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Morphology Control of Silicalite/HZSM-5 Composite Catalysts for the Formation of *Para*-Xylene

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Abstract Single- and poly-crystalline silicalite/HZSM-5 core-shell composite catalysts were synthesized by optimizing the silicalite coating conditions. At low molar ratios of SiO_2 (fumed silica) and TPAOH in the coating solutions, a crystal growth of silicalite layer on the HZSM-5 surface was dominant instead of a homogeneous nucleation in the solution. The mass gain after the coating was also inhibited at low molar ratios of silica source and TPAOH. High *para*-selectivities of silicalite/HZSM-5 composites in the toluene alkylation with methanol were obtained over the single crystal-like silicalite/H-ZSM-5 composite catalyst prepared by one coating process.

Keywords ZSM-5 · Silicalite · Alkylation · Single crystal · Core-shell composite · *Para*-selectivity

1 Introduction

The market demand of *para*-xylene is considerable because it is important raw material for many chemical processes. The separation of *p*-xylene from its isomers; *o*-; *m*-xylenes and other aromatic compounds requires high cost with much energy consumption in the conventional method. The selective formation of *p*-xylene over medium pore size ZSM-5 zeolite is an efficient and energy saving method for *p*-xylene production [1]. However, the secondary isomerization of *p*-xylene into its isomers, *o*-; *m*-xylenes is one of important factors that reduces the selectivity. Pretreatment or external surface modification methods to deactivate external acid sites or to narrow the pore-mouth openings of ZSM-5 catalytic particles have found to enhance the *para*-selectivity such as the impregnation of phosphorous, MgO, boron [2, 3], chemical vapor deposition (CVD) [4–7], chemical liquid deposition (CLD) [5, 8–12], and others [13–26]. Recently, Breen had reported an impregnation of HZSM-5 with boric acid, giving more than 99.9% of *para*-selectivity with the toluene conversions of 3.5–7.9% [11].

In our previous studies, ZSM-5 catalysts were coated by an inactive polycrystalline silicalite layer under hydrothermal conditions for *p*-xylene production [23–26]. The synthesized silicalite/HZSM-5 composites with different Si/Al ratios and with variety of crystal sizes showed not only high *p*-xylene selectivities but also high toluene conversions in the alkylation reaction of toluene with methanol. The interlayer between silicalite and HZSM-5 was directly connected together [26]. However, the deposited polycrystals after the second synthesis were randomly oriented and were not densely packed. Thus, repeated coating processes were required for obtaining highly selective catalysts. These polycrystalline layers seem to have a low mechanical strength and will 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/ZSM-5 composites. Thus, the mass gain of the products after the coating was very large in our previous reports. Considering 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

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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. The alkylation of toluene with methanol was performed using the composite catalysts with different morphologies.

2 Experimental

2.1 Catalyst Preparation and Characterization

HZSM-5 crystals were used as a core for the silicalite coatings. The preparation of HZSM-5 was described in our previous reports [25]. HZSM-5 catalyst with a Si/Al ratio of 100 was prepared by hydrothermal synthesis at 453 K for 24 h. The synthesis solution consisted of tetraethoxysilane (TEOS), aluminum nitrate [$Al(NO_3)_3 \cdot 9H_2O$], sodium hydroxide (NaOH), and tetrapropylammonium bromide (TPABr). The molar ratio was: 2.0 SiO_2:0.01 Al_2O_3:0.5 TPABr:0.25 Na_2O:120 · H_2O.

The precursor solution for the silicalite coatings consisted of fumed silica (Aerosil 200; Wako Pure Chemical Industries Co., Ltd.) and TEOS as silica sources, tetraprophylammonium hydroxide (TPAOH; Wako Pure Chemical Industries Co., Ltd.), TPABr, deionized water (H_2O), and ethanol (EtOH). The molar ratios of the coating solutions were shown on the Table 1. Here, approximately 0.3 g of HZSM-5 crystals was immersed in 15 g of the precursor solution. The crystallization was carried out in a closed Teflon-lined stainless steel vessel under autogenous pressure at 453 K for 24 h. To stir the solution during the hydrothermal synthesis, the vessel was rotated in an oven. The products were then calcined at 873 K for 5 h to remove TPA cations remaining in their structures. The final products were characterized by X-ray diffraction (XRD) recorded on a Rigaku Miniflex using Cu$K\alpha$ radiation and scanning electron microscope (SEM) on a Hitachi S-2250N.

2.2 Catalytic Test

Alkylation of toluene with methanol over the HZSM-5 and silicalite/H-ZSM-5 catalysts was performed using a fixed bed reactor at 673 K. The space time W/F is fixed at 0.11 kg-catalyst h mol^{-1} with the molar ratio of methanol/toluene was 1.0. The products of alkylation were analyzed by a gas chromatograph GC-2014 (Shimadzu Co.) equipped with a flame ionization detector (FID) using a Xylene Master column PRC 7791 (50 m, 0.32 mm).

3 Results and Discussion

3.1 Morphology of Silicalite/H-ZSM-5 Composite

Table 1 lists the effects of molar ratios of the coating solutions on the mass gain of the products after coating. XRD patterns of all the coated samples (data not shown) did not contain reflection peaks for amorphous silica and

Table 1 Molar ratios of the coating solutions and the mass gain of the products

Silica source	Sample	Molar ratios x SiO_2:y TPAOH:z TPABr:8 EtOH:120 · H_2O	Coating time	Mass gain [%]
Fumed silica	A1	$x = 2.0$, $y = 0.12$, $z = 0$	1	+167
	A2	$x = 2.0$, $y = 0.12$, $z = 0.12$	1	+194
	A3	$x = 2.0$, $y = 0.06$, $z = 0.06$	1	+88
	A4	$x = 2.0$, $y = 0.03$, $z = 0.09$	1	+56
	A5	$x = 1.0$, $y = 0.12$, $z = 0$	1	+127
	A6	$x = 0.5$, $y = 0.12$, $z = 0$	1	+40
	A7-1	$x = 0.5$, $y = 0.06$, $z = 0$	1	+51
	A7-2	$x = 0.5$, $y = 0.06$, $z = 0$	2	–
	A8	$x = 0.5$, $y = 0.03$, $z = 0$	1	+36
TEOS	T1	$x = 2.0$, $y = 0.5$, $z = 0$	1	+180
	T2	$x = 1.5$, $y = 0.5$, $z = 0$	1	+151
	T3	$x = 1.0$, $y = 0.12$, $z = 0$	1	+120
	T4	$x = 1.0$, $y = 0.06$, $z = 0$	1	+71
	T5	$x = 0.5$, $y = 0.12$, $z = 0$	1	+65
	T6	$x = 0.5$, $y = 0.06$, $z = 0$	1	+44
	T7	$x = 0.5$, $y = 0.03$, $z = 0$	1	+35

impurities other than an MFI structure, indicating that the mass gain is due to the formation of silicalite crystals.

Here, two different silica sources (fumed silica and TEOS) were used for the silicalite coating. The samples are labeled as A1–A8 (fumed silica) and T1–T7 (TEOS). The mass gain (%) of the products was calculated as the mass increase after the coating divided by the mass of HZSM-5 core zeolites. The mass gain was too large at high molar ratio of TPAOH/silica sources (A1&A2; T1&T2) due to the formation of silicalite crystals through a homogeneous nucleation in the coating solution.

Figures 1 and 2 show the SEM images of uncoated and coated catalysts. A number of undesired silicalite crystals

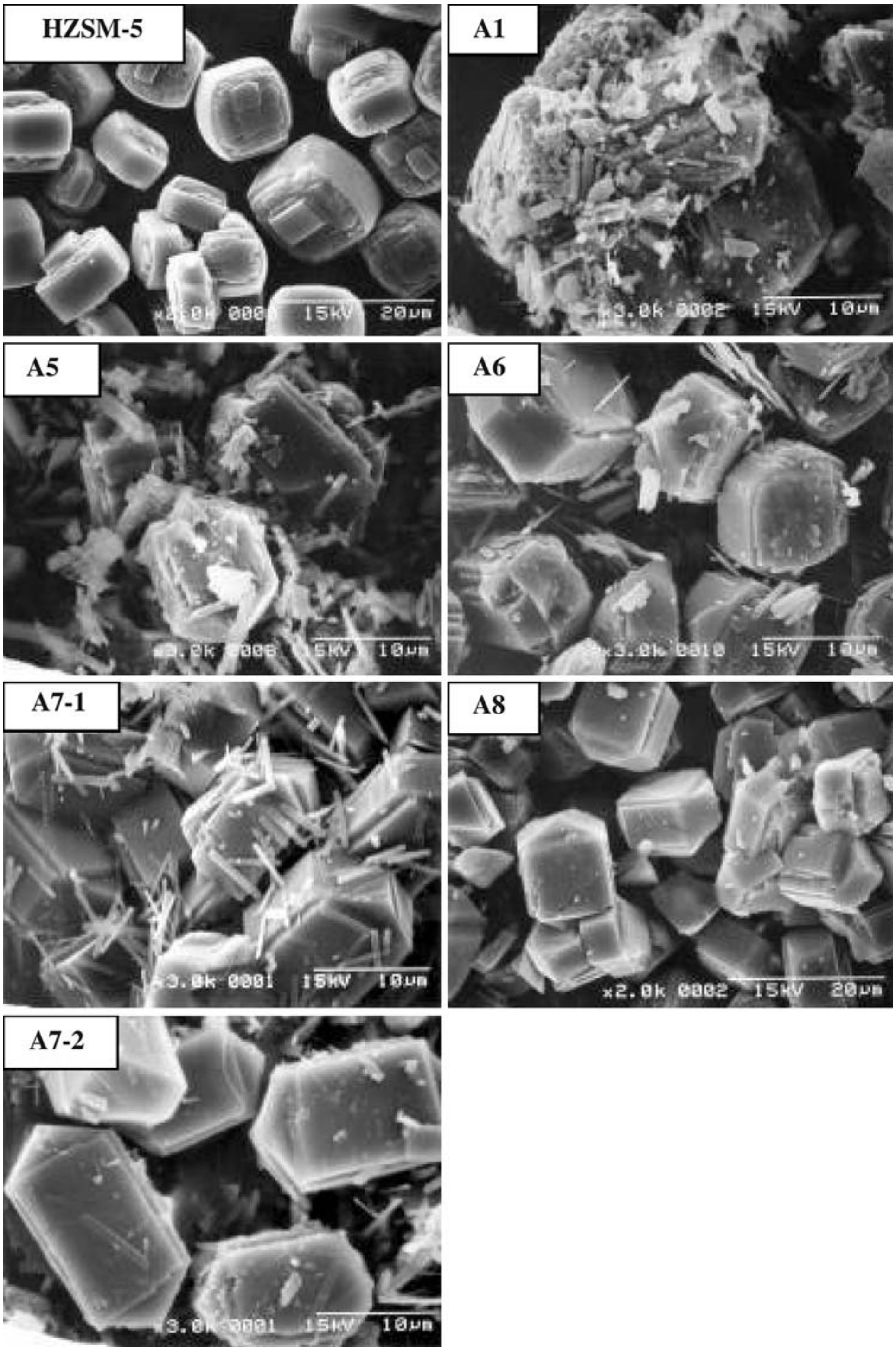

Fig. 1 SEM images of HZSM-5 and silicalite/HZSM-5 composites prepared using fumed silica

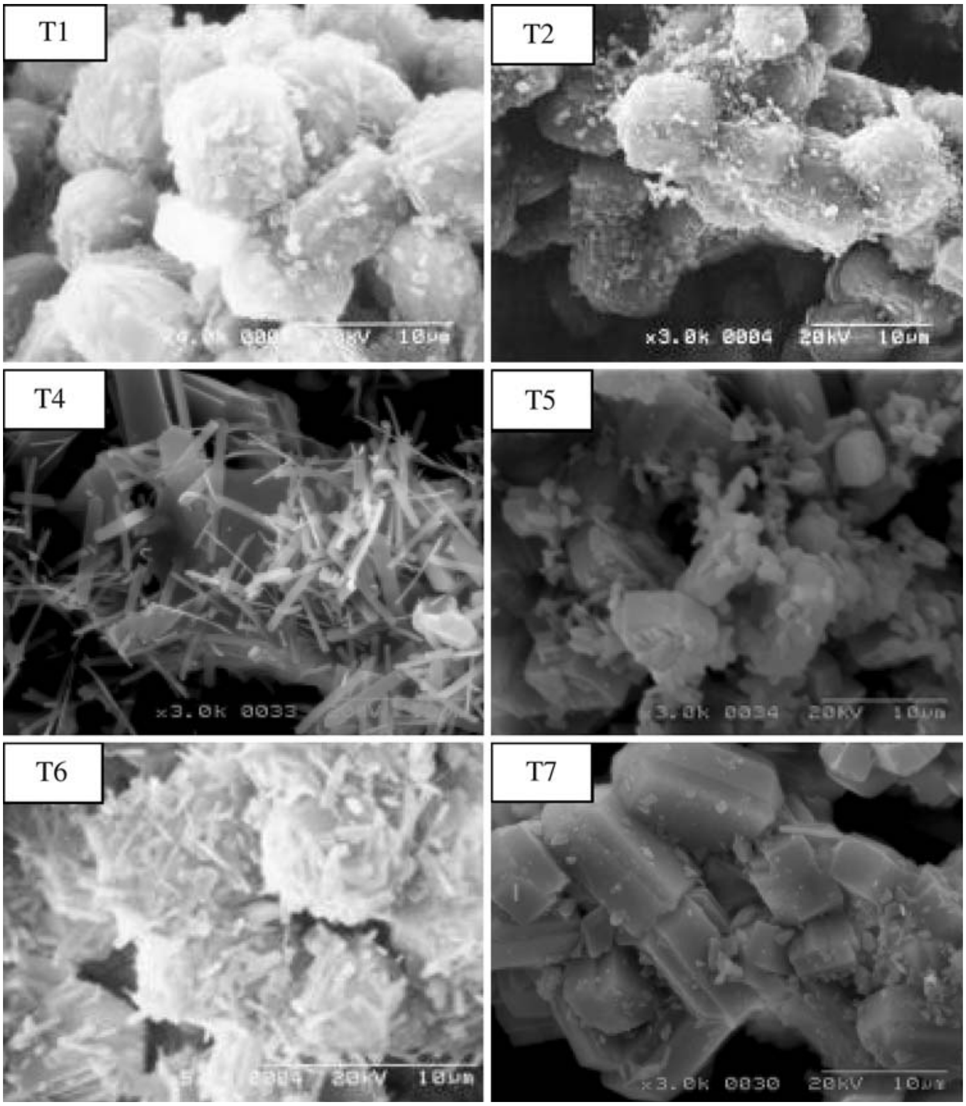

Fig. 2 SEM images of silicalite/HZSM-5 composites coated using TEOS

were formed in the liquid phase and randomly deposited on the silicalite/H-ZSM-5 composites at high silica and TPAOH concentrations. The morphology of the A1 sample was considerably different from that of uncoated HZSM-5. The silicalite-coated HZSM-5 crystals were intergrown each other substantially, which might cause grain boundaries between crystals.

From the SEM observation, we classified the products into polyclystals (p) and single crystals (s) by their morphology. The composites with a large amount of undesired and randomly deposited silicalite crystals were composed of polycrystals (p). On the other hand, composite crystals with a thin silicalite layer grown on the HZSM-5 surface look like single crystal (s). Figure 3 shows the effect of SiO_2 and TPAOH molar ratios in the coating solutions on the morphology of the composite crystals. Single crystals-like silicalite/HZSM-5 composites were obtained at low molar ratios of SiO_2 (fumed silica) and TPAOH. 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. To completely prevent the formation of undesired silicalite crystals, TPA ions-free coating conditions should be developed and will be reported in the future.

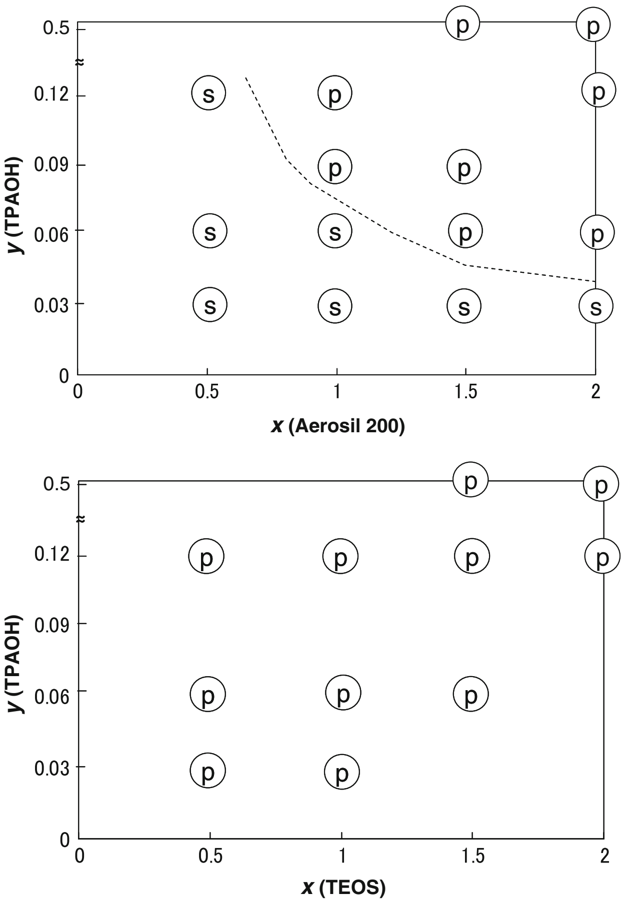

Fig. 3 Effect of molar ratios of the coating solutions on the morphology of the products. The symbols (s and p) represent single crystals (s) and polycrystals (p), respectively. The molar ratiosof the solutions are x SiO_2: y TPAOH: z TPABr: 8 EtOH: 120 H_2O

3.2 Catalytic Performances of HZSM-5 and Silicalite/HZSM-5 Catalysts

Alkylation of toluene with methanol was carried out over the uncoated HZSM-5 and silicalite/HZSM-5 catalysts. The molar fraction of produced *p*-xylene in all the produced xylene isomers is defined as the *para*-selectivity. The reaction results were shown in Table 2. Regardless of the difference in the synthesis conditions, the coated catalysts provided higher *para*-selectivities compared to that of uncoated one.

For the catalysts prepared using TEOS as a silica source, the order of *para*-selectivity was T5 > T1 > T4, T6 > T7. The *para*-selectivity was significantly affected by the TEOS/TPAOH molar ratios. The medium TPAOH and TEOS concentration (T5) resulted in higher selectivity than that of the other samples. The formation of randomly deposited silicalite crystals on the surface of HZSM-5 crystals was clearly observed on T4 and T6. The result indicates that the formation of silicalite layer and alkalinity of coating solution, as mentioned above, affected on the *para*-selectivity of those silicalite/H-ZSM-5 catalysts.

The toluene conversions for the composite catalysts were increased at higher molar ratios of silica sources. High silica concentration resulted in a formation of a densely-packed silicalite layer on the HZSM-5 zeolite. But, toluene conversion decreased due to the diffusion limitation. In addition, decrease in toluene conversion was also caused by the presence of undesired silicalite crystals that were hard to be separated from the silicalite/HZSM-5 composites.

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

	Uncoated	A1	A6	A7-1	A7-2	A8	T1	T4	T5	T6	T7
Toluene conversion [%]	46.7	35.3	36.5	39.4	33.3	38.6	34.5	38.0	43.9	46.6	41.7
Selectivity of xylenes [%]											
p-xylene	75.6	97.5	98.3	98.7	99.1	99.6	97.3	94.3	98.7	94.2	85.6
m-xylene	15.1	1.5	1.1	0.7	0.4	<0.1	1.86	4.01	0.7	3.4	12.29
o-xylene	9.3	1.0	0.6	0.6	0.5	0.3	0.86	1.72	0.6	2.6	5.12
Product composition [%]											
Benzene	–	–	–	–	–	–	–	–	–	–	–
Ethylbenzene	0.18	0.16	0.22	0.17	0.13	0.15	0.12	0.36	0.21	0.12	0.16
p-xylene	31.74	30.17	29.66	34.26	28.99	31.38	25.04	29.94	37.33	40.18	28.87
m-xylene	6.33	0.47	0.32	0.27	0.11	–	0.48	1.27	0.94	1.45	4.29
o-xylene	3.93	0.31	0.19	0.20	0.14	0.08	0.22	0.55	0.67	1.00	1.79
p-ethyltoluene	4.05	3.31	5.28	3.29	2.95	5.73	3.96	4.41	2.41	2.11	3.01
m-ethyltoluene	1.61	0.09	0.10	0.06	0.04	0.03	0.22	0.28	1.34	1.29	0.37
o-ethyltoluene	0.01	0.02	0.02	–	–	–	2.92	0.67	0.18	0.27	1.99
Trimethylbenzene	5.31	0.78	0.72	1.10	0.91	1.02	0.20	0.24	0.71	–	0.27

For the catalysts prepared using fumed silica, the order of selectivity of was A8 > A7-1 > A6 > A1, in which the *para*-selectivity of A8 reached to 99.6% after one coating. The A8 sample is classified into the single crystals. These results indicate that single crystal-like catalysts prepared at lower concentration of SiO_2 (fumed silica) and TPAOH in the solutions show higher *para*-selectivity. As mentioned above, high concentrations of silica source and TPAOH accelerate a nucleation and crystal growth and then, polycrystalline silicalite layers are formed.

The effect of the coating time was also investigated. The reaction results for A7-1 and A7-2 were shown in Table 2. With repeated coatings, the *para*-selectivity was enhanced and reached to 99.1% (A7-2). Similarly to the previous reports [25, 26], we need repeated coating processes to obtain *para*-selectivity higher than 99% for the polycrystals-type composite catalysts. In the present study, however, we could control the morphology of the silicalite/HZSM-5 composite and prepare highly *para*-selective composite catalyst by only one coating process.

Another reason for the low *para*-selectivities of silicalite/HZSM-5 composites prepared at high TPAOH concentrations might be high alkalinity of the solutions. In high alkaline coating solutions, aluminum species of the core HZSM-5 would be dissolved into the coating solution. Then, these aluminum ions would be incorporated into the external surface of the composite catalysts.

The single crystal catalysts show higher *para*-selectivity over the polycrystals catalysts. The single crystal-like zeolite composites are thought to have high mechanical strength compared to the polycrystals. In addition, a homogeneous nucleation was inhibited in the synthesis conditions for single crystals. The high selectivity was achieved by only one coating. The improved coating method in this study gives a strong advantage from the viewpoint of industrial application.

4 Conclusions

The *para*-selectivity of the composite catalysts was significantly affected by the synthesis conditions. The catalysts prepared at lower concentration of SiO_2 (fumed silica) and TPA ions in the coating solutions showed higher *para*-selectivity. Excellent *para*-selectivity of 99.6% 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.

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