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Zeolite membrane on catalyst particles for selective formation of *p*-xylene in the disproportionation of toluene

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Received (in Cambridge, UK) 14th June 2001, Accepted 1st August 2001
First published as an Advance Article on the web 29th August 2001

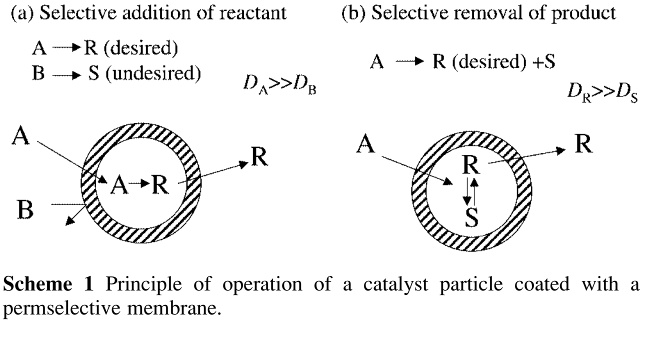
The selective formation of *p*-xylene is shown in toluene disproportionation using a new catalyst which is surrounded with a permselective membrane.

New technologies using inorganic membrane reactors have become of interest with the development of preparation methods for metal and ceramic membranes. The basic concept of the membrane reactor is a coupling of a catalyst with a membrane that gives (1) selective addition of reactants to the reaction zone and (2) selective removal of products from the reaction zone. Although the preparation of zeolite membranes on porous supports has been extensively studied,[1–9] the number of reports regarding membrane reactors combined with zeolite membranes is still small.[10,11] Recently, titania plate-supported platinum catalysts covered with a silicalite layer have been developed by van der Pauil *et al.*[12–14] who used titania/Pt/silicalite composites for hydrogenation of linear and branched alkenes. They showed that the yield of the hydrogenation of linear alkenes was much higher than that of branched alkenes because of a high diffusivity (D) of linear alkenes through the silicalite layer.

In this study, we developed catalyst particles coated with a permselective membrane. The reaction models for the potential applications using this type of catalyst particle are shown in Scheme 1. In the first example, if the diffusivity of reactant A is much larger than that of B, reactant A selectively diffuses to a catalyst particle through a membrane. The undesired reaction B to S or the adsorption of B as a poison on the catalyst can be prevented. In the second example, the reaction has a limited yield or selectivity controlled by the reaction equilibrium according to thermodynamics. The selective removal of desired product R from the catalyst particle gives enhancement of selectivity when the diffusivity of product R is much greater than S.

A catalyst with a permselective membrane has a larger membrane area per unit reactor volume compared to conventional membrane reactors. This is one of the most advantageous points of this catalyst considering practical applications since the membranes with large membrane areas without pinholes or cracks are difficult to prepare in many cases.

In this study, a silica-alumina catalyst covered with a silicalite membrane was used for disproportionation of toluene to produce benzene and xylene isomers, which is an example of the reaction shown in Scheme 1(b). An amorphous acid catalyst, silica-alumina, was first used in the industrial process of toluene disproportionation.[15] Following this, zeolite catalysts such as mordenite, faujasite and ZSM-5 were reported to be very active in catalyzing toluene disproportionation. However, the selectivity of *p*-xylene production was close to the thermodynamic equilibrium. To overcome this, various improvements have been carried out using medium pore zeolites, such as dealuminated MCM-22[16] and ZSM-5[17] modified with P and Mg. The high *para*-selectivity over modified MCM-22 and ZSM-5 can be explained by 'restricted transition-state selectivity' or 'product selectivity' inside the zeolite pores.



Scheme 1 Principle of operation of a catalyst particle coated with a permselective membrane.

The silica-alumina/silicalite catalyst was prepared as follows: silica-alumina particles (Nikki Chemical Co., Ltd.) with composition of 82 wt% SiO_2 and 13 wt% Al_2O_3 were crushed to *ca.* 1 mm in size. The starting sol for the zeolite coating consisted of colloidal silica (Nissan Chemical Industries, Ltd.), tetrapropylammonium bromide (TPABr) and tetrapropylammonium hydroxide (TPAOH) (Wako Pure Chemical Industries Co., Ltd.) and deionized water. The silica-alumina particles were placed in the bottom of the sol with a molar ratio of 3 SiO_2 : 0.3 TPABr : 0.3 TPAOH : 130 H_2O. The crystallization was carried out in an autoclave at 453 K for 24 h. The product was calcined in air at 773 K for 5 h with a heating rate of 0.8 K min^{-1} and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and catalytic tests.

XRD patterns of silica-alumina particles and zeolite-coated silica-alumina particles are shown in Fig. 1. No amorphous phase was observed in the XRD pattern of the silicalite-coated sample. The observed peaks are similar to the reported XRD patterns of silicalite powder, indicating that randomly oriented polycrystalline silicalite was formed on the silica-alumina particles. Fig. 2 shows SEM images of the obtained particles with different magnifications. The size of the silicalite crystals formed on the silica-alumina was about 5 μm.

The disproportionation of toluene was performed using a fixed-bed reactor (i.d. 4 mm) with a continuous flow system under atmospheric pressure. The feed rate of toluene was 2.16 mg min^{-1}. The catalyst weight and the flow rate of helium carrier were 1.3 g and 10 ml min^{-1}, respectively. Reaction

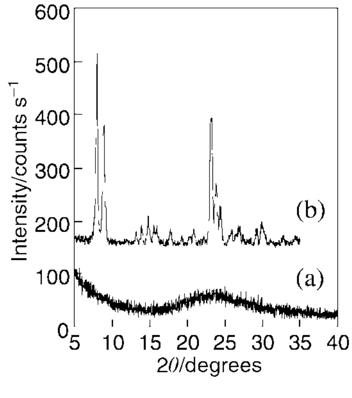


Fig. 1 XRD patterns of (a) silica-alumina particles and (b) silicalite-coated silica-alumina particles.

DOI: 10.1039/b105256j

Table 1 Results of toluene disproportionation

Catalyst	T/K	WHSV[a]	Yield of xylene (%)	Fraction of xylene (%)			Ref.
				p	m	o	
Silicalite/SA[b]	673	0.1	0.08	100	0	0	This work
	823	0.1	0.4	91	5	4	This work
SA	673	0.1	1.5	23	52	25	This work
Silicalite	673	0.1	0.0	—	—	—	This work
H-MCM-22	573	0.1	7.8	85.3	14.4	0.3	16
P-ZSM-5	873	10	21	97	2	1	17
Mg-ZSM-5	823	3.5	10.9	88	10	2	17
Thermodynamic equilibrium	673		—	22	54	24	
	823		—	22	54	24	

[a] WHSV: weight hourly space velocity, (g of feed)/(g of catalyst) h^{-1}. [b] SA = silica-alumina.

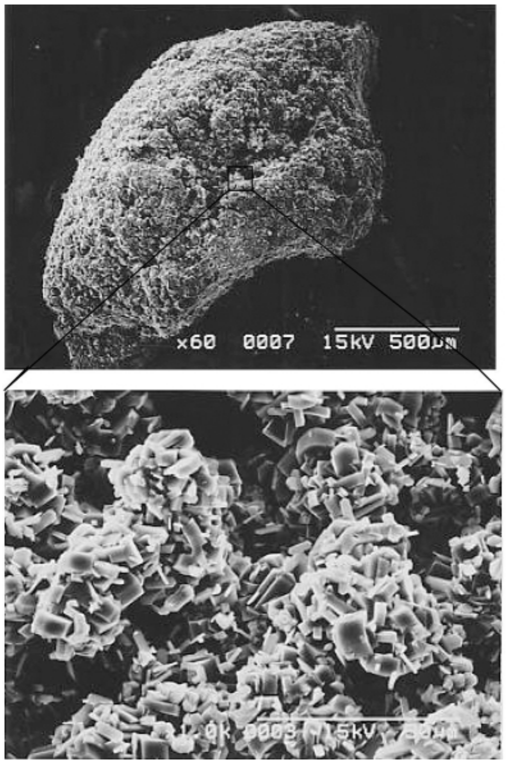


Fig. 2 SEM images of a silicalite-coated silica-alumina particle.

temperatures used were 723 and 823 K and the products were directly introduced to an FID gas chromatograph.

Table 1 lists the yields of the xylene isomers and the fraction of each xylene. The distribution of xylene isomers was very close to their equilibrium value over the silica-alumina catalyst without silicalite coating. On the other hand, the fraction of *p*-xylene in xylene isomers (*para*-selectivity) over the silicalite-coated catalyst largely exceeded the equilibrium value of about 22%. The selective permeation of *p*-xylene through silicalite membranes has been reported by several groups.[18–20] The high *para*-selectivity in the toluene disproportionation is caused by the selective removal of *p*-xylene from the silica-alumina particles, which leads to an apparent equilibrium shift between xylene isomers. The activity of the silicalite-coated catalyst was lower than that of the non-coated catalyst because of diffusion resistance through the membrane. A remarkable increase in the yield of xylenes was found at high temperature (823 K) owing to an increase in activated diffusivity of xylene through the silicalite membrane. When silicalite crystals without silica-alumina particles were used for the reaction, no catalytic activity was observed. Therefore, the silicalite membrane on the catalyst is believed to act not as a catalyst but as a separator.

High *para*-selectivity over shape-selective zeolite catalysts has been reported previously[16,17] (listed in Table 1). However, the mechanism of selective *p*-xylene production in this study is different from those observed in shape-selective zeolite catalysts. Here, the high *para*-selectivity does not result from 'product shape-selectivity' but from the selective removal of the produced *p*-xylene as seen in membrane reactors. The great potential of catalyst particles coated with a permselective membrane has been shown.

We would like to thank GHAS laboratory at Osaka University for the XRD and SEM measurements.

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