



## Catalytic cracking of polypropylene using aluminosilicate catalysts



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### ABSTRACT

The microporous and mesoporous structured aluminosilicate materials MCM-22 and SBA-15, respectively, were successfully synthesized by hydrothermal treatment and then modified to H-Al derivatives. All prepared catalysts were investigated for their physicochemical features, including the surface area, pore volume and acidity, using powder X-ray diffraction, N<sub>2</sub> adsorption-desorption, <sup>27</sup>Al NMR spectroscopy, temperature programmed desorption of ammonia and scanning electron microscopy. The derived catalysts were then utilized for the catalytic cracking of polypropylene (PP) in a batch reactor at atmospheric pressure, 350–400 °C for 30 min with a catalyst loading of 10 wt% (of the PP mass) and a nitrogen flow of 20 mL min<sup>-1</sup>. Under these conditions, the PP conversion value was over 97% and 80% for the acid H-Al-SBA-15 and H-MCM-22 catalysts, respectively. For the mesoporous H-Al-SBA-15 catalyst, the major product was a liquid fraction (mostly low temperature distillate oil), such as C<sub>7</sub>–C<sub>8</sub> hydrocarbons, with a boiling point similar to that of gasoline. With the microporous H-MCM-22 catalyst, the main products were gases that principally consisted of *n*-butane, C<sub>5</sub><sup>+</sup> hydrocarbons and propene.

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### 1. Introduction

Polypropylene (PP), a typical thermoplastic polymer, is ubiquitously present in every field of our life, and has been applied in housewares, furniture, automobile and appliance parts, packaging products, textile and stationery. However, the increased use of PP has concurrently led to the problem of increasing levels of PP waste, which is already a serious environmental problem. Therefore, the recycling of PP waste is necessary to reduce the problem of its disposal. Plastic recycling is typically classified into the two categories of physical and chemical processes. In the chemical recycling process, plastic wastes are cracked under a high temperature [1–3], including thermal and catalytic cracking methods [4]. Thermal cracking has been investigated over a high operating temperature, typically more than 500 °C and even up to 900 °C [5,6]. Therefore, the addition of a suitable catalyst is of interest to reduce the otherwise required high reaction temperature. Another advantage of the catalytic cracking process is it can occur at a lower degradation temperature compared to the thermal cracking process [7]. After the cracking procedure, the gas, liquid fuel or raw chemical materials are obtained as the final products. Several materials have previously been evaluated as catalysts for plastic cracking,

including clay, amorphous alumina-silica (Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>), zeolite and mesoporous catalysts [8–15].

The microporous zeolite catalysts have excellent properties for polymer degradation, as their strong acidity can break carbon-carbon bonds [16,17]. Accordingly, several zeolite types have been utilized in the cracking of polymers, such as ZSM-5, BEA, zeolite Y and clinoptilolite. In addition, the zeolite-type MCM-22 material, which consists of MWW layers with a medium-pore size, has attracted a considerable amount of attention in the catalysis community, such as in the alkylation of benzene, dehydration of glycerol and cracking reactions [18–20]. However, the use of MCM-22 catalyst in the pyrolysis of polymers is poorly researched. Nevertheless, the small pore size of zeolite is limiting as it hinders the access of bulky molecules to the acid sites located inside the channel. Also, coke is deposited inside the pores and on the surface of the catalyst, which then results in pore closure and catalyst deactivation. That said, in the polymer cracking process, these zeolite catalysts have provided a high selectivity for gas products [8]. Alternatively, mesoporous materials have been developed for the catalytic degradation of polymers like PP with a high product selectivity for liquid products with properties like gasoline [21,22]. However, these previous works, which have performed the catalytic polymer cracking in a semi-batch reactor, have still used the mesoporous catalyst at a high temperature of around 400–500 °C [6,9]. The pyrolysis of a mixed polymer waste has been determined over zeolite and non-zeolite catalyst types, such as ZSM-5 and

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MCM-41, respectively, where the zeolite catalyst exhibited a higher yield of volatile products than the non-zeolite material, but the non-zeolite MCM-41 catalyst, with its large mesopores and weaker acid sites, provided a higher olefin product mixture yield with a wide carbon number distribution [8]. Furthermore, kaolinite and  $\text{Al}_2\text{O}_3\text{-SiO}_2$  have been used in the degradation of PP at 400–550 °C in a semi-batch reactor, where the  $\text{Al}_2\text{O}_3\text{-SiO}_2$  catalyst decreased the reaction time and increased the liquid product yield. In addition, the  $\text{Al}_2\text{O}_3\text{-SiO}_2$  catalyst showed a better activity than the kaolinite catalyst, with a maximum oil yield of 91% and 89.5%, respectively [9]. On the other hand, the mesoporous SBA-15 is widely used as a catalyst in several chemical reactions. This material has a large surface area and pore sizes between 20 and 300 Å with a large pore diameter. However, SBA-15 is a pure siliceous form with a low acidity level compared to microporous materials like zeolite. Therefore, an increased acidity level of mesoporous materials has been developed by the addition of aluminum ions into the framework [16]. The degradation of PP using aluminum loaded MCM-41 and SBA-15 catalysts led to the heavier molecules being further degraded in the presence of these catalysts to produce lighter hydrocarbons of  $<C_{14}$  [21].

An interesting alternative process for degrading plastic waste is based on the use of solid-acid porous catalysts, which can be operated under a lower reaction temperature for a shorter time. Therefore, this research reported here investigated the effects of the acid catalyst type and cracking temperature on PP cracking using the mesoporous Al-SBA-15 and microporous MCM-22 materials as catalysts. Each material type was prepared from two different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios, and they were compared as catalysts under the same reaction condition for their catalytic efficiency in terms of the substrate conversion level and the product yield and selectivity. The final products were categorized as liquid, gas and residue phases, with the composition of each phase then further characterized. The product selectivity was found to depend on the catalyst type. Their catalytic activity is discussed in terms of the relationship between the physicochemical properties of the catalyst and the cracking performance.

## 2. Experimental

### 2.1. Synthesis of catalysts

The mesoporous SBA-15 was synthesized by hydrothermal treatment using the triblock copolymer Pluronic P123 ( $\text{PEO}_{20}\text{-PPO}_{70}\text{-PEO}_{20}$ , average molecular weight = 5800; Aldrich) as the template and tetraethyl orthosilicate (TEOS:  $\geq 98.0\%$ ; Fluka) as the silica source with a gel composition of TEOS: 0.0165 P123: 5.88 HCl: 192  $\text{H}_2\text{O}$  mole ratio. In addition, the effect of alumina impregnated SBA-15 (Na-Al-SBA-15) was studied by post-synthesis impregnation using a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  mole ratio of 30 and 60 [23,24] to derive the Na-Al-SBA-15(30) and Na-Al-SBA-15(60) catalysts, respectively. In a typical procedure, 0.5 g of SBA-15 was stirred in 50 mL of sodium aluminate ( $\text{NaAlO}_2$ , Riedel-deHaën, reagent grade) solution at room temperature for 12 h, where the  $\text{NaAlO}_2$  solution contained 0.046 g or 0.023 g of  $\text{NaAlO}_2$ . After that, the solid material was filtered, washed with deionized water and dried at 70 °C overnight to obtain the respective Na-Al-SBA-15 catalyst.

The microporous MCM-22 was synthesized by hydrothermal treatment as previously reported [25,26], using hexamethyleneimine (HMI:  $\geq 97.0\%$ , Fluka), fumed  $\text{SiO}_2$  (Cab-o-sil®M-5),  $\text{NaAlO}_2$ , sodium hydroxide ( $\text{NaOH}$ :  $\geq 99.0\%$ ; Lab-Scan) and deionized water as the starting materials. For the procedure, 25 g of fumed  $\text{SiO}_2$ , 3.5 g of  $\text{NaOH}$  and 150 g of  $\text{H}_2\text{O}$  were mixed in a four-necked round bottom flask for 1 h to obtain a white solution. Then 37 g of HMI was added dropwise under vigorous stirring for 1 h,

followed by the  $\text{NaAlO}_2$  solution under continuous stirring for 1 h. All steps were prepared at room temperature. The gel mixture was transferred into a Parr autoclave reactor, model 4843, and crystallized at 140 °C for 7 d. The gel composition was  $\text{SiO}_2$ : 0.15  $\text{NaO}_2$ : 0.033  $\text{Al}_2\text{O}_3$ : 0.9 HMI: 40  $\text{H}_2\text{O}$  for a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 30, denoted as Na-MCM-22(30), or altered to give a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 60 and denoted as Na-MCM-22(60).

In addition,  $\text{Na}^+$  ion exchange for  $\text{H}^+$  of these synthesized catalysts was performed using ammonium chloride ( $\text{NH}_4\text{Cl}$ : reagent grade, Fluka), and the resulting catalysts were denoted by the prefix H in place of Na (H-Al-SBA-15(30), H-Al-SBA-15(60), H-MCM-22(30) and H-MCM-22(60)). For ion exchange, 0.5 g of catalyst was refluxed with 50 mL of 0.01 M  $\text{NH}_4\text{Cl}$  at 70 °C for 24 h. After that, the solution was filtered, washed with deionized water and dried at 70 °C overnight. Finally, all materials were calcined at 550 °C for 5 h.

The spent catalysts, after polymer cracking at 380 °C, were reused by washing with hexane several times and then dried at 80 °C overnight. After that, the spent catalyst was calcined at 550 °C for 5 h in order to remove the solid coke from the catalyst pores. These materials were denoted as reused Al-SBA-15(30) and reused MCM-22(60). The pyrolysis condition for the reused catalyst was the optimized condition for fresh catalysts, with a reaction temperature of 380 °C for 30 min and using 10 wt% of reused catalyst.

### 2.2. Characterization of the catalysts

The structure of the prepared materials was determined by X-ray diffractometry (XRD) using a Rigaku D/MAX-2200 Ultima+ X-ray diffractometer equipped with  $\text{Cu K}\alpha$  radiation at 40 kV and 30 mA. The scanning range was measured between 0.5° and 3° for the SBA-15 catalyst and between 2° and 40° for the MCM-22 material, with a scan speed of 1.0° and 5.0°  $\text{min}^{-1}$ , respectively. For the SBA-15 materials, the scattering slit, divergent slit and receiving slit were set up at 0.05°, 0.5° and 0.15 mm, respectively, while that for the MCM-22 catalyst was 0.5°, 0.5° and 0.3 mm, respectively. The Brunauer-Emmett-Teller (BET) specific surface area and Barrett-Joyner-Halender (BJH) pore size and volume of all the catalysts were identified by nitrogen ( $\text{N}_2$ ) adsorption/desorption using a BEL Japan, BELSORP-mini instrument and analyzing the data. The adsorption isotherms were determined at 77 K using highly pure  $\text{N}_2$  as an adsorbate. Each sample (~0.04 g) was weighted exactly and pretreated at 400 °C for 3 h before each measurement. The position of the aluminum atoms in the material framework was investigated by  $^{27}\text{Al}$ -magnetic angle spinning-nuclear magnetic resonance spectrometry (MAS-NMR) using a Bruker Advance DPX 300 MHz NMR spectrometer operating at 78 MHz. The acidic property of each porous material was measured using temperature-programmed desorption of ammonia ( $\text{NH}_3\text{-TPD}$ ) with a thermal conductivity detector (TCD). Before each measurement, the catalyst was pretreated at 500 °C for 2 h under a helium gas flow and then cooled down at 150 °C. The adsorption of ammonia was investigated between 100 and 600 °C at a 10 °C  $\text{min}^{-1}$  heating rate. Scanning electron microscopy (SEM) was used to determine the morphology and particle size of the materials using a JEOL JSM-5401 LV scanning electron microscope at 15 kV of acceleration voltage.

### 2.3. Catalytic cracking of PP waste

The pyrolysis cracking activity of plastic was performed using PP pellets from PTT Global Chemical PCL. The properties of this polymer were  $M_w$  of 250,000, density of 0.9  $\text{g cm}^{-3}$ , melt flow index of 1.05  $\text{g min}^{-1}$ , melting point of 160–170 °C and average size of 0.4 mm. The PP waste was obtained from drinking water glasses. All waste samples were cleaned and cut into the small pieces of

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