Journal of the Chinese Chemical Society, **2000**, *47*, 1237-1242 **1237**

Vapor-Phase Aldolization of n-Butyraldehyde to 2-Ethyl-2-Hexenal over Solid-Base Catalysts

Wei-de Zhu (• • • •) and An-Nan Ko* (• • • •)
Department of Chemistry, Tunghai University, Taichung, Taiwan, R.O.C.

Vapor-phase aldol condensation of n-butyraldehyde to 2-ethyl-2-hexenal was studied at 1 atm and 150~300 °C in a fixed-bed, integral-flow reactor by using NaX, KX, γ-Al_2O_3 and Na/NaOH/γ-Al_2O_3 catalysts. Ion exchange of NaX zeolite with potassium acetate solution results in a decrease of crystallinity and apparent lowering of surface area, whereas the basic strength is enhanced. Treatment of γ-Al_2O_3 with NaOH and Na causes a large decrease of the surface area but strong enhancement of the catalyst basicity. The catalytic activity on the basis of unit surface area is in the order Na/NaOH/γ-Al_2O_3 > KXU > KXW > NaX >γ-Al_2O_3, in accordance with the relative catalyst basic strength. The molar ratio of trimeric to dimeric products increases with increasing the reaction temperature and the catalyst basic strength except for Na/NaOH/γ-Al_2O_3. Very high selectivity of 2-ethyl-2-hexenal (>98.5%) was observed for reactions over NaX zeolite at 150 °C. Based on the FT-IR and the catalytic results, the reaction paths are proposed as follows: self-aldol condensation of n-butyraldehyde, followed by dehydration produces 2-ethyl-2-hexenal, which then reacts with n-butyraldehyde and successively dehydrates to 2,4-diethyl-2,4-octadienal and 1,3,5-triethylbenzene. For the reaction over NaX, the calculated Arrhenius frequency factor and activation energy are 314 mol/g·h and 32.6 kJ/mol, respectively.

INTRODUCTION

2-Ethylhexanol is an important raw material for the manufacture of di-2-ethylhexanol phthalate (DOP) by reacting with phthalic acid. DOP can be applied to the industries of plastics, capacitors and synthetic lubricating oils. 2-Ethylhexanol is made from hydrogenation of 2-ethyl-2-hexenal (2E2H) which is conventionally prepared from n-butyraldehyde via self-condensation in sodium hydroxide solution.[1] However, the disadvantages of such a process include corrosion, separation procedures, and environmental problems due to the use of sodium hydroxide. Therefore solid base catalysts have been utilized recently, viz. anion ion exchange resin,[2] metal carboxylate,[3] titanium dioxide,[4] alkaline earth oxide,[5-7] aluminum oxide,[5,8] iron (III) oxide,[8] chromium oxide,[8] reduced tin supported on SiO_2,[9] metal oxides[10] or mixed metal oxides supported on SiO_2,[11] zeolites X and Y,[5,12,13] mixed metal oxides (MgO-Al_2O_3, CaO-Al_2O_3)[14] and molecular sieves VPI-5 and $AlPO_4$-8.[15]

For self-condensation of n-butyraldehyde over alkaline earth oxide and γ-alumina in the liquid phase, aldol condensation to the dimer (2-ethyl-3-hydroxyhexanal) occurred on basic sites, followed by Tischenko-type cross-esterification of the dimer with n-butyraldehyde to trimeric glycol ester (TGE) on both basic and acidic sites. High and quite small selectivity of the aldol condensation dimer (ACD) and the trimer (TGE) were found using alkali ion-modified aluminas, respectively. The activity of X zeolites was lowest among the catalysts studied and it was enhanced by ion exchange with excess alkali ions.[5] In the reactions over alkaline earth oxide, zirconium oxide and lanthanum oxide, the active site is proposed to be the surface O^{2-} and the rate-determining step is α-H abstraction.[7] With type X and Y zeolites in n-butyraldehyde condensation, M^+NaX was much more active than M^+NaY, $M^{n+}NaX$ or $M^{n+}Y$.[12] For the reaction over alkali metal zeolites, the catalyst activity followed the order of CsNaY > NaY > LiNa > MgO > Al_2O_3. It was inferred that the presence of both basic and acidic sites exhibited a higher activity.[13]

Despite the above descriptions of the reported catalytic results, the reaction paths and associated mechanisms over zeolite X in the gas phase still remain unclear. In addition, no kinetic data was reported for reactions using NaX. In this study, the aldol condensation of n-butyraldehyde over X-type zeolites, γ-Al_2O_3 and Na/NaOH/γ-Al_2O_3 was investigated at atmospheric pressure and in the temperature range of 150~300 °C. Highly selective formation of 2E2H is observed for reactions over NaX zeolite at 150 °C. The catalytic results are correlated to the catalyst properties. For reactions over NaX zeolite, the reaction paths and associated mechanisms are proposed, according to the FT-IR and the catalytic results. Furthermore, the kinetic parameters are estimated.

EXPERIMENTAL SECTION

Catalyst Preparation

To prepare KX samples,[16] 20 g NaX zeolite (Si/Al = 1.23, Strem) was added with stirring into 1000 mL 0.4 M potassium acetate solution at 60 °C for 24 h. Then the solution was filtered. After the fourth exchange, the catalysts were separated into two parts. One part was washed with de-ionized water, dried at 100 °C for 3 h and calcined at 400 °C for 4 h. The resulting catalyst is denoted as KXW. Another part of the sample was not washed with de-ionized water and is denoted as KXU.

To prepare Na/NaOH/γ-Al_2O_3,[17] 30 g γ-Al_2O_3 (Strem) was calcined at 500 °C for 12 h. Then 4.5 g NaOH (R.D.H.) was added into γ-Al_2O_3 with stirring at 320 °C for 3 h under flowing N_2 gas. Finally 1.2 g sodium metal was added into the above mixture with stirring at 320 °C for 1 h under an inert atmosphere of nitrogen.

Catalyst Characterization

The XRD powder patterns of catalyst samples NaX, KXU, and KXW were determined with an X-ray diffractometer (Shimadzu XD-7). The BET surface area of the catalysts was obtained with a sorption analyzer (Quantachrome Quantasorb). The basicity and acidity were determined by temperature-programmed desorption of carbon dioxide and ammonia, respectively. Before adsorption, 0.1 g of catalyst sample was heated under helium flow (40 mL/min NTP) with a rate of 10 °C/min from 110 to 500 °C to remove water from the sample; the sample was then cooled to room temperature. Measured pulses of carbon dioxide gas or ammonia (pulse volume, 0.5 mL NTP) were injected into helium gas and carried through the sample until adsorption saturated. Then the temperature was increased to 110 °C and it was kept there for 2 h to remove the physisorbed carbon dioxide or ammonia. Finally, the system was heated from 110 to 500 °C at 10 °C per minute and kept at 500 °C for 25 min. The TPD diagrams were obtained by monitoring the desorbed gas with a thermal conductivity detector. The adsorption behavior of n-butyraldehyde vapor on the surface of NaX was determined with a FT-IR spectrometer (Perkin-Elmer 2000) using a MCT mid-IR detector. NaX powder was pressed into a disk (~20 mg cm^{-2}) and the wafer was evacuated at 400 °C for 2 h. Different IR spectra were recorded for adsorption of n-butyraldehyde vapor (~20 torr) at 20 °C and subsequent desorption at 100 °C, 200 °C, and 300 °C. All spectra were measured at 20 °C.

Catalytic Reaction

The catalytic reaction was carried out at 150~300 °C and 1 atm in a fixed-bed, integral-flow reactor (1.1 cm I.D. × 32 cm). Before the reaction, the catalyst was activated in flowing air at 400 °C for 2 h and then adjusted to the reaction temperature with flowing nitrogen gas. Reagent grade n-butyraldehyde (R.D.H.) was fed into the reactor via a micropump (Razel A-99). The values of W/F (g·h/mol) refers to the weight of catalyst per unit feed rate of n-butyraldehyde. The reaction products were identified with a GC-MS (HP 5989 B Mass Spectrometer) and periodically analyzed with a G.C. (HP 5890 series II) equipped with a PONA column (Supelco 0.2 mm × 50 m) and a flame-ionization detector.

RESULTS AND DISCUSSION

Treatment of NaX zeolite with potassium acetate solution results in a similar XRD powder pattern except for a smaller peak intensity, indicating a decrease of crystallinity. The BET surface areas are 363, 297, 302, 212 and 44 m^2/g for NaX, KXU, KXW, γ-Al_2O_3 and Na/NaOH/γ-Al_2O_3, respectively. According to the TPD of carbon dioxide results, the basic strength decreases in the following order: Na/NaOH/γ-Al_2O_3 > KXU > KXW > NaX > γ-Al_2O_3, whereas the acidic strength shows the reverse trend. The strong basicities of Na/NaOH/Al_2O_3 and KXU are consistent with some reports in the literature; Na/NaOH/Al_2O_3 exhibits super basicity[17,18] and KXU has higher basicity than KXW due to its larger amount of potassium ion and the possible generation of strong basic sites in the zeolite cavities.[16]

In the catalytic reaction of n-butyraldehyde, the major product is 2E2H, while the minor products include 2-ethyl-3-hexenal (2E3H), 2-ethylhexanal (2EH), 2,4-diethyl-2,4-octadienal (DEO), and 1,3,5-triethylbenzene (TEB). These products, other than 2E2H, are quite different from those observed in the liquid phase reaction over MgO, CaO and γ-Al_2O_3 at 0 and 50 °C where the main products were 2-ethyl-3-hydroxyhexanal (2E3HH) and trimeric glycol ester.[5] In this study, the reaction temperature is much higher, thus facilitating the dehydration of the aldol 2E3HH to 2E2H and thus allowing further reaction between 2E2H and n-butyraldehyde to form other products such as DEO and TEB. The conversion of n-butyraldehyde and the product selectivities are calculated on the basis of converted n-butyraldehyde. Table 1 shows the catalytic results obtained from reactions over various catalysts. As the catalysts deactivated during the process time, the initial activity and selectivity, viz. data obtained at time-on-stream 8 min, are reported. The conversion follows the decreasing order of KXU > KXW ≒ NaX > Na/NaOH/γ-Al_2O_3 > γ-Al_2O_3 on a unit weight catalyst basis. However, the order becomes Na/NaOH/γ-Al_2O_3 > KXU > KXW > NaX > γ-Al_2O_3, according to the activity per unit area of catalysts, in accordance with the trend of catalyst basic strength. In Table 1 the dimer includes 2E2H, 2EH and 2E3H, while the trimer involves DEO and TEB. The molar ratio of trimer to dimer increases with increasing catalyst basic strength and the reaction temperature, showing the favorable formation of trimer

Table 1. Initial Catalytic Results of n-Butyraldehyde over Solid Base Catalysts. Reaction Conditions: W/F, (33.5 ± 1) g·h/mol; Time-on-stream 8 min

Catalyst	Surface area	Reaction	Conversion	Selectivity (mol%)					Conversion	Trimer
	(m^2/g)	temperature (°C)	(mol%)	2E2H	2E3H	2EH	DEO	TEB	Surface area	Dimer
NaX	363	150	70.3	99.1	0.87	0	0	0	0.19	0
		200	82.5	96.0	1.9	0.21	1.7	0.23	0.23	0.02
		250	83.0	87.4	2.8	0.60	7.7	1.5	0.23	0.10
		300	83.2	68.2	3.9	4.1	15.8	8.0	0.23	0.31
KXW	302	200	81.9	94.0	1.5	0.26	3.9	0.34	0.27	0.04
KXU	297	200	90.3	93.6	1.6	0.20	4.1	0.50	0.30	0.05
γ-Al_2O_3	212	300	11.8	85.8	6.6	7.6	0	0	0.06	0
Na/NaOH/γ-Al_2O_3	44	300	23.8	89.9	5.1	5.0	0	0	0.54	0

on strong base catalyst and at severe reaction condition. Although Na/NaOH/γ-Al_2O_3 exhibits the strongest basic strength, no trimer is found and the possible reason may be due to its extremely small acidity. Similar catalytic features were reported in the liquid phase aldol condensation of n-butyraldehyde.[5]

Table 2 shows the effect of W/F values on the product yields. As W/F values increase, the yields of 2E2H and DEO decrease with concomitant increase of TEB. Small variation in the yields of 2EH and 2E3H are observed. Fig. 1 shows the FT-IR spectra of n-butyraldehyde vapor adsorbed on NaX zeolite with subsequent evacuation at 100, 200 and 300 °C. The band at ca. 1715 cm^{-1} is attributed to the stretch of carbonyl group while the bands at ca. 1409 and 1462 cm^{-1} are ascribed to the bending modes of methyl and CH_2 group. The band at ca. 2870 cm^{-1} corresponds to the C-H stretching mode of α-carbon. As the evacuated temperature is increased to 100 °C, a new band at ca. 1674 cm^{-1} appears, implying the C=C stretching mode due to the formation of 2E2H. Further increase of evacuated temperature to 200 and 300 °C results in the decrease of the band 1674 cm^{-1} as well as the apparent increase of the new band at ca. 1579 cm^{-1}. Such a band infers the C=C stretching mode of the aromatic compound TEB. Based on the above catalytic and FT-IR results, the reaction paths are shown in Fig. 2. Aldol condensation of n-butyraldehyde on the catalyst basic sites produces 2E3HH (step I), which is easily dehydrated to 2E2H on acidic sites (step II). Further cross condensation between 2E2H and n-butyraldehyde on basic sites forms 2,4-diethyl-3-hydroxy-4-octenal (DEHO) (step III), followed by dehydration to DEO (step IV). Finally, successive dehydration of DEO on acid sites yields TEB (step V). Neither 2E3HH nor DEHO was found in the reaction products, indicating the relatively high reaction rates of step II and IV. Consequently, both basic and acidic sites with adequate strength are necessary for the formation of DEO and TEB from n-butyraldehyde. The absence of these two products by using γ-Al_2O_3 and Na/NaOH/γ-Al_2O_3 as catalysts (Table 1) is attributed to their weak basic and acidic strength, respectively. Fig. 3 illustrates the reaction mechanism for the forma-

Table 2. Effect of W/F Values on Product Yields. NaX; 300 °C; Time-on-stream 8 min

W/F	Product yield (mol%)				
(g·h/mol)	2E2H	2E3H	2EH	DEO	TEB
33.6	56.8	3.2	3.4	13.2	6.6
74.1	42.2	5.6	7.1	7.9	20.9
146.4	15.4	4.8	6.7	2.7	69.3

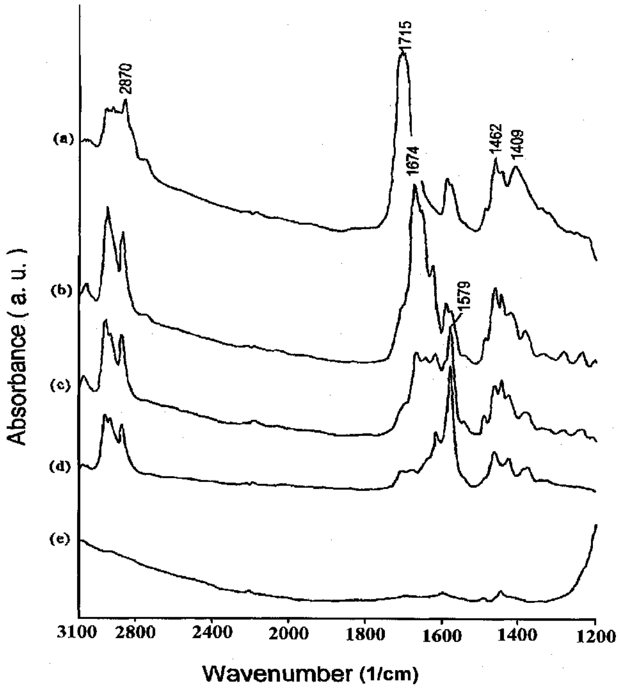

Fig. 1. FT-IR absorption spectra of adsorbed n-butyraldehyde at different evacuated temperatures: (a) 20 °C; (b) 100 °C; (c) 200 °C; (d) 300 °C; (e) NaX.

tion of 2E2H. The catalyst basic sites abstract a hydrogen ion from the α carbon of n-butyraldehyde to form carbanion A, which attacks carbonyl carbon of n-butyraldehyde to form 2E3HH (step I), followed by dehydration on the acidic sites to produce 2E2H (step II).

To investigate the reaction kinetics of n-butyraldehyde to 2E2H over NaX zeolite, the following reaction sequences and rate equations are proposed: [8]

$$B + L_B \Leftrightarrow BL_B \quad (1)$$
$$B + BL_B \Leftrightarrow B_2L_B \quad (2)$$
$$B_2L_B \rightarrow W + E + L_B \quad (3)$$
$$W + L_B \Leftrightarrow WL_B \quad (4)$$
$$E + L_B \Leftrightarrow EL_B \quad (5)$$

Where L_B, B, W and E represent Lewis basic sites, n-butyraldehyde, water and 2E2H. Since 2E3HH is not detected in the reaction products, step 2 is considered as the rate-determining step that leads to the following rate equation (A):

$$-\gamma_B = k\,K_BC_B^2/(1 + K_BC_B + K_WC_W + K_EC_E) \quad (A)$$

where k, K_i and C_i refer to the rate constant, adsorption-desorption equilibrium constant and concentration of the ith compound, respectively. Since the concentrations of n-butyraldehyde, water and 2E2H are relatively high, the following equation (B) is reasonably valid.

$$K_BC_B + K_WC_W + K_EC_E > 1 \quad (B)$$

Let C_O and X be the initial concentration and the conversion of n-butyraldehyde, respectively. Then equation (A) leads to equation (C).

$$-\gamma_B = k\,C_O\,(1 - X)^2/(1 + K_{rel}X) \quad (C)$$

where K_{rel} is defined as follows:

$$K_{rel} = [(K_W + K_E)/2K_B] - 1 \quad (D)$$

Integration of equation (C) gives equation (E):

$$X/(1\text{-}X) + K_{rel}\,[X/(1\text{-}X) + \ln(1\text{-}X)] = k\,(W/F) \quad (E)$$

In the reaction of n-butyraldehyde over NaX zeolite at 150~200 °C and W/F 3.94~34.5 g h/mol, all of the 2E2H selectivities were larger than 97.2% and no 2E3HH was observed. These results propose the above rate equations are applicable to this reaction system. Fig. 4 shows the conversion as a function of W/F values at different temperatures. The curves are obtained from non-linear regression fitting according to equa-

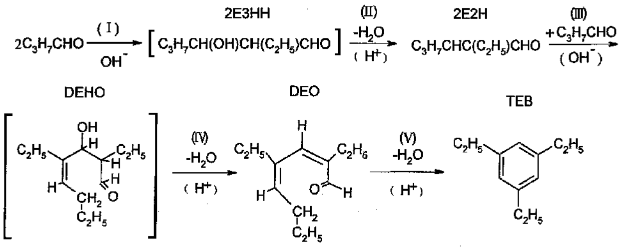

Fig. 2. The reaction paths in the aldol condensation of n-butyraldehyde.

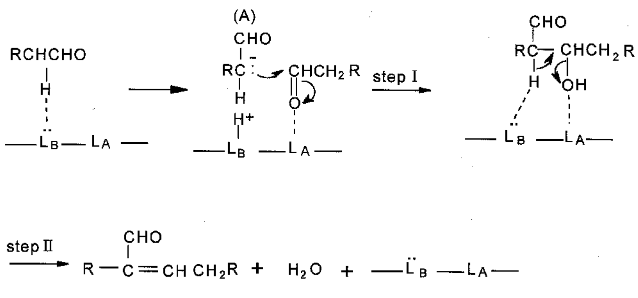

Fig. 3. The proposed reaction mechanism for the formation of 2E2H. R = C_2H_5; L_B = Lews basic site; L_A = Lewis acid site.

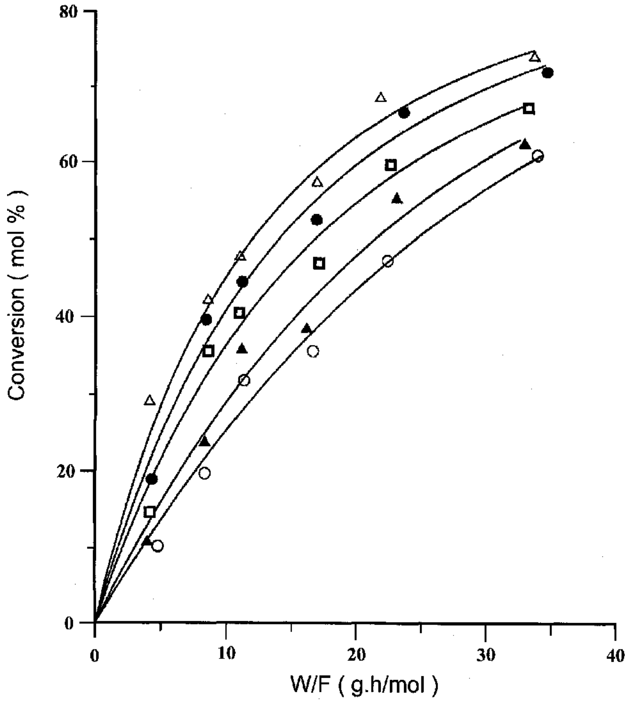

Fig. 4. Evaluation on the rate constant of n-butyraldehyde reaction over NaX zeolite. (O) 150 °C; (▲)162 °C; ( )175 °C; (●)187 °C; (Δ)200 °C.

Table 3. Kinetic Parameters for the Reaction of n-Butyraldehyde over NaX

Reaction Temperature (℃)	k (mol/g h)	K_{rel}	Ea (kJ/mol)	A (mol/g h)
150	0.030	-0.897		
162	0.036	-0.786		
175	0.053	-0.406	32.6	314
187	0.063	-0.430		
200	0.077	-0.307		

tion (E). Table 3 indicates the calculated kinetic parameters. Fig. 5 shows the Arrhenius plot of ln k versus 1/T. The activation energy and frequency factor are 32.6 kJ/mol and 314 mol/g h, respectively, for gas phase reaction of n-butyraldehyde. The corresponding data are 40.1 kJ/mol and 191 mol/g h for vapor phase aldolization of acetaldehyde.[19] In addition, such a value of activation energy is smaller than those in the liquid phase reaction at 165~210 °C using Al_2O_3, Fe_2O_3 and Cr_2O_3. The corresponding activation energies were 62.0, 54.4 and 48.1 kJ/mol.[8]

CONCLUSION

In the vapor phase aldol condensation of n-butyraldehyde over X-type zeolite and γ-Al_2O_3 type catalysts, both the catalytic activity and the molar ratio of trimeric to dimeric products increase with increasing the reaction temperature and the catalyst basic strength except for Na/NaOH/γ-Al_2O_3. According to the FT-IR and the catalytic results, self-aldolization of n-butyraldehyde produces 2-ethyl-3-hydroxyhexanal, followed by quick dehydration to 2-ethyl-2-hexenal. Further cross condensation between 2-ethyl-2-hexenal and n-butyraldehyde, followed by successive dehydration yields 2,4-diethyl-2,4-octadienal and 1,3,5-triethylbenzene. Very high selectivity (>98.5%) of 2E2H is attained for reactions over NaX zeolie at 150 °C and W/F 33.8 g h/mol during a process time of 90 min. The estimated Arrhenius frequency factor and activation energy are 314 mol/g h and 32.6 kJ/mol, respectively, for the aldolization of n-butyraldehyde over NaX zeolite.

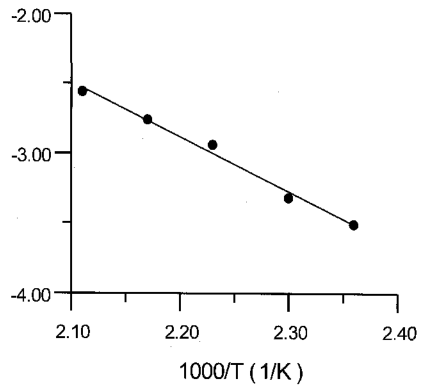

Fig. 5. Arrhenius plot for n-butyraldehyde reaction over NaX zeolite.

ACKNOWLEDGEMENT

We thank the National Science Council of the Republic of China for financial support.

Received May 12, 2000.

Key Words

Aldol condensation; n-Butyraldehyde; 2-Ethyl-2-hexenal; NaX zeolite; Solid base catalyst.

REFERENCES

1. Weissermel, K.; Arpe, H.-J. *Industrial Organic Chemistry*, Lindey, C. R., Translator; 3rd ed.; VCH: New York, 1997, p 138.
2. Tanabe, K.; Misono, M.; Ono, Y.; Hattori, H. *New Solid Acids and Bases. Their Catalytic Properties*; Kodansha Ltd.: Tokyo, 1989, p 179.
3. Papa, A. J. U. S. Patent 4, 528, 405, 1985.
4. Morris, D. L. U. S. Patent 4, 316, 990, 1985.
5. Tsuji, H.; Yagi, F.; Hattori, H.; Kita, H. *J. Catal.* **1994**, *148*, 759.
6. Kwok, T. J.; Watkins, W. C. PCT Int. Appl. WO 9735, 825, 1997.
7. Zhang, G.; Hattori, H.; Tanabe, K. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2070.
8. Nondek, L.; Malek, J. *Collect. Czech. Chem. Commun.* **1984**, *44*, 2384.
9. Swift, H. E.; Bozik, J. E.; Massoth, F. E. *J. Catal.* **1969**, *15*, 407.
10. Moggi, P.; Albanesi, G. *Appl. Catal.* **1991**, *68*, 285.
11. Moggi, P.; Albanesi, G. *React. Kinet. Catal. Lett.* **1983**, *22*, 247.
12. Isakov, Ya. I.; Usachev, N. Ya.; Isakova, T. A. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1985**, 1965. [From *C. A.* **1986**, *105*, 42293q].
13. Rode, E. J.; Gee, P. E.; Marquez, L. N.; Uemura, T.; Bazargani, M. *Catal. Lett.* **1991**, *9*, 103.
14. Nondek, L.; Malek, J. *Chem. Prum.* **1980**, *30*, 74.

15. Isakov, Ya. I.; Minachev, Kh. M.; Tome, R.; Tissler, A.; Oehlmann, G.; Kalinin, V. P.; Isakova, T. A. *Izv. Akad. Nauk, Ser. Khim.* **1994**, 2123. [From *C. A.* **1996**, *124*, 86331x].
16. Tsuji, H.; Yagi, F.; Hattori, H. *Chem. Lett.* **1991**, 1881.
17. Suzukamo, G.; Fukao, M.; Hibi, T.; Tanaka, K.; Chikaishi, K. in *Acid-Base Catalysis*, Tanabe, K.; Hattori, H.; Yamaguchi, T., Eds., Proceedings of the International Symposium on Acid-Base Catalysis, Sapporo, Nov. 28-Dec. 1, 1988, Kodansha Ltd.: Tokyo, 1989, p 405.
18. Tanabe, K.; Misono, M.; Ono, Y.; Hattori, H. *New Solid Acids and Bases. Their Catalytic Properties*, Kodansha Ltd.: Tokyo, 1989, p 211.
19. Chang, Y.-C.; Ko, A.-N. *Appl. Catal. A* **2000**, *190*, 149.