increasingly stringent regulations, the desulfurization of diesel fuel has become an important research subject. An earlier industrial technique for the desulfurization of diesel was the hydro-desulfurization (HDS) process (Babich and Moulijn 2003; Duarte *et al.* 2011; Zannikos *et al.* 1995). In HDS, sulfur-containing compounds were converted to hydrogen sulfide (H₂S) and other hydrocarbons via extreme temperature and pressure conditions using hydrogen as the converter. Therefore, the HDS process was not only very expensive but was also environmentally dangerous due to the highly inflammable nature of hydrogen. Recently, several alternative, greener desulfurization processes have been proposed (Ahmad *et al.* 2009; Marin-Rosas *et al.* 2010; Salem and Hamid 1997; Seredych and Bandosz 2010; Shakirullah *et al.* 2009; Velu *et al.* 2003; Weitkamp *et al.* 1991).

Some of the techniques reported include extractive desulfurization (EDS), selective adsorptive desulfurization (SAD) (Subhan *et al.* 2012), and oxidative desulfurization (ODS) (Dharaskar *et al.* 2014; Lü *et al.* 2014; Wei *et al.* 2009). Some of these techniques have limitations. For instance, the extractant used in the ODS and EDS processes are usually flammable and contain volatile organic compounds (VOCs) which are also known for their environmental and safety impacts (Gao *et al.* 2010; Gui *et al.* 2010). The adsorption-based approaches appear particularly attractive due to their simpler flow sheets and lower hydrogen requirements (Ahmad *et al.* 2014; Dasgupta *et al.* 2013; Hussain *et al.* 2012; Sisani *et al.* 2014).

Due to the possibility of selective heating, microwave energy has attracted considerable attention in the field of desulfurization, where it has been found that microwave heating makes the process more effective. With microwaves, energy can be delivered to reacting molecules at a much greater rate compared to conventional heating, which is a more efficient way to heat since microwaves allow faster and more uniform heating. Ibe *et al.* (2007) applied microwave heating to facilitate the desulfurization of poisoned mono-nitrogen oxide (NO_x) storage-reduction (NSR) catalysts. They concluded that high catalyst temperatures did not need to be reached in order to achieve the desorption of sulfur species. Therefore, the use of microwave heating provided an efficient way to promote the regeneration of the NSR catalysts. Wei *et al.* (2009) investigated the simultaneous desulfurization and denitrification from stimulated flue gas by a microwave reactor with potassium permanganate and zeolite. They found that the microwave reactor could be used in the oxidation of sulphur dioxide (SO₂) to sulfate with a desulfurization efficiency of 96.8%. The addition of zeolite to microwave potassium permanganate increased the microwave removal efficiency of SO₂ from 16.5% to 43.5%. Microwave-assisted oxidative desulfurization of sour natural gas condensate via a combination of sulfuric and nitric acids was investigated by Moaseri *et al.* (2014). They found that that the ODS efficiency of sore condensate

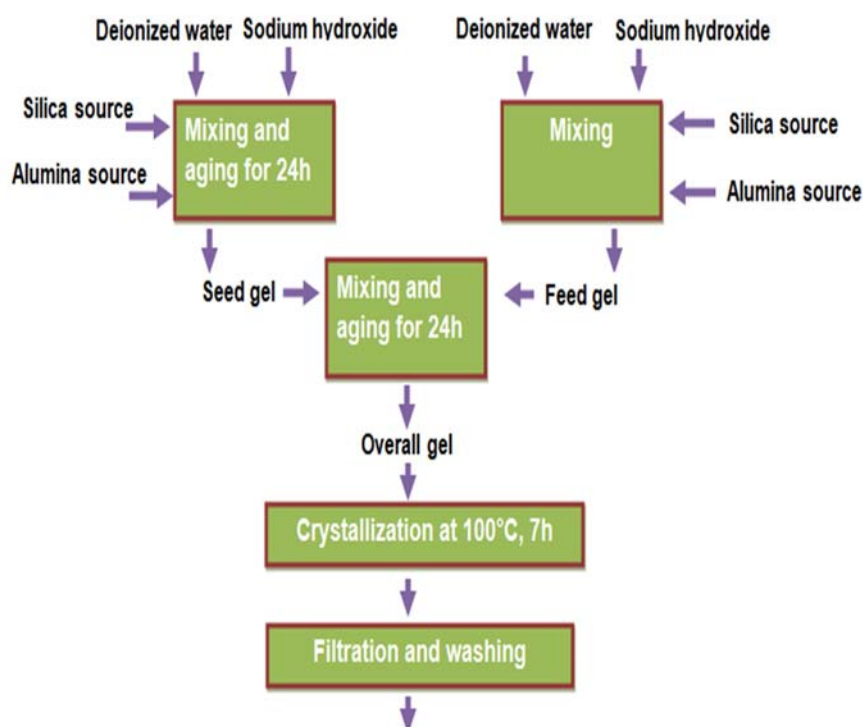


Figure 1. Flow diagram for the synthesis of zeolite Y.

by the combination of sulfuric acid (H₂SO₄) and nitric acid (HNO₃) was improved by 30% in the presence of microwave radiation.

This work was aimed at the desulfurization of model fuel using a cost effective and environmentally friendly technique. The suitability of a synthesized zeolite Y impregnated with lanthanum metal for microwave-assisted selective adsorptive desulfurization of a model fuel was investigated.

2. Materials and Methods

2.1 Synthesis of Zeolite NaY

Zeolite Y in the NaY form was synthesized by adapting the verified method of the Synthesis Commission of the International Zeolite Association (Harry, 2001; Ginter *et al.* 1992). This process involved preparation of seed and feedstock gels, and a general gel using sodium hydroxide, sodium aluminate, aluminium hydroxide, and distilled water. This general gel was crystallized through a template-free, low

temperature crystallization method inside a polypropylene bottle (Fig. 1).

2.2 Transformation to Zeolite RE Y

The synthesized zeolite NaY was protonated by an ion exchange reaction to make zeolite HY. A 1.0 M solution of NH₄Cl was prepared and exchanged with zeolite NaY at 80 °C using a ratio of 10 ml of solution to 1 g of solid and stirred for 20 minutes (Du *et al.* 2013; Gao *et al.* 2012). After the exchange reaction, the slurry was suction filtered using a vacuum pump and washed thoroughly with distilled water, then dried at 110 °C for six hours. The zeolite HY formed was impregnated with rare earth metal (La). The reaction was carried out using an ion exchange wet-impregnation method: a 0.5 M solution of lanthanum chloride (LaCl₃) was prepared and mixed with the protonated zeolite (HY) at 80 °C using a ratio of 12.5 ml of solution to 1 g of solid and stirring the solution for one hour (Du *et al.* 2013; Gao *et al.* 2012). The product was then filtered using a vacuum pump and washed thoroughly with distilled water. The wet cake of zeolite was hydrothermally calcined at

650 °C in air for two hours, resulting in zeolite RE Y.

2.3 Characterization

X-ray diffraction (XRD) patterns were measured using a MiniFlex 600 X-ray diffractometer at 40 kV and 10 mA with Cu K α radiation ($\lambda = 0.15418$ nm,) (Rigaku, Tokyo, Japan). The samples were scanned from 20–80 °C (2θ) at a rate of 0.02 °C/min. X-ray fluorescence (XRF) analysis was carried out using a MiniPal 4 X-ray fluorescence analyser (PANalytical B.V., Almelo, The Netherlands). Fourier transform infrared (FTIR) spectroscopy was applied mainly to study the chemical structure of the catalysts. The infrared spectra of the catalyst samples were measured at wavelengths ranging from 400–4000 cm^{-1} using a Frontier FT-IR spectrometer (PerkinElmer, Waltham, Massachusetts, USA). The morphology of the samples was analyzed with field emission scanning electron microscope JSM-7600F (JEOL, Inc., Tokyo, Japan) and by a TEM-1230 high contrast transmission electron microscope (TEM) (JEOL). The BET surface area and total pore volume were measured using Autosorb-1 nitrogen adsorption apparatus (Quantachrome Instruments, Boynton Beach, Florida, USA). All samples were degassed at 300 °C for four hours prior to the measurement.

2.4 Desulfurization of Model Diesel

The RE Y form of the synthesized zeolite Y was used as the catalyst for the desulfurization of the model diesel using the microwave-assisted technique. The model oil used was prepared by dissolving 200 ppm of thiophene (Sigma-Aldrich, Co., St. Louis, Missouri, USA) in n-heptane (Sigma-Aldrich) and pouring 10 g of model oil into the pressure vessel of a microwave reactor (Milestone, Inc., Sorisole, Italy) and 1 wt% of the RE Y zeolite was also added. The pressure vessel was torqued and inserted in the workstation of the reactor. The reactor's thermocouple was then inserted in the thermowell and the reactor was programmed for variable time and temperature runs. After each run, the reactor content was allowed to cool for 30 minutes. At the end of this process, the torque was loosened, and the vessel content was removed. The resulting mixture was centrifuged at 10,000 rpm for 10 minutes in an Avanti™ J-251 high performance centrifuge (Beckman Coulter, Brea, California, USA). The

resulting raw liquid product was analysed using a Clarus 600C GC/MS system (PerkinElmer).

3. Results and Discussion

3.1 Catalyst Characteristics

Figure 2 shows the XRD patterns of the commercial and synthesized zeolite Y. The zeolite Y peaks could be observed in both XRD patterns at Bragg's angles of 6, 10, 12, 16, 19, 20, 24, 27, 31, and 32° (Harry 2001; Ginter *et al.* 1992; Treacy and Higgins, 2001). The intensities of the characteristic peaks for zeolite Y at Bragg's angles of 6.13, 10.0, 11.8, and 15.5° were 1795, 718, 527 and 693 counts, respectively, for the synthesized zeolite NaY, whereas those of the commercial zeolite Y were 2176, 847, 416, and 698 counts, respectively. Therefore, using the commercial zeolite Y as a reference, and using Equation (1) (Pal *et al.* 2013), the crystallinity of the synthesized zeolite Y was evaluated as 89.5%.

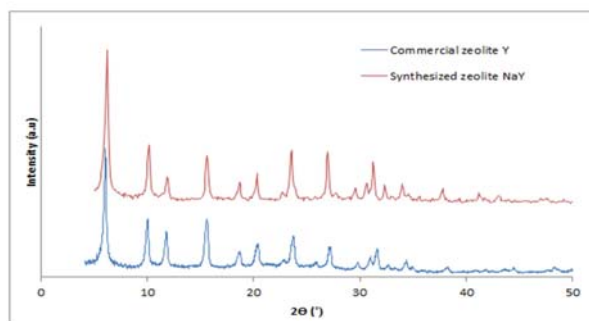


Figure 2. XRD patterns of the synthesized and commercial zeolite Y.

Table 1 presents the XRF result of the synthesized zeolite Y, reflecting the fact that the zeolite contained low concentrations of impurities, with a measurement generally below 1 wt%. The Si/Al molar ratio was 5.2 and the loss on ignition (LOI) was 26 wt%.

Figures 3a–d show the structural morphology of the synthesized zeolite NaY at magnifications of 8,000, 15,000, 30,000, and 45,000, respectively. The macrographs show that the zeolite Y at magnifications of 100,000, 200,000, 300,000 and 400,000 times. The clear boundary shapes of the crystals are very obvious. Although the crystal

$$\text{Crystallinity} = \frac{\text{Intensity of the characteristic XRD peak of the product}}{\text{Intensity of the characteristic peak of the reference XRD pattern}} \times 100 \quad (1)$$

Table 1. Chemical composition of the synthesized zeolite Y.

Metal oxides	Wt %
Al ₂ O ₃	17.98
SiO ₂	54.75
K ₂ O	0.04
CaO	0.27
TiO ₂	0.09
Cr ₂ O ₃	0.04
MnO	0.03
Fe ₂ O ₃	0.3
CuO	ND
LOI	26

ND: Not determined

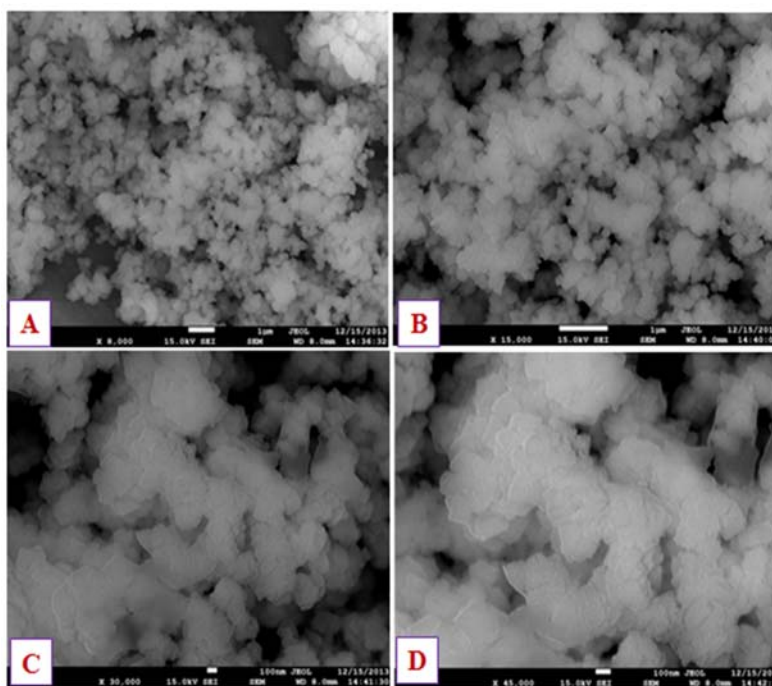


Figure 3. SEM images for the synthesized zeolite NaY at various magnifications: (A) 8000; (B) 15000; (C) 30000 and (D) 45000.

Table 2. BET results for the synthesized zeolite Y.

Sample	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore Diameter (Å)
-synthesized	980.9	0.3494	14.25
Commercial	601.8	0.2500	16.40

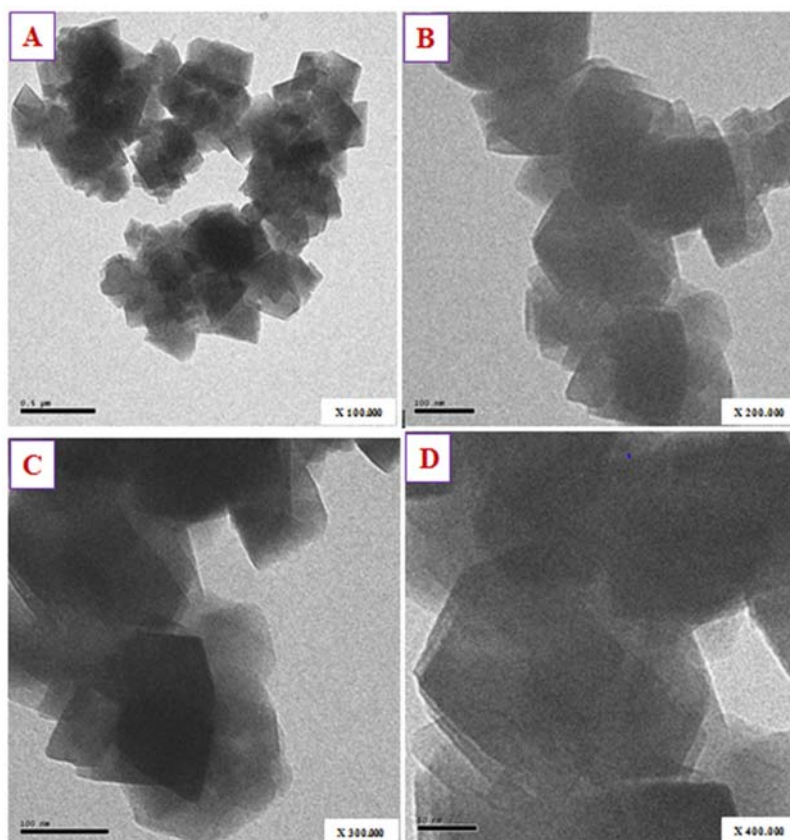


Figure 4. TEM images for the synthesized zeolite NaY at various magnifications: (A) 100000; (B) 200000; (C) 300000 and (D) 400000.

average crystal size was estimated as 200 nm. Figure 4 also shows the TEM images of the synthesized zeolite Y at magnifications of 100,000, 200,000, 300,000 and 400,000 times. The clear boundary shapes of the crystals are very obvious. Although the crystal images overlap extensively, the boundary edges of the unit tetrahedral crystal shape is obvious. The average crystal size was estimated as 200 nm.

BET analysis for the synthesized and commercial zeolite Y shows that the specific surface area of the synthesized zeolite Y was 63%

higher and the pore volume was 40% higher than that of the commercial zeolite Y (Table 2). However, the pore diameter of the commercial zeolite Y was 15% higher than that of the synthesized zeolite Y.

3.2 Desulfurization of Model Diesel

The sulfur reduction at variable reaction times and temperatures for the microwave-assisted desulfurization of model petroleum oil using the prepared zeolite RE Y catalyst is shown in Figs. 5 and 6, respectively. Figure 5 shows the sulfur

reduction for reactions carried out at 100 °C at variable times. The maximum sulfur reduction was observed at 15 minutes when the sulphur reduction was 74%. Figure 6 shows the sulfur reduction for the reactions carried out at 10 minutes for variable temperatures. There was a continuous progressive increase in sulfur reduction throughout the runs, with the maximum sulphur reduction (74%) occurring at 150 °C.

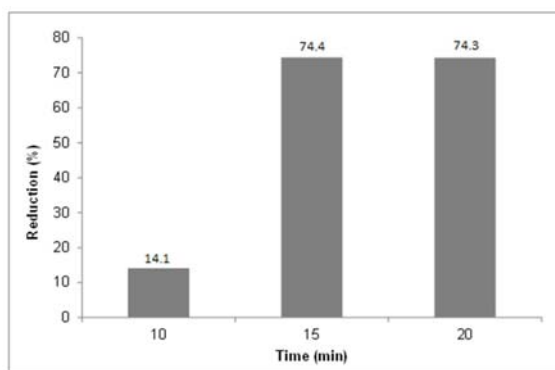


Figure 5. Trend of microwave desulfurization of model diesel at variable time.

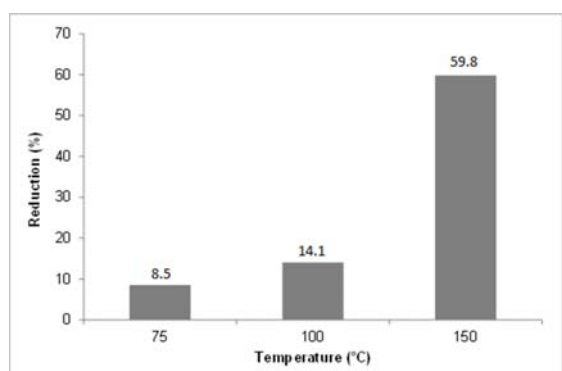


Figure 6. Trend of microwave desulfurization of model diesel at variable temperature.

Figures 7 and 8 show the FTIR spectra of the synthesized catalyst before and after the reaction. The spectra were similar except that the spent zeolite showed the presence of strange bands at wavelengths 1450 and 2930 cm^{-1} for both the variable temperatures and time curves. These bands were due to the adsorption of sulfur (Song *et al.* 2013) and were completely absent in the fresh catalyst spectrum. It could also be observed that for the variable time runs, the sample at 15 minutes showed a larger band area while for the variable temperature runs, the sample at 150 °C

showed the largest band area. Hence, the synthesized catalyst showed a potent effect on the desulfurization of the model diesel fuel, while the FTIR analysis of the catalyst before and after the reactions showed that the mode of desulphurization employed by the catalyst was adsorptive desulfurization. The extent of desulfurization recorded by this work compares closely with the work of Fallah *et al.* (2015), who reported using a different approach.

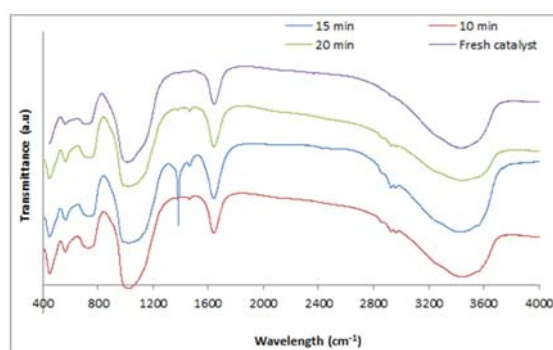


Figure 7. FTIR spectra of the fresh and used catalysts for the desulfurization at variable time.

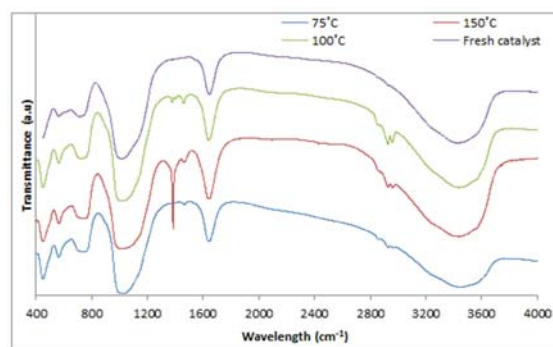


Figure 8. FTIR spectra of the fresh and used catalyst for the desulfurization at variable temperatures.

4. Conclusions

A microporous zeolite Y having 89.5% crystallinity, a 980.9 m^2/g surface area, a 0.3494 cm^3/g pore volume, and a 200 nm crystal size was synthesized. The Si/Al molar ratio of the synthesized zeolite was 5.2 and the LOI was 26%. The synthesized zeolite was effective for adsorptive desulfurization of a model fuel, having the best efficiency of 75% in a microwave-assisted desulfurization carried out at 100 °C for 15 minutes. The high desulfurization effect was likely

due to the higher efficiency impact of microwave energy in the interaction between sulfur in thiophene and HO-La(OSiAl).

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