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Readily recyclable catalysts of zeolite nanoparticles linked with polymer chains

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ABSTRACT

Aggregates of zeolite nanoparticles were linked together with polypropylene oxide or polydimethylsiloxane polymer chains, and were used as catalysts for liquid-phase reactions. The polymer-linked catalysts showed high catalytic activity in esterification of acetic acid with 1-propanol and hydrolysis of ethyl acetate, and were readily separated from reaction mixtures by decantation. Moreover, the linkage with the polymer chains enhanced shape selectivity in esterification of acetic acid with cyclohexanol and dehydration of 1-phenylethanol because of passivating the external acid sites of the zeolite with the polymer.

1. Introduction

Zeolites are often used as solid acid catalysts because of their high surface areas and shape selectivities owing to their uniform micropores. The catalytic activity of zeolites depends on particle size [1–4]. For a high catalytic activity, usually small particles of zeolites are preferable [1–11]. The ratio of external to internal surface areas increases with decreasing particle size. Thus, zeolite nanoparticles have higher external surface areas, which possess high activities, particularly in the reactions of bulky reactants [11]. In addition, these nanoparticles reduce the path lengths of the diffusion of reactants, leading to the effective use of active sites deep inside the micropores. Many research groups have reported on zeolite nanoparticles [12–24]. However, when the nanoparticles, which usually form aggregates, are used as catalysts, it is difficult to separate even the aggregates of the nanoparticles from the reaction mixtures via filtration or decantation in order to reuse them. To solve this drawback, binders are generally used to form large structures such as pellets. Another drawback is the loss of shape selectivity. Reactions over acid sites on an external surface are non-shape selective.

In this study, we report novel catalysts that are readily separated from the reaction mixture via decantation and possess shape selectivity. The catalysts were prepared by linking aggregates of ZSM-5 nanoparticles together with polydimethylsiloxane (PDMS) and polypropylene oxide (PPO) as hydrophobic and hydrophilic polymers, respectively; these complexes can be handled as large particles. These polymers were terminated by alkoxysilyl groups, which reacted with silanol groups on the external surfaces of the nanoparticles [25]. The zeolite-polymer composites had been already reported [26,27], but they were finally calcined to remove the polymers, leading to mesopore formation. For example, Song et al. successfully made bulky and mesoporous particles from self-assembly of zeolite nanoparticles with polymer, which showed almost the same catalytic activity as zeolite nanoparticles and could be separated by filtration [27]. However, they had high external surface showing low shape selectivity. In this work, we demonstrated that the use of the zeolite-polymer composites without calcination enhanced shape selectivity owing to passivation of the external acid sites with the polymer.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of nanoZSM-5

We prepared ZSM-5 nanoparticles (represented as nanoZSM-5) via Grieken's method [22]. Tetraethoxysilane (Shin-Etsu Chemical Co.) was added to an aqueous solution of tetrapropylammonium hydroxide (TPAOH, Tokyo Chemical Industry Co.) and aluminum nitrate (Kanto Kagaku), and the mixture was stirred for 3 h. Ethanol was removed from the mixture using a rotary evaporator, and then water amount was adjusted to the gel ratio (Na_2O:Al_2O_3:SiO_2:TPAOH:H_2O = 1:1:100:17.8:542). The gel in an

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autoclave was heated at 170 °C for 48 h under a static condition. The solid product was separated by centrifugation, washed several times with distilled water, dried overnight at 100 °C and calcined in air at 550 °C for 7 h.

2.1.2. Synthesis of triethoxysilyl-terminated PDMS

Triethoxysilyl-terminated PDMS was synthesized by the hydrosilylation of vinyl-terminated PDMS (molecular weight: 6000; Gelest) with triethoxysilane (Tokyo Chemical Industry Co.) catalyzed by Pt/carbon. The mixture of 0.30 g of Pt/carbon (2% (w/w) Pt), 3.2 g of vinyl-terminated PDMS, 40 mL of dry toluene and 0.29 mL of triethoxysilane was refluxed for one night under a nitrogen atmosphere. The Pt catalyst was removed by filtration, and toluene and unreacted triethoxysilane were removed by vacuum. The ratio of unreacted vinyl groups in the obtained polymer was 27% (determined by NMR analysis, see Supplementary Data, Fig. S1). We obtained (3-methyldimethoxysilyl)propyl terminated PPO (molecular weight: 600–800) from Gelest.

2.1.3. Linkage with the polymers

In a Schlenk flask, triethoxysilyl-terminated PDMS (3.2 g) or (3-methyldimethoxysilyl)propyl terminated polypropylene oxide (2.26 g) was mixed with nanoZSM-5 (2.0 g) dispersed in dry ethyl acetate formed by sonication. After removal of ethyl acetate by vacuum, the mixture was heated at 100 °C for 17 h. The resultant catalyst was thoroughly washed with toluene and collected by decantation. Finally remnants of toluene in the catalyst were removed by vacuum. The catalysts linked with polydimethylsiloxane and polypropylene oxide are represented as PDMS-nanoZSM-5 and PPO-nanoZSM-5, respectively.

2.2. Reaction procedures

2.2.1. Esterification of acetic acid with 1-propanol or cyclohexanol

In a 50-mL flask, the polymer-linked zeolite (0.17 g excluding the polymer weight), toluene (10 mL) as a solvent and acetic acid (93 mmol) was mixed and heated at 100 °C. Alcohol (93 mmol) was added to the mixture and the reaction started. Products are analyzed by gas chromatography. Dodecane was used as an internal standard.

2.2.2. Hydrolysis of ethyl acetate

Hydrolysis of ethyl acetate was performed in a 50-mL autoclave. The polymer-linked zeolite (0.13 g excluding the polymer weight), ethyl acetate (1.0 g) and water (19 g) were put into the autoclave. The hydrolysis was performed at 100 °C. After the reaction, the autoclave was cooled, and cyclohexanone as an internal standard was added to the reaction mixture.

2.2.3. Dehydration of 1-phenylethanol

In a 30-mL flask, the polymer-linked zeolite (0.10 g excluding the polymer weight), toluene (10 mL) as a solvent and 1-phenylethanol (5 g) was mixed and heated at 110 °C. Products are analyzed by gas chromatography. Dodecane was used as an internal standard.

In all reactions, mass balances were almost 100%; errors were less than 2.5%.

2.2.4. Recycling the catalyst

The used catalyst was recovered by decantation. The catalyst with 5 mL of the solvent was decanted from the reaction mixture after settling for 1 min, and 15 mL of the solvent was added to the catalyst. After stirring for 3 min and settling for 1 min, we decanted the mixture again. This entire process was carried out three times. After recovery of the used catalyst, we reused the catalyst for the reaction.

2.3. Catalyst characterization

Powdered X-ray diffraction (XRD) data was recorded with a Rigaku Multi Flex (Rigaku) using CuKα radiation. Field emission scanning electron microscopy (FE-SEM) images were taken using a S4500 (Hitachi) operated at an accelerating voltage of 2.0 kV. To examine the particle size, dynamic light scattering (DLS) measurement was performed using an LB-500 (Horiba). Before measurement, particles were dispersed in water using sonication for 30 min. Infra-red spectroscopic analysis of the catalysts was using FT/IR-460 plus (JASCO). The samples were pressed into self-supporting wafer, and then placed into the spectrometer.

3. Results and discussion

3.1. Polymer-linked zeolite

We prepared ZSM-5 nanoparticles (nanoZSM-5) via Grieken's method [22]. Powdered XRD results showed that the crystallite size of the nanoparticles was 30 nm (see Supplementary Data, Fig. S2). SEM observation (Fig. 1a) revealed that nanoparticles formed as aggregates of small particles (ca. 30 nm). The aggregates, with their size around 300 nm, were determined using analyses of the morphology and DLS of the nanoparticles (Fig. 1). Thus, we linked the small aggregates of the nanoparticles with polymers. BET and external surface areas of nanoZSM-5 were 479 and 64 $m^2 g^{-1}$, respectively. The Si/Al ratios obtained from elemental analysis and temperature programmed desorption of ammonia were the same, 58.

To confirm the linkage of two aggregates of nanoparticle, we used mono-triethoxysilylated polydimethylsiloxane instead of the polysiloxane terminated by triethoxysilyl groups at both the ends. The catalyst prepared from the mono-silylated polymer (monoPDMS-nanoZSM-5) was powdery, whereas PDMS-nanoZSM-5 was block (see Supplementary Data, Fig. S3). After the catalysts (0.1 g) were dispersed in 50-mL toluene by stirring for 1 h, the mixture settled for 1 min, and 40 mL of the supernatant was removed. We dried and weighed the remains. PDMS-nanoZSM-5 was almost recovered; however, recoveries of monoPDMS-nanoZSM-5 and nanoZSM-5 were 34% and 40%, respectively, indicating linkage between the particles with the polymer. Recovery of monoPDMS-nanoZSM-5 was slightly lower than that of nanoZSM-5, because hydrophobicity of PDMS probably makes monoPDMS-nanoZSM-5 dispersed in toluene more than nanoZSM-5 with hydrophobic external surface due to hydroxyl groups.

Infra-red analysis of the polymer-linked zeolites revealed that polymer structure remained after linkage between nanoZSM-5 and the polymers (see Supplementary Data, Fig. S4). ^{29}Si MAS NMR spectra of the polymer-linked zeolites showed slight decrease of the Q3($HOSi^*(OSi)_3$)/Q4($Si^*(OSi)_4$) ratio (see Supplementary Data, Fig. S5), indicating that the polymers were linked with nano-ZSM-5 by the reaction of silanol groups in nanoZSM-5 with alkoxysilyl groups in the polymers. The amounts of nanoZSM-5 in the polymer-linked zeolites were examined by elemental analysis. PDMS- and PPO-nanoZSM-5 contained 35 and 53%(w/w) of nanoZSM-5, respectively. The numbers of PDMS and PPO per the external surface area of nanoZSM-5 were estimated to be 2.8 and 12 nm^{-2}. The PPO number was higher, possibly because part of PPO was immobilized by one side of the polymer chain due to much shorter length of PPO (3 nm) than the size of the aggregates.

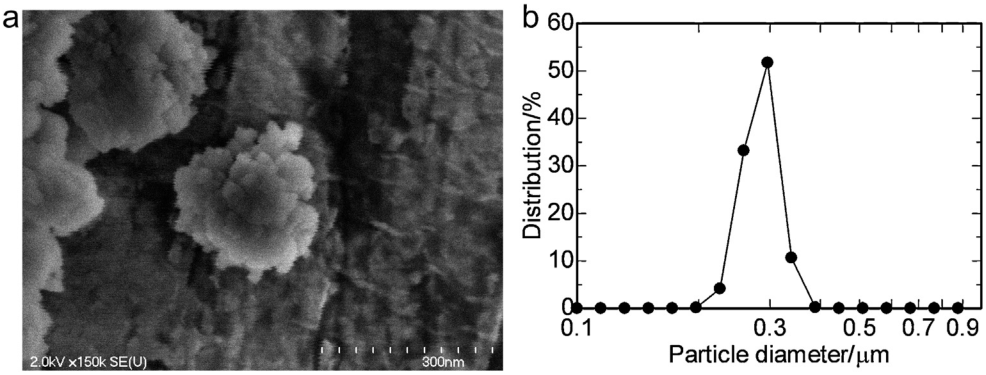

Fig. 1. ZSM-5 nanoparticles. (a) FE-SEM image and (b) particle size distribution.

3.2. Esterification of acetic acid with 1-propanol

We carried out the esterification of acetic acid with 1-propanol in toluene using the polymer-linked catalysts; Fig. 2 shows the results. The catalytic activities of the two polymer-linked nanoZSM-5 catalysts were lower than that of nano-ZSM-5, however the difference was very small. Thus, the linkage with the polymer hardly decreased the activity. To passivate acid sites on the external surface of nanoZSM-5, we added 2,4-dimethylquinoline (100 mg), which cannot enter the micropores, to nanoZSM-5 (0.5 g) and washed it thoroughly with toluene. This catalyst also produced the same yield as nanoZSM-5. In the esterification with 1-propanol, the role of the external acid sites was not important; i.e. most of the acid sites of the zeolite were inside the micropores and they mainly worked. Possibly rapid diffusion of the reactants and the products inside the micropores did not decrease the catalytic activity. Actually, a conventional ZSM-5 (Si/Al = 57) with lower external surface area also showed the same catalytic activity as nanoZSM-5.

The effect of reaction temperature on reaction rate was examined. Since the esterification proceeded without catalysts, actual initial rates of the catalytic reaction were calculated by subtraction of initial rates of non-catalytic reaction from overall initial rates. Arrhenius plots of the actual initial rates at reaction temperatures between 80 and 109 °C are shown in Fig. 3. Slopes obtained by use of nanoZSM-5 and PDMS-nanoZSM-5 were the same, and apparent activation energy was 59.1 and 58.7 kJ mol^{-1}, respectively. No change in the activation energy indicates that heat transfer and diffusion of molecules through the polymer were not important to determine the reaction rate.

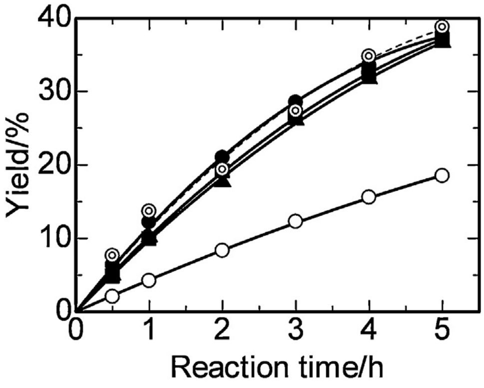

Fig. 2. Time courses of propyl acetate yield in the esterification of acetic acid with 1-propanol. Without catalyst: open circle; non-linked nanoZSM-5: double circle; dimethylquinoline-adsorbed nanoZSM-5: solid circle; PDMS-nanoZSM-5: square; PPO-nanoZSM-5: triangle. Amounts of acetic acid, 1-propanol and toluene were 93 mmol, 93 mmol and 10 mL, respectively. The catalyst amount excluding polymer weight was 0.17 g. Reaction temperature was 100 °C.

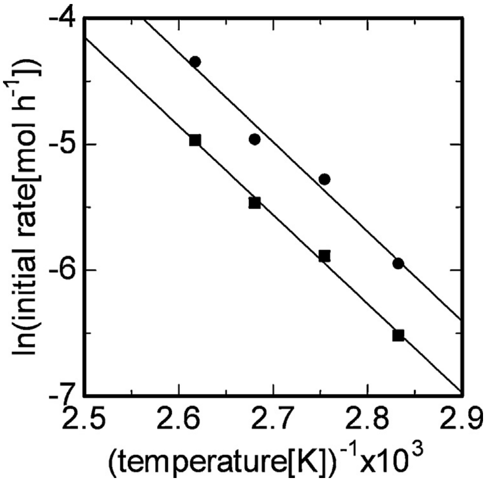

Fig. 3. Arrhenius plot of the initial reaction rates caused by the catalysts. Non-linked nanoZSM-5: circle; PDMS-linked nanoZSM-5; square. Amounts of acetic acid, 1-propanol and toluene were 93 mmol, 93 mmol and 10 mL, respectively. The catalyst amount excluding polymer weight was 0.17 g.

We reused the catalysts for the esterification. The used catalyst was recovered by decantation. Only the yield obtained using the PDMS-nanoZSM-5 catalyst did not change with reuse (Table 1). All the PDMS-nanoZSM-5 catalyst was recovered by decantation, whereas recoveries of PPO-nanoZSM-5 and nanoZSM-5 were 96 and 93%, respectively. As mentioned above, recovery of nanoZMS-5 dispersed in pure toluene was low (40%). NanoZSM-5 had high area of the external surface area and a large amount of silanol groups on the external surface [28], which showed hydrophilic property. In

Table 1
Esterification of acetic acid with 1-propanol and hydrolysis of ethyl acetate.

Reaction	Polymer	Product yield (%)		Catalyst recovery (%)
		Fresh catalyst	Recycled catalyst	
Esterification	None	38	31	93
	PDMS	38	37	99
	PPO	37	31	96
Hydrolysis	None	79	31	71
	PDMS	67	63	99
	PPO	82	80	99

Esterification: 100 °C for 5 h, acetic acid 93 mmol, propanol 93 mmol, toluene 10 mL, nanoZSM-5 0.17 g. Hydrolysis: 100 °C for 5 h, 5% ethyl acetate aqueous solution 20 mL, ZSM-5 0.13 g.

Table 2
Recycling test of PDMS-nanoZSM-5 catalyst in the esterification of acetic acid with 1-propanol.

Recycling number	Propyl acetate yield (%)	Ratio of recycled catalyst amount to parent catalyst amount (%)
Fresh	38	100
1	37	99
2	35	87
3	31	79
4	32	78
5	33	76

Amounts of acetic acid, 1-propanol and toluene were 93 mmol, 93 mmol and 10 mL, respectively. The parent catalyst amount excluding polymer weight was 0.17 g. Reaction was performed at 100 °C for 5 h.

Table 3
Recycling test of PPO-nanoZSM-5 catalyst in the hydrolysis of ethyl acetate.

Recycling number	Ethanol yield (%)	Ratio of recycled catalyst amount to parent catalyst amount (%)
Fresh	82	100
1	80	99
2	71	90
3	66	83
4	69	82
5	69	82

Amounts of ethyl acetate and water were 1.0 g and 19 g, respectively. The catalyst amount excluding polymer weight was 0.13 g. Reaction was performed at 100 °C for 5 h.

the esterification, water was formed as a byproduct and adsorbed in hydrophilic nanoZSM-5. Thus, adsorption of water enhanced sedimentation of nanoZSM-5 and increased its recovery from the reaction mixture; however it was still lower than PDMS-nanoZSM-5 recovery. We used the best catalyst (PDMS-nanoZSM-5) in the esterification for a recycling test. After recycling the catalyst 5 times, the catalytic activity yet remained high (Table 2), demonstrating that the catalyst linked with PDMS was reusable. After the reaction at reflux temperature (109 °C), the PDMS-nanoZSM-5 catalyst was reused. The shape of the catalyst was not changed, and the catalytic activity at 100 °C after the reaction at 109 °C was almost the same as that of a new catalyst, indicating that PDMS-nanoZSM-5 was still stable at 109 °C.

3.3. Hydrolysis of ethyl acetate

When we hydrolyzed ethyl acetate in water at 100 °C for 5 h, the ethanol yield obtained using PPO-nanoZSM-5 was 82%, which was close to that obtained using nanoZSM-5 (Fig. 4 and Table 1). Ogawa et al. have compared the catalytic activities of ZSM-5 and octadecyl-immobilized ZSM-5 in hydrolysis of ethyl acetate [29]. Immobilization of organic groups passivated the external acid sites; however, they showed the same activity. In the hydrolysis of ethyl acetate, the role of the external acid sites was not important. This was consistent with our result. After the reaction, many bubbles on PDMS-nanoZSM-5 were observed (see supplementary data, Fig. S7). Because PDMS is hydrophobic, PDMS-nanoZSM-5 repelled the aqueous solution of ethyl acetate and all acid sites in PDMS-nanoZSM-5 could not be used as the catalyst, thereby demonstrating lower activity. The reuse test of the catalysts revealed that only PPO-nanoZSM-5 showed an original activity. Because nanoZSM-5 is hydrophilic, decantation led to low recovery (71%). PDMS-nanoZSM-5 recovery was almost 100%; however, the yield still remained low. Table 3 shows the results of the recycling test of PPO-nanoZSM-5. Loss of the catalyst increased with an increase in the number of recycling steps; however, the yield was still high (69%).

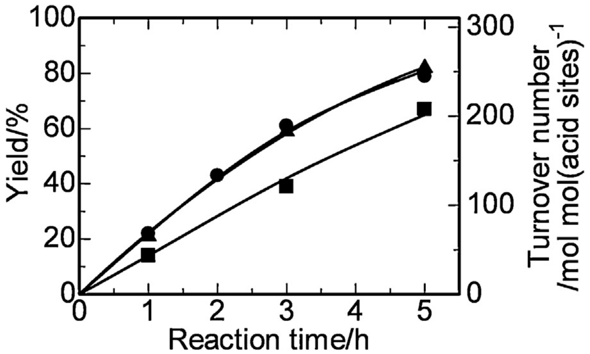

Fig. 4. Time courses of ethanol yield (turnover number) in the hydrolysis of ethyl acetate. Non-linked nanoZSM-5: circle; PDMS-nanoZSM-5: square; PPO-nanoZSM-5: triangle. Amounts of ethyl acetate and water were 1.0 g and 19 g, respectively. The catalyst amount excluding polymer weight was 0.13 g. Reaction temperature was 100 °C.

When PPO-nanoZSM-5 was used at 150 °C for 5 h, the yield was 90%, which was the same as 91% yield obtained by the reaction using nanoZSM-5. However, PPO-nanoZSM-5 was dispersed in the solvent, and could not be separated from the reaction mixture. Thus, PPO-nanoZSM-5 was not stable at 150 °C under reaction conditions for hydrolysis. Ether bonds can be hydrolyzed in the presence of water and acids. Possibly higher reaction temperature accelerated hydrolysis of the ether bonds catalyzed by acetic acid and/or the acid sites of nanoZSM-5 in the presence of a large amount of water.

The esterification and hydrolysis results indicated that a highly active catalyst that is easily separated from the reaction mixture could be obtained by linking the nanoparticles with the proper type of polymer, i.e. hydrophobic and hydrophilic polymers are suitable for reactions in organic and aqueous solvents, respectively.

3.4. Esterification of acetic acid with cyclohexanol

The polymers were bound to the external surface of the zeolite. Therefore, access of the reactants to the external surface was possibly blocked by the polymer chains, and consequently the acid sites on the external surface were passivated. We tested esterification of acetic acid with cyclohexanol as a more bulky alcohol than with 1-propanol to examine shape selectivity. Viswanadham et al. reported that nano-sized ZSM-5 catalyst was more active than a conventional ZSM-5 in the esterification of acetic acid with cyclohexanol because of the large surface area and high pore volume of nano-sized ZSM-5 [10], suggesting that the esterification proceeded mainly on the external surface. Fig. 5 shows the results obtained using the polymer-linked nanoZSM-5. When we used nanoZSM-5 as the catalyst, the yield of cyclohexyl acetate was 13% after 5 h. The activity of the conventional ZSM-5 (the yield was 10%) was lower than that of nanoZSM-5, corresponding to Viswanadham's results. Use of PDMS- and PPO-nanoZSM-5 resulted in the same yield (ca. 7%) as the non-catalyzed reaction, suggesting that linkage with the polymers passivated the external acid sites. To passivate the external sites, nanoZSM-5 was exposed to 2,4-dimethylquinoline and was used as the catalyst. The time course of the yield was similar to that obtained from the non-catalyzed reaction. Cyclohexanol could enter the micropore; however, under these reaction conditions, esterification with cyclohexanol did not proceed, possibly because the diffusion of cyclohexanol in the micropores was so slow that the reaction at the acid sites inside the micropores did not proceed. Therefore, the polymer chains passivated the external sites in PDMS- and PPO-nanoZSM-5.

Table 4
Dehydration of 1-phenylethanol.

Catalyst	Conversion (%)	Turnover frequency (mol mol(acid sites)$^{-1}$ min^{-1})[a]	Selectivity (%)	
			Styrene	Bis(1-phenylethyl) ether
NanoZSM-5	90	22	73	27
NanoZSM-5[b]	53	25	73	27
Conventional ZSM-5	65	15	81	19
PDMS-nanoZSM-5	59	14	99	1
SAC-13[c]	95	23	14	86
Amberlyst 15DRY[b]	22	5.3	23	77

Reaction conditions: 1-Phenylethanol 5.0 g, toluene 10 g, nanoZSM-5 0.10 g, reaction temperature 110 °C, reaction time 1 h.

[a] Amounts of acid sites in zeolites were determined by TPD.

[b] NanoZSM-5 0.050 g, reaction time 20 min.

[c] Amount of acid sites was same as that of nanoZSM-5.

3.5. Dehydration of 1-phenylethanol

Lange and Otten reported that 1-phenylethanol dehydration over various zeolite catalysts gave styrene and bis(1-phenylethyl) ether, formed by intra- and inter-molecular dehydration, respectively, and that the medium-pore zeolites delivered a higher styrene yield than the large-pore zeolites or the mesoporous materials [30]. Shape selectivity depending on micropore size seemed to determine the selectivity for styrene. To confirm the shape selectivity, we also performed 1-phenylethanol dehydration. Use of nanoZSM-5 resulted in both products, and the selectivity for styrene was 73%, as shown in Table 4. When PDMS-nanoZSM-5 was used, the conversion decreased to 59%, and the selectivity for styrene increased to 99%. To compare selectivities for styrene at the same conversion, the amount of nanoZSM-5 catalyst and reaction time were adjusted. The reaction using a half amount of nanoZSM-5 for 20 min resulted in 53% conversion close to 59% obtained using PDMS-ZSM-5. When nanoZSM-5 was used as a catalyst, the selectivity (73%) did not change with conversions. Thus, the intra- and inter-molecular dehydrations were parallel reactions. The PDMS linkage enhanced the selectivity for styrene from 73% to 99%, indicating that the ether was formed at the external acid sites and that the sites were passivated owing to linkage with PDMS. When a conventional ZSM-5 having lower external surface area than nanoZSM-5 was used, the conversion was lower (65%) and the selectivity was higher (81%). This also showed that the ether was formed at the external acid sites of ZSM-5. Ion exchanged resins, SAC-13 (Aldrich) and Amberlyst 15DRY (Organo Corp.), showed very low styrene selectivities.

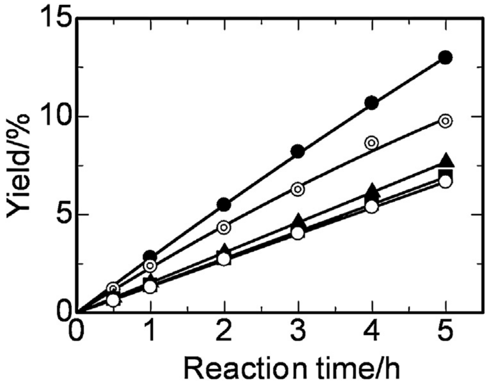

Fig. 5. Time courses of cyclohexyl acetate yield in the esterification of acetic acid with cyclohexanol. Without catalyst: open circle; non-linked nanoZSM-5: solid circle; PDMS-nanoZSM-5: square; PPO-nanoZSM-5: triangle; conventional ZSM-5: double circle. Amounts of acetic acid, cyclohexanol and toluene were 93 mmol, 93 mmol and 10 mL, respectively. The catalyst amount excluding polymer weight was 0.17 g. Reaction temperature was 100 °C.

4. Conclusions

We linked aggregates of highly active ZSM-5 nanoparticles with PDMS or PPO to conquer the drawback of a difficult separation from the reaction mixture, and selected the proper type of polymer that led to high activities. Furthermore, polymer-linked nanoZSM-5 increased the shape selectivity because of passivation of the external acid sites with the polymer. Therefore, the polymer-linked catalyst can be applied to various liquid-phase reactions, especially reactions expected to demonstrate shape selectivity. Moreover, our report suggests that the polymer linkage can make not only nano-sized zeolite catalysts but also other nano-materials easy to reuse.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2013.07.008.

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