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ALDOL CONDENSATION IN GASEOUS PHASE BY ZEOLITE CATALYSTS

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Vapour-phase reactions of, in situ, prepared formaldehyde with methyl propionate were studied using X, Y and ZSM-5 zeolite catalysts. Base properties of these zeolites were enhanced by KOH or NaN_3 treatment. The niobium and molybdenum ZSM-5 zeolite supported oxides were also tested for their catalytic activity. The results are discussed in terms of an ability of zeolite catalysts to synthesize methyl methacrylate.

Keywords: Aldol condensation. methyl methacylate synthesis, methyl propionate, formaldehyde, zeolites, acidity and basicity.

1. Introduction

Aldol condensation reactions are generally performed in liquid homogeneous phase with bases added as catalysts. There are few references in the chemical literature [1–7] concerning the aldol reactions in gaseous phase by heterogeneous catalysts. It is known that vapour phase aldol condensation of formaldehyde with methyl ethyl ketone, n-butyraldehyde, acetic acid, methyl acetate, and methyl propionate can be performed resulted in a formation of, respectively, isopropenyl methyl ketone, ethyl vinyl ketone and isopropenyl vinyl ketone, 2-ethylacrolein, acrylic acid, methyl acrylate or methyl methacrylate. As regards the catalysts, both acidic and basic components have been claimed in patents to be useful. Since the discovering of zeolites they have been widely studied as the convenient heterogeneous catalysts, inter alia, of aldol condensation [8–13]. The catalytic activity of X, Y and ZSM-5 zeolites additionally modified by alkali metals (NaOH, KOH, CsCl, NaN_3) or niobium and molybdenum oxides in synthesis of methyl methacrylate is the subject of the present study.

2. Experimental

Samples of NaX and NaY zeolites ($SiO_2/Al_2O_3 = 2.37$ and 4.72 respectively) were ion exchanged three times at 363 K in 0.5 M solutions of KCl and CsCl.

After the exchange procedure the samples were washed with distilled water and dried in air at 393 K for 3 h. NaZSM5 and KZSM5 produced according to the ion exchange procedure from their hydrogen forms ($SiO_2/Al_2O_3 = 70$ and 700) adjusting pH at 7 were subsequently washed with 0.001 M NaOH (KOH) and dried in air at 393 K. The degree of ion exchange of potassium and cesium in X and Y zeolites was better than 88%, the difference being Na^+ cations. In the case of ZSM-5 zeolites the degree of ion exchange for cesium was 80% and for potassium or sodium better than 95%. The preparation of KY-KOH and KZSM-5 [70]-KOH involved a washing of KY with 0.1 N KOH solution and dried and calcined at 623 K, in situ, in the catalytic reactor in dry argon stream. Zeolite samples before azide impregnation were calcined at 723 K and impregnated with an azide slurry in methanol, containing 2.14 mmole of NaN_3 per g of zeolite. These zeolite-azide adducts were dried at 773 K in situ in the catalytic reactor. Niobium and molybdenum zeolite supported oxides (5% wt.) were prepared from niobium pentachloride methanol solution and ammonium paramolybdate, then dried and calcined at 773 K.

For catalytic testing a continuous-flow fixed-bed tubular microreactor was used. Reaction was studied at 623 K, operating at atmospheric pressure with 3.5 fold molar excess of methyl propionate to formaldehyde. The latter was fed as trioxane soluble in methyl propionate. The products were analyzed by gas chromatographs: 2.5 m column of Chromosorb 101 and 5 m column of 10% (wt) of didodecyl phthalate on Chromosorb WAW.

3. Results and discussion

The more significant results from the experiments are given in table 1.

It can be shown that condensation between formaldehyde feeded as trioxane and methyl propionate to give, after dehydration, methyl methacrylate

$$\begin{aligned} CH_3CH_2COOCH_3 + CH_2O &= CH_3CH(CH_2OH)COOCH_3 \\ &= CH_3C(CH_2)COOCH_3 + H_2O \end{aligned}$$

strongly depends on the zeolite treatment method. H-ZSM5 zeolite catalyst is so strongly acidic that dehydration of the oxygenated compounds has resulted mainly in the formation of hydrocarbons. The highest conversion of the substrates and a good selectivity to methyl methacrylate (74.1%) was obtained over potassium Y zeolite additionally treated with potassium hydroxide. Impregnation of sodium azide on CsX, NaZSM-5 and CsZSM-5 zeolites, followed by its thermal decomposition to metallic sodium, resulted in the decreasing of catalytic activity of zeolite with slight increasing of selectivity. The metal zeolite supported oxides (Nb_2O_5, MoO_3) did not show a significant influence on the zeolite activity in contrary to Nb_2O_5/SiO_2 catalyst [6]. In all cases the hydrolysis of methyl

Table 1
Synthesis of methyl methacrylate from methyl propionate and formaldehyde

Catalyst	Conversion (%) of		Selectivity to methyl methacrylate	
	MetPr	CH_2O	vs. MetPr	vs. CH_2O
KY	8.1	43.9	20.4	12.8
KY-KOH	13.8	69.6	74.1	50.1
CsX	15.2	81.6	31.6	20.0
CsX-NaN_3 (5%)	8.9	45.0	18.2	12.2
CsZSM-5 [70]	8.8	41.0	28.8	21.0
KZSM-5 [70] *	14.3	98.0	35.3	18.1
KZSM-5 [70] **	10.1	46.7	26.4	20.0
KZSM-5 [70]-KOH	16.4	98.0	38.2	22.4
NaZSM-5 [70]	8.5	82.0	28.4	10.4
HZSM-5 [70] ***	35.3	100.0	3.3	4.0
HZSM-5 [700]	5.3	3.0	0.2	0.2
CsZSM-5 [70]-NaN_3 (5%)	4.3	40.3	50.2	18.1
NaZSM-5 [70]-NaN_3 (5%)	5.2	40.8	34.0	14.7
KZSM-5 [70]-Nb_2O_5 (5%)	7.8	40.7	43.0	28.2
NaZSM-5 [700]-MoO_2 (5%)	5.6	33.7	65.7	37.0
Nb_2O_5/SiO_2 (ref. [6])	20.0	58.0	38.0	44.5

Conditions: 633 K, contact time 4.1 s, MetPr/CH_2O = 3.4.
[70], [700] and (5%) indicate, respectively, the mole ratio of silica to alumina in the zeolite and percentage amount of sodium azide, niobium and molybdenum oxide.
*,** Contact time 4,1 s and 0,5 s, respectively.
*** Hydrocarbons are predominantly formed.

propionate resulted in a decreasing of the reaction selectivity. Partial hydrolysis of methyl methacrylate over all catalysts prepared from ZSM-5 [70] was also observed. The important side reaction resulted in a decreasing of the selectivity to methyl methacrylate versus formaldehyde, was an acid catalysed disproportionation of formaldehyde. A decreasing of contact time by a dilution of the gaseous substrates with argon decreases the selectivity to methyl methacrylate versus methyl propionate probably due to a competitive strong adsorption of H_2O which is active in hydrolysis. In contrary, a dilution of formaldehyde is required (disproportionation of formaldehyde is less favourable) resulted in the increase selectivity to methyl methacrylate. Hydrolysis of esters and disproportionation of aldehydes are, both, acid catalyzed reactions. Our results indicate that even the treatment of KZSM-5 zeolite with KOH solution (0.1 N) has not eliminated all sites active in hydrolysis.

Zeng et al. [14] found the basic sites on alkali metal exchanged zeolites detectable by carbon dioxide adsorption. However the amount of residual acid sites was always several times greater than those of basic ones. The origin of these acid sites is postulated by Lercher et al. [15] to be arisen from the polarized residual water molecules adsorbed on accessible alkali metal cations (Li, Na, K or

Cs) exchanged in ZSM-5 zeolites (IR OH absorption band at 3695–3683 cm^{-1} which disappeared after adsorption of ammonia). In the later paper [16] the authors suggest that acid centers present in alkali metal exchanged ZSM-5 zeolites arise also from zeolite lattice defects.

It can be concluded that it is impossible to remove all zeolitic acidity by alkali metal ion-exchange method, a washing with alkali metal hydroxide or sodium azide impregnation. It seems that in the case of catalysts under study, both, the basic and acidic center are active in aldol condensation of methyl propionate formaldehyde in gaseous phase.

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