A Novel Modification for Silicalite-1 with High Stability and Selectivity in Vapor Phase Beckmann Rearrangement of Cyclohexanone Oxime

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This paper presents a novel modification of highly siliceous MFI zeolites with hydrofluoric acid treatment: Silicalite-1 undergone such treatment exhibited remarkable improvements in stability and selectivity for Beckmann rearrangement of cyclohexanone oxime, which are even much better than those obtained by basic modification.

ε-Caprolactam, the raw material of nylon-6, is produced industrially by liquid phase Beckmann rearrangement of cyclohexanone oxime using concentrated sulfuric acid catalyst, which is a source of pollution and equipment corrosion. Thus, many efforts have been focused on the research of solid acid catalysts for their environmental friendly manufacture.[1,2] Among them, zeolites of MFI-type, in particular those with a high silica/alumina ratio, prove to be the most promising catalysts for the transformation of oximes into amides.

It has been well illustrated in the literature that silanols on zeolites surface are of great significance for Beckmann rearrangement reaction.[3–8] For example, Sato et al.[3] proposed that the terminal silanols on highly siliceous MFI zeolite are the active sites. On the contrary, Kitamura et al.[4] reported that the selectivity to lactam was improved greatly when the terminal silanol groups were eliminated, indicating that the terminal silanol groups promoted the formation of by-products. On the other hand, Hölderich and co-workers[5,6] investigated the catalysis of vapor phase Beckmann rearrangement over the parent and various modified zeolites silicalite-1 and suggested that the silanol nests were the most favorable active sites for Beckmann rearrangement due to the adjustment of acid strength caused by the hydrogen bond, while terminal silanols were the least favorable. These results suggest that the catalytic performance of highly siliceous MFI zeolite will be improved if the distribution of various types of silanols can be adjusted by a suitable way. Hence, many efforts have been concentrated on the adjustment of silanols on zeolites surface.[5,6,9–11] Until now, treating high siliceous MFI zeolites with nitrogen-containing basic solutions, which was developed by Sumitomo Company,[10] has been considered to be the most effective modification method. However, thus treated catalysts still deactivated at a relatively quick rate with time on stream. Therefore, it is still interesting and of great significance to explore other effective modification methods for highly siliceous MFI zeolites applied in vapor phase Beckmann rearrangement reaction.

Besides its widely use in surface etching, hydrofluoric acid treatment is also an effective method of surface rehydroxylation for silica.[12,13] However, to the best of our knowledge, such treatment for highly siliceous zeolites has not been reported so far. In this paper, we report that zeolite silicalite-1 modified with hydrofluoric acid exhibited remarkable improvements in stability and selectivity for vapor phase Beckmann rearrangement of cyclohexanone oxime, which are even much better than those obtained by basic treatment which has been considered to be the most effective modification method up to date.

Silicalite-1 was hydrothermally prepared by conventional procedure from TEOS, TPAOH, and water at 120 °C for 48 h. White solid produced was washed, separated, dried at 100 °C, and calcined at 600 °C for 4 h in air. To this crystal was added 7.5 wt % ammonium nitrate solution to carry out ion exchange treatment at 90 °C for 1 h and repeated for 3 times and then the crystal was washed and separated. Finally, the crystal was dried at 100 °C and calcined at 550 °C for 4 h in air. The resulting crystal was referred as catalyst S-1.

Hydrofluoric acid treatment was carried out in an autoclave under autogenous pressure. 0.04 wt % HF with the mass ratio of HF to S-1 of 10:1 was added. The treatment was carried out at 80–90 °C for 1 h and was repeated for 3 times. The crystal obtained was washed, separated, dried and named as FS-1. The basic treatment was performed in a similar way as hydrofluoric acid treatment except that a mixture of ammonium nitrate (7.5 wt %) and aqueous ammonia solution (28 wt %) with the mass ratio of 3:1 was used and the resulting crystal was calcined at 550 °C for 4 h in air. The catalyst with basic treatment was named as NS-1.

The Beckmann rearrangement reaction was carried out in a fixed-bed reactor at 370 °C under atmosphere pressure. The mixture of cyclohexanone oxime (30 wt %) and ethanol was injected to the reactor along with N_2 as the carrier gas. The weight hourly-space-velocity (WHSV) of cyclohexanone oxime was $8\,h^{-1}$. The effluent products were collected and analyzed by gas chromatograph (HP 4890, HP-1 capillary column, flame ionization detector). The major by-products formed are cyclohexanone, cyanopentane, and cyanopentene, which is in accordance with the literature.[9]

The changes of oxime conversion with time on stream over the different catalysts are compared in Figure 1. It was found that each catalyst exhibited a high initial oxime conversion about 99%, while their deactivation rate was quite different. The untreated catalyst S-1 underwent a quick activity loss and its conversion dropped to 66.9% after 21 h reaction. The deactivation rate of S-1 was greatly slow down after modification and catalyst NS-1 gave a conversion of 88.3% after 29 h reaction. Particularly, catalyst modified with hydrofluoric acid exhibited the lowest deactivation rate. Its conversion remained nearly 96% after a relatively long reaction time of 53 h (almost two times longer than that for NS-1 catalyst). Unlike the conversion of oxime, no significant change in the selectivity to caprolactam with time on stream was observed over all three catalysts. The average selec-

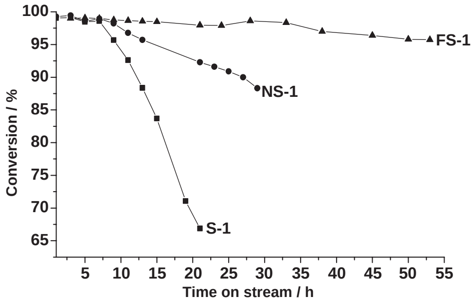

Figure 1. Variation of oxime conversion with reaction time over different silicalite-1 catalysts. Reaction conditions: $T = 370\,^{\circ}\mathrm{C}$, $P = 0.1\,\mathrm{MPa}$, $\mathrm{WHSV} = 8\,\mathrm{h}^{-1}$, solvent: ethanol, carrier gas: N_2, flow rate of $N_2 = 60\,\mathrm{mL\,min}^{-1}$.

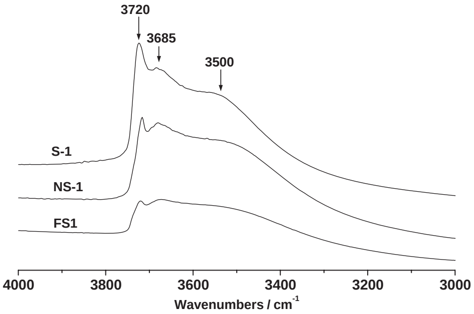

Figure 2. FT-IR spectra of different silicalite-1 catalysts.

tivity to lactam of S-1, NS-1, and FS-1 was 93.6, 93.2 and 96.1%, respectively, the highest value being observed on FS-1. The above results show that hydrofluoric acid modification for silicalite-1 significantly improves its catalytic performance for the Beckmann rearrangement of cyclohexanone oxime; and that the improvements are even much better than those obtained by basic treatment which has been considered to be the most effective modification method up to date.

To clarify the effect of HF modification on catalytic behavior of silicalite-1 for Beckmann arrangement reaction, the FT-IR spectra of FS-1 and S-1 together with NS-1 were measured. As shown in Figure 2, three peaks were detected and assigned to terminal silanols ($\approx 3720\,\mathrm{cm}^{-1}$), vicinal silanols ($\approx 3685\,\mathrm{cm}^{-1}$) and silanol nests ($\approx 3500\,\mathrm{cm}^{-1}$), respectively. The first one belongs to isolated silanols while the latter two to silanols associated by hydrogen bonding. By comparing the intensities of different silanols, we obtained that the ratio of the associated silanols to the isolated silanols decreased in the order: FS-1 > NS-1 $\gg$ S-1. This order agrees well with that of catalytic performance. The good relationship between the catalytic behavior and the ratio of the associated silanols to the isolated silanols can be explained as follows: (1) It has been reported that the associated silanols are favorable than the isolated counterparts for the selective formation of lactam.[3,4] On the other hand, it was also reported that the isolated terminal silanols promote the non-selective conversion of cyclohexanone oxime,[4,9] which makes the lactam selectivity decrease and the catalyst deactivate quickly. Accordingly, higher ratio of the associated silanols to the isolated silanols means higher selectivity for caprolactam formation and less coke precursor production, which in consequence delay the deactivation of catalyst.[11] (2) It has been demonstrated that the rearrangement to ε-caprolactam from cyclohexanone oxime can be catalyzed by silanols around $100\,^{\circ}\mathrm{C}$, while the desorption of the originally produced ε-caprolactam from catalyst surface occurs at a considerably higher temperature ($>350\,^{\circ}\mathrm{C}$).[3,14] If the produced ε-caprolactam can not desorb from catalysts surface smoothly, it may transfer to coke or other by-products, which lowers the selectivity to lactam and shortens catalyst life.[3,15] On the other hand, Barrett et al.[12] and Kohler et al.[13] verified experimentally that the terminal silanols possess a higher adsorptivity for basic compounds than the associated silanols. It is proposed that most of the hydrogens may be involved in H-bonding in associated silanols; as a result there is little reactive hydrogen to react with basic compounds.[16] The above results implied that the desorption rate of the produced caprolactam from silicalite-1 catalyst surface depends greatly on the ratio of the associated silanols to the isolated silanols. The higher the ratio the easier the desorption of the produced caprolactam from catalyst surface, which results in higher stability and selectivity for caprolactam synthesis.

In conclusion, compared with untreated samples, silicalite-1 with hydrofluoric acid treatment exhibited a much lower deactivation rate and higher selectivity to lactam in Beckmann rearrangement of cyclohexanone oxime. The stability and selectivity of zeolite silicalite-1 for the vapor phase Beckmann rearrangement of cyclohexanone oxime was closely dependent on the ratio of the associated silanols to the isolated silanols, which accounts for the excellent catalytic performance of HF modified silicalite-1.

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