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Catalytic degradation of high-density polyethylene over SAPO-34 synthesized with various templates

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Abstract−A variety of SAPO-34 catalysts were prepared using various templates, such as tetraethylammonium hydroxide (TEAOH), diethylamine (DEA), and a mixture of TEAOH and DEA, and then applied for the first time to the pyrolysis of high-density polyethylene (HDPE). The crystal morphology and physicochemical properties were affected by the type of template employed. In particular, an inexpensive SAPO-34 catalyst, with good crystal properties and catalytic performance, was obtained using a mixed-template of DEA and TEAOH. Through N_2 isotherm, XRD, SEM and NH_3 TPD the effects of the mixed-template on the crystal morphology and acidity were investigated. The catalytic activity of SAPO-34 in the pyrolysis of HDPE was improved with the use of a mixed-template, due to the crystal size, surface area and acidity.

Key words: SAPO-34, High Density Polyethylene, Mixed-template, Crystal Morphology

INTRODUCTION

The recycling of plastic wastes as feedstock has drawn much attention as it converts plastic wastes into valuable products. Furthermore, feedstock recycling has been recognized as more environmentally benign than conventional treatment methods, such as landfill or incineration. Accordingly, feedstock recycling of plastic wastes is an emerging research field. Since polyolefins account for over 70% of the total plastic waste generated, feedstock recycling of polyolefins has been extensively studied [1,2]. In particular, catalytic pyrolysis improves product selectivity and reduces energy input. Catalysts, such as HZSM-5, HY, natural zeolite, fly ash derived catalyst, Ferrierite, MCM-41, MCM-48 and SBA-15, have been studied for the catalytic pyrolysis of plastics [1-5]. However, few investigations into the catalytic pyrolysis of polyethylene over silicoaluminophosphate (SAPO) materials have been reported, even though the material has a high potential for polyethylene recycling. Since the first report of SAPO catalysts by Union Carbide in the 1980s, they have received a great deal of attention with respect to various reactions due to their unique physicochemical properties.

Until now, of the SAPO catalysts, only SAPO-37, with a faujasite structure, has been applied to polyethylene degradation. It was reported that the activation energy for HDPE alone decreased from 290 kJ mol^{-1} to 220 kJ mol^{-1} with 25%SAPO-37/HDPE, providing evidence that SAPO-37 is an effective catalyst for polyethylene degradation [6].

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SAPO-34, one of the main catalysts in the SAPO family, has been studied for various catalytic applications and, most notably, has shown excellent performance in the catalytic conversion of methanol into olefins, such as ethylene and propylene, which is known as the MTO process [7,8]. Thus, the potential exists for the degradation of high-density polyethylene (HDPE) into light olefins.

Furthermore, the template plays an important role in the preparation of molecular sieves, such as zeolite, SAPO and so on [9]. A molecular sieve structure can be prepared from various templates; however, different physicochemical properties might be observed according to the type of template used during the preparation, although different templates give rise to molecular sieves with similar structures. Therefore, the catalytic activities could also differ. In the preparation of SAPO-34, it is possible to use various organic-amine templates, such as tetraethyl ammonium hydroxide (TEAOH), morpholine, diethylamine (DEA), triethylamine (TEA), dipropylamine (DPA) and isopropylamine (IPA) [9]. Among the templates of SAPO-34, TEAOH has become well-known as it gives rise to good catalytic properties for various reactions, especially the MTO reaction. Since TEAOH is expensive, its adoption for the commercial production of SAPO-34 is difficult. Conversely, SAPO-34 prepared with morpholine or DEA has a larger crystallite size, resulting in lower catalytic activity.

In this study, SAPO-34 was applied for the first time for the degradation of HDPE. Especially, the template effect of the SAPO-34 catalyst on the degradation of HDPE was investigated. The physicochemical characteristics of the SAPO-34s prepared via various templates were also examined to verify the effects of the template on the degradation of HDPE. It is important to mention that research

on the synthesis and characterization of SAPO-34 using a mixed-template is relatively scarce.

EXPERIMENTAL

1. Catalyst Preparation

In our study, SAPO-34 was prepared using a hydrothermal method with a 2.0 template: 0.3 SiO_2 : 1.0 Al_2O_3 : 1.0 P_2O_5 : 50 H_2O. The precursors of Al, P and Si were aluminium isopropoxide (98%, Acros), phosphoric acid (85%, Samchun Chemicals) and fumed silica (Aldrich), respectively. The pure or mixed compounds of TEAOH and DEA were used as the template. A synthetic gel with the above molar ratio was introduced into a Teflon cup in a Parr autoclave, and then crystallized for 24 hr at 200 °C and 160 rpm. After crystallization, the prepared sample was filtered, dried at 110 °C for 10 hr and calcinated at 600 °C for 10 hr.

2. Catalyst Characterization

The powder XRD pattern was determined by X-ray diffraction (Rigaku D/MAX-IIIB), using Cu-Kα radiation (λ=0.15418 nm) at a scan rate of 4°/min. The shape and size of the crystallite were observed by SEM (JSM-840 Scanning Microscope). The surface acidities of the catalysts were measured by NH_3-TPD (BEL-CAT TPD analyzer). 0.1 g of catalyst was pretreated at 600 °C for 3 hr to remove the adsorbed water. NH_3 was sufficiently adsorbed at 100 °C for 1 hr, with He then purged for 30 min to remove any weakly adsorbed NH_3. The desorption profile was recorded from 100 to 600 °C, at 10 °C /min intervals. The surface area and pore property were measured by N_2 adsorption (Micromeritics 2010). All samples were evacuated at 350 °C prior to measurement. Because thermogravimetric analysis can provide useful kinetic data about pyrolysis [10-12], the catalytic degradation kinetics of the polyethylene over the catalysts was evaluated using thermogravimetric analysis (TGA 2050, TA Instrument), performed with 10.0 mg of a 10 : 1 sample : catalyst ratio (w/w) between 30 and 600 °C, with a linear heating rate of 10 °C/min, under a nitrogen atmosphere at a flow rate of 90 mL/min. The average particle sizes of the catalysts used in this study ranged from 0.5 to 10 micron according to the template type.

3. Catalytic Activity Measurement

Catalytic pyrolysis of HDPE was carried out in a fixed bed reactor system (Fig. 1). The pyrolysis reactor was U-type quartz, with an inner volume of 50.0 mL, height of 160 mm and internal diameter of 15 mm. The reactor was charged with HDPE (1.0 g) and 0.1 g of the catalyst (HDPE : SAPO-34=10 : 1). The average particle size of the catalysts used in this study ranged from 0.5 to 10 micron according to the template type. Prior to the experiments, all the experimental systems were purged with inert nitrogen for 1 hr, at a flow rate of 50.0 mL/min. The furnace was indirectly electrically heated to the desired reaction temperature. After the furnace temperature reached 500 °C, the desired reaction temperature, the reactor was inserted into the furnace. Thereafter, the catalytic pyrolysis reaction continued for 1 h. The temperatures of the experimental systems were adjusted with a PID temperature controller and monitored with two thermocouples (K type). The gaseous products were sampled by using a Teflon gas bag, with their compositions then analyzed. The oil and gaseous products were analyzed by gas chromatography/mass spectrometry (GC/MS (HP 5973)) and gas chromatography, equipped with flame ionization detection (GC-FID (ACME 6000, Young Lin Instrument Co., Ltd), respectively, with helium as the carrier gas. The columns used were an HP-5MS (30 m×0.25 mm×0.25 μm) capillary column for the GC/MS and an HP-plot Al_2O_3/KCl (50 m×0.32 mm×8.0 μm) for the GC/FID.

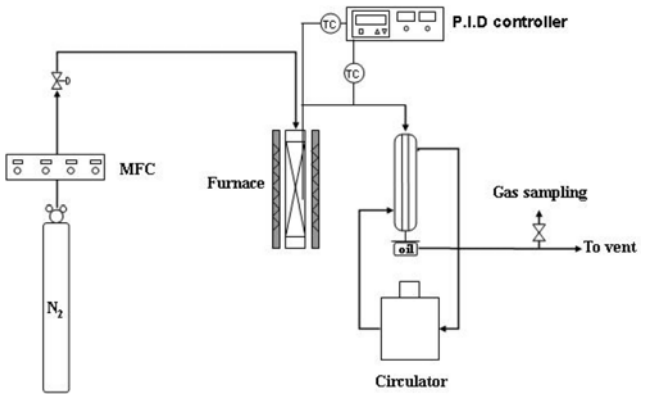

Fig. 1. Schematic diagram of the experimental apparatus.

RESULTS AND DISCUSSION

1. Catalyst Characterization

The effect of the template in the preparation of SAPO molecular sieve was observed by XRD and SEM. In Fig. 2, all samples show the characteristic peaks of SAPO-34 in the XRD measurement, which has already been reported [13]. However, the intensity of each peak differed according to the type of template, indicating that the extent of crystallization and the size of crystallite SAPO-34 were dependent on the type of template. In Fig. 3, the SEM observation shows cubic structure shape, which could be easily observed for SAPO-34 having chabazite structure. As expected from the XRD results, the size of crystallite SAPO-34 from the DEA was over 5.0 μm, which is much bigger than that from other templates. It is well known that the size of crystallite SAPO-34 affects the catalytic activities, especially in the MTO reaction [14]. Likewise, it might be expected that the conversion of HDPE would be dependent on the SAPO-34

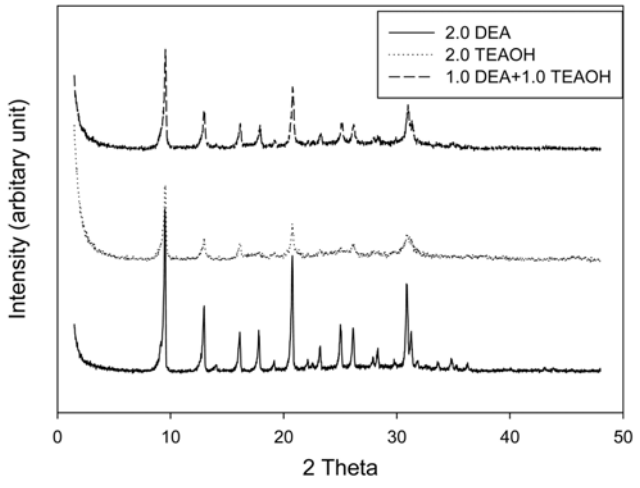

Fig. 2. XRD patterns of SAPO-34 catalysts with respect to template type.

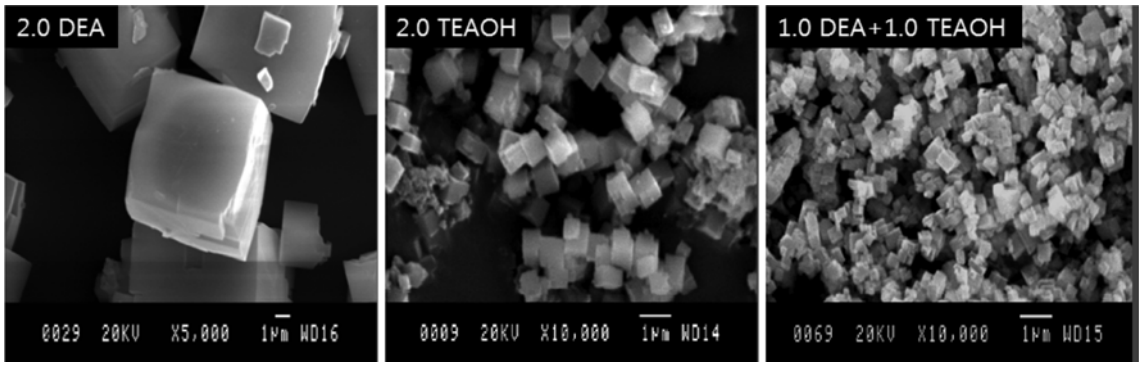

Fig. 3. SEM images of SAPO-34 catalysts with respect to template type.

Table 1. Physical properties of SAPO-34 catalysts with respect to template type

Sample	S_{BET} ($m^2\ g^{-1}$)	Micro surface area* ($m^2\ g^{-1}$)	External surface area ($m^2\ g^{-1}$)	Total pore volume ($cm^3\ g^{-1}$)	Micropore volume* ($cm^3\ g^{-1}$)	Mesopore volume ($cm^3\ g^{-1}$)
2.0 DEA	732.6	718.9	13.7	0.269	0.263	0.006
2.0 TEAOH	544.5	502.5	41.9	0.263	0.228	0.035
1.0 DEA+1.0 TEAOH	715.9	656.2	59.7	0.354	0.247	0.107

*Obtained from t-plot method

crystal size. Using TEAOH, a well developed submicron SAPO-34 could be formed. However, as mentioned before, the commercial process for the synthesis of SAPO with TEAOH could not be developed due to the high price of TEAOH. Therefore, our attention was focused on the development of an economical, highly active SAPO-34, with a submicron size by the reducing the amount or excluding the TEAOH used. By decreasing the TEAOH content, the crystallinity of SAPO-34 has been reported to be lowered and the crystal size increased [9]. For example, other types of SAPO, such as SAPO-5 and SAPO-11 rather than SAPO-34, were formed with a TEAOH/Al_2O_3 mol ratio of 0.5. When the TEAOH/Al_2O_3 mol ratio was 1.0, pure SAPO-34 crystallite was well developed; however, the crystal size grew by over 1 μm [9]. In addition, when a mixed template of (1.0DEA+1.0TEAOH)/Al_2O_3 was used instead of a 2.0TEAOH/Al_2O_3 template composition, a good crystal of SAPO-34 was obtained, with a crystal size under the submicron level; it also showed better catalytic activity for the MTO reaction [9]. As shown in Fig. 3, by using the mixed template of DEA+TEAOH, SAPO-34 with a good crystallinity and 0.5 μm crystal size was also successfully prepared in this study. It might be inferred that one of the two templates played a major role in the formation of the SAPO-34 crystal structure and the other could promote the increase in the dispersion, resulting in a decreased crystal size. The physical properties of the prepared SAPO-34 are summarized in Table 1. The surface area and volume of the micropore and mesopore of SAPO-34 from TEAOH were 544.5 m^2/g, 0.228 and 0.035 cm^3/g, respectively. SAPO-34 from DEA had a larger surface area, but its external surface area was relatively small due to its large crystal size. The surface area and pore volume especially, as well as the external surface area and mesopore volume of SAPO-34 by the DEA+TEAOH mixed-template were greatly enhanced. As shown in Fig. 4, the amount of N_2 in the isotherm of SAPO-34 (DEA+TEAOH) was greatly increased compared to that of SAPO-34 (TEAOH). This might

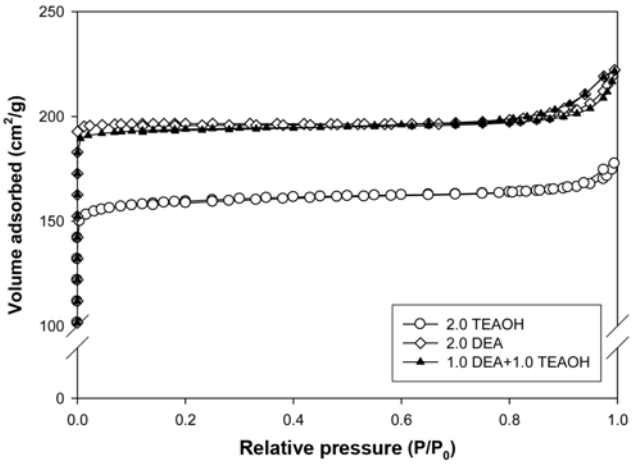

Fig. 4. N_2 adsorption-desorption isotherms of SAPO-34 catalysts with respect to template type.

Table 2. NH_3-TPD results of SAPO-34 catalysts with respect to template type

Samples	Amount of desorbed ammonia (mmol g^{-1})		Total amount (mmol/g)
	LT (<300 °C)	HT (>300 °C)	
2.0 DEA	0.0363	0.0893	0.1256
2.0 TEAOH	0.0506	0.1138	0.1644
1.0 DEA+1.0 TEAOH	0.0420	0.1168	0.1588

have been because of the good crystallinity and smaller crystal size derived from the effect of the mixed template of DEA+TEAOH.

The acid properties from NH_3-TPD of SAPO-34 synthesized with

various templates are summarized in Table 2. Two distinct desorption peaks at 200 and 400 °C were observed, indicating the existence of two acid sites with different acid strengths. The desorption peak below 300 °C represents a weak acid site due to the surface hydroxyl group, and the peak above 300 °C was due to a strong acid site in the framework of SAPO-34 [13].

As indicated in Table 2, the acidity of SAPO-34 from TEAOH was higher than that of SAPO-34 from either DEA or DEA+TEAOH. However, the number of strong acid sites of SAPO-34 from DEA+TEAOH was slightly greater than that of SAPO-34 from TEAOH.

2. Catalytic Activity

The catalytic activities of the SAPO-34 synthesized using various templates were evaluated by thermogravimetry, which monitors the weight loss upon applying a temperature ramp in a nitrogen atmosphere and maintaining a polymer-to-zeolite mass ratio of 10. The profiles of the HDPE conversion *versus* temperature over SAPO-34 catalysts are shown in Fig. 5. The catalytic degradation of HDPE was shown to greatly depend on the template. The degradation behavior of the HDPE over the SAPO-34 synthesized with DEA was similar to that with no catalyst. However, the degradation temperature was shifted to 30 K lower in the presence of the SAPO-34 synthesized with TEAOH. Furthermore, the SAPO-34 synthesized with a mixed-template showed the highest catalytic ability for HDPE degradation.

Although the SAPO-34 from DEA showed the highest surface area (Table 1), its external surface area was the lowest of all the SAPO-34s. The external surface area has been reported to be very important for the catalytic cracking of plastic [15]. Large plastic fragments are cracked on the external surface of the catalyst and then enter into the pores for further cracking. Therefore, the lowest activity of the SAPO-34 from DEA may have been due to its small external surface area (large crystal size, Fig. 3) and low acidity (Table 2). Also, for the SAPO-34 from TEAOH, with the smallest surface area, but moderate (or considerable amount) external surface area, the catalytic activity was higher than that of the SAPO-34 from

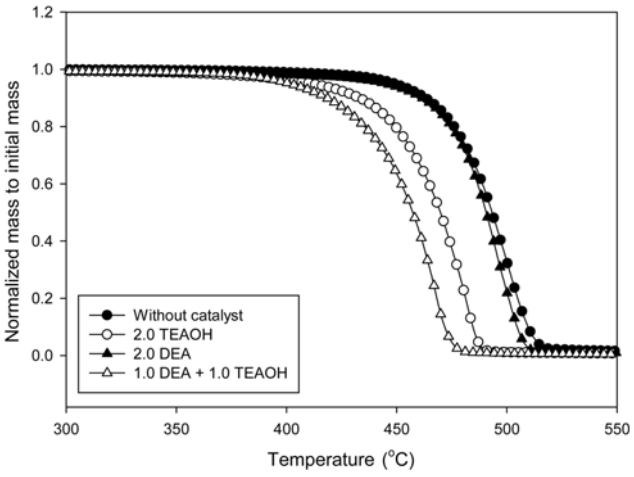

Fig. 5. Catalytic degradation of HDPE over SAPO-34 catalysts with respect to template type.

Table 3. Product distribution of HDPE degradation of SAPO-34 with respect to template type

Catalyst	Without catalyst	2.0 DEA	2.0 TEAOH	1.0 DEA+ 1.0 TEAOH
Conversion (%)	99.3	100	100	100
Yield (wt%)				
Oil	88.3	86.0	63.1	60.1
Gas	11.0	14.0	36.9	39.9

Temperature: 500 °C, HDPE: catalyst (w/w)=10 : 1

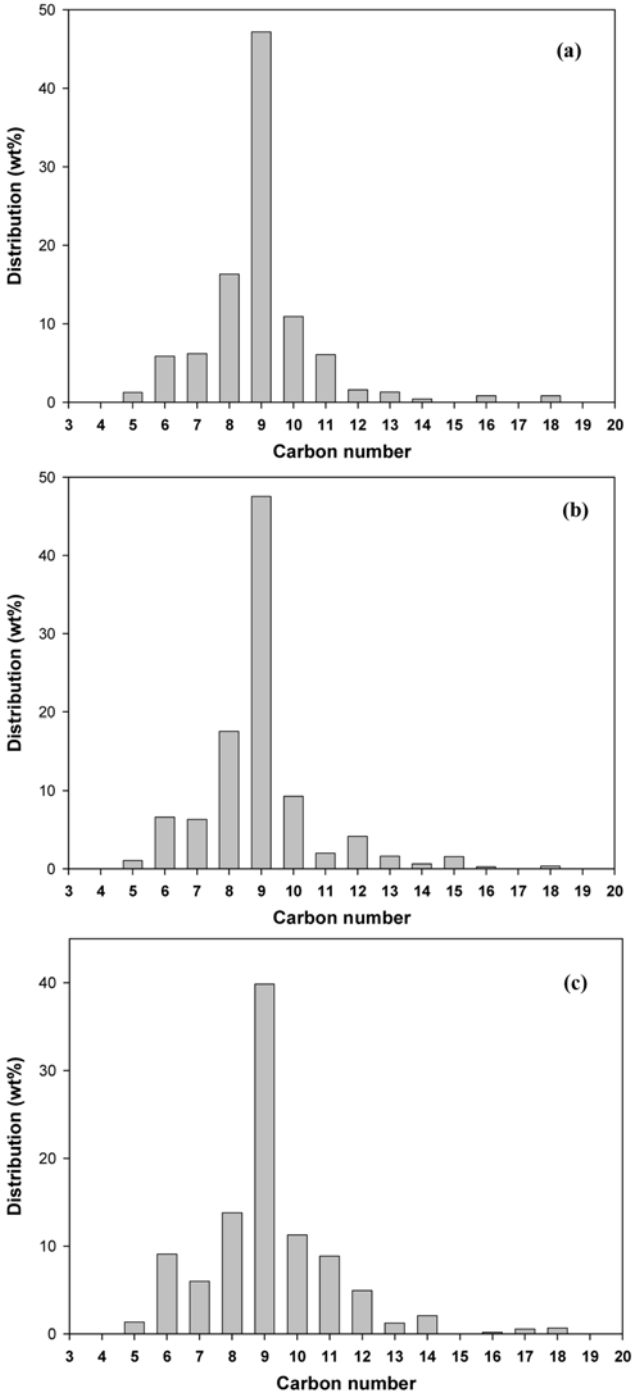

Fig. 6. Product distribution of oil (a) from SAPO-34 with 2.0 TEAOH (b) from SAPO-34 with DEA+TEAOH (c) from SAPO-34 with 2.0 DEA.

Table 4. Product distribution of gas of SAPO-34 with respect to template type

Catalyst	Without catalyst	2.0 DEA	2.0 TEAOH	1.0 DEA+ 1.0 TEAOH
Selectivity (wt%)				
CH_4	2.4	3.0	1.9	2.7
C_2H_4	10.2	5.8	5.2	6.2
C_2H_6	6.8	6.2	3.8	4.3
C_3H_6	10.7	34.0	33.7	34.8
C_3H_8	0.2	5.0	4.2	3.8
C_4H_8 (*c*-,*t*-,*n*-,*i*-)	34.3	44.3	49.6	46.6
C_4H_{10} (*i*-,*n*-)	35.4	1.7	1.6	1.6
Σparaffins	44.8	15.9	11.5	12.4
Σolefins	55.2	84.1	88.5	87.6

Temperature: 500 ºC, HDPE: catalyst (w/w)=10 : 1

DEA, due to its large external surface area (smaller crystal size) and greater number of acid sites compared to the SAPO-34 from DEA. The highest catalytic activity of the SAPO-34 from the mixed-template can be ascribed to the combination of a large external surface area (small crystal size) and high acidity.

Table 3 shows the product distribution following HDPE degradation. All of the catalysts increased the yield of gas, but was greatest for the SAPO-34 from the mixed-template. The increased ability to crack the HDPE into gas may also be related to the physical properties of the SAPO-34, such as external surface area, acidity and crystal size. The dominant factors seemed to be the crystal size and acidity.

Table 4 and Fig. 6 show the product distributions of the gases and liquids, respectively. All of the catalysts showed higher selectivity to olefins, especially the more valuable propylene from gas (Table 4). Because the SAPO-34 exhibited high selectivity for olefins in the MTO process, due to its small pore size and acidity, the high selectivity to olefin for degradation of HDPE might also be the same. In the liquid product distribution, most of the hydrocarbons were C_5 to C_{13} hydrocarbons. The distribution patterns were almost symmetrical around C_9 hydrocarbons. Because the pore sizes of all the SAPO-34s were small, it is difficult for higher hydrocarbons, such as C_{13+}, to diffuse out of the pores.

CONCLUSIONS

Mixed-templates, such as DEA-TEAOH, can give well-developed SAPO-34 structures and good crystal sizes, in the submicron region, under the same synthetic conditions as those of a single template. Furthermore, the SAPO-34 catalyst prepared using the mixed-template possessed superior catalytic activity in the degradation of HDPE compared to those prepared using single templates. The mixed-template gave sufficient acidity in the synthesis of SAPO-34, as well as a good crystallinity and crystal size.

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