Chapter 6
CVD of Silica for the Shape Selective Reaction

Abstract Chemical vapor deposition (CVD) of silicon alkoxide on the external surface of zeolite is proposed to realize the shape selective reaction and adsorption. Formation, characterization and control function of the silica overlayer on zeolites, mordenite, ZSM-5, A, and Y-zeolites are elucidated. The fine control of the pore-opening size of zeolite is an example of the molecular engineering of zeolites.

6.1 Reactants and Products Shape Selectivity, Concept and Definition

Shape selectivity is a concept for the selective formation of the desired product based on the zeolite catalysts. The generation of the shape selectivity is realized only with the micro porosity of zeolites effectively utilized. Various energy-saving processes of the catalytic reaction and the adsorption separation are realized by utilizing the excellent property of the shape selectivity on zeolites. Thus, the enhancement of the shape selectivity has been studied extensively from various view-points. The study on the selective production using the modified zeolites is a subject which is most typical on the zeolite catalysts. It includes utilizations of various available reagents, effective modification processing, and preparation mechanism.

Shape selectivity is divided into following three categories, as shown in Fig. 6.1. Reactant selectivity is defined as that any molecule which cannot enter into the pore does not react. In a similar way, product selectivity is defined as that any molecule which cannot be desorbed from the pore is not produced. Transition-state selectivity is not usual but has been indicated in a following, i.e., any product of which intermediate in the transition state is not formed inside the pore is not formed [1]. The latter selectivity should be caused by the three dimensional inherent structure of the zeolite, and will not be a subject in the present description. Improvement of the reactant and product selectivity based upon the control of pore-opening size is reviewed in this chapter.
6.2 Chemical Vapor Deposition of Silica and the Procedure

Niwa et al. have found that chemical vapor deposition of silica on the external surface of zeolite remarkably (in some cases, perfectly) enhances the shape selectivity [2]. The chemical vapor deposition (CVD) method has been studied extensively on various zeolites. Usually, silicon tetra-alkoxide, i.e., Si(OCH$_3$)$_4$ or Si(OC$_2$H$_5$)$_4$,

(I) Reactant selectivity

(II) Product selectivity

Fig. 6.1 Three categories of the shape selectivity in zeolites