Catalysis Communications 64 (2015) 1–5

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Positive effect of secondary structure creation in mordenites on alkylation of benzene with 1-tetradecene

Michal Horňáček *, Pavol Hudec, Klaudia Velebná, Peter Lovás

Department of Petroleum Processing and Petrochemistry, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovakia

ARTICLE INFO

Article history:
Received 2 October 2014
Received in revised form 20 January 2015
Accepted 22 January 2015
Available online 23 January 2015

Keywords:
Mordenite
Mesoporous structure
Acidity
Alkylation
Aromatics
l-Alkenes

ABSTRACT

The liquid-phase alkylation of benzene with 1-tetradecene was realized over dealuminated mordenites with different mesoporous surface areas and three different levels of acidity. The mordenite catalysts were characterized by N_2-sorption, FTIR pyridine adsorption, and TPDA. The number of Brønsted acid sites decreases; however, it represents a higher proportion of the total acidity. Alkylation results demonstrated that the mordenite activity in alkylation accelerated with increasing mesoporous surface area in spite of the lower total acidity. This fact indicates that the accessibility of acid sites and the internal mass transport in mordenite channels play a significant role in liquid-phase alkylation of aromatics with 1-alkenes.

1. Introduction

Alkylation of benzene with long-chain l-alkenes is applied much of the petroleum industry. A great amount of linear alkylbenzenes is used as material for the production of detergents for domestic and industrial use and for the preparation of various special synthetic oils [1,2]. Among all alkylbenzene isomers, production of 2-alkylbenzene (linear alkylbenzenes) is preferred because it yields detergents with better emulsivity and biodegradability for several applications [3,4].

At the present, alkylbenzenes are manufactured via alkylation of benzene with l-alkenes over Friedel–Crafts catalysts, such as HF, H_2SO_4, or others [5]. These types of Friedel–Crafts catalysts are highly toxic, create a substantial amount of waste, and cause severe corrosion problems [6]. Based on the latter, a great effort is expended to replace these F–C catalysts by solid acid catalysts such as zeolites; for example, zeolite Y [7–9], beta zeolite [10,11], mordenites [12,13], heteropolyacids [14], clays [15] and ionic liquids [16] have been widely investigated for this reaction.

Mordenite seems to be a suitable catalyst for the alkylation of aromatics with 1-alkenes. Mordenite provides high selectivity to 2-phenyl isomers up to ca. 75–80% [17]. This is due to its relatively narrow parallel 12-MR elliptical channels with the dimensions of 0.65 × 0.70 nm. However, the overall activity is significantly lower than those of Y-zeolite [18] due to the limiting internal diffusion as a consequence of narrower pores. The activity of mordenite can be improved by dealumination. Removing of aluminum from the mordenite framework results in the elimination of acid sites and in a decrease of the total acidity [19]. On the other hand, dealumination of mordenite leads to the creation of a secondary mesoporous structure that has a significant positive effect on the improvement of internal diffusion properties, increasing the catalytic activity and at the same time preserving the shape selectivity [19].

Bordoloi et al. [20] reported the use of mesoporous AlMCM-41/Beta zeolite composite catalyst for liquid-phase alkylation of benzene with different 1-alkenes. The synthesized composite catalyst had a BJH average mesopore diameter of 2.98 nm, and their acidity was 0.29 mmol/g. The authors performed the alkylation reaction using the benzene:1-alkene molecular ratio of 10:1 at temperatures ranging from 80 °C to 160 °C. It was shown that the composite material was less active than the dealuminated or desilicated mordenites [19,12]. The conversion of 1-dodecene was only 48% at the temperature of 120 °C in the 120 min of reaction time. Selectivity to the 2-phenyl isomer was comparable with mesoporous mordenite. Aluminum chloride-grafted mesoporous molecular sieves were tested as catalysts in alkylation of benzene with 1-dodecene in the study of Dubé and co-workers [21]. The prepared catalyst had a very high total acidity of ca. 2 mmol/g as was determined by TPD of ammonia and pore diameter of 5.3 nm. The authors performed the alkylation of benzene at room temperature and the molar ratio of benzene:1-dodecene was 12.5:1. Conversion of 1-dodecene in the 15 min of reaction time was 100%, selectivity to 2-phenyl isomer was 54%, and the content of linear alkylbenzenes was 85%. Desilicated mordenites provide practically the same conversion of 1-alkenes, but on the other hand they show a higher value of selectivity to 2-phenyl isomer (70%), and the overall content of linear alkylbenzenes is also

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* Corresponding author.
E-mail address: michal.hornacek@stuba.sk (M. Horňáček).

http://dx.doi.org/10.1016/j.catcom.2015.01.018

higher (98%) [12] at a much lower total acidity of 0.4 mmol/g. Dealuminated mordenites with a low total acidity of ca. 0.27 mmol/g are very selective to 2-phenyl isomer (87%) at comparable values of 1-alkene conversion and with comparable content of linear alkylbenzenes [19]. Total acidity is not the most important factor that affects the catalyst activity and the composition of the products in alkylation of benzene with 1-alkenes. This process is limited by the mass transfer, the diffusion of the feed and products, and the access to the active sites of mordenites [22].

The aim of this work is to study the influence of the secondary structure created by the mordenite dealumination on the activity in the benzene alkylation with 1-tetradecene in liquid-phase using catalysts with the same acidity.

2. Experimental

2.1. Catalyst preparation

From the samples of different synthetic mordenites with various starting Si/Al ratios prepared in our laboratory by different combinations of chemical and thermal treatment, nine samples divided into three series were chosen for this study, including three triplets with three different acidities. Parent Na-forms of mordenites were received from the Research Institute for Hydrocarbons and Petroleum Gases in Bratislava. Chemical treatment consisted of mixing the mordenite suspension with a solution (ratio 1:10) of NaOH, HCl, and NH_4NO_3 at 90 °C for 3 h at concentrations and repetitions as indicated in Table 1. Thermal treatment was carried out in deep bed conditions at 560 °C and 780 °C for 3 h. The specifications of samples and the methods of their modifications are listed in Table 1.

2.2. Characterization of catalysts

Textural properties were determined by physical adsorption of nitrogen at the temperature of liquid nitrogen using ASAP-2400 equipment (Micromeritics). Before the measurement, samples were degased at 350 °C under vacuum of 2 Pa overnight. Adsorption data were evaluated using a BET-isotherm with the linearization in the standard range of relative pressure ($p/p_0 = 0.05–0.30$). The micro-mesoporous character ($S_t = S_{mezo}$, V_{micro}) was determined using the t-plot method with the linearization of t in the range of 0.03–0.50 nm. The total acidity was determined by the standard TPD of ammonia method. Before adsorption of ammonia, the samples (0.3000 g) were treated in situ at 480 °C for 2 h in a flow of He and then cooled to 220 °C in a He atmosphere. Adsorption of ammonia was done at 220 °C using an NH_3/He mixture. Ammonia desorption was carried out in the temperature range of 220–700 °C in a flow of He. During desorption the effluent was led to the solution of 0.05 M H_2SO_4. The amount of desorbed ammonia was determined by titration of the excess of H_2SO_4 with 0.05 M NaOH. Analysis of Brønsted and Lewis acidity was performed by room-temperature infrared spectroscopy of pyridine adsorbed at 150 °C using a FTIR Genesis (Mattson-Unicam) spectrometer. Self-supported wafers (surface density ca. 8 mg/cm^2) were activated at 450 °C under a vacuum of 10^{-4} Pa for 3 h. The amount of Brønsted and Lewis acid sites was determined based on the integrated area absorbances at 1550 and 1450 cm^{-1}, respectively, in correlation with their extinction coefficients [23].

2.3. Catalytic tests

Alkylation of benzene with 1-tetradecene was carried out in a mixed batch reactor (1500 rpm, 100 mL) at the temperature of 120 °C and nitrogen pressure of 0.5 MPa. For each experiment, 80 g of reaction mixture of benzene and 1-tetradecene with a molar ratio of 8.6:1 was used. 2 g of freshly calcinated catalyst (450 °C/3 h) was added to the reaction mixture just before the experiment. Liquid samples were taken from the bottom of the reactor during the experiment via a sampling valve. Samples of reaction products were cooled in an ice trap. Samples for the analysis were taken in the following way: the first sample was taken after reaching the reaction temperature (120 °C), i.e., 30 min after the heating was started; next, samples were taken each 30 min up to the reaction time of 240 min. The feed and reaction products were analyzed using a gas chromatograph (Hewlett–Packard 5890 A, Series II) with FID and a capillary column HP-1. Structures of alkenes and alkylbenzenes in the reaction mixture were verified by GC–MS using a MS25RFA Kratos, Manchester equipment. Conversion of 1-tetradecene was calculated as a percentage of alkylbenzenes in the sum of alkenes and all products. Selectivity to 2-phenyl isomer was determined as a percentage of 2-tetradecyl benzene in all products.

3. Results and discussion

As seen in Table 2, three triplets of dealuminated mordenite samples have acidity of 1.45 ± 0.03 (M-1.4), 0.95 ± 0.04 (M-0.9), and 0.38 ± 0.02 (M-0.3) mmol/g, respectively. Examples of TPDA curves for three chosen mordenite samples with different acidities in Fig. 1 show very similar profiles with the maximum at about 550 °C, indicating that for all three acidity levels the greatest acidity portion is concentrated in centers with the highest acid strength. For each triplet of samples with similar acidity, the TPDA profiles are practically the same. The evaluation of acidity by FTIR of adsorbed pyridine shows that it is predominantly concentrated in Brønsted acid sites, whose portion on the total acidity increases from about 65% from sample M-1.4/36 up to over 90% for all samples M-0.3 (see Table 2).

Fig. 2 displays examples of different adsorption isotherms of mordenites with small, high, and average values of mesopore surface area calculated using the t-plot method. The texture characteristics of all nine mordenite samples are presented in Table 2. The shapes of the adsorption isotherms of the mordenite samples are similar: they show a narrow hysteresis loop without meaningful steps that do not

Table 1
Methods of mordenite catalyst treatment.

Sample	Si/Al initial	Method of the treatment
M-1.4/36	8.9	4 × 0.5 M HCl
M-1.4/52	6.4	4 × 1 M HCl
M-1.4/66	6.4	5 × NH_4NO_3, DB[a]—560 °C, 5 × 0.5 M HCl
M-0.9/44	8.9	1 × 1 M HCl, 5 × 1 M NH_4NO_3, 5 × 1 M HCl
M-0.9/59	7.0	5 × 1 M HCl
M-0.9/93	8.9	2 × 0.2 M NaOH, 5 × 1 M NH_4NO_3, 5 × 1 M HCl
M-0.3/101	8.9	2 × 0.2 M NaOH, 5 × 1 M NH_4NO_3, DB[a]—780 °C, 5 × 1 M HCl
M-0.3/133	5.4	5 × 1 M NH_4NO_3, DB[a]—780 °C, 5 × 1 M HCl
M-0.3/141	5.4	2 × 0.2 M NaOH, 5 × 1 M NH_4NO_3, DB[a]—780 °C, 5 × 1 M HCl

[a] DB = deep bed treatment at indicated temperature for 3 h.

Table 2
Acid and textural properties of prepared mordenites.

Sample assay	S_{BET} (m^2/g)	S_t (m^2/g)	V_{micro} (cm^3/g)	D_p (nm)	Total acidity[a] (mmol/g)	BAS[b] (mmol/g)
M-1.4/36	347	36	0.201	–	1.43	0.93
M-1.4/52	410	52	0.176	–	1.47	1.15
M-1.4/66	446	66	0.168	–	1.42	1.16
M-0.9/44	360	44	0.191	–	0.91	0.77
M-0.9/59	423	59	0.185	–	0.99	0.83
M-0.9/93	445	93	0.171	–	0.94	0.85
M-0.3/101	425	101	0.175	5	0.36	0.33
M-0.3/133	445	133	0.171	5	0.36	0.34
M-0.3/141	471	141	0.166	6	0.40	0.37

[a] Total acidity determined by TPD of ammonia.

[b] Brønsted acid sites determined by FTIR spectra of adsorbed pyridine.