

Silicoaluminophosphate molecular sieves as a hydrocarbon trap

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Abstract

Silicoaluminophosphate molecular sieves with AFI, AFO, AEL and CHA topologies have been investigated as a hydrocarbon trap by studying the temperature programmed desorption of toluene. The pore diameter is increased in the following order: SAPO-34 ($d_p = 0.38$ nm) < SAPO-11 (0.39 nm × 0.63 nm) < SAPO-41 (0.43 nm × 0.70 nm) < SAPO-5 (0.73 nm). The capacity to adsorb hydrocarbon increases with increase of pore width. The effect of hydrothermal treatment over SAPO-5 shows that the stability is not affected significantly up to a temperature of 700 °C. Moreover, Si substitution is playing an important role in desorption temperature while capacity to adsorb toluene is mostly influenced by pore diameter.

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1. Introduction

The increasing concern about the air pollution on the environment has led the catalyst manufacturers to focus on the control of cold start emission control. During the first 2 min of the US FTP test about 80% of the total hydrocarbons are released (often causing failure in the cycle of federal test procedure (FTP)) [1–3]. As a consequence, a significant attention has been paid over the past three decades developing a method to treat automobile exhaust on the new technologies such as close coupled catalysts, electrically heated catalysts and hydrocarbon traps to convert these hydrocarbons (HC) during cold start. Among these technologies, hydrocarbon trapping aims at adsorbing hydrocarbons from the exhaust stream when the temperature of the catalytic system is low and releasing them when the temperature is raised to the light-off point [4–13].

In recent years, several studies have been explored as potential solutions to the cold start emissions [14–16]. The studies have met with varying degrees of success due to the wide range of conditions found in a vehicle exhaust [17–20]. Zeolites were found to be the preferred adsorbents, due to

their stability under these conditions. Many of these studies have been focusing medium and large pore zeolites [16,21–27]. Czaplewski et al. [28] showed that one-dimensional zeolites can also be an effective material for this purpose, where one can observe a control release of smaller hydrocarbons in presence of aromatic molecule.

Ever since the introduction of silicoaluminophosphate molecular sieves [29] they have been employed for many important applications including lube dewaxing and MTO process. A wide distribution of acid sites and one-dimensional nature appear to contribute to their performance [30,31]. Substitution of silicon in a neutral aluminophosphate will generate acid sites of different strengths and this may provide a much stronger interaction with the hydrocarbons which could result in desorption of trapped hydrocarbons relatively at a higher temperature. Moreover, the structure of SAPO molecular sieves cover a wide range of unique structures with different pore widths, of which, some are analogous to zeolites [32].

In the present investigation, we have explored the possibility of utilizing silicoaluminophosphate molecular sieves, viz. SAPO-5 (AFI topology), SAPO-41 (AFO topology), SAPO-11 (AEL topology) and SAPO-34 (CHA topology) for the trapping of hydrocarbons in the applications of cold start emission control with a particular

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aim to elucidate the influence of the pore diameter on the hydrocarbon trapping. No studies have been reported on such systems. The pore diameter is increased in the following order: SAPO-34 ($d_p = 0.38$ nm) < SAPO-11 (0.39 nm \times 0.63 nm) < SAPO-41 (0.43 nm \times 0.70 nm) < SAPO-5 (0.73 nm). In addition, the effect of hydrothermal treatment and the influence of Si substitution on the desorption temperature are also reported.

2. Experimental

Synthesis conditions of silicoaluminophosphate molecular sieves of different topologies are given in Table 1. In typical synthesis, pseudoboehmite (Catapal B, 74% Al₂O₃) was first dispersed in a solution containing orthophosphoric acid (Merck, 85%) and water, and the mixture was stirred for about 1 h at room temperature. Thereafter, silicon source was added and continued stirring for further 30 min. Then structure-directing agent (SDA) was slowly added and the stirring was maintained for additional 2 h. The homogeneous gel was transferred in a Teflon lined autoclave and heated under autogenous pressure in a static condition. After crystallization, the solids were recovered by filtration and dried at 100 °C for overnight. Afterward, calcination was carried out by heating the samples to a temperature of 540 °C in a flow of nitrogen, and subsequently, maintained at the same temperature for about 5 h in air.

The samples were characterized by XRD, SEM, ²⁷Al–²⁹Si–³¹P NMR, and chemical analysis.

Toluene was used as a probe molecule for this study. The temperature-programmed desorption (TPD) of toluene was carried out by using a gas chromatograph (Shimadzu GC-9A) with a thermal conductivity detector. Sample (ca. 50 mg) was placed in a quartz tube of 4 mm i.d., between the quartz wool. Subsequently, the sample was activated in a flow of helium at 300 °C for about 2 h. After cooling the column to a temperature of 50 °C, toluene was injected

(pulse method) until saturation. Desorption was performed by a 90 °C hold method that is heating the column from 50 to 90 °C at a heating rate of 20 °C/min and maintained at the same temperature for about 10 min to desorb weakly adsorbed toluene. Subsequently, the samples were heated to 390 °C at the rate of 20 °C/min and kept at 390 °C for an additional 10 min. The toluene desorption profile was recorded with a dedicated printer attached to the instrument. All TPD experiments were carried out under a flow of helium with a flow rate of 50 ml/min. In addition, the reproducibility of desorbed amount of toluene was confirmed by a repeated TPD experiment over SAPO-5 without further activation.

3. Results and discussion

3.1. Characterization

The X-ray powder diffraction patterns of both as-synthesized and calcined samples closely resemble those reported in the literature [33–35] and confirm the phase purity and crystallinity of the samples prepared in this study (Fig. 1). The $n_{Si}/n_{(Al+P)}$ ratio of all the samples is summarized in Table 2. The $n_{Si}/n_{(Al+P)}$ ratio determined by ICP shows that AEL and AFO structures have a lower tolerance toward the incorporation of foreign elements as compared to AFI structure. Similar findings have also been reported in the recent studies [36,37]. The substitution of silicon in the AIPO- n neutral framework creates a negative charge in the framework which is balanced by a bridging proton imparting Brønsted acidity in the SAPO- n samples [38–40].

Fig. 2 shows the SEM image of all the SAPO- n samples with the crystallites of micron range particles. SAPO-34 exhibits the rhombohedral shape of micro crystals with average dimensions of 10 μm, which is typical for these systems [41,42].

Table 1
Synthesis conditions of silicoaluminophosphate molecular sieves

Sample	Structure type	Gel composition x SiO ₂ : y Al ₂ O ₃ : z P ₂ O ₅ : m R: n H ₂ O; x : y : z : m : n	Silicon source	SDA, R	Crystallization time and temperature
SAPO-5	AFI, 0.73 nm, 12 MR, one-dimensional	0.5:1:1:0.77:20.3	Tetraethyl orthosilicate (Fluka)	Triethylamine	36 h, 200 °C
SAPO-41	AFO, 0.43 nm \times 0.7 nm, 10 MR, one-dimensional	0.1:0.85:1:3:50	Fumed silica (Cabosil)	Dipropylamine	34 h, 200 °C
SAPO-11	AEL, 0.63 nm \times 0.39 nm, 10 MR, one-dimensional	0.5:1:1.25:2.37: 156:1.8 HF	Tetraethyl orthosilicate (Fluka)	Dipropylamine	18 h, 145 °C
SAPO-34	CHA, 0.38 nm, 8 MR, three-dimensional	1.08:1:1.06: 2.09:66	Fumed silica (Cabosil)	Morpholine	24 h, 28 °C; 24 h, 200 °C
SAPO-5 (0.15)	AFI, 0.73 nm, 12 MR, one-dimensional	0.2:1:1:1.9:40	Tetraethyl orthosilicate (Fluka)	Tripropylamine	48 h, 125 °C; 48 h, 150 °C
AIPO-5	AFI, 0.73 nm, 12 MR, one-dimensional	0:1:1:0.77:20.3		Triethylamine	36 h, 200 °C

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