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## Synthesis and Catalytic Properties of Ti-rich TS-1

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### Introduction

Zeolite TS-1 is an active, highly selective and environmentally benign catalyst for a number of industrially important organic oxidation reactions in the presence of aqueous H<sub>2</sub>O<sub>2</sub> solution. Typical reactions include the conversion of alkanes to alcohols, alkene epoxidation, phenol oxidation and ketone ammoximation *etc.* The catalytic property of TS-1 depends on the lattice Ti content, which is, however, always less than 2 wt.%. The effective way to increase the Ti content in the framework of TS-1 is still a huge challenge. Thangaraj et al. reported that 8 Ti ions could be incorporated in the lattice sites per unit cell with an improved method [1], but Schuchardt and his coworkers claimed that there was no difference in the framework Ti content for the samples synthesized with the Enichem route and the Thangaraj method [2].

Isomorphous substitution of metal atoms for Si in zeolites is not only related to zeolite structures and the chemical nature of metals but also strongly influenced by the crystallization mechanism. Attempts were made to increase the lattice Ti content in TS-1 by harmonizing the hydrolysis rate of Ti alkoxide with that of silicate species as well as the nucleation and crystal growth rates. We have found the potential of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>; the presence of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> in the crystallization gel not only considerably increased the framework Ti content without forming extraframework Ti species but also improved the hydrophobicity of the prepared TS-1 catalyst, consequently showing significantly improved activity for the oxidation of a variety of organic substrates.

### Materials and Methods

TS-1 samples were synthesized basically according to the same procedures as those reported by the Enichem group [3] except that (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> was added after removing alcohol. When the Si/Ti ratio in the synthesis gel was lower than 50, a certain amount of H<sub>2</sub>O<sub>2</sub> aqueous solution was added before the addition of TPAOH. The solution was heated in a water bath kept at 55 – 60 °C for about 4 h. Occasionally, a small amount of water was added during the heating process to compensate the vaporized portion. After totally evaporating alcohol, the clear solution was cooled down, and ammonium carbonate was added. The composition of the final gel was maintained in the range of 0.3(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>:SiO<sub>2</sub>:(0-0.2)TiO<sub>2</sub>:0.5 TPAOH:35H<sub>2</sub>O. The crystallization was carried out at 170 °C for 3 to 6 days to produce TS-1(YNU) samples.

### Results and Discussion

It was found that the coordination states of Ti species in the samples were markedly different when different synthesis methods were used. The diffuse reflectance (DR) UV-vis spectra showed that there was a considerable amount of octahedral Ti species in the as-

synthesized and calcined Enichem samples synthesized from a gel with a Si/Ti ratio of 50, as evidenced by the presence of an intense band around 260 nm. In contrast, extraframework Ti species were negligibly observed in the YNU samples. After acid washing of calcined samples, a small amount of octahedral Ti species and Ti oxides were still present in the Enichem samples. Nevertheless, if the Enichem samples were also treated with acid before calcination, no extraframework Ti species could be detected. The Si/Ti ratio in the prepared Enichem catalysts reached a minimum of 58.3. The samples synthesized with the Thangaraj method gave similar results. In contrast, if (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> was introduced in the synthesis gel, the Ti content in the catalyst increased with increasing Ti amount in the gel when the Si/Ti ratio in the gel was larger than 20. Thus TS-1 catalysts with a Si/Ti ratio of 37-40 were obtained by the YNU method. The unit-cell volume of the TS-1 catalyst prepared from the YNU system linearly increased with increasing Ti content, providing evidence that more Ti cations in the samples have been incorporated in the framework. This is also confirmed by the development of the 960 cm<sup>-1</sup> band in IR spectra.

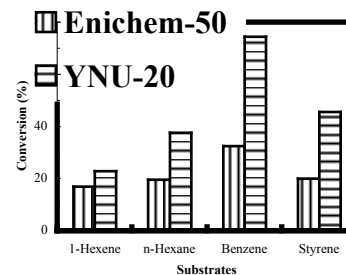


Fig. 1. Catalytic performance of TS-1 samples synthesized with different methods.

The YNU sample exhibited much higher catalytic activity than the Enichem sample as shown in Fig. 1. This is not only due to the higher Ti content in the framework, but also might result from the increase in hydrophobicity. In the case of YNU samples, crystals are well crystalline, as evidenced by high Q<sup>2</sup>/Q<sup>3</sup> ratios. In contrast, more defective sites were present in the Enichem samples. The higher hydrophobicity of the well-crystallized YNU samples would lead to the higher oxidation activity. The Enichem samples are not only relatively hydrophilic but might contain more ((SiO)<sub>3</sub>TiOH) species since the incorporation of Ti atoms in the framework may occur via the insertion of Ti in the defective sites of silicalite-1.

The difference toward oxidation catalysis may be accounted for by the modified crystallization mechanism in the presence of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> and the resulting difference in the pathway to isomorphous substitution of Ti for Si.

### Significance

A new route to the synthesis of TS-1 having high oxidation activity has been developed with (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> as a crystallization-mediating agent.

### References

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3. Clerici, M.G., Bellussi, G., Romano, U. *J. Catal.* 129, 159 (1991).