Catal Lett (2009) 128:203–209
DOI 10.1007/s10562-008-9738-4

Na-Y Zeolite as a Highly Active Catalyst for the Hydroamination of α,β-Unsaturated Compounds with Aromatic Amines

Kenichi Komura · Ryuichi Hongo · Jinya Tsutsui · Yoshihiro Sugi

Received: 6 August 2008 / Accepted: 16 October 2008 / Published online: 22 November 2008

Abstract Hydroamination of α,β-unsaturated compounds with less reactive aromatic amines was investigated over Na-Y zeolite. Aniline gave the 99% conversion at 100 °C for 5 h over Na-Y zeolite, resulting in the formation of *N*-[2-(methoxycarbonyl)ethyl]aniline with excellent mono-selectivity. However, aromatic amines having an electron-withdrawing functional group gave moderate conversions. The reactions using recovered catalyst also occurred without significant decrease in the catalytic activity during four recycles. The regeneration of used Na-Y zeolite can be performed by the calcination. Solid-state ^{13}C MAS NMR measurement revealed that methyl acrylate was effectively activated by Na-Y zeolite.

Keywords Na-Y zeolite · Hydroamination · α,β-Unsaturated compound · Aromatic amine

1 Introduction

Nitrogen-containing organic compounds are important key substances in organic synthesis for fine and functional chemicals, particularly, medicines and agrochemicals. The hydroamination, i.e., the direct addition of an amine to an unsaturated compound, is the most straightforward synthetic method among the number of tools to form C–N bond [1–5]. This reaction gives directly β-amino acid ester derivatives from α,β-carbonyl compounds. However, previous attempts have been focused on aliphatic amines because they have higher basicity than aromatic amines [6–13]. It is expected to find the catalysts with high performances even for less reactive aromatic amines, resulting in offering green chemical process.

Recently, the replacement of homogenous catalysts to solid catalysts has been recognized as one of the promising ways for establishing the green chemical manufacturing of fine chemicals. Zeolites, having uniform three-dimensional pores such as Y and β zeolites, are one of the most probable candidates for the purposes. We have recently reported some proton-type zeolites such as H-Y and H-BEA zeolites had high catalytic activity in the reaction of less reactive aromatic amine such as aniline [14, 15].

Here, we describe the hydroamination over Na-Y zeolite including the reaction profile and reactions of less reactive aromatic amines with methyl acrylate and of aniline with α,β-unsaturated compounds.

2 Experimental

Na-Y and H-Y zeolite (SiO_2/Al_2O_3 (SAR) = 5.6, HSZ-320NAA and HSZ-320 HOA) and H-MOR and Na-MOR (SAR = 25, HSZ-650HOA and HSZ-620) were purchased from Tosoh Corporation, Tokyo, Japan, and H-BEA (SAR = 25, CP 814B-25), Zeolyst International, Valley Forge, PA, USA. Na-LTA (SAR = 1.0) was used as a commercially available molecular sieves 4A (Aldrich). Na-BEA was prepared according to the literature [16]. Prior to use, all samples were calcined under air flow: room temperature to 550 °C (programmed rate 1 °C/min), 550 °C for 7 h.

In a typical reaction, Na-Y zeolite (0.10 g) was suspended in distilled toluene (4.0 mL), and amine (1.0 mmol) and methyl acrylate (2.0 mmol) were added to the suspension. The reaction mixture was heated to 100 °C

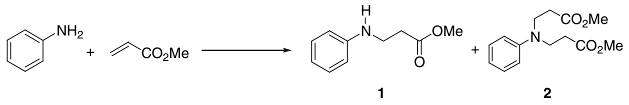
K. Komura · R. Hongo · J. Tsutsui · Y. Sugi (✉)
Department of Materials Science and Technology, Faculty of Engineering, Gifu University, Gifu 501-1193, Japan
e-mail: sugi@apchem.gifu-u.ac.jp

with stirring for 5 h. After reaction, the reaction mixture was filtered and the filtrate was analyzed by a gas chromatography (Shimadzu GC-14B with an Ultra-1 capillary column, 25 m, 0.32 μm thick layer; Agilent Technol.) using biphenyl as an internal standard. Products were also analyzed by GC-MS (Shimadzu MS-5000 with an Ultra-1 capillary column (above mentioned) and ^{1}H-NMR spectra by using a JEOL ECA-500 FT-NMR spectrometer for the identification and selectivity for the products. ^{13}C NMR (in $CDCl_3$ solvent using TMS as an internal standard) and solid ^{13}C MAS NMR (using a 4 mm zirconia rotor spinning at 10 kHz) were also carried out using the same spectrometer.

3 Results and Discussion

Hydroamination of aniline with methyl acrylate usually offers the mixture of mono- (*N*-[2-(methoxycarbonyl) ethyl]aniline, **1**) and di-adduct (*N*,*N*-bis[2-(methoxycarbonyl)ethyl]aniline, **2**), respectively, shown in Scheme 1. Di-adduct **2** is formed by the further reaction of **1** and methyl acrylate [14].

Table 1 shows catalytic activities of zeolites on the hydroamination of amine with methyl acrylate. The reaction did not occur in the absence of zeolites. Among sodium type zeolites, Na-Y zeolite with three-dimensional 12-MR pore-entrances had the highest catalytic activity: the reaction was completed within 5 h, resulting in the selective formation of **1**. Na-BEA also showed the good catalytic activity although the formation of **2** (8.6%) was accompanied. However, Na-LTA with three-dimensional 8-MR pore entrances gave low catalytic activity, and no reaction occurred over Na-MOR with two-dimensional 12-MR and 8-MR pore entrances. These results indicate that pore size and dimension of zeolite are critical even for sodium type zeolites in this reaction.



Scheme 1

Table 1 Hydroamination of aniline with methyl acrylate over zeolite catalysts[a]

Zeolite[b]	Conversion of amine (%)	Selectivity (%)	
		1	**2**
None	0	–	–
Na-Y (5.6)[b,c]	99	99	1
Na-BEA (100)[b,c]	78	91	9
Na-MOR (20)[b,c]	0	–	–
Na-LTA (1.0)[b,c]	10	100	0
H-Y (5.6)[c]	91	90	10
H-Y (30)[c]	57	95	5
H-BEA (25)[c]	85	80	20
H-MOR(25)[c]	12	100	0

[a] Reaction conditions: amine (1.0 mmol); methyl acrylate (2.0 mmol); zeolite (0.10 g); solvent: toluene (4.0 mL). temperature: 100 °C. period: 18 h

[b] Reaction period: 5 h

[c] Values in parenthesis are SiO_2/Al_2O_3 ratios

H-Y zeolite also showed the high performances although the catalytic activities were lower than Na-Y zeolite as typical results shown in Table 1 [14]. Interestingly, these results show that Na-Y zeolite with no acidic characters is highly active as well as H-Y zeolite with strong acidity. We thus examined the study on reaction parameters to know the scope of the catalysis by Na-Y.

Figure 1 shows the influences of reaction temperature on the hydroamination over Na-Y zeolite. Catalytic activity increased with increasing reaction temperature (aniline conversions: 6% at 50 °C, 39% at 60 °C, 78% at 70 °C and 97% at 80 °C), and almost complete conversion of aniline (>99%) was observed over 100 °C. Selectivity of mono-adduct was kept >99% even at high temperature such as 120 °C. These results mean that reaction temperature is essential in the hydroamination over Na-Y zeolite catalyst; however, that does not significantly affect the mono-selectivity.

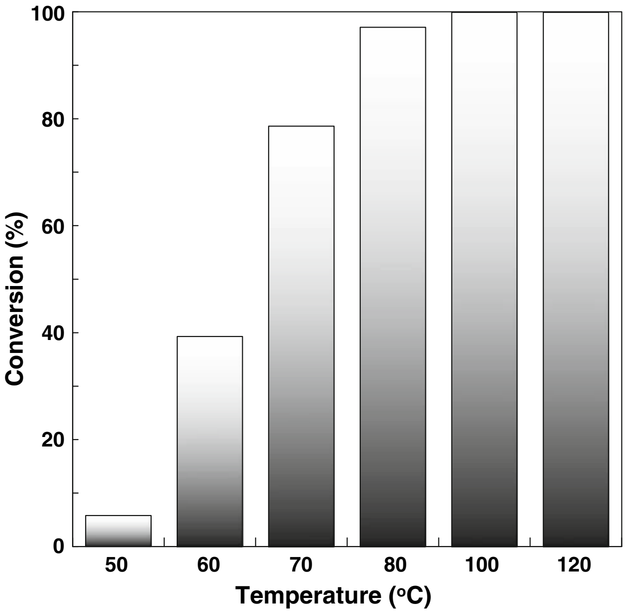


Fig. 1 The influences of reaction temperature on the hydroamination of methyl acrylate with aniline over Na-Y zeolite. Reaction conditions: substrates: amine 1.0 mmol and methyl acrylate 2.0 mmol catalyst: Na-Y 0.10 g. solvent: toluene 4.0 mL. period: 5 h

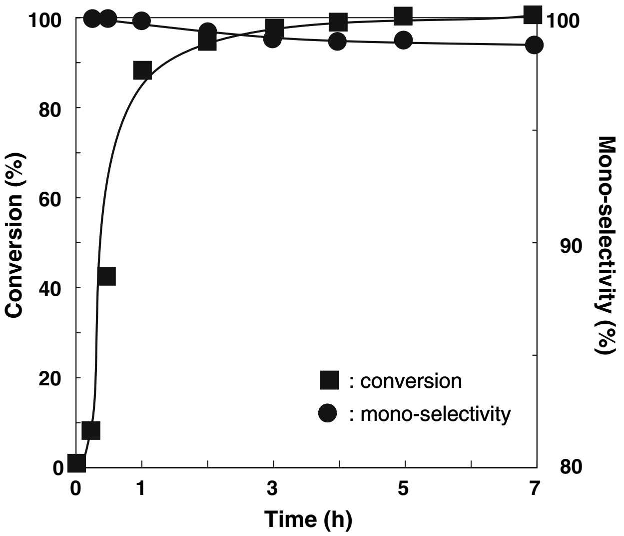


Fig. 2 Reaction profile in the hydroamination of methyl acrylate with aniline over Na-Y zeolite. Reaction conditions: substrates: amine 1.0 mmol and methyl acrylate 2.0 mmol catalyst: Na-Y 0.10 g solvent: toluene 4.0 mL temperature: 100 °C

Figure 2 shows the influences of reaction period on the hydroamination over Na-Y zeolite at 100 °C. It is clear that the conversion of aniline reached >90% within 1 h, and the complete conversion was observed within 5 h. Mono-selectivity kept high even on prolonged reaction period: 99% after 1 h to 98% after 18 h. However, the mono-selectivity decreased with period for H-Y zeolite as discussed in previous paper. These results indicate that the reaction over Na-Y zeolite are much selective than H-Y zeolite.

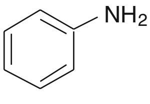
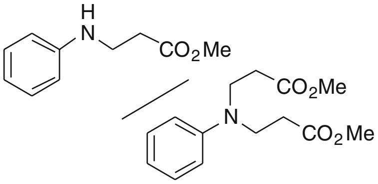
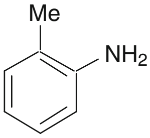
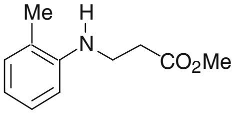
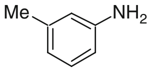
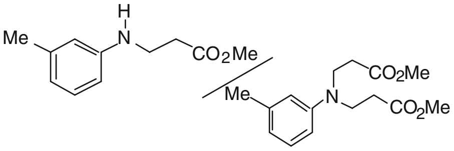
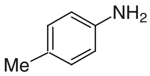
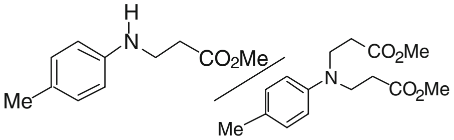
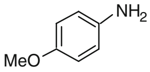
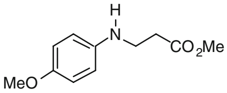
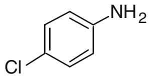
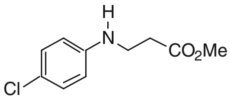
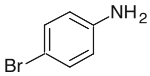
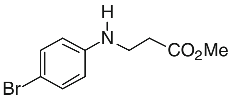
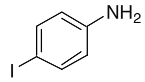
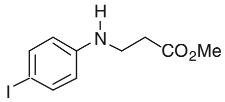
Table 2 summarizes the influences of aromatic amines on the hydroamination with methyl acrylate over Na-Y zeolite at 100 °C. Na-Y zeolite showed good to excellent catalytic activities for aniline, toluidine isomers and *p*-anisidine (entries 1–5). Interest catalytic feature was observed in reactions of toluidine isomers (entries 2–4): *p*-toluidine was the most reactive among the isomers; however, *o*- and *m*-toluidines gave corresponding products with moderate conversions. This is due to the bulkiness of toluidine isomers: *p*-toluidine can most easily enter into the Na-Y pores and the product ester can also diffuse out most easily from its pores. In contrast, Na-Y zeolite had remarkably low reactivities for aromatic amines with an electron-withdrawing group (entries 6–8) because of the lower basicity of nitrogen atom by the halogen substituent. These results means that electron-donation to benzene ring accelerates the hydroamination over Na-Y zeolite.

Table 3 shows the influences of α,β-unsaturated compounds on the hydroamination with aniline. Methyl acrylate gave the mixture of mono- and di-adduct with quantitative conversion of amine as discussed above (entry 1); however, *tert*-butyl acrylate had lower reactivity in 30% conversion (entry 2). This is due to the bulkiness of substrate. Na-Y zeolite effectively catalyzed the reactions of acrylonitrile and acrylic acid to afford the corresponding β-aminopropionitrile and β-aminopropionic acid without the formation of di-adduct product (entries 3 and 4). Both methyl crotonate and methyl methacrylate gave the products with around 30% conversions (entries 5 and 6). The addition of aniline occurred regioselectively at β-position to give β-amino acid esters. However, acrylamide and styrene were inactive for the hydroamination with aniline (entries 7 and 8). These results indicate that catalytic activity is affected by type of α,β-unsaturated compounds.

One of the most attractive advantages using a solid catalysis is the recyclability of catalyst. Figure 3 shows the activities of recycled Na-Y zeolite in the hydroamination of methyl acrylate with aniline. The catalyst used for the reaction was separated by filtration, washed with toluene, and then reused after drying at 80 °C for overnight. The catalytic activity was kept high during four recycles with 99% of mono-selectivity; however, the catalytic activity was decreased in fifth recycle (81%). The decrease is due to the accumulated coke and/or coke-precursor onto the zeolite during the catalysis judging from TG-DTA profiles of recycled catalysts shown in Fig. 4. The peaks were observed in the range of 200–300 °C and 500–600 °C; the former peak is due to adsorbed organic compounds and the latter is due to coke and/or its precursor, respectively. The amount of coke also increased by recycling, and saturated in fourth recycle (5.17 wt% at 500–600 °C). The accumulation of adsorbed organic compounds inside the zeolite channel may also decrease the catalytic active sites because they prevent the access of the reactants. These results correspond well to the results of recycle experiment shown in Fig. 3. The catalytic activity of recycled catalyst was regenerated by the calcination under air flow (6* in Fig. 3) resulting in the formation of the product in 96% conversion.

It is interesting that Na-Y zeolite has high activity for the hydroamination of aniline although it has no acidic character. To elucidate the mechanism of the catalysis of Na-Y zeolite, solid-state NMR is one of the most important techniques to give information of electron environment of molecules. We measured the ^{13}C MAS NMR spectra of methyl acrylate adsorpted Na-Y zeolite and ^{13}C NMR of methyl acrylate in $CDCl_3$ solution as shown in Fig. 5, and found that the downfield shifts of β- and carbonyl carbons were observed; 166.6–169.9 ppm at carbonyl carbon and 130.7–133.7 ppm at β-carbon, respectively. These results indicate that methyl acrylate was activated in the high electrostatic field of Na-Y zeolite, resulting in enhancement of the electron acceptance at β-carbon, and that these activities are due to the Lewis acidity induced by the

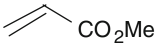
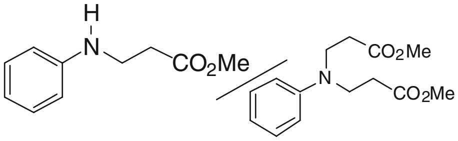
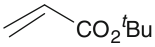
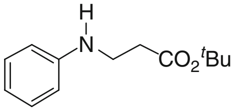
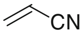
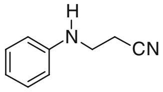
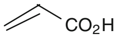
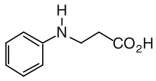
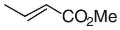
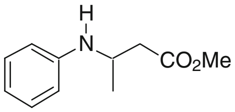
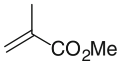
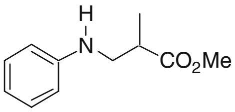
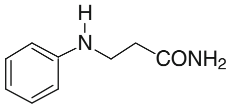
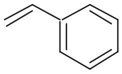
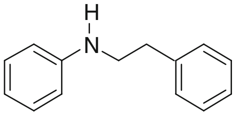
Table 2 Results of the hydroamination of methyl acrylate with various aromatic primary amines over Na-Y zeolite[a]

Entry	Amine	Product	Conversion of amine (%)	Selectivity (%)	
				Mono	Di
1			99	99	1
2			70	100	0
3			64	98	2
4			85	93	7
5			81	100	0
6			33	100	0
7			20	100	0
8			36	100	0

---

[a] Reaction conditions: amine (1.0 mmol); methyl acrylate (2.0 mmol); Na-Y (0.10 g). solvent: toluene (4.0 mL). temperature: 100 °C. period: 5 h

Table 3 Influences of the α,β-unsaturated compounds for the hydroamination with aniline over Na-Y zeolite[a]

Entry	α,β-unsaturated compound	Product	Conversion of amine (%)[b]	Selectivity (%)	
				Mono	Di
1			99	99	1
2			30	100	0
3			98	100	0
4			81	100	0
5			30	100	0
6			26	100	0
7			0	–	–
8			0	–	–

---

[a] Reaction was carried out using amine (1.0 mmol), α,β-unsaturated compound (2.0 mmol) and Na-Y (0.10 g) in toluene (4.0 mL) at 100 °C for 5 h

electron static field of Na-Y zeolite. The hydroamination of methyl acrylate with aniline proceeds *via* the conjugated addition of amine at the electron deficient β-carbon of adsorbed methyl acrylate (Scheme 2). Recently, Onaka et al. reported similar type of activation of carbonyl carbon in the carbony-ene reaction of formaldehyde and conjugate addition of acrolein over Na-Y zeolite as a catalyst [17–19].

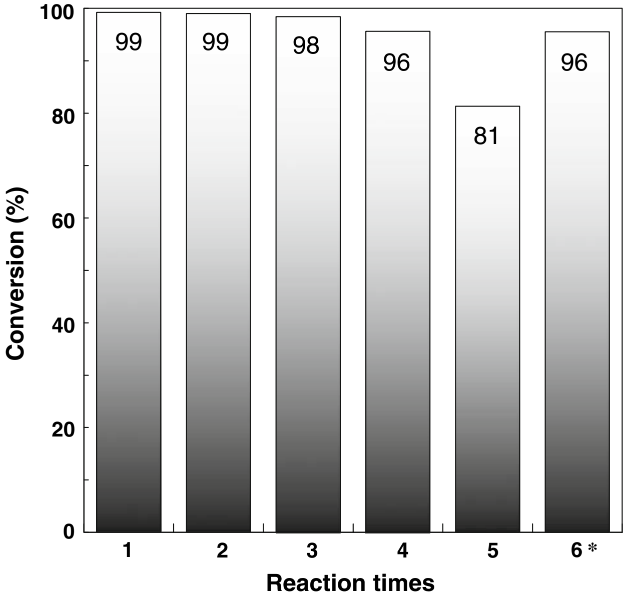


Fig. 3 Recycling of Na-Y zeolite in the hydroamination. Reaction conditions: substrates: amine 1.0 mmol and methyl acrylate 2.0 mmol catalyst: Na-Y 0.10 g solvent: toluene 4.0 mL temperature: 100 °C period: 5 h

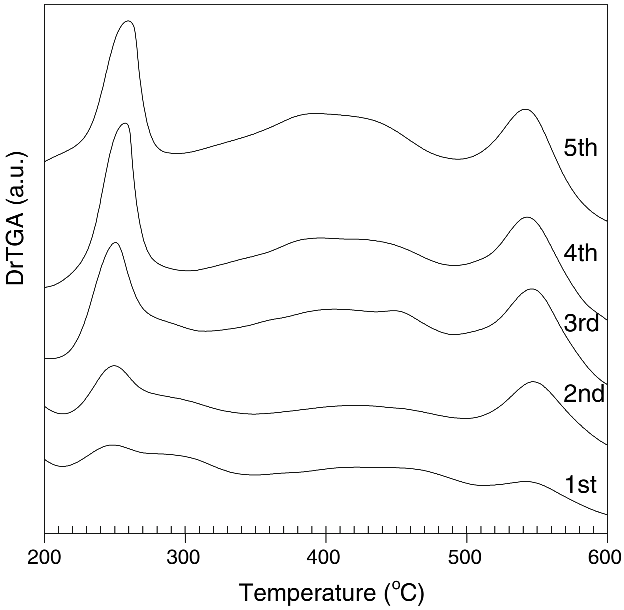


Fig. 4 TG profiles of recycled Na-Y zeolites

Both of Na- and H-Y zeolites show the same regioselectivities for the reactions of methyl methacrylate and crotonate with aniline giving β-anilino esters. These results indicate that the similar type of activation by proton on H-Y is responsible for the hydroamination as we proposed in the previous paper [14]. However, there are some unclear phenomena to understand the differences between the catalyses of Na- and H-Y zeolites.

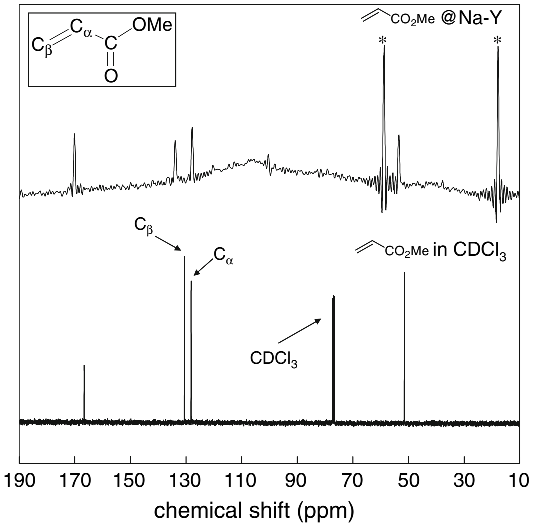
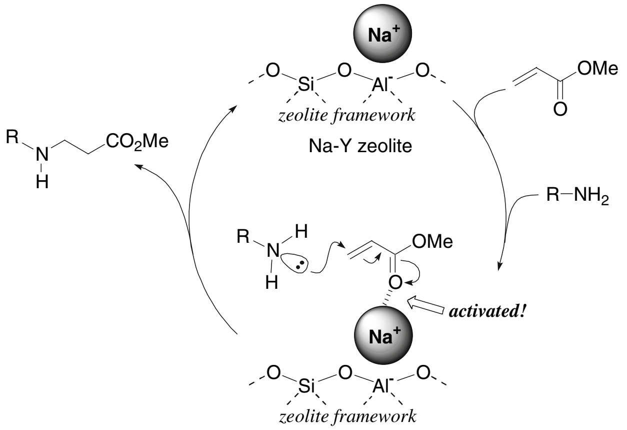


Fig. 5 Solid-state ^{13}C MAS NMR spectra of methyl acrylate adsorpted Na-Y zeolite (top) and ^{13}C NMR of methyl acrylate in $CDCl_3$ (bottom)



Scheme 2 Proposed mechanism for the hydroamination over Na-Y zeolite

4 Conclusion

The hydroamination of aromatic amines with methyl acrylate was examined over Na-Y zeolite. Na-Y zeolite showed high catalytic activity, resulting in the formation of β-amino acid esters for 5 h at 100 °C; however, amines with an electron-withdrawing functional group gave products in moderate conversion because of their lower basicity. Na-Y zeolite gave the excellent conversions for an acrylic acid and an acrylonitrile without the formation of di-adduct.

The reactions using recovered catalyst also occurred without significant decrease in catalytic activity during four recycles. The regeneration of used Na-Y zeolite can be performed by the calcination in air stream. Solid-state ^{13}C MAS NMR measurement reveals that methyl acrylate is effectively activated by Na-Y zeolite, showing the downfield shift of β-carbon and carbonyl moieties.

Further aspects on the catalysis over Na-Y zeolite in hydroamination are under the investigation, and will be discussed elsewhere in near future.

Acknowledgment A part of this work was financially supported by Grant-in Aid for Scientific Research (B) 16310056 and 19310060, the Japan Society for the Promotion of Science (JSPS).

References

1. Venuto PB (1994) Microporous Mater 2:297
2. Davis ME (1998) Microporous Mesoporous Mater 21:173
3. Taube R (1996) In: Cornils B, Herrmann WA (eds) Applied homogeneous catalysis with organometallic compound, vol 1. VCH, Weinheim, p 507
4. Hölderich WF (2000) Catal Today 62:115
5. Domeier W, Armor JN, Hölderich WF (2000) J Mol Catal A: Chem 156:255
6. Deka RC, Hirao K (2002) J Mol Catal A: Chem 181:275
7. Smith JW (1961) J Chem Soc 81
8. Loh TP, LL Wei (1998) Synlett 975
9. Fadini L, Togni A (2003) Chem Commun 30
10. Li K, Horton PN, Hursthouse MB, Hii KK (2003) J Organometal Chem 665:250
11. Azizi N, Saidi MR (2004) Tetrahedron 60:383
12. Xu LW, Li L, Xia CG (2004) Helv Chim Acta 87:1522
13. Surendra K, Krishnaveni NS, Sridhar R, Rao KR (2006) Tetrahedron Lett 47:2125
14. Horniakova J, Komura K, Osaki H, Kubota Y, Sugi Y (2005) Catal Lett 102:191
15. Komura K, Tsutsui J, Hongo R, Sugi Y (2007) Stud Surf Sci Catal 170B:1111
16. Matsukata M, Ogura M, Oaki T, Rao PRHP, Nomura M, Kikuchi E (1999) Top Catal 9:1441
17. Okachi T, Onaka M (2004) J Am Chem Soc 126:2306
18. Imachi S, Onaka M (2005) Chem Lett 35:708
19. Kobayashi K, Igura Y, Imachi S, Masui Y, Onaka M (2007) Chem Lett 36:60