



# Robust surface-modified Beta zeolite for selective production of lighter fuels by steam-assisted catalytic cracking from heavy oil

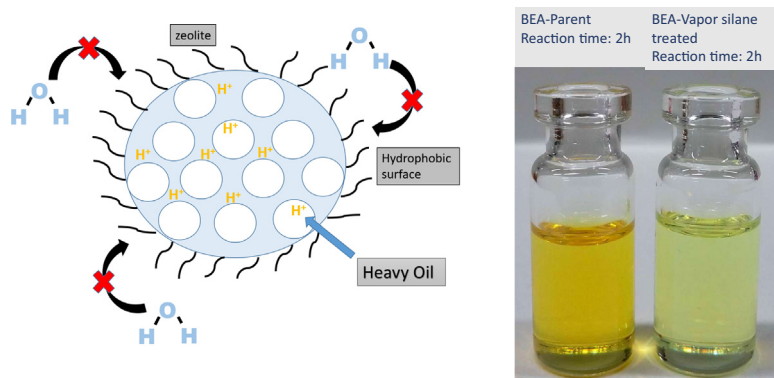


Umer Khalil<sup>a</sup>, Oki Muraza<sup>a,\*</sup>, Hisaki Kondoh<sup>b</sup>, Gaku Watanabe<sup>b</sup>, Yuta Nakasaka<sup>b</sup>, Adnan Al-Amer<sup>a</sup>, Takao Masuda<sup>b</sup>

<sup>a</sup> Center of Excellence in Nanotechnology & Chemical Engineering Department, King Fahd University of Petroleum and Minerals, Saudi Arabia

<sup>b</sup> Division of Chemical Process Engineering, Faculty of Engineering, Hokkaido University, N13 W8, Kita-ku, Sapporo, Hokkaido 060-8628, Japan

## GRAPHICAL ABSTRACT



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## ABSTRACT

Production of lighter hydrocarbons were maximized by steam-assisted catalytic cracking of heavy oil over silane treated Beta catalysts. Steaming environment may cause dealumination of zeolites and affect the stability of zeolites. Herein, we improved the hydrophobicity and stability of the Beta zeolite catalyst ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 150$ ) by modifying its surface using triphenyl silane through vapor phase deposition technique. Parent Beta and silane treated Beta catalysts were tested in fixed-bed flow reactor for steam-assisted catalytic cracking of atmospheric residue. It was found that the modified Beta catalyst retained its crystallinity and phase purity after reaction. Moreover, coke formation was also reduced significantly over silane treated Beta catalysts. This indicates the increase in the stability of catalysts. Furthermore, the yields of gases, gasoline ( $\text{C}_7\text{--C}_{13}$ ) and gas oil ( $\text{C}_{14}\text{--C}_{20}$ ) over a silane treated Beta zeolite catalyst were 11.6 mol%, 55.7 mol% and 3.7 mol% respectively for 2 h reaction time.

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## 1. Introduction

Recovery of unconventional fossil fuels became more important in the last few decades as conventional fossil reserves will not last

forever. Proven reserves which include mostly conventional crude oil are approximately 1.47 trillion bbl and according to a recent study these reserves will sustain up to next forty years at the current level of production [1]. Therefore, developing new technologies to utilize unconventional oil resources such as shale oil, tar sand and extra heavy oil is on demand. Hydrous pyrolysis or also known as aquathermolysis, is referred to a cracking of hydrocarbon

\* Corresponding author.

E-mail address: [omuraza@kfupm.edu.sa](mailto:omuraza@kfupm.edu.sa) (O. Muraza).

in presence of water. Although this concept originates from the formation of crude oil from kerogen through catagenesis but this concept has given a commercial application when the first superheated steam was used to extract heavy oil from wells [2]. Thermal cracking in the presence of water was first named as aquathermolysis by Hyne et al. [3].

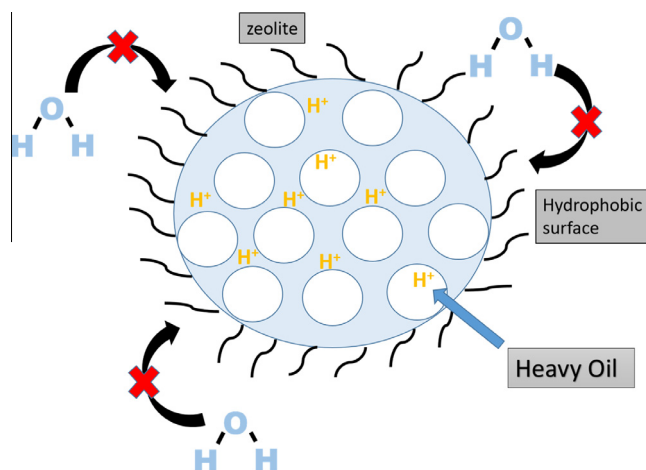
It was reported that thermal cracking in the presence of steam decreases the coke formation and increase the production of lighter olefins [4–6]. Zeolite catalysts are found to be active and stable acid catalysts for cracking reactions. Cracking of n-hexane over ZSM-5 catalyst in the presence of steam showed a decrease in amount of coke formed and also increased in lighter yield [7]. Coke formation in heavy oil cracking is more severe as heavy oil contains heavy metals, which can poisoned catalysts very rapidly. Hence, steam catalytic cracking of heavy oil can minimize coke formation and also increase lighter component yield. It was also found that zeolite catalysts lead to dealumination in the steaming environment [8]. Dealumination decreases acidity and eventually causes irreversible deactivation. The need to upgrade heavy oil and biomass in the presence of water or steam has stimulated numerous research activities to develop highly stable catalysts in an aqueous environment [2,9]. Caeiro et al. studied the effect of the phosphorus addition on the hydrothermal stability of H-MFI in steam environment [10]. Impregnation of different Si/Al ratios of ZSM-5 zeolites with phosphorus in  $H_3PO_4$  form was reported by Blasco et al. [11]. Hydrophobic siliceous ferrierite was reported, for instance, by the introduction of pyridine and sodium fluoride [12]. Organosilane treated zeolite also showed stable structure after exposure to hot water [13,14].

The objective of this work was to develop hydrophobic Beta (BEA) zeolite catalysts using organosilane groups as surface modifier reagents. This work has been focused on steam-assisted cracking of heavy oil (atmospheric residue) to enhance the lighter component yield over silane treated Beta zeolite catalyst. Beta zeolite has three-dimensional 12-ring framework structure with elliptical opening  $0.76 \times 0.64$  nm. Large pore BEA zeolite catalyst with  $SiO_2/Al_2O_3$  of 150 was treated with triphenyl silane to make its outer surface water resistive. Silane compound with kinetic diameter larger than the pore size of BEA zeolite was deposited on the surface through vapor chemical deposition technique. Steaming environment decreased amount of coke while de-alumination prevented by silane treatment of the external surface of BEA zeolite. Stability and yield of lighter component was reported after 2 h and 4 h reaction tests. Combined effect of steam and catalyst modification was studied on the cracking of heavy oil to get lighter component yield. Previously, metal oxide catalysts have been extensively used for cracking of heavy oil in the presence of steam where steam was used to make active sites on metal oxides [15–17]. It was observed that gaseous product constituted high percentage of  $H_2$  and  $CO_2$  which indicates large amount of coke [16]. In this study zeolites were preferred over metal oxides because of their high activity, crystallinity and stability. Coke formation and dealumination problems associated with zeolites were overcome using steam and surface modification of zeolite catalysts. Moreover zeolite catalysts were found to be more selective toward olefins unlike metal oxides. Scheme 1 shows the overview of hydrophobic zeolite in heavy oil upgrading.

## 2. Experimental

### 2.1. Surface modification of catalyst using silane compounds

Beta zeolite catalyst (BEA) with  $SiO_2/Al_2O_3$  150 was provided by Catalysis Society of Japan. Firstly, BEA catalyst was ion exchanged using conventional method [18,19], typically, 1 g of catalyst was



**Scheme 1.** Schematic overview of hydrophobic zeolite in heavy oil upgrading.

suspended in 20 g of 2 M ammonium nitrate ( $NH_4(NO_3)$ ) solution and the solution was heated under stirring for 3 h. The final solution was centrifuged to remove ( $NH_4(NO_3)$ ) solution from the catalyst. This procedure was repeated thrice. Finally  $NH_4^+$ -BEA zeolite was dried at 373 K for 12 h.  $NH_4^+$ -BEA was first pelletized to get ca. 0.3 mm in diameter pellets and then calcined at 823 K for 3 h in an air stream. After calcinations, H-BEA was used as BEA-parent catalyst in cracking reactions. While for BEA-silane treated samples, the pelletized  $NH_4^+$ -BEA were used directly in silane treatment. Triphenyl silane was used as a silane reagent.  $NH_4^+$ -BEA pellets in a packed bed reactor were first air calcined at 823 K, then H-BEA zeolite was exposed to the vapor of triphenyl silane at 373–393 K in a  $N_2$  stream. After 1 h feed of silane was stopped to remove the physically adsorb silane compounds on surface. Zeolite was brought in the contact with silane compound vapor twice [20]. Finally modified catalyst was used as BEA-silane treated catalyst in the heavy oil cracking reaction.

### 2.2. Characterization of catalyst

All BEA zeolite catalysts structure and phase purity was confirmed by using X-ray diffractometer (Ultima IV, Rigaku). Texture properties of catalysts were obtained using an  $N_2$  adsorption isotherm (Belsorp mini, BEL Japan). Acidity was measured using the  $NH_3$ -TPD method. A 1.0%  $NH_3$  was used as the carrier gas at 373–823 K temperature range and  $5 K min^{-1}$  heating rate was maintained. To establish measurement under complete adsorption equilibrium conditions,  $NH_3$  molecules desorption from acid sites of zeolite was performed under a 1.0%  $NH_3$ -He atmosphere [21]. Brønsted acid sites (BAS) and Lewis acid sites (LAS) were measured using Fourier transform infrared (FT-IR) equipped with pyridine adsorption support. Diffuse reflectance infrared Fourier transform (DRIFT) spectrometer with mercury cadmium telluride (MCT) detector (FT/IR-4100, JASCO) was used. A total of 200 Scans were averaged for each spectrum. Sample was pre-treated in vacuum at 723 K for 12 h and then pyridine was adsorbed onto the sample at 373 K for 2 h. Nitrogen was introduced to remove physically adsorbed pyridine at 373 K for 0.5 h. Lastly, sample acidity was measured via FT-IR analysis at 373 K [22].

### 2.3. Steam assisted catalytic cracking of heavy oil

Fixed-bed type reactor was used for cracking of atmospheric residue (AR) with steam at a reaction temperature of 743 K and a pressure of 1 atm for 2 and 4 h. Reactor setup is shown in Fig. 1. AR was diluted with toluene at 10% to reduce its viscosity. Toluene

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