Methylation of 2-naphthol over molecular sieves

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The mesoporous molecular sieves of the type MCM-41 with different pore openings (40, 64 and 80 Å) were used as catalysts in the gas-phase methylation of 2-naphthol by methanol at 473 K. Their catalytic activity was compared with that of BEA, SAPO-5 and SAPO-11. The molar ratio of 2-naphthol : methanol was varied from 1 : 4 to 1 : 6. The alkylation of the hydroxyl group (O-alkylation) as well as of the aromatic ring (C-alkylation) proceeded. The best yield of 2-methoxynaphthalene was achieved using MCM-41 40 Å and molar ratio 2-naphthol : methanol = 1 : 6.

Keywords: MCM-41, BEA, SAPO-5, SAPO-11, 2-methoxynaphthalene

1. Introduction

The design of environmentally friendly catalysts is a challenge for the contemporary catalytic science. A great deal of investigations are related to zeolites and zeolite similar structure of solids. The mesoporous molecular sieves may catalyze reactions of large size molecules. The synthesis of 2-methoxynaphthalene (nerolin), a raw material in the production of pharmaceuticals [1], is accomplished by methanol and concentrated sulfuric acid [2], dimethylsulfate or diazomethane [3,4]. Aluminosilicate was used instead of sulfuric acid [5]. The interest in 2-methoxynaphthalene acylation in the presence of zeolite catalysts increased [6,7]. Zeolite catalysts were successfully applied in phenol alkylation [8]. It was found that C-alkylation requires stronger acid sites than those responsible for O-alkylation, although some C-alkylation derivatives might be formed by intramolecular rearrangement of the ethers. The aim of the present investigation was to find optimal conditions for O-alkylation of 2-naphthol by methanol using mesoporous molecular sieves of the type of MCM-41 with different pore openings (40, 64 or 80 Å) as catalysts. The catalytic properties of MCM-41, BEA, SAPO-5 and SAPO-11 in this reaction were compared.

2. Experimental

2.1. Catalysts

The molecular sieves were synthesized according to the literature data (table 1). Synthesis A from [9] was applied for MCM-41 with pore size of 40 Å, while the two other MCM-41 samples were prepared according to synthesis D. The samples were characterized by X-ray diffraction and raster electron microscopy. The crystallinity of BEA was checked using (203)-reflex at $2\theta = 22.4°$. The quality of the MCM-41 structure was checked from the shape and the intensity of the peak at $2\theta = 2.26°$. EDAX (energy dispersion analysis of X-ray) was used for the determination of the Si/Al ratio. The pore size distribution has been analysed by measuring the adsorption and the desorption isotherms of nitrogen and analysing these curves with the Kelvin equation using a system from Carlo–Erba Instruments, model Sorptomatic 1900.

Cyclohexanol and benzyl alcohol were applied to characterize the acid and base properties of the catalysts. Cyclohexene from cyclohexanol at 438 K (figure 1) was an

Table 1
Characteristics of the molecular sieves used.

Catalyst	Pore diameter (Å)	Si/Al	Template	Ref.
MCM-41	40	36.7	$C_{16}H_{33}(CH_3)_3NOH/Cl$	[9,10]
	64	12.4		[9,10]
	80	12.4		[9,10]
BEA	5.7 × 7.5; 5.6 × 6.5	9	TEA-Br	[11]
SAPO-5	7.3		Tripropylamine	[12]
SAPO-11	3.9 × 6.3		Dipropylamine	[12]

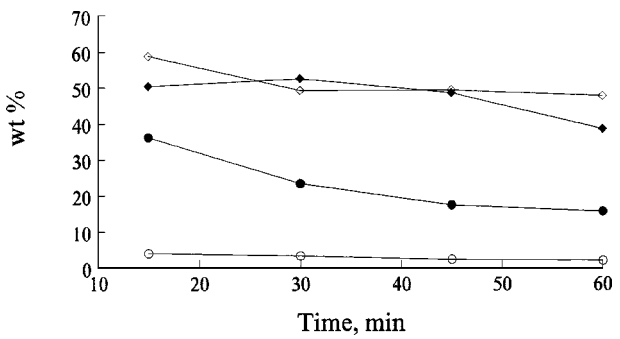

Figure 1. Cyclohexene yield (wt%) from cyclohexanol at 438 K in the presence of MCM-41: 40 (♦), 64 (◇) and 80 Å (○); and BEA (●); 0.15 g catalyst, WHSV = 18.6 h^{-1}.

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indication for the presence of Brønsted acid sites. In accordance with our previous investigations [14] benzyl alcohol was converted at 573 K to toluene on the Brønsted acid sites via the benzyl cation, while the basic sites activated the dehydrogenation to benzaldehyde.

2.2. Methods

The experiments were performed in a quartz fixed-bed flow reactor at atmospheric pressure. The catalysts (1.0 g) were preliminary pressed, crushed and sieved. The particles with dimensions of 1.25–2.50 mm were activated at 723 K under air flow during 3 h before the experiments and then cooled down to the reaction temperature. All the catalysts were re-used after regeneration under air flow at 773 K during 5 h and their catalytic activity restored, except MCM-41 80 Å. Some quantity of 2-methoxynaphthalene was kept on the catalysts and released under air flow. The amount of coke varied between 2.5 and 4.7 wt% from the 2-naphthol feed.

The reaction products were analyzed after 1 h on stream using a Hewlett–Packard GC-MSD 5971 with a HP-5MS (30 m $\times$ 0.25 mm) capillary column.

3. Results

3.1. Methylation over MCM-41

Given the solubility of 2-naphthol in methanol we used the latter as a solvent permitting the easier introduction of the reagents mixture into the catalytic reactor. An excess of 5 moles methanol per mole 2-naphthol gave a homogeneous solution that was gradually introduced to the catalyst bed. Experiments at different temperatures were carried out (table 2). It was found that at 473 K the best yield of 2-methoxynaphthalene was achieved. At this temperature the minimal amount of by-products appeared. Side reactions, mainly C-alkylation and also dehydroxylation, took place especially at 673 K.The C-alkylation dominated over O-alkylation. Besides dimethyl-2-naphthols, 1- and 2-methylnaphthalene were found, the presence of which has to be explained by dehydroxylation of 2-naphthol and methylation of naphthalene obtained. The origin of tetrahydronaphthalene has to be related to hydrogenation of naphthalene. Hydrogen is usually released by coking. The yields of 2-methoxynaphthalene at 473 and 573 K were similar, but more by-products were formed at higher temperature. The reaction temperature applied for the comparison of all the studied catalysts was 473 K. Three samples of MCM-41 with pore openings of 40, 64 and 80 Å were examined as catalysts for 2-naphthol methylation (table 3). The molar ratio 2-naphthol : methanol was varied between 1 : 4 and 1 : 6. Increasing the methanol excess resulted in higher conversion of 2-naphthol and better yield of 2-methoxynaphthalene except on the sample MCM-41 80 Å, that was not so active also in cyclohexanol dehydration (figure 1). Best results were obtained in the presence of MCM-41 40 Å. The amount of dimethyl-2-naphthols reached 13% on the sample with 64 Å pore diameter.

Table 2
Influence of the temperature on the methylation of 2-naphthol on MCM-41 40 Å (1 g).[a]

Temp. (K)	Products (wt%)								
	Methanol	Tetrahydro-naphthalene	Naphthalene	1-methyl-naphthalene	2-methyl-naphthalene	2-methoxy-naphthalene	2-hydroxy-naphthalene	5,7-dimethyl-2-naphthol	1,5-dimethyl-2-naphthol
473	23.5	0.6	0.5	–	–	49.0	20.0	2.1	0.9
573	14.8	0.9	5.2	1.3	1.8	46.5	15.0	6.3	7.5
673	3.7	6.8	6.0	3.6	4.7	7.8	40.2	4.3	22.9

[a] Molar ratio of 2-naphthol : methanol = 1 : 5, WHSV = 6.3 h^{-1}.

Table 3
Methylation of 2-naphthol on MCM-41 at 473 K.

Pore diameter (Å)	WHSV (h^{-1})	2-naphthol : methanol (moles)	Products (wt%)						
			Methanol	Tetrahydro-naphthalene	Naphthalene	2-methoxy-naphthalene	2-naphthol	5,7-dimethyl-2-naphthol	1,5-dimethyl-2-naphthol
40	5.7	1 : 4	25.8	–	–	34.3	34.8	2.2	2.3
	6.3	1 : 5	23.5	0.6	0.5	49.0	20.0	2.1	0.9
	7.0	1 : 6	34.0	–	–	50.0	12.7	2.7	0.6
64	5.7	1 : 4	36.1	–	–	27.7	34.7	0.5	1.0
	6.3	1 : 5	31.8	–	–	29.3	31.4	3.5	4.0
	7.0	1 : 6	34.3	–	–	28.8	23.9	5.3	7.7
80	5.7	1 : 4	41.5	–	–	22.5	35.8	0.2	–
	6.3	1 : 5	33.0	–	0.1	28.0	35.6	1.8	1.5
	7.0	1 : 6	35.0	–	–	13.0	50.0	0.6	1.4

Table 4
Methylation of 2-naphthol on BEA at 473 K.

WHSV (h^{-1})	2-naphthol : methanol (moles)	Products (wt%)								
		Methanol	Tetrahydro-naphthalene	Naphthalene	1-methyl-naphthalene	2-methyl-naphthalene	2-methoxy-naphthalene	2-naphthol	5,7-dimethyl-2-naphthol	1,5-dimethyl-2-naphthol
5.7	1 : 4	33.0	–	0.2	0.2	0.3	23.7	38.6	2.2	1.8
6.3	1 : 5	32.3	0.2	2.9	0.9	1.7	25.5	18.0	8.8	9.7
7.0	1 : 6	28.0	0.2	0.7	0.5	2.2	26.0	30.0	3.5	8.9

Table 5
Methylation of 2-naphthol on SAPO molecular sieves at 473 K catalyst.

Catalyst	WHSV (h^{-1})	2-naphthol : methanol (moles)	Products (wt%)				
			Methanol	2-methoxy-naphthalene	2-naphthol	5,7-dimethyl-2-naphthol	1,5-dimethyl-2-naphthol
SAPO-5	5.7	1 : 4	27.4	26.7	42.5	1.6	1.8
	6.3	1 : 5	27.7	27.0	42.7	1.2	1.4
	7.0	1 : 6	29.4	28.0	39.5	1.2	1.9
SAPO-11	5.7	1 : 4	26.8	16.6	55.3	1.3	–
	6.3	1 : 5	31.0	21.0	46.0	0.4	1.6
	7.0	1 : 6	33.0	22.0	37.6	5.0	2.4

3.2. Methylation on BEA

The wide pore zeolite BEA (table 1) seemed suitable for 2-naphthol alkylation. Similar zeolites were active in acylation of 2-methoxynaphthalene [6,7]. The yield of 2-methoxynaphthalene reached 26% (table 4). The excess of methanol favorized the formation of C-methylated products. Dehydroxylation of 2-naphthol was considerable.

3.3. Methylation on SAPO molecular sieves

It has been shown [15] that SAPO-5 and SAPO-11 are active in pinacol rearrangement proceeding usually in the presence of strong mineral acids. Although the silico-aluminophosphate molecular sieves SAPO-5 and SAPO-11 have completely different composition and structure, compared with MCM-41 and BEA, both showed to be active catalysts in 2-naphthol methylation (table 5). The yields of 2-methoxynaphthalene are comparable with that of BEA. SAPO-5 showed better activity and selectivity than BEA. No dehydroxylation of 2-naphthol occurred in the presence of SAPO-5 and SAPO-11.

4. Discussion

The presented results definitely show that two main factors regulate the selectivity in the O-alkylation of 2-naphthol: pore dimensions of the catalyst and its acid properties. The role of the pore dimensions in the O-alkylation of 2-naphthol is demonstrated by the best performance of MCM-41 40 Å. The selectivity in 2-methoxynaphthalene formation is comparable with that of SAPO-5.

The zeolite BEA has a three-dimensional network of 12-ring channels with two different types of pores [16]. The Si/Al ratio in BEA which we used as catalyst ensures high concentration of Brønsted acid sites, that was proved by the cyclohexanol test (figure 1). The high acidity of BEA and the complicated pore structure probably favor the side reactions, namely dehydroxylation of 2-naphthol and C-methylation. In this respect catalysts with milder acidity like MCM-41 should be preferred in 2-naphthol O-methylation than BEA. Even SAPO-5 and SAPO-11 should be recommended as rather good catalysts because of the lack of dehydroxylation products. As seen from [14] the acidity of SAPO molecular sieves is comparable with that of concentrated sulfuric acid, but the pore dimensions of SAPO-11 influence its activity in 2-naphthol methylation.

5. Conclusions

All the studied molecular sieves of the types of MCM-41, BEA, SAPO-5 and SAPO-11 are active catalysts in 2-naphthol alkylation in excess methanol at 473 K. In all cases some dimethyl-2-naphthols are formed also. The best yields of 2-methoxynaphthalene are obtained in the presence of MCM-41 40 Å.

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