Catal Lett (2008) 123:259–263
DOI 10.1007/s10562-008-9416-6

Selective Isopropylation of Isobutylbenzene over H-Mordenite in Supercritical CO_2 Medium: Remarkable Enhancement in Catalytic Activity and Selectivity for 4-Isobutylcumene

Subhash Chandra Laha · Kenichi Komura · Yoshihiro Sugi

Received: 5 December 2007 / Accepted: 24 January 2008 / Published online: 20 February 2008

Abstract Remarkable enhancement in the catalytic activity and selectivity for the formation of 4-isobutylcumene (4-IBC) was observed in the isopropylation of isobutylbenzene (IBB) over highly dealuminated H-mordenite in supercritical CO_2 (*sc*-CO_2) medium. Thermogravimetric analyses confirm that reduced coking of the catalysts in *sc*-CO_2 medium and stronger acid sites in dealuminated H-mordenite (MOR) are the key factors for superior activity and selectivity for 4-IBC.

Keywords Supercritical CO_2 · Dealuminated H-mordenite · Isobutylbenzene · 4-Isobutylcumene

1 Introduction

The Friedel-Crafts alkylation of aromatics catalyzed by solid acids such as zeolites is of significant industrial and pharmaceutical interests [1–3]. Selective liquid-phase isopropylation of isobutylbenzene (IBB) to 3- and 4-isobutylcumene (IBCs) derivatives over H-beta (BEA) zeolite has been reported recently [4]. 3-and 4-IBCs are important precursors for the synthesis of antioxidants, pharmaceuticals, fragrances, fine chemicals, etc. [5–7]. The results obtained under conventional liquid-phase reaction conditions; however, showed low conversion of isobutylbenzene ($\sim$21 mol%) and moderate selectivity for more relevant 4-IBC ($\sim$47 mol%), and the coke amount of the used catalyst was found to be as high as 20 wt.% [8].

In general, all solid acid catalysts, for instance, zeolites with confined micropores, suffer a major set back for its typical deactivation due to coke-formation on the active sites of the catalysts [9, 10]. One of the most important challenges for green catalytic processes is, therefore, to control the diffusion of the reactant(s) and product(s) from active sites to minimize the on-site coke-formation due subsequent acid-catalyzed transformations. Supercritical fluids, such as supercritical CO_2 (*sc*-CO_2), are becoming more attractive media for carrying out chemical reactions, since they offer enhanced solubility of reactants and products which can be tuned by variation of pressure and temperature, faster heat transfer from catalysts to dense gases, and easier product separation into reaction step [11–13]. Moreover, due to high density and low viscosity of *sc*-CO_2, an increased solubility of higher molecular weight carbon-rich compounds like polyaromatic hydrocarbons could be achieved under the reaction conditions (minimize the catalyst deactivation), establishing it as an inevitable choice for specified type of chemical reactions [14–18].

In this paper, we report, for the first time, the isopropylation of isobutylbenzene to isobutylcumenes in *sc*-CO_2 medium. In particular, we emphasize our results on dealuminated H-mordenite catalysts and the impact of *sc*-CO_2 medium for achieving higher conversion and more importantly higher selectivity for 4-IBC.

2 Experimental

H-mordenite (MOR(26)[1]: HSZ-640HOA; MOR(110): HSZ-690HOA) and H-ZSM-5 (MFI(54): HZS-850-NHA as

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

---

[1] The numbers in the parenthesis denote SiO2/Al2O3 ratios of zeolites.

NH_4-form) were obtained from TOSOH Corporation, Tokyo, Japan. H-Y (FAU(30): CBV720; FAU(80): CBV780) and H-Beta (BEA(26): CP814B-25) zeolites were obtained from Zeolyst International, Conshohochen, PA, USA. ZSM-11 (MEL(49)) zeolite was obtained from N. E. CHEMCAT Corporation, Tokyo, Japan. BEA(100) was synthesized according to the literature [19]. They were calcined at 550 °C in air for 6 h prior to use.

The isopropylation of isobutylbenzene was carried out in a 100 mL SUS-316 autoclave (equipped with an agitator) using dry ice as the source of CO_2. After the reaction, the reactor was depressurized very slowly after cooling it in ice bath. The contents of the reactor were extracted with acetone and analyzed by Shimadzu GC-18 gas chromatograph equipped with an Ultra-1 capillary column ((25 m × 0.2 mm × 0.33 μm), Agilent Technologies). The products were identified by GC-IR (Perkin Elmer, GC-IR 2000) and GC-MS (Shimadzu GC-MS5000).

3 Results and Discussion

Figure 1 shows the influences of zeolites on the isopropylation of isobutylbenzene (IBB) at 150 °C under 11 MPa of CO_2 pressure. Although the IBB conversion was ~17%, MOR(26) gave a very high selectivity for 4-IBC (~77%), and there were no 2-IBC and diisopropylisobutylbenzene (DIPIBB) isomers formed. On the other hand, high selectivity for 4-IBC couldn't be achieved over BEA(26) and FAU(30) zeolites, although the conversion of IBB was moderate (~40%). However, MFI(54) and MEL(49) showed no catalytic activity as compared to those of MOR, BEA, and FAU zeolites. These selectivity patterns are in conformity according to the pore diameter and dimensionality of these zeolites and imply low shape selectivity for BEA and FAU zeolites, and MFI has much smaller pore diameter and dimensionality for the catalysis. The existence of dense and strong acid sites on the zeolites also triggered the formation of 2-isobutylcumene (2-IBC), DIPIBB, and other products in higher proportion. Further, dense acid sites in aluminum-rich catalysts caused the coke deposition in higher amounts in the catalysts. Obviously, higher amounts of coke deposited in the catalysts during the isopropylation reduced the catalytic activity, the effect of which was most significant particularly in the case of one-dimensional MOR, in comparison to three-dimensional BEA and FAU zeolites.

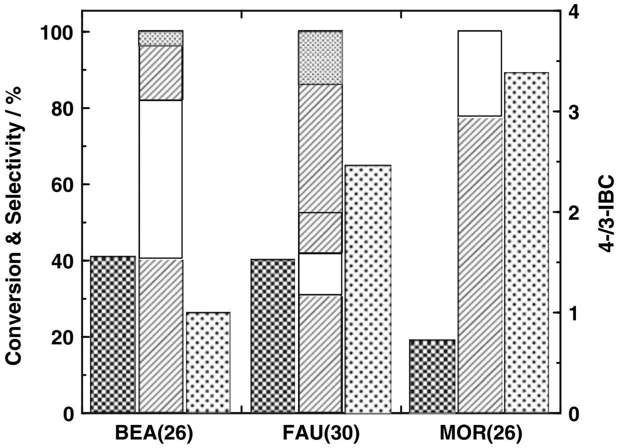

Fig. 1 Selective isopropylation of isobutylbenzene (IBB) over zeolites catalysts. Reaction conditions: isobutylbenzene, 3.35 g (25 mmol); 2-propanol: 1.50 g (25 mmol); catalyst, 0.50 g; CO_2 pressure, 11 MPa; temperature, 150 °C; reaction time, 12 h. Legends —▩: IBB conversion. Selectivity— ▨: 4-IBC; ☐: 3-IBC; ▨: 2-IBC; ▒: DIPIBB, and ▨: others. ░: 4-/3-IBC ratio

Table 1 summarizes the isopropylation of IBB over the zeolites with high SiO_2/Al_2O_3 ratio at 150 °C under 11 MPa of CO_2 pressure. Dealuminated H-mordenite (MOR(110)) showed a remarkable fivefold increase in the IBB conversion (~86%) along with a very high selectivity for 4-IBC (~81%). The coke formation of MOR(110) during the reaction was much lower than that of MOR(26). These phenomena observed over MOR(110) are directly related to the low deactivation of the catalyst in *sc*-CO_2 medium as well as the decrease in the acidity by the dealumination previously proposed in several papers [20–23]. Moreover, the pore dimensionality and pore structures of the H-mordenite also played an important role for achieving higher selectivity of 4-IBC. However, further decrease in the Al-content in H-mordenite zeolites showed a decrease in the IBB conversion suggesting low deactivation of the catalyst couldn't overcome the declining catalytic activity due to much lower acid density (data not shown). H-BEA(100) and FAU(80) zeolites also gave very low IBB conversion (2–10%) owing to lower acid density. MFI(54) and MEL(49) were found inactive under the same reaction conditions owing to steric limitations.

Figure 2 shows the influence of the atmosphere of the isopropylation of IBB at 150 °C over MOR(110). The reaction in *sc*-CO_2 medium gave the very high conversion (~80%) with high selectivity for 4-IBC (80%). On the other hand, the conventional liquid-phase reaction under autogeneous pressure in hexane showed lower conversions in comparison to that in *sc*-CO_2 medium (Fig. 2). The conversion under 11 MPa of N_2 pressure without solvent also gave lower conversion than that in *sc*-CO_2 medium, however, higher than that in hexane. The selectivity for 4-IBC in hexane was much less (~67%) compared to that under *sc*-CO_2 conditions; however, the selectivity under N_2 pressure was almost the same as under *sc*-CO_2 atmosphere. In all cases, there is no formation of 2-IBC, and small amount of DIPIBB isomers (1.0–1.2%) were also identified in the product mixture. These results mean that *sc*-CO_2

Table 1 Isopropylation of isobutylbenzene over different zeolite catalysts[a]

Catalysts	Conv./mol%	Selectivity/mol%				4-/3-IBC	Coke amounts/wt%[b]
		2-IBC	3-IBC	4-IBC	DIPIBB		
MOR(26)	18.5	–	22.9	77.1	–	3.36	3.5
MOR(110)	85.6	–	19.6	80.4	–	4.10	1.0
BEA(100)	9.7	7.3	40.0	52.7	–	1.32	–
FAU(80)	2.4	28.7	25.8	45.5	–	1.76	–
MFI(54)	0	–	–	–	–	–	–
MEL(49)	0	–	–	–	–	–	–
Ce/MOR(110)[c]	32.6	–	18.4	81.6	–	4.44	–
MOR(110)[d]	47.3	–	17.8	82.2	–	4.62	–
MOR(110)[e]	79.7	–	19.4	80.6	–	4.15	–

[a] Reaction conditions: same as given in Fig. 1 or as stated in the footnote

[b] Estimated from weigh loss of used catalyst from 350 °C to 650 °C in TG profiles

[c] MOR(110) contains 5 wt.% CeO_2

[d] 2nd run for MOR(110) after just filtration and subsequent drying of the catalyst

[e] 1st recycle for MOR(110) after subsequent calcination of the used catalyst

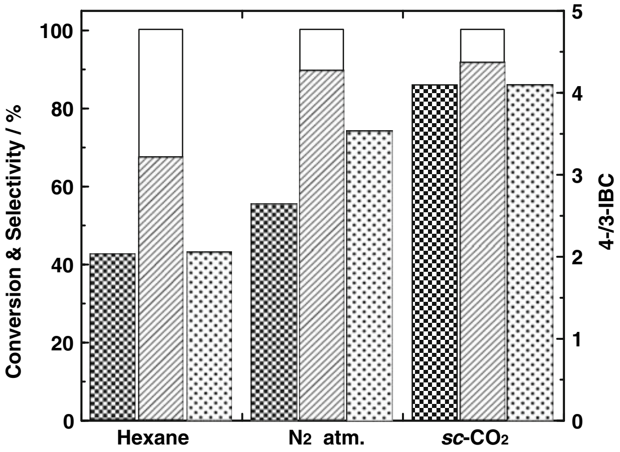

Fig. 2 Selective isopropylation of IBB over dealuminated MOR(110) under different reaction conditions. Reaction conditions: isobutylbenzene, 3.35 g (25 mmol); 2-propanol: 1.50 g (25 mmol); catalyst, 0.50 g; CO_2 pressure, 11 MPa; temperature, 150 °C; reaction time, 12 h, or as stated in the footnote. The conventional reaction was carried out in hexane under autogeneous pressure. Under N_2 atmosphere, the reaction was either carried out 11 MPa of N_2 pressure. Legends: see in Fig. 1

works as the excellent reaction medium for the isopropylation of IBB. As expected, the reaction carried out with neat reactants under autogeneous pressure also produced similar results to that observed under 11 MPa of N_2 pressure, indicating the inert N_2 gas has no effect in the IBB isopropylation reaction. The faster diffusion of reactants/products and efficient removal of coke precursors from the zeolitic channels, promoted by *sc*-CO_2 medium, are the main feature for higher IBB conversion and selectivity for 4-IBC.

We previously proposed the deactivation of external acid sites by the modification of MOR with CeO_2 [24, 25]. The modification of MOR(110) catalyst with 5 wt.% cerium dioxide (CeO_2) (Ce/MOR(110)) emerged as a better shape-selective catalyst compared to its parent MOR(110); however, a sharp decrease in the catalytic activity was noticed demonstrating the deposition of CeO_2 plausibly blocked the active acid sites in substantial amounts (Table 1).

Remarkable results were obtained when MOR(110) was reused for the 2nd run directly after filtration and subsequent drying. The results as given in Table 1 showed the highest selectivity for 4-IBC. Nevertheless, the IBB conversion dropped down considerably, but higher than Ce/MOR(110), indicating 1 wt.% coke (vide infra) formed during the 1st run could effectively sit on the active sites and reduce the IBB conversion. In fact, the channel width reduction due to coking, plausibly, facilitated the formation of 4-IBC in higher proportion. In addition, recycling studies (three times) of the catalysts (e.g. MOR(110)) confirmed that the catalysts retained its activity and impart similar product selectivity with respect to the fresh catalyst (Table 1).

The influence of the reaction time on the isopropylation of IBB at 150 °C over MOR(110) is shown in Fig. 3. The IBB conversion increased with reaction period under *sc*-CO_2 medium; however, the selectivity for 4-IBC decreased slightly with reaction time: the ratio of 4-IBC/3-IBC (4-/3-IBC) was also gradually decreased from 4.2 to 4.0, although 2-IBC was not detected even after 18 h. The continuation of the reaction resulted in saturation of the IBB conversion; however, the formation of a small amount of DIPIBB (1.2%) was also detected at the same time. It is obvious to presume that the formation of 3-IBC and DIPIBB isomers was catalyzed by external acid sites.

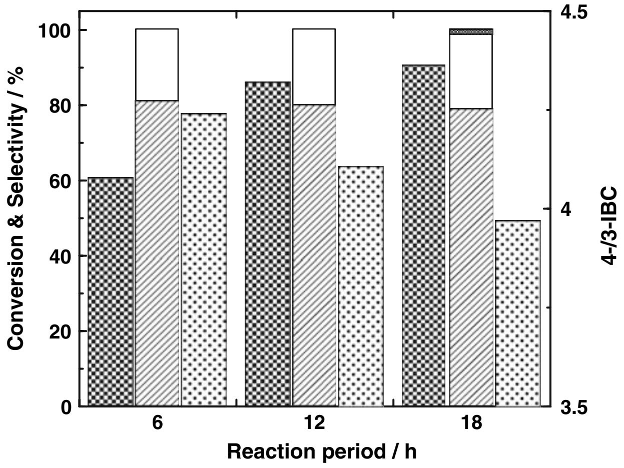

Fig. 3 The influence of reaction time on the isopropylation of IBB over MOR(110). Reaction conditions: isobutylbenzene, 3.35 g (25 mmol); 2-propanol: 1.50 g (25 mmol); catalyst, 0.50 g; CO_2 pressure, 11 MPa; temperature, 150 °C; reaction time: 6, 12, and 18 h. Legends: see in Fig. 1

The influence of the reaction temperature on the isopropylation of IBB under 11 MPa of CO_2 pressure over MOR(110) is shown in Fig. 4. As expected, the IBB conversion increased with temperature while the selectivity for 4-IBC gradually decreased from 82.3% at 130 °C to 79.6% at 170 °C. On the contrary, the formation of 3-IBC and DIPIBB (0.5% at 170 °C) were slightly increased with temperature compelling the 4-IBC/3-IBC ratio to decrease. Nevertheless, 2-IBC was not found even at 170 °C. It is obvious to presume that the formation of 3-IBC and DIPIBB isomers was catalyzed by external acid sites.

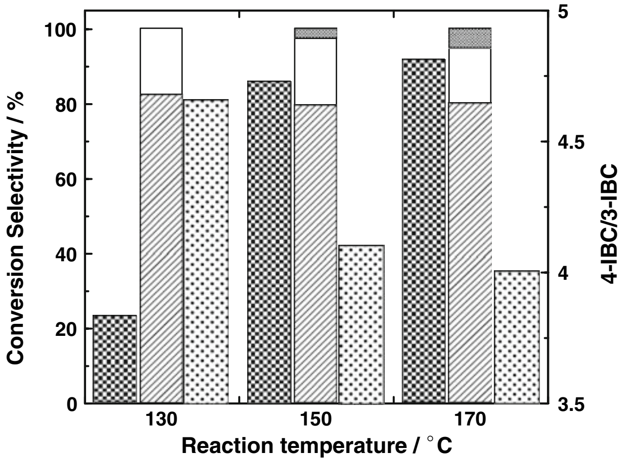

Fig. 4 The influence of reaction temperature on the isopropylation of IBB over MOR(110). Reaction conditions: isobutylbenzene, 3.35 g (25 mmol); 2-propanol: 1.50 g (25 mmol); catalyst, 0.50 g; CO_2 pressure, 11 MPa; temperature, 130, 150, and 170 °C; reaction time, 12 h. Legends: see in Fig. 1

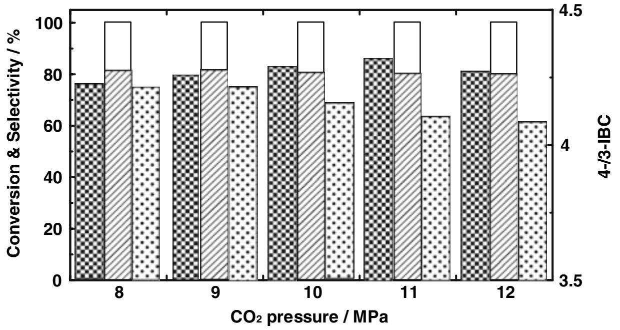

Fig. 5 The influence of CO_2 pressure on the isopropylation of IBB over MOR(110). Reaction conditions: isobutylbenzene, 3.35 g (25 mmol); 2-propanol: 1.50 g (25 mmol); catalyst, 0.50 g; CO_2 pressure: 8, 9, 10, 11, and 12 MPa; reaction time: 12 h. Legends: see in Fig. 1

Figure 5 shows the influence of CO_2 pressure on the isopropylation of IBB at 150 °C over MOR(110). The IBB conversion increased almost linearly up to 11 MPa of CO_2 pressure. However, further increment in the CO_2 pressure decreased the IBB conversion due to higher CO_2 density. It is important, however, to note that the selectivity for 4-IBC represented as 4-/3-IBC ratio remained almost constant with the variation of CO_2 pressure. Nevertheless, higher CO_2 concentration reduce the coke deposition on the catalysts which probably allowed the formation of 3-IBC in slight higher fraction.

Coke-deposition over acidic sites is considered as one of principal reasons for the rapid deactivation of the catalyst. Enhanced catalyst performances in *sc*-CO_2 achieved due to lower coke deposition. This is visually observed with different colors of the catalysts used after the reaction: off-white in *sc*-CO_2 medium and dark yellow in hexane and under N_2 pressure. Thermogravimetric analyses of the used catalysts reveal that soft coke (~1 wt.%) (weight loss in the range of 350–650 °C) was predominantly found in the catalyst used under *sc*-CO_2 medium (Fig. 6). However, the

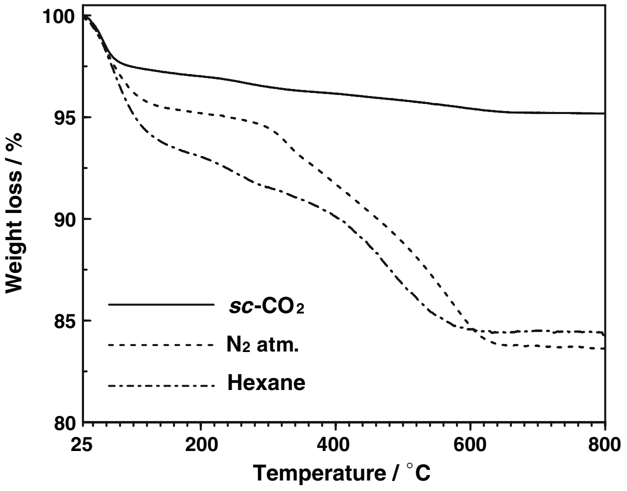

Fig. 6 TG profiles of the catalyst after the reaction. Reaction conditions: see in Fig. 2

catalysts after the reaction in hexane and under N_2 pressure without solvent contained much higher amounts of coke: 10 wt.% in hexane and 12–14 wt.% under N_2 pressure. These results unambiguously prove the superiority of *sc*-CO_2 medium for chemical transformations that are prone to coke-formation.

Strategically, this approach is significant for the shape-selective *para*-isopropylation of various aromatic compounds. The selective formation of the least bulky 4,4′-diisopropylbiphenyl (4,4′-DIPB) and 2,6-diisopropylnaphthalene (2,6-DIPN) was observed in the isopropylation of 4-isopropylbiphenyl and 2-isopropylnaphthalene. These results demonstrate that *sc*-CO_2 medium is a potential system to prevent deactivation of the catalyst by severe coking and to improve selectivity of the desired product(s). Further, the catalysis in *sc*-CO_2 medium can also get rid of huge quantity of organic wastes, and simplify the post-reaction separation processes. The detailed results and discussion will be given in the near future.

4 Conclusions

Supercritical CO_2 as reaction medium can remarkably enhance the catalytic activity and selectivity (4-IBC) in the isopropylation of isobutylbenzene over H-mordenite. The *sc*-CO_2 medium renders the intra-channel active acid sites free by faster diffusion of reactants and products through the zeolite catalysts and also by efficient dissolution of coke precursors thus formed in small quantities. Thus, the deactivation of the catalyst could be reduced substantially, while the shape-selectivity could still be exploited.

These results demonstrate that *sc*-CO_2 medium can prevent deactivation of the catalyst by severe coking and improve selectivity of the desired product(s), resulting in opening new aspects of green catalysis. Further investigations on these aspects are currently ongoing and will be reported in due course.

Acknowledgment A part of this work was financially supported by a Grant-in Aid for Scientific Research (B) 19310060, the Japan Society for the Promotion of Science (JSPS). S. C. Laha gratefully acknowledges JSPS for the postdoctoral fellowship.

References

1. Pujado PR, Rabo JA, Antos GJ, Gembicki SA (1992) Catal Today 13:113
2. Venuto PB (1994) Microporous Mater 2:297
3. Cejka J, Wichterlova B (2002) Catal Rev Sci Eng 44:375
4. Perego C, Ingallina P (2002) Catal Today 73:3
5. Franck HG, Stadelhofer JW (1988) In: Industrial aromatic chemistry, Springer-Verlag, Berlin
6. Harrington PJ, Lodewijk E (1997) Org Process Res Develop 1:72
7. Sheldon RA (1992) Chem Ind 7:903
8. Venkatesan C, Chidambaram M, Kamble KR, Singh AP (2003) Catal Lett 85:171
9. Bibby DM, Howe RF, McLellan GD (1992) Appl Catal A: Gen 93:1
10. Perot G, Guisnet M (1990) J Mol Catal 61:173
11. Clifford A (1998) In: Fundamentals of supercritical fluids. Oxford University Press, Oxford
12. Noyori R (2005) Chem Commun 1807
13. Baiker A (1999) Chem Rev 99:453
14. Hitzler MG, Smail FR, Ross SK, Poliakoff M (1998) Chem Commun 359
15. Petkovic LM, Ginosar DM, Burch KC (2005) J Catal 234:328
16. Kamalakar G, Komura K, Sugi Y (2006) Ind Eng Chem Res 45:6118
17. Amandi R, Licence P, Ross SK, Aaltonen O, Poliakoff M (2005) Org Process Res Dev 9:451
18. Gläser R, Weitkamp J (2003) Ind Eng Chem Res 42:6294
19. Matsukata M, Ogura M, Oakai T, Rao PRHP, Nomura M, Kikuchi E (1999) Top Catal 9:1441
20. Sugi Y, Kubota Y (1997) In Spivey JJ (ed) Catalysis, vol 13. Royal Soc Chem pp 55–84
21. Lee GS, Maj JJ, Rocke SC, Garces JM (1989) Catal Lett 2:243
22. Neuber N, Karge HG, Weitkamp J (1988) Catal Today 3:11
23. Karge HG, Weitkamp L (1986) Chem Ind Techn 58:946
24. Kim J-H, Sugi Y, Matsuzaki T, Hanaoka T, Kubota Y, Tu X, Matsumoto M, Nakata S, Kato A, Seo G, Pak C (1995) Appl Catal A: Gen 131:15
25. Tawada S, Sugi Y, Kubota Y, Imada Y, Hanaoka T, Matsuzaki T, Nakajima K, Kunimori K, Kim J-H (2000) Catal Today 60:243