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学位論文名	MFI Zeolite Catalysts for Selective Production of para-Xylene and Light Olefins （パラキシレンおよび低級オレフィンの選択的合成を目指したMFI型ゼオライト触媒の開発）
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論文内容の要旨

Introduction

Zeolites have shown many advantages in practical applications especially in the field of separation and catalysis. In fact, many reactions using zeolite catalysts in the industry are controlled by kinetics and thermodynamics in the way that is not favourable for the target products. The catalyst modifications are expected to obtain desired components at the highest reactant conversion. For those reasons, the active sites of zeolite catalysts should be controlled properly through the modifications. The combination of zeolite layer with catalyst particles and the chemical treatments to control the active sites of zeolite catalyst have shown many advantages from the view point of large scale application.

The concept of thesis is the development of new catalyst design through controlling of active sites of H-ZSM-5 catalytic particles to improve product selectivities.

In this study, the chapters 2-6 focus on the control of location of acid sites on the external surface of synthesized H-ZSM-5 particles by an inactive silicalite-1 layer for the production of *p*-xylene through the alkylation, disproportionation and isomerization reactions. In addition, the morphology of the synthesized silicalite-1/H-ZSM-5 composite crystals was controlled effectively by changing the synthesis compositions.

Chapter 7 concentrates on the control of acid-strength distribution of H-ZSM-5 by a chemical treatment method for the light olefin production in the methanol-to-olefin reaction.

1. Core-Shell Silicalite-1/H-ZSM-5 Composite Catalysts

The processes of the formation of dialkyl-benzene from monoalkyl-benzene such as disproportionation and alkylation are one of the most important processes in chemical industry. The separation of *p*-xylene from its isomers; *o*-; *m*-xylenes and from other aromatics requires high cost with much energy consumption. Since the late 1960s, ZSM-5 catalysts have been extremely studied because of high selectivity for *p*-isomer, the most valuable compound for commercial use, especially for the production of polyester resin and fibers. However, the *para*-selectivity significantly decreases because of the acid sites on the external surface and at the pore-mouth openings of zeolite particles, which causes the secondary isomerization of *para*-xylene into its isomers. To enhance *para*-selectivity, Miyamoto et al. [Adv. Mater. 17 (2005) 1985] have developed a novel composite catalyst consisting of zeolite crystals combined with an inactive silicalite layer giving up to 99% *para*-selectivity, respectively. However, the morphology of the composite crystals had still been not controlled yet. In addition, the effects of reaction process variables were also not investigated in their work.

In this study, new types of silicalite-1/H-ZSM-5 composite catalysts were developed based on controlling external acid sites and the crystalline morphology by changing the synthesis compositions. The synthesized catalysts were then used for the production of *p*-xylene through the alkylation, disproportionation and isomerization reactions at different reaction conditions.

1. 1. Effect of Si/Al ratios in the core HZSM-5 on the growth of silicalite layer (Chapter 2)

H-ZSM-5 zeolites with different Si/Al ratios of 30, 50 and 70 were coated with an inactive thin silicalite-1 layer under hydrothermal conditions used for the alkylation of toluene with methanol to produce *p*-xylene. The catalytic properties of the silicalite-1/H-ZSM-5 composites were carried out at different reaction conditions. Firstly, HZSM-5 catalysts with different Si/Al ratios were synthesized then coated by silicalite-1 layer by a repeated coating process. Then, the silicalite-1 overgrowth on H-ZSM-5 with different Si/Al ratios was studied. The thickness, structure, and quality of the silicalite layer, as well as catalytic performances were also investigated.

The results showed that the silicalite layers thus formed comprised oriented polycrystals of a few micrometers that grew on the surface of the substrate H-ZSM-5 in the early stage of synthesis. The presence of Al in the H-ZSM-5 must affect on formation of the polycrystalline layer (Fig. 1). When applied in the alkylation of toluene with methanol, the silicalite-1/H-ZSM-5 catalysts with different Si/Al ratios showed excellent *para*-selectivity, >99.9% under all of the reaction conditions (Table 1). The toluene conversions over the silicalite/H-ZSM-5 catalyst were almost constant, indicating that the silicalite coating inhibited coke formation on the external surface of H-ZSM-5.

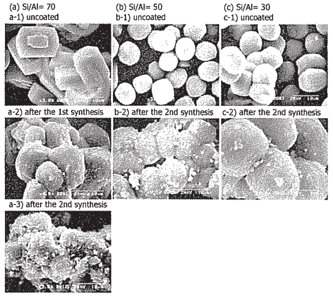

Fig. 1 SEM images of H-ZSM-5 and silicalite/H-ZSM-5 crystals.

Table 1. Alkylation of toluene with methanol over H-ZSM-5 and silicalite/H-ZSM-5.

	silicalite/H-ZSM-5(30)		silicalite/H-ZSM-5(50)		silicalite/H-ZSM-5(70)	
	toluene conversion [%]	*para*-selectivity [%]	toluene conversion [%]	*para*-selectivity [%]	toluene conversion [%]	*para*-selectivity [%]
H-ZSM-5*	63	40	65	38	65	49
silicalite/H-ZSM-5**	42	>99.9	52	>99.9	55	>99.9

Reaction temperature: 673 K, Reaction time: 60 min, * W/F= 0.09 [kg-catalyst h mol^{-1}], ** W/F= 0.15 [kg-catalyst h mol^{-1}]

1.2 Effect of crystal size of core HZSM-5 on silicalite overgrowth, and structure of the interface between silicalite and ZSM-5 (Chapter 3)

The influence of the crystal sizes on the catalytic activity and deactivation behavior of silicalite-1/HZSM-5 catalysts was studied in the alkylation of toluene with methanol. In addition, the crystalline structure of the interface between silicalite-1 and H-ZSM-5 was observed carefully. The reasons for the high *para*-selectivity and high toluene conversion were discussed from the viewpoint of the structure of the composite. HZSM-5 catalysts with different crystal sizes with the same Si/Al ratio of 70 were synthesized under hydrothermal conditions. The crystal sizes were controlled by changing the synthesis conditions. Polycrystalline silicalite layers were formed on H-ZSM-5 with different crystal sizes of 5–30 µm by repeated coating times (Fig. 2). The catalysts were then used for the alkylation of toluene with methanol to produce *p*-xylene. The interlayer between silicalite-1 layer and the core HZSM-5 was observed by TEM observations [Fig. 4].

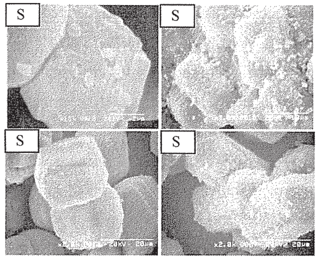

Fig. 2 SEM images of different crystal sizes of silicalite/H-ZSM-5 composite.

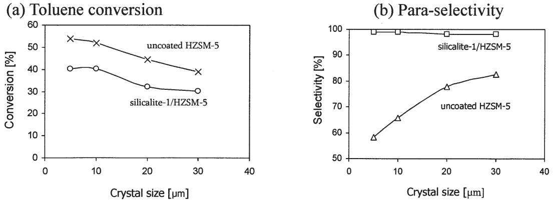
(a) Toluene conversion
(b) Para-selectivity

Fig. 3 Toluene conversion and *p*-xylene selectivity in toluene alkylation as a function of crystal size of the zeolite catalysts. T = 673K, W/F = 0.14 [kg-cat h mol^{-1}], [MeOH]/ [toluene] = 1.0. Reaction time = 60 min.

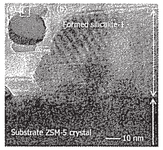

Fig. 4 TEM image of the composite crystal (a) and the HREM image at the interface between silicalite-1 and H-ZSM-5 (b) at 120 kV.

The reaction results (Fig. 3) showed that the conversion and selectivity are as a function of crystal sizes, in which the silicalite-1/H-ZSM-5 composite with a crystal size of 5 µm showed high *para*-xylene selectivity (nearly 100%), and the toluene conversion over the silicalite-1/H-ZSM-5 composite (5 µm) was high and stable with reaction time. Small H-ZSM-5 silicalite core-shell composites of 5 µm are expected for industrial applications.

Para-selectivity slightly decreased with increasing crystal size and the catalyst with a large crystal size rapidly deactivated, indicating that the large crystals could not be fully covered with a silicalite layer. The acid site on the external surface for the large crystal must contribute to the deactivation. High catalytic activity and selectivity of silicalite-1/H-ZSM-5 composites must be caused by the direct pore-to-pore connection between H-ZSM-5 and silicalite.

1.3 New-type composite catalysts: Morphology control for high performance catalysts (Chapter 4)

Considering that the deposited polycrystals after the second synthesis were randomly oriented and were not densely packed in our previous studies. Thus, repeated coating processes were required for obtaining highly selective catalysts. The polycrystalline layers seem to have a low mechanical strength and would become a problem in severe conditions such as in fluidized bed reactors. Another problem is a homogeneous nucleation of silicalite crystals in the solution. Namely, the silicalite crystals formed not only on the ZSM-5 surface but also in the solution. It is not easy to separate the silicalite crystals formed in the solution from the silicalite-1/ZSM-5 composites. Thus, the mass gain of the products after the coatings caused by silicalite-1 was very large.

The thin silicalite layer on the surface of HZSM-5 crystals, the mass gain was mainly due to the homogeneous nucleation of silicalite in the liquid phase. The presence of silicalite crystals without catalytic activity would reduce the efficiency of catalysts. Furthermore, the repeated silicalite coating synthesis seems to be complicated from the viewpoint of large-scale application. In this work, morphology of the silicalite/HZSM-5 composite crystals was studied by changing the molar ratios of silica source and structure directing agent (SDA) in the coating solutions. Polycrystalline (p) and singlecrystalline (s) composites were obtained by changing the coating compositions using different silica sources of fumed silica and TEOS as shown in Figs. 5&6. Single composite crystals were obtained at low molar ratios of SiO_2 (fumed silica) and TPAOH (SDA). At high molar ratios of silica source and TPAOH, a homogeneous nucleation in the solution was apparently dominant instead of a crystal growth of silicalite layer on the HZSM-5 surface. The mass gain was also very large at high molar ratios of SiO_2 and TPAOH. On the other hand, single crystal-like composites could not be obtained by using TEOS as a silica source, which can be explained by high nucleation rate caused by high solubility of TEOS. A decrease of the molar ratio of silica sources and TPA ions would prevent the intergrowth and the formation of undesired silicalite crystals resulting in a decrease of a mass gain after the coating. The presence of TPA ions accelerates the nucleation and crystal growth of silicalite in the liquid phase.

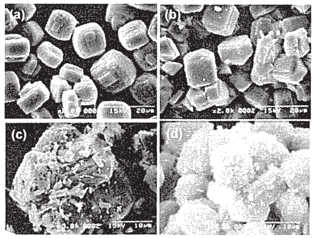

Fig. 5 Selected SEM images of (a) HZSM-5; single-(b) and poly-(c) crystalline silicalite/ZSM-5 synthesized from fumed silica; (d) poly-crystalline silicalite/ZSM-5 synthesized from TEOS.

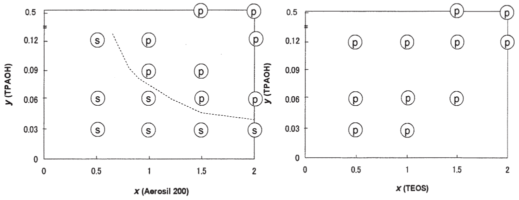

Fig. 6 Effect of molar ratios of the coating solutions on the morphology of the products. The symbols (s and p) represent single crystals (s) and polycrystals (p), respectively. The molar ratios of the solutions are x SiO_2: y TPAOH: z TPABr: 8 EtOH: 120 H_2O.

The alkylation of toluene with methanol was performed using some selected composite catalysts with different morphologies. Regardless of the difference in the synthesis conditions, the coated catalysts provided higher *para*-selectivities compared to that of uncoated one. Here, the reaction data of some selected samples were shown in Table 2.

Table 2. Alkylation results of uncoated HZSM-5 and silicalite-1/H-ZSM-5 catalysts.

	H-ZSM-5	silicalite/ZSM-5$^{(b)}$	silicalite/ZSM-5$^{(c)}$	silicalite/ZSM-5$^{(d)}$
Composite crystal type	-	s	p	p
Toluene conversion [%]	46.7	38.6	35.3	34.5
Selectivity of xylenes [%]				
p-xylene	75.6	99.6	97.5	97.3
m-xylene	15.1	<0.1	1.5	1.86
o-xylene	9.3	0.3	1.0	0.86

The *para*-selectivity of the composite catalysts was significantly affected by the synthesis conditions. The catalysts prepared at lower concentration of silica source and SDA in the coating solutions showed higher *para*-selectivity. Excellent *para*-selectivity of 99.6% with nearly 40% of toluene conversion could be obtained over the single crystal-like composite crystals prepared by only one coating process. Revised synthesis conditions inhibited a homogeneous nucleation of silicalite in the solution. The mass gain of the single crystals was much reduced, and very thin silicalite layer was formed on the HZSM-5 surface. Morphology of silicalite/HZSM-5 composite catalyst was controlled by the synthesis conditions in this work.

1.4 Toluene disproportionation for *p*-xylene production over composite catalysts (Chapter 5)

In the previous work, the developed a silicalite-1/H-ZSM-5 composite catalyst were used for the alkylation of toluene with methanol to produce *p*-xylene. The *para*-selectivities (the molar fraction of produced *p*-xylene in all the produced xylene isomers) were excellent (>99.8%). However, the fraction of *p*-xylene in the total final products was not high as expected because by-products were formed by series of side reactions of methanol to hydrocarbons (MTH). The side reactions were very hard to be controlled in the alkylation reaction because the MTH reaction occurs over weak acid sites of H-ZSM-5 catalyst even at low temperature. The huge of by-products in the final products also make complicated separation processes in the practical application. Toluene disproportionation over ZSM-5 zeolite catalysts is one of candidates for reducing the fraction of by-products. Generally, the catalytic activity of ZSM-5 catalyst in the disproportionation of toluene is low compared to the toluene alkylation with methanol. In this work, silicalite-1/HZSM-5 composites with different Si/Al ratios of 50, 70 and 100 were synthesized and used for the toluene disproportionation. The effect of Si/Al ratios and reaction conditions on the selectivity and yield of *p*-xylene was also studied.

Table 3. The disproportionation of toluene over H-ZSM-5(70) and silicalite-1/H-ZSM-5(70) at 873 K, reaction time: 90 min, *W/F*= 0.44 [kg-catalyst h mol^{-1}].

	Silicalite-1/H-ZSM-5(70)	H-ZSM-5(70)
Conversion of toluene [%]	25.86	33.42
Product composition [%]		
Benzene	15.02	17.37
p-Xylene	8.80	6.32
m-Xylene	1.29	2.77
o-Xylene	0.35	0.79
Ethyl toluenes	0.19	0.74
Trimethyl benzenes	0.24	5.44
Selectivity of xylenes [%]		
p-Xylene	84.64	63.99
m-Xylene	11.71	28.05
o-Xylene	3.65	7.96
Fraction of C_1-C_5 (%)	D.L.	D.L.
Fraction of aromatics (%)	100	100

High fraction of *p*-xylene in the final product with a small amount of by-products was observed while the selectivity to *p*-xylene was still kept at high level. In addition, the catalyst lifetime was improved through the disproportionation of toluene over the composite catalyst due to the absence of olefins produced from methanol as a coke precursor. The *para*-selectivity was increased and reached 84.6% after coating by a silicalite layer (Table 3). But, it was hard to improve further the selectivity at these reaction conditions, which would be caused by an increase of diffusivity of other xylene isomers (*o*- and *m*-xylenes) through the ZSM-5 zeolite channels. The *para*-yield was increased over the coated samples with Si/Al of 50 and 70 after coating. However, *para*-yield decreased over the sample with a Si/Al of 100 because of a lower toluene conversion. To enhance the *para*-selectivity, hydrogen gas was introduced to the feed of toluene reactant at the rate of 15 ml/min as seen in the designs for the industrial units of disproportionation and alkylation reactions. The *para*-selectivities were much improved. However, the decrease of toluene conversions occurred as a lower residence time of toluene in the reactor as shown in Fig. 7.

For the effect of reaction temperatures, this study suggests that toluene disproportionation should be carried out at high temperature to get high yields of *p*-xylene.

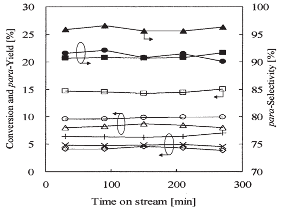

Fig. 7 Toluene disproportionation over silicalite-1/H-ZSM-5 with different Si/Al ratios of 50; 70; 100 carried out with the feed of hydrogen of 15 ml/min at 873 K; *W/F*=0.44 [kg-cat h mol^{-1}]; Toluene conversion: □: 50; O: 70; Δ: 100; *para*-Selectivity: ■:50; ●:70; ▲: 100; *para*-Yield: +: 50; ×: 70; ◊:100).

1.5 Synthesis of H-ZSM-5 nanocrystals for highly-active catalyst (Chapter 6)

A unique synthesis method to form uniform nanoscale HZSM-5 (500 nm) by incorporating Al species dissolved from FAU zeolite and αAl_2O_3 was found. The samples synthesized using the FAU zeolite and Al_2O_3 particles are designated as ZSM-5(F), ZSM-5(A). For comparison, different MFI zeolites were synthesized using $Al(NO_3)_3$ and without aluminum source are named as ZSM-5(N) and silicalite-1. The samples were synthesized under hydrothermal and agitational conditions. The ZSM-5(F) was then coated by silicalite-1 to study the effect of silicalite-1 coating on ZSM-5 nano particles through the alkylation of toluene with methanol.

Fig. 8 shows the crystal surfaces of the prepared samples. The silicalite-1 crystal and ZSM-5(N) have a smooth surface. For ZSM-5(F) and ZSM-5(A), the dissolved Al species might be fragments of the FAU framework in a subnanometer scale and fragment of alumina. These fragments must have partially inhibited a crystallization of ZSM-5 and created a large number of defects formed on the external surface resulting in rough surface of these nano particles.

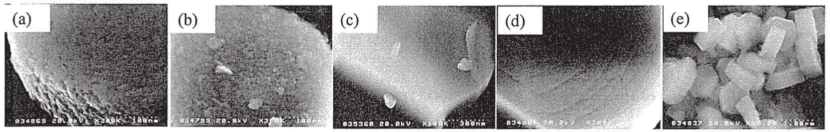

Fig. 8 FE-SEM of (a): ZSM-5(F); (b): ZSM-5(A); (c): ZSM-5(N); (d) silicalite-1; (e): silicalite-1/HZSM-5

From the table 4, the ZSM-5(F) catalyst has expressed very high catalytic activity in the alkylation reaction of toluene with methanol (toluene conversion was about 80%). The *para*-selectivity of ZSM-5(F) was much increased after coating by silicalite-1, about 58%, respectively. However, it was hard to increase further *para*-selectivity. This might be caused by incorporated aluminum from nanoscale ZSM-5(F) released easily to the silicalite solution during the coating process, which causes the reconstruction of external acid sites on the silicalite-1/ZSM-5 (F) composite. It is hard to deactivate the external surface activity of nanoscale ZSM-5 catalytic particles by silicalite-1 coating.

Table 4. Toluene alkylation with methanol (D.L: Below detection limit).

	ZSM-5(F)	ZSM-5(A)	ZSM-5(N)	silicalite/HZSM-5(F)
Crystal size [μm]	0.4	0.5	1.2	1.0
Conversion of toluene [%]	81	51	54	61.3
Fraction of xylenes [%]				
p-xylene	23.8	23.1	76.8	54.2
m-xylene	49.1	53.0	13.7	32.0
o-xylene	27.1	23.9	9.6	13.9

2. Control acid strength distribution: H-ZSM-5 treated with H_3PO_4 for selective production of light olefin in MTO reaction (Chapter 7)

The demand of light olefins (ethylene, propylene) has been rising year by year because they are important starting materials for many chemical processes, especially propylene. Nowadays, the raw material of methanol can be easily produced from the abundant natural gas, so the methanol-to-olefin (MTO) reaction has gaining interest recently. Fig. 9 shows the MTO reaction mechanism over zeolite catalysts.

HZSM-5 catalyst with the medium pore size (ca. 0.55 nm) is one of the candidates to enhance the catalytic lifetime. However, the strong acid sites of the catalyst result in large fraction of by-products through oligomerization reactions, especially aromatic compounds.

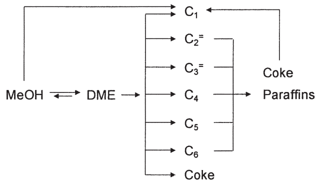

Fig. 9 MTO reaction mechanism

In this work, HZSM-5 catalysts were modified with H_3PO_4 for the production of light olefins in MTO reaction. The H-ZSM-5 catalyst was treated with H_3PO_4 solutions with various concentrations. The mass ratios of phosphorous (P) in the solutions to H-ZSM-5 were 0.01, 0.02, 0.03, 0.045 and 0.055. Hereafter, the H-ZSM-5 samples modified with H_3PO_4 (P-HZSM-5) were designated as: 1P-Z, 2P-Z, 3P-Z, 4.5P-Z and 5.5P-Z. After calcination, the samples were washed with deionized water to remove excess H_3PO_4 on the catalysts. After the washing, the samples were renamed as: W1P-Z, W2P-Z, W3P-Z, W4.5P-Z and W5.5P-Z. Fig. 10 shows the NH_3-TPD profiles of the catalysts before and after treatments. The peak intensity of strong acid sites (523-723K) of modified catalysts decreased with the increase of phosphorous incorporation. The removal of excess H_3PO_4 after washing resulted in a partial recovery of strong acid sites for washed P-HZSM-5 samples.

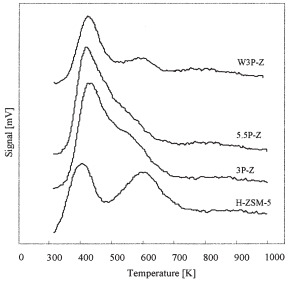

Fig. 10 NH_3-TPD profiles of H-ZSM-5 and P-HZSM-5 catalyst

The selectivities to olefin over P-HZSM-5 in the MTO reactions were significantly improved by the H_3PO_4 treatments. With increasing the phosphorous content in P-HZSM-5, the selectivity to ethene and aromatics noticeably decreased due to weakening acid strength of the strong acid sites of H-ZSM-5 by dealumination. The highest selectivity to propylene over modified P-HZSM-5 reached up to 57% as shown in Table 5, which is very high compared to that of other reports, with a small amount of by-products of aromatics.

Table 5. Methanol conversion and product selectivity over HZSM-5 and P-HZSM-5 catalyst at 723K after 30 min.

Catalyst	Conversion (%)	Selectivity (%)								
		C_1	$C_2^{=}$	C_3	$C_3^{=}$	C_4	$C_4^{=}$	C_5~	DME	Aromatics
H-ZSM-5	100	1.45	22.5	3.12	39.04	3.71	13.41	5.77	0	11.0
1P-Z	100	1.69	19.91	2.42	44.07	3.30	16.43	7.88	0	4.31
2P-Z	100	1.86	17.35	1.28	48.35	2.10	17.99	8.15	0	2.94
3P-Z	100	1.90	8.89	0.73	54.88	1.58	17.10	13.88	0	1.26
4.5P-Z	86.78	4.82	6.76	0.42	52.63	0.69	18.3	14.7	0.62	1.05
5.5P-Z	71.07	1.27	2.27	0.42	0.54	0.42	0.32	0.25	94.51	0
W1P-Z	100	2.06	21.98	3.78	37.25	5.23	14.69	7.59	0	7.41
W2P-Z	100	2.56	22.57	3.31	40.74	4.28	15.13	6.99	0	4.41
W3P-Z	100	1.47	19.86	2.37	45.73	2.82	16.66	8.09	0	2.99
W4.5P-Z	100	1.22	9.59	0.58	56.96	0.95	18.84	10.72	0	1.14
W5.5P-Z	97.4	2.59	11.37	0.43	52.91	0.93	16.16	14.42	0	1.09

論文審査の結果の要旨

化学工業のプロセスでは、化学反応によって目的成分が純粋で得られるケースはほとんどなく、生成物中に副生成物や未反応の反応物が含まれる。生成物の分離・精製には、多大なエネルギーが必要となるため、プロセス全体の省エネルギー化および低コスト化のためには、高選択性触媒の開発が重要となる。

代表的な固体酸触媒であるゼオライトは、構造に起因した分子レベルのミクロ細孔を有しており、形状選択性を利用した反応が期待されている。しかし、実際のプロセスでは、ゼオライトの形状選択性が最大限に利用されていない場合が多い。例えば、ゼオライトの細孔径は、ちょうどパラキシレンの大きさと等しいため、パラキシレンの製造に使われている。細孔内ではメタキシレンやオルトキシレンよりもパラキシレンが選択的に生成する。しかし、細孔内で生成したパラキシレンは触媒粒子表面で異性化してしまい、結果としてパラキシレンの選択性は著しく低下してしまう。

2〜6章では、選択性向上を目的とした「活性点の位置を制御する手法」について述べている。ZSM-5（MFI）型ゼオライト触媒のまわりに、触媒機能をもたないゼオライトであるシリカライトをコーティングした。このコアシェル構造ゼオライト触媒が極めて高いパラキシレン選択性を示すことを実証した。本手法により結晶外表面の活性点を効果的に被覆し、パラキシレンの異性化を抑制することができた。2および3章では、コアゼオライトの結晶径、シリカ/アルミナ比を変化させ、得られた構造触媒の活性・選択性を評価した。4章では、コーティング溶液の組成を変えることにより、コンポジット触媒の形状を制御した。構造規定剤である有機アンモニウム塩およびシリカ源であるフュームドシリカの濃度を低くすることによって、ゼオライトの均一核発生を抑制し、コアゼオライトがそのまま結晶成長した単結晶型ゼオライトコンポジットの合成に成功した。本触媒は、多結晶型触媒よりも、高いパラキシレン選択性を示した。また、5章では、トルエンの不均化について、6章では、ゼオライトナノクリスタルの合成と反応性についての研究成果をまとめている。

一方、7章では、メタノールからオレフィンを製造する反応（MTO反応）におけるプロピレン選択性の向上を目指し、H-ZSM-5触媒の「酸強度分布を制御する手法」を開発した。ゼオライトをリン酸で処理することにより、強い酸点が消滅することを見出した。結果として、芳香族化合物の生成を抑制し、プロピレン選択性が55%以上となった。この値は報告された中で最高値である。また、コーク析出に起因する活性劣化を抑制できた。

以上、本論文は、生成物選択性の向上を目的として、触媒の活性点の制御法を開発したものであり、博士（工学）の学位論文として価値あるものと認める。