

## Strong Basic Sites Accelerate the Deactivation of Oxide Catalysts Supported on FSM-16 for the Vapor-Phase Beckmann Rearrangement of Cyclohexanone Oxime

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The acidic and basic properties of FSM-16-supported  $\text{Al}_2\text{O}_3$ , ZnO or CdO were determined by the temperature-programmed desorption (TPD) of ethylamine. Relationship of the deactivation rate of the catalyst during the vapor-phase Beckmann rearrangement with the acidic and basic properties was studied. It was found that the deactivation was accelerated with an increase in the amount of the strong basic sites.

On the H-ZSM-5 catalyst, the correlations between coke and polymer formation during the vapor-phase Beckmann rearrangement and the amount of the strongly acidic sites determined by the ammonia-TPD or IR spectroscopy were studied.<sup>1-3</sup> These studies suggested that the formation of coke and polymer proceeded on the strongly acidic sites and the formation was a cause for the catalyst deactivation. On the other hand, it was reported that mesoporous-silicas (FSM-16 and MCM-41) having no strongly acidic sites were also deactivated during the reaction.<sup>4</sup> This fact suggests that there are some other causes for the catalyst deactivation than the coke and polymer formation on the strongly acidic sites.

It is known that the  $\epsilon$ -caprolactam, i.e., the objective product of the reaction, is transferred into nylon 6 by the anion polymerization. Therefore, basic sites on the catalyst may cause the catalyst deactivation. We simultaneously determined the acidity and the basicity of the catalysts and then compared to the deactivation rates of the catalysts. The determinations of the acidity and the basicity were carried out by the ethylamine-TPD method, a modified method of the triethylamine-TPD method proposed by Yamaguchi, et al.<sup>5</sup>

We adopted some metal oxides supported on the FSM-16 as the catalysts. The FSM-16 has a honeycomb-like structure of uniform pores, which are much larger in diameter than those of the H-ZSM-5. Cyclohexanone oxime (CHO), the reactant, is likely accessible to all the acidic and the basic sites measured by the TPD. Therefore, the FSM-16-supported catalysts are suitable for studying the relationship between the catalytic performance and the properties characterized by the TPD.

FSM-16 was prepared as stated in a previous paper,<sup>6</sup> pressed into disks, crushed and sieved into a 32-42 mesh size. The FSM-16-supported oxide (oxide/FSM-16) was prepared by the incipient wetness method. The catalysts were calcined at 500 °C for 3 h in air. FSM-16-supported zinc and cadmium oxides were not calcined. The BET surface areas of the catalysts were determined by using an ASAP 2000 (Micromeritics Co.). XRD were measured by using RAD-1A (Rigaku Co.) (Cu-K $\alpha$ ). The BET areas of oxides supported on FSM-16 (e.g. BET areas of CdO(8wt%)/FSM-16 and  $\text{Al}_2\text{O}_3$ (8wt%)/FSM-16 were 796 and 546  $\text{m}^2 \text{g}^{-1}$ , respectively) were less than the original support (1065  $\text{m}^2 \text{g}^{-1}$ ). Intensities of all the XRD peaks of the catalysts were less than those of FSM-16. Thus the pore structure of the catalysts were slightly destroyed by the impregnation process.

A conventional fixed bed flow reactor was used for the reaction runs. A 100 mg sample of a catalyst was fixed by quartz wool in the Pyrex glass reactor (10 mm i.d.) and pre-treated at 350 °C for 1 h. An 8 wt% benzene solution of CHO was then fed by a "Micro-feeder" (Furue Science Co.) at the rate of 10  $\text{cm}^3\text{-liquid h}^{-1}$  into the pre-heated zone of the reactor and vaporized (W/F=15 g-cat. h  $\text{mol-CHO}^{-1}$ ). The effluent product mixture was trapped in an ice-cooled trap and analyzed by GC (Shimadzu GC-8A with 3m-long OV-17 columns).

The ethylamine-TPD was measured by use of a conventional TPD apparatus. Catalyst samples were pre-treated at 500 °C or 350 °C in air for 3 h and in a pure nitrogen stream for 1 h, then equilibrated with a nitrogen stream containing 49 kPa of ethylamine vapor at 100 °C. They were washed with pure nitrogen and then treated by washing with nitrogen containing 0.61 kPa of water vapor for 3 h as the steam treatment. TPD runs were carried out by elevating the temperature of the sample from 100 to 600 °C at a rate of 3 °C  $\text{min}^{-1}$ , with repeatedly analyzing the effluent gas by GC with FID (Shimadzu GC-8A with 1 m-long Chromosorb 103 columns).

An exemplary ethylamine-TPD spectrum of a catalyst was shown in Figure 1. The vertical axis showed desorption rate

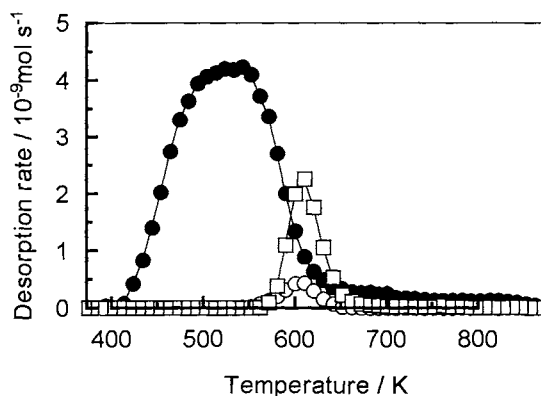


Figure 1. TPD spectrum of ethylamine on ZnO/FSM-16 (1.2 mol/kg). (○) ethylene, (●) ethylamine and (□) acetonitrile.

and the horizontal axis showed sample temperature. Acetonitrile generates via dehydrogenation of ethylamine on the sites by a strong base. Ethylene generates via elimination of  $\text{NH}_3$  from ethylamine on the sites by a strong acid. The amount of strong basic sites and acid sites were estimated from the desorbed amounts of acetonitrile and ethylene, respectively.<sup>5</sup> Detail of the analyses will be reported in our forthcoming paper.

CHO conversions over 97% were observed for all of the catalysts in 30 minutes. The CL selectivity was improved when increased amount of oxides are supported and reached its

maximum at 12wt% for  $\text{Al}_2\text{O}_3$ , 7.3wt% for ZnO and 3.9wt% for CdO. The maximum CL selectivity was 63, 69% and 77%, respectively.

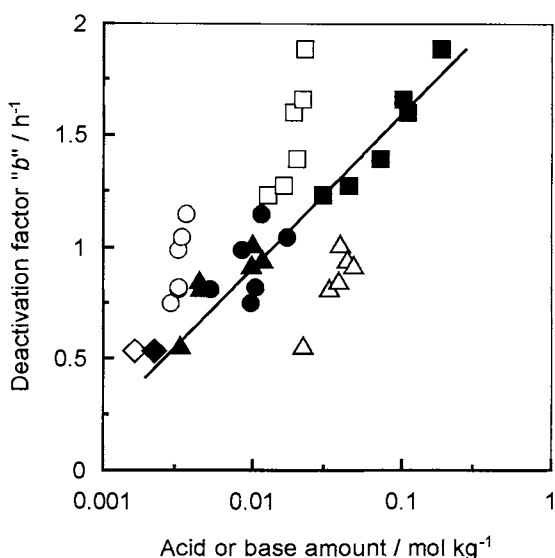
Most solid catalysts are known to deactivate during the Beckmann rearrangement and the deactivation prevents the catalysts from being industrially applied. The oxides supported on FSM-16 were also deactivated and the deposition of coke was observed on the spent catalysts. After the reaction for 4 h, the BET areas of FSM-16 and  $\text{Al}_2\text{O}_3/\text{FSM-16}$  drastically decreased from 1065 to 6.6 and 546 to  $8.7 \text{ m}^2 \text{ g}^{-1}$ , respectively. Since FSM-16 is structurally stable and its BET area remained constant after calcination at  $550 \text{ }^\circ\text{C}$ , these decreases in BET areas were probably due to the deposition of coke and resultant filling of their mesopores.

Deactivation of the catalysts were estimated by a well-known equation for the deactivation by the deposition of coke or polymeric substances:

$$x(t) = a \exp(-bt)$$

where  $x(t)$  is the conversion of CHO at process time  $t$ , constant  $a$  is the initial conversion and constant  $b$  is a deactivation factor. Our reaction data were well explained by this equation.

Figure 2 shows the relationships of the deactivation factor  $b$



**Figure 2.** Relationships between the deactivation factor " $b$ " and acid or base amounts. (○), (□), (△), (◇) Strong acid sites on CdO/FSM-16, ZnO/FSM-16,  $\text{Al}_2\text{O}_3/\text{FSM-16}$  and FSM-16, respectively; (●), (■), (▲), (◆) strong base sites on CdO/FSM-16, ZnO/FSM-16,  $\text{Al}_2\text{O}_3/\text{FSM-16}$  and FSM-16, respectively.

with the acidity and the basicity of the catalysts. The correlation was seen between strong basic amounts and deactivation factor  $b$ . This relation clearly indicates a contribution of the basic sites to the deactivation. It is well known that  $\epsilon$ -caprolactam (CL) form nylon 6 by the anionic polymerization initiated by a base. Therefore, we suggest that the basic sites on the surface initiate the polymerization of CL and that the resultant polymers deactivate the catalysts. This is supported by the facts that retardation of the deactivation and improvement of the CL selectivity are achieved by replacing the nitrogen carrier by a  $\text{CO}_2$  stream<sup>7</sup> or in the presence of oxygen compounds such as alcohols on various zeolite catalysts.<sup>4,8,9</sup> The acidic  $\text{CO}_2$  and alcohols are likely to block the basic sites to retard the deactivation. We suppose that strong basic sites on siliceous FSM-16 are caused by impurities in it, and that  $\text{CO}_2$  and alcohol blocks the strong basic sites by adsorption. However, the addition of alcohols brings about a new problem to separate the alcohols from the product.

We proposed here that the existence of the strong basic sites caused the deactivation of the catalysts. To minimize the catalyst deactivation rate, it is probably necessary to suppress the formation of the strong basic sites on the catalyst.

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