SHAPE SELECTIVE ALKYLATION OF POLYNUCLEAR AROMATICS WITH MORDENITE-TYPE CATALYSTS: A HIGH YIELD SYNTHESIS OF 4,4′-DIISOPROPYLBIPHENYL

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Unique dealuminated mordenite zeolites with a high proportion of mesopores behave as shape selective catalysts in the liquid phase alkylation of biphenyl with propylene. Dealumination reduces deactivation and the mesopores enhance diffusion. High yields of 4,4′-diisopropylbiphenyl (> 70%) are observed.

1. Introduction

Shape selective reactions on zeolites have been the subject of numerous publications [1]. In particular, ZSM-5 type zeolites have proven utility for the production of para substituted isomers such as p-xylene, p-ethyltoluene, etc. However, little is known about the use of mordenite as a catalyst for shape selective alkylations. As pointed out by Jacobs and Martens [2], mordenite strictly does not behave as a shape selective zeolite.

The rapid deactivation of acidic mordenite catalysts in gas phase alkylation of benzene with olefins limits the use of this zeolite in many practical applications [3]. Deactivation is associated with pore plugging via formation of coke deposits in the pores of acidic zeolites and increases with the framework Al density [4]. Walsh and Rollman suggests that the alkylation of aromatics is the initial reaction in coke formation [5].

We report here on novel dealuminated H-mordenite catalysts (DHM) for the alkylation of biphenyl with propylene to produce 4,4′-diisopropylbiphenyl (DIPB) in high yield as an example of the alkylation of polynuclear aromatics with olefins. The para para dialkylates of polynuclear aromatic hydrocarbons are valuable intermediates in the preparation of monomers to make thermotropic liquid crystal polymers.

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2. Experimental

A one-liter stirred tank reactor from Autoclave Engineers was used. The reactor was purged with propylene first and then heated to reaction temperature. Typical reaction conditions are: 8.34 kg (wt) cm^{-2} of propylene, 523 K, 2000 rpm stirring rate, 500 g of biphenyl, and 10 g of mordenite catalyst. Samples of the reaction mixture were analyzed using a Hewlett Packard 5890 GC unit equipped with flame ionization detector and a 30 m DB-5 capillary column. The H forms of the listed zeolites were used as catalysts. For dealumination, Na-Mordenite (NaM) was converted to H-mordenite (HM) by exchange with 1N HCl and then calcined at about 973 K. The resulting HM was heated at reflux in 6N HNO_3, washed in water, and activated in air at about 973 K for 2 hrs. This procedure was repeated (1X, 2X, etc.) to make catalysts with lower Al content and different pore properties. X-ray powder diffraction, BET surface area and chemical composition were used to characterize the catalysts.

3. Results and discussion

The results of screening a variety of acidic catalysts for the shape selective alkylation of biphenyl with propylene to make DIPB are summarized in table 1. Liquid phase alkylation with propylene fed on demand maintains a low propylene concentration which is needed to limit olefin side reactions, because Bronsted acid sites catalyze the oligomerization and polymerization of olefins, even at room temperature [6]. The reaction was typically allowed to proceed for about 20 hours at 523 K. The best results are obtained with 12-member ring zeolites (table 1), and in particular with DHM which give high conversion of biphenyl and high yields of DIPB (table 2).

Table 1
Performance of acidic catalysts in the alkylation of biphenyl (BP) with propylene at 523 K for the production of DIPB. Results refer to product analysis after 20 hrs of reaction in batch runs using 500 g of BP and 10 g of catalyst at 8.43 kg (wt) cm^{-2} propylene pressure and stirring rate of 2000 rpm.

Catalyst	% BP conversion [1]	% Selectivity [2]	% DIPB yield [3]
H_3PO_4	48	1.9	0.9
Zeolite Y	90	6.7	6.0
Zeolite L	73	3.8	2.8
Offretite	96.4	14.7	14.2
ZSM-5	5	–	–
Zeolon 100	21	3.8	0.8
DHM-2X	98	73.5	72

[1] % Conversion = % BP converted.

[2] % Selectivity = 100 * DIPB/[BP converted].

[3] % DIPB yield = % Selectivity * % Conversion/100.

Table 2
Composition, surface area, pore distribution and yield of mordenite catalysts in the alkylation of BP with propylene to make DIPB.

Catalyst	SiO_2/Al_2O_3 molar	% yield DIPB		BET m^2/g	micro cm^3/g	meso cm^3/g
		1 hr	20 hrs			
Zeolon 100	10	0	0.8	319	0.133	0.061
Zeolon 1X	144	3	28.6	465	0.184	0.087
Zeolon 2X	213	15	41.4	496	0.170	0.123
DHM-1X	256	35	56.2	428	0.208	0.200
DHM-2X	2600	56	72	382	0.149	0.227

As the SiO_2/Al_2O_3 ratio of the HM increase, the yield of DIPB also increases. Dealumination not only reduces the number of acid sites but also modifies the pore distribution of the catalysts resulting in an increase in their total pore volume (as determined by N_2 adsorption), and in particular in an increase of the mesopore volume (20–1000 Å) as shown in table 2. If the formation of DIPB is diffusion limited, the higher yield observed with DHM may be due to the improved diffusion via creation of additional mesopores. However, the higher yields could also be related to a lower deactivation rate in the DHM.

It is more difficult to dealuminate Zeolon 100 samples and at comparable levels of dealumination they have less mesopore volume than DHM. Zeolon 2X and DHM-1X (table 2) have similar composition but their performance appears to be related to the mesopore volume. By selection of the mordenite source we have identified materials which can be readily dealuminated with formation of significant mesopore volume. Eventually, as the mesopore volume increases, the creation of mesopores at the expense of micropores results in a loss of crystallinity.

Zeolon 100 gives low yields of DIPB and readily cokes during a single batch run. In contrast to Zeolon catalysts, DHM ($SiO_2/Al_2O_3 > 50$), remain active and selective after several batch runs without intermediate regeneration. The performance of the Zeolon 100 and the DHM appear to be related not only to the dealumination levels but also to the synthesis of the mordenite precursors, which result in differences in composition, particle size, morphology, and the presence of related structures in polycrystalline samples [7]. A detailed account of these observations will be given elsewhere [8].

The shape selectivity of the catalyst is probably due to spatial constraints imposed on the biphenyl and alkylated biphenyl molecules within the 12-member ring channels of mordenite. The amount of biphenyl adsorbed in the micropores of DHM (9.9 cm^3/100 g) is comparable to the benzene uptake (10 cm^3/100 g). Mordenite has a total pore volume of 21 cm^3/100 g, with 11 cm^3/100 g in the main channel, and the remaining 10 cm^3 in the 8-member ring channels [9]. Itabashi et al. [10] give evidence for a two layer packing of benzene in the 12-ring channels of mordenite with low Na content. Preliminary XRD and adsorption data on DHM support a similar packing for biphenyl involving partial overlap of the aromatic rings. Thus, the shape selectivity appears to be related also to the packing of the reactants and the geometry of the mordenite pores. We propose the term "reactant assisted shape selectivity" for this phenomenon.

The complete occupation of the 12-member ring channel in mordenite by polynuclear aromatic molecules under liquid phase conditions suggests that propylene may diffuse into the crystals – at least in part – via the 8-member ring channels. Thus, HM appears to behave as a two-dimensional pore zeolite under our reaction conditions. Adsorption of propylene in the side channels of mordenite and competitive reaction data to be reported elsewhere support this hypothesis [8]. Since the diffusion of biphenyl into mordenite is limited to the 12-ring channels and propylene uses the lateral 8-ring pores, the production of DIPB is a good example of molecular traffic control.

Biphenyl adsorption in Zeolon 100 results in a color change from white to purple, whereas DHM samples adsorb biphenyl but remain white. Incomplete desorption of biphenyl from the purple samples on heating reflects a strong interaction between the aromatic rings and Zeolon 100 which results in coke formation within the zeolite. However, biphenyl easily desorbs from DHM on heating with little or no irreversible adsorption. Both the adsorption and desorption of biphenyl are more facile for DHM.

Dealumination limits coke formation due to a weaker interaction of biphenyl and its alkylated products with the zeolite catalyst, and also reduces polymerization of propylene. Finally, dealumination reduces the number of acid sites in the crystals (perhaps more on the external surfaces), and may result in a reduction of competing non-shape selective reactions such as isomerization of para para, to para meta isomers.

4. Conclusions

We describe the first use of mordenite for the shape selective alkylation of polynuclear aromatics. We introduce reactant induced shape selectivity as a new concept, which depends on the unique match between the zeolite pore structure and the packing and size of the reactant molecules. Besides, we demonstrate the modification of selected mordenites to convert them into catalysts suitable for industrial application. These achievements result in high yield of DIPB and low deactivation of the DHM catalysts. We have extended this discovery to a variety of polynuclear aromatics and alkylating agents which will be discussed elsewhere [8].

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