

## LETTERS

### SSZ-33: A Promising Material for Use as a Hydrocarbon Trap

S. P. Elangovan,<sup>†</sup> Masaru Ogura,<sup>†</sup> Mark E. Davis,<sup>‡</sup> and Tatsuya Okubo<sup>\*,†</sup>

*Department of Chemical System Engineering, The University of Tokyo,  
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan, and Chemical Engineering,  
California Institute of Technology, Pasadena, California 91125*

*Received: June 16, 2004; In Final Form: July 26, 2004*

SSZ-33 is tested for possible application as a hydrocarbon trap by investigating the temperature-programmed desorption behavior of toluene (used as a probe molecule) and the results are compared to those obtained with zeolites  $\beta$ , Y, mordenite, and ZSM-5. SSZ-33 shows higher adsorption capacity than the other zeolites at the conditions used here, and as well as better hydrothermal stability than zeolite  $\beta$ , and is therefore identified as a promising candidate for use as a hydrocarbon trap in cold-start emission control.

#### 1. Introduction

SSZ-33 is a molecular sieve with intersecting 10- and 12-membered ring (MR) pores and possesses a unique combination of reaction activity, selectivity, and stability not found in other materials.<sup>1</sup> Figure 1 depicts the framework topology of SSZ-33 along with zeolite  $\beta$ . The 12- and 10-MR channels of SSZ-33 connect to form a large void volume at the intersections. This type of porosity endows SSZ-33 with interesting adsorption properties. Depending on the size of the diffusing molecule, transport can occur in the 12 ring pore system or in both types of pores. A limited number of catalytic reactions have been investigated with SSZ-33.<sup>2–5</sup>

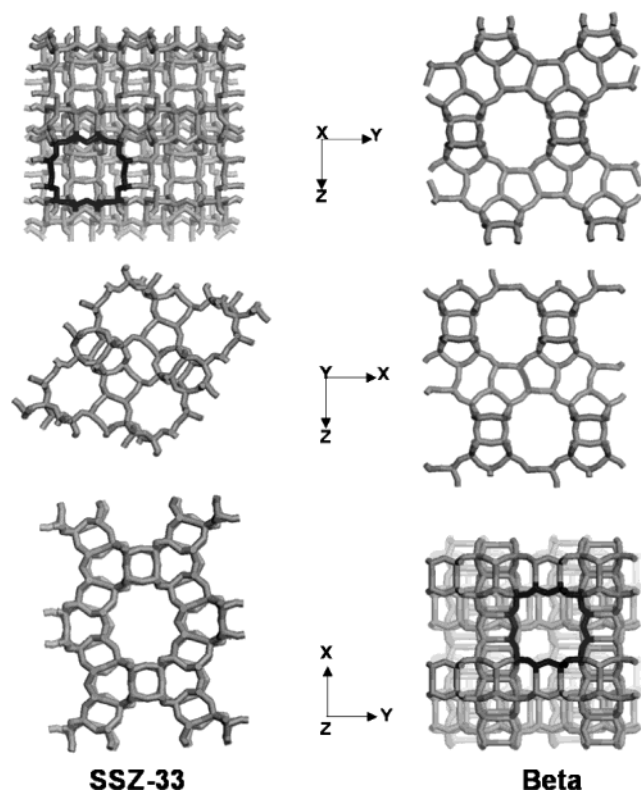
Vehicles equipped with a conventional three way catalytic converter consist of precious metals supported on washcoat layer, which in turn is deposited on a monolithic carrier. Fresh catalysts start to operate at ca. 170 °C, while aged catalysts work only at ca. 200–225 °C. The catalysts require 1–2 min to reach these temperatures, and during this time, 70–80% of the tailpipe hydrocarbon (HC) emissions occur, often causing

failure in the cycle of federal test procedure (FTP). The FTP is a standardized laboratory method for new vehicles testing that is comprised of two simulated environments; namely, city and highway. The selected preproduction of prototypes of new vehicle models are driven by a trained driver in a laboratory on a dynamometer. The future low emissions standards are forcing automobile and catalyst manufacturers to focus on reducing the cold start HC emissions. Consequently, control of emissions during this cold start period is essential. At temperatures where the catalyst is not able to convert HC effectively, hydrocarbon adsorber systems should trap the HC molecules and desorption should occur in the ideal case at temperatures exceeding catalyst light-off. The critical factors for any emission trap are the adsorption capacity and desorption temperature (must be higher than the catalyst operating temperature). Zeolites have been found to be the preferred adsorbents for this application due to their stability under these conditions. Many studies have been focusing on medium and large pore zeolites, but the types of zeolites used have not been identified. A series of zeolites ( $\beta$ , ZSM-5, mordenite, and Y) have been investigated for their hydrocarbon adsorption capacity under a variety of conditions.<sup>6–9</sup> Previous investigations have thus far found zeolite  $\beta$  to be a promising material for this application. However, the aged

\* Corresponding author. Fax: +81-3-5800-3806 E-mail: okubo@chemsys.t.u-tokyo.ac.jp.

<sup>†</sup> The University of Tokyo.

<sup>‡</sup> California Institute of Technology.

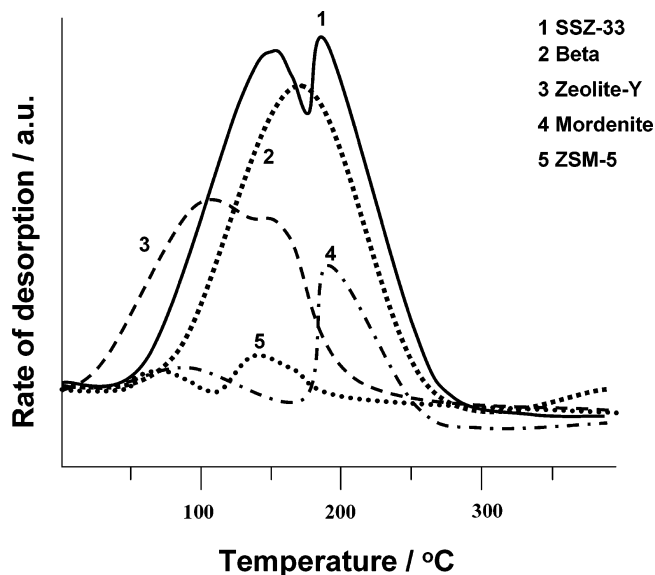


**Figure 1.** Framework structure of SSZ-33 (CON topology) along with  $\beta$  (BEA topology).

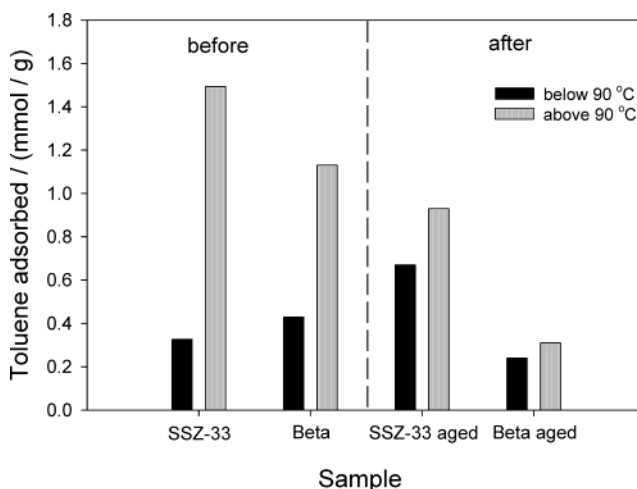
catalysts degraded performance in trapping the HC due to a low hydrothermal stability. Hence, it is essential to find a material that possesses a better adsorption capacity and hydrothermal stability than zeolite  $\beta$  for this application. In this communication, we report the temperature-programmed desorption of toluene (used as a probe molecule) with SSZ-33 and compare the results to those obtained with zeolites  $\beta$ , Y, mordenite, and ZSM-5 as a test to ascertain whether SSZ-33 could be of potential use for the HC trap application for cold start emission control.

## 2. Experimental Section

SSZ-33 was synthesized, and posttreatment was carried out according to the procedure reported in the literature.<sup>2</sup> After the treatment, the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio was found to be 60. Zeolites  $\beta$  ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$ ), mordenite ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 10.2$ ), and ZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 23.8$ ) were obtained from Tosoh Corporation and zeolite Y ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.6$ ) was supplied by Catalysts & Chemicals Ind. Co., Ltd. All materials used in this study were in the H-form, and they were obtained by a 3-fold ion-exchange with 0.1 M ammonium nitrate solution. 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 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°/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°/min and kept at 390



**Figure 2.** Desorption rate of toluene as a function of temperature.



**Figure 3.** Desorption amounts of toluene from SSZ-33 and  $\beta$  before and after hydrothermal treatment.

°C for an additional 10 min. All the TPD experiments were carried out under a flow of helium with a flow rate of 50 mL/min.

## 3. Results and Discussion

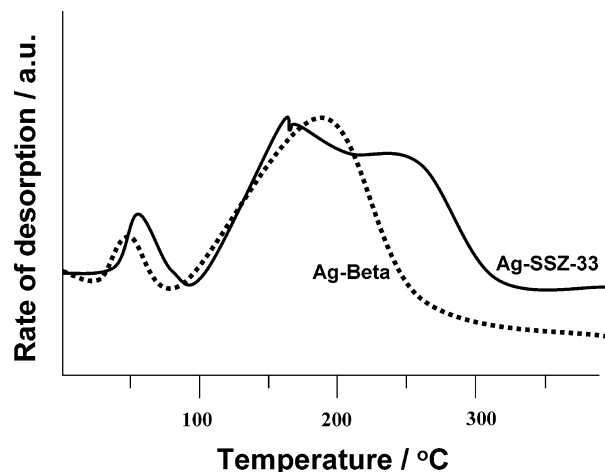
The rate of desorption of toluene as a function of temperature from the samples described above is depicted in Figure 2 and shows the superior performance of SSZ-33 over the other materials used in this study. Zeolite Y, ZSM-5, and mordenite desorb toluene at a relatively low temperature. The end temperature of toluene desorption decreases in the following order; SSZ-33 >  $\beta$  > mordenite > Y > ZSM-5. In comparison to the materials used in this study, SSZ-33 shows an enhanced high-temperature desorption over the other zeolites that could be ascribed to the larger amount of toluene adsorbed. In particular, SSZ-33 exhibits two sharp maxima at ca. 150 and 200 °C. This behavior is ascribed to the unique pore system of SSZ-33 in which desorption from the 10-MR channel occurs at a relatively higher temperature, but further work is necessary in order to conclusively prove this hypothesis. From these preliminary studies, SSZ-33 and  $\beta$  were chosen for a more detailed comparison of the adsorption capacity and stability.

**TABLE 1: Micropore Volume and Crystal Size of the Samples**

sample	micropore volume (cm <sup>3</sup> /g)	crystal size (as determined by SEM) (μm)
SSZ-33	0.21	1–2
SSZ-33, aged	0.21	
β	0.20	<1
β, aged	0.16	

For practical applications of the HC trap, the material should be stable for a sufficiently long time and for higher temperature treatments that involve temperature swings of up to 800 °C. To study the stability of these materials, hydrothermal treatment was carried out in the presence of 10% H<sub>2</sub>O at 800 °C for about 5 h in a stream of air with a flow of 25 mL/min. The materials after the hydrothermal treatment are denoted as an aged sample. Figure 3 shows the amount of toluene desorbed from SSZ-33 and β and their aged samples. It is clear from the data shown in the figure that the capacity of SSZ-33 is about 1.25 times larger than that of β. The capacity and the desorption temperature of SSZ-33 are superior to those of zeolite β when considering the requirements in the HC cold trap application. There is a decrease in the adsorption capacity after hydrothermal treatment of SSZ-33. The total amount desorbed from the fresh SSZ-33 is 1.82 mmol/g and is decreased to 1.60 mmol/g after the hydrothermal treatment. By comparison with zeolite β, the desorption from a fresh sample amounts to 1.49 mmol/g, while after the hydrothermal treatment it is only 0.56 mmol/g. It has been suggested that a part of the adsorption capacity of β originates from faults in the structure. The mild steaming may cause structural changes that in turn cause a marked difference in the adsorption capacity.<sup>10</sup> This hypothesis is further supported by nitrogen adsorption measurements of SSZ-33 and β, before and after hydrothermal treatment. Table 1 presents the micropore volume of these samples. SSZ-33 possesses a micropore volume of 0.21 cm<sup>3</sup>/g which is not decreased after hydrothermal treatment while for β the micropore volume is decreased to 0.16 cm<sup>3</sup>/g from 0.20 cm<sup>3</sup>/g.

It is believed that metal exchange over zeolites can lead to higher desorption temperatures of HC by increasing the strength of the interactions between the solid and the adsorbed molecule.<sup>6,11,12</sup> In an attempt to test this hypothesis, silver exchange was carried out with SSZ-33 and zeolite β. Figure 4 shows the rate of desorption of toluene from Ag-β and Ag-SSZ-33. Further increases in the desorption temperatures are observed

**Figure 4.** Comparison between Ag-SSZ-33 and Ag-β.

from the silver containing zeolites over their acidic counterparts, and a better performance is obtained from SSZ-33 over β.

#### 4. Conclusions

We have found that SSZ-33 possesses higher capacity for the adsorption of toluene and reveal greater hydrothermal stability compared to zeolite β. These results suggest that SSZ-33 may perform well in HC trap applications for cold start emission control.

#### References and Notes

- (1) Lobo, R. F.; Pan, M.; Chan, I.; Li, H.; Medrud, R. C.; Zones, S. I.; Crozier, P. A.; Davis, M. E. *Science* **1993**, 262, 1543.
- (2) Dartt, C. B.; Davis, M. E. *Appl. Catal., A* **1996**, 143, 53.
- (3) Jones, C. W.; Zones, S. I.; Davis, M. E. *Microporous Mesoporous Mater.* **1999**, 28, 471.
- (4) Adair, B.; Chen, C. Y.; Wan, K. T.; Davis, M. E. *Microporous Mater.*, **1996**, 7, 261.
- (5) Corma, A. *Microporous Mesoporous Mater.* **1998**, 21, 487.
- (6) Burke, N. R.; Trimm, D. L.; Howe, R. F. *Appl. Catal., B* **2003**, 46, 97.
- (7) Lafyatis, D. S.; Ansell, G. P.; Bennett, S. C.; Frost, J. C.; Millington, P. J.; Rajaram, R. R.; Walker, A. P.; Ballinger, T. H. *Appl. Catal., B* **1998**, 18, 123.
- (8) Noda, N.; Takahashi, A.; Shibagaki, Y.; Mizuno, H. *SAE Tech. Pap. Ser.* **1998**, 980423.
- (9) Czaplewski, K. F.; Reitz, T. L.; Kim, Y. J.; Snurr, R. Q. *Microporous Mesoporous Mater.* **2002**, 56, 55.
- (10) Kunkelar, P. J.; Zuurdeeg, B. J.; van der Waal, J. C.; van Bokhoven, J. A.; Koningsberger, D. C.; van Bekkum, H. *J. Catal.* **1998**, 180, 234.
- (11) Liu, X.; Lampert, J. K.; Arendarskii, D. A.; Farrauto, R. J. *Appl. Catal., B* **2001**, 35, 125.
- (12) Yamamoto, S. *PETROTECH* **2003**, 26, 119.