FRIES REARRANGEMENT OF PHENYL ACETATE OVER ZSM-5 BASED CATALYSTS*

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Catalysts based on samples of ZSM-5, differing in Si/Al ratio were applied in the Fries rearrangement of phenyl acetate. Experiments were carried out in batch reactors at 180°C and continuously at various temperatures both in liquid phase and gas phase. A reaction scheme is proposed.

The catalytic conversion of aromatic esters to aromatic hydroxy ketones, commonly referred to as Fries rearrangement, is a useful synthetic method[1] for the preparation of intermediates. The reaction is acid catalyzed and may be carried out equally well with Lewis or Brønsted acids. $AlCl_3$, the classical Friedel–Crafts catalyst is extensively applied; the Fries rearrangement generally requires a more than equimolar quantity of the catalyst which forms complexes with both substrate and products[2]. Isolation of the products requires a hydrolysis step and the used catalyst cannot be recovered or regenerated and presents a disposal problem.

Replacing the classical catalyst systems by a zeolite based catalyst has e.g. the potential advantages that a heterogeneous regenerable catalyst can be used and that shape selectivity might be exploited. Strongly acidic zeolites such as Y, ZSM-5 and Nu2 have been reported as catalysts for the Fries rearrangement of phenyl acetate (Scheme 1) in the gas phase at 400°C (refs[3,4]) and in the liquid phase at 170°C (ref.[5]). The reported results show, however, a poor stability and massive byproduct formation.

We have extended the above mentioned studies using catalyst samples based on various zeolites in batch reactions and in continuous experiments both in gas phase and liquid phase. Here we report on results obtained with catalysts based on a number of samples of ZSM-5 differing in Si/Al ratio. The effect of channel size is touched upon in comparative liquid phase batch experiments using catalysts based on zeolite Beta and ZSM-5, respectively. Zeolite Beta is more active but its selectivity

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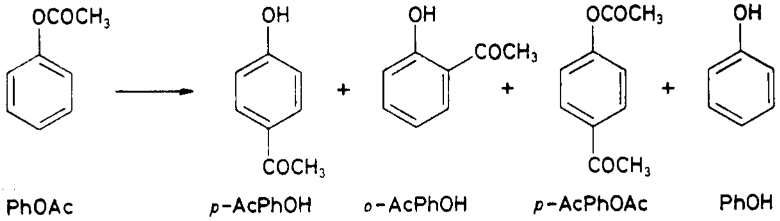
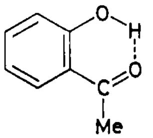
is much lower due to side reactions, leading to other products than phenol, *p*-AcPhOH, *o*-AcPhOH and *p*-AcPhOAc.



PhOAc phenylacetate ; *p*-AcPhOH *p*-acetylphenol ; *o*-AcPhOH *o*-acetylphenol ; *p*-AcPhOAc *p*-acetylphenylacetate ; PhOH phenol

SCHEME 1



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In the continuous liquid and gas phase experiments the selectivity of ZSM-5 depends strongly on the reaction temperature. In gas phase experiments high temperature favours phenol formation as a product of hydrolysis and thermolysis reactions.

EXPERIMENTAL

Zeolite catalyst preparation and characterization. All zeolite samples were received from CU Chemische Fabrik Uetikon. Samples of ZSM-5 were calcined at 550°C for 8 h, exchanged at 80°C with 1M-HCl for 1 h (3×), dried and calcined a second time at 550°C for six hours. Zeolite Beta was exchanged with 0·1M-HCl for one hour at room temperature and then calcined at 550°C. The crystallinity of the solid products was checked by X-ray diffraction. Elemental analysis was done by atomic absorption spectroscopy (Varian SpectrAA-10). The zeolites were also analysed with the BET method (Micromeritics ASAP-2000) and crystallite size was measured by scanning electron microscopy (Hitachi S-900). The results are given in Table I.

Reaction conditions. Batch reaction with phenyl acetate were performed with stirring (450 rpm) at 180°C and 200°C and at atmospheric pressure (1·5 g). Freshly activated (500°C, 2 h) catalyst was added to 7·5 g dried phenyl acetate. Samples were taken periodically and analysed by GC (HP 5890 2, crosslinked methyl silicone column). In some cases sulfolane was used as a solvent. Continuous experiments were carried out at atmospheric pressure in a fixed bed up-flow reactor. The binder-free granulated catalyst (1·5 g, particle size 0·4—0·7 mm) was packed into a stainless steel tube of 8 mm I.D. and activated in a flow of nitrogen at 500°C for 10 h. Continuous reactions were performed over a temperature range of 180—420°C at a WHSV of 0·86 h^{-1} for the liquid phase and 1·7 h^{-1} for the gas phase reactions. In batch reactions, the first samples contained a relatively large amount of phenol due to traces of water in the system leading to a adulteration of the measured values in selectivity.

Definitions. WHSV: weight of reactor feed per unit weight of catalyst per hour. Conversion (x): mole % of starting material (PhOAc) consumed. Selectivity (y): mole % of the sum of products (o-AcPhOH, p-AcPhOH, p-AcPhOAc) obtained divided by the mole % of starting materials consumed, normalized to 100%.

RESULTS AND DISCUSSION

ZSM-5 (Si/Al = 20) or Beta in Batch Reactions

In batch reactions at 180°C, the activity and selectivity depend strongly on the zeolite type. The catalyst based on zeolite Beta (Fig. 1) is very active and initially a fast reaction is observed with a high selectivity, prolonged transformation results mainly in formation of other components.

The ZSM-5 (Si/Al = 20) based catalyst (Fig. 2) has a much lower rate of reaction compared to the Beta material but a higher selectivity. Byproduct formation is not observed and the product has a much higher p/o ratio which may be an indication of shape selectivity.

Zeolite Beta consists of a 3-dimensional, 12-ring channel system with a high degree of stacking disorder[6]. Compared to the medium pore zeolite ZSM-5 (10 ring system) migration of the reactant molecules is limited to a smaller extent by diffusion, presumably resulting in a much higher reaction rate for zeolite Beta.

Effect of Si/Al Ratio on the Performance of ZSM-5 Catalysts

The number of acid sites has a strong effect on catalyst activity in the Fries rearrangement of phenyl acetate. As shown in Figs 3 and 4, the conversion and selectivity depend strongly on the Si/Al ratio of the catalysts.

TABLE I

Characteristics of zeolite catalysts

Zeolite	Zeolite type	Si/Al ratio	Crystallite size	Surface area BET, $m^2 g^{-1}$
PZ 2	ZSM-5	20	<1 μm	428
PZ 6	ZSM-5	83	1 μm	379
PZ 8	ZSM-5	120	3 μm	355
PZ 10	ZSM-5	250	3 μm	368
FB2/G	BETA	10	<1 μm	628

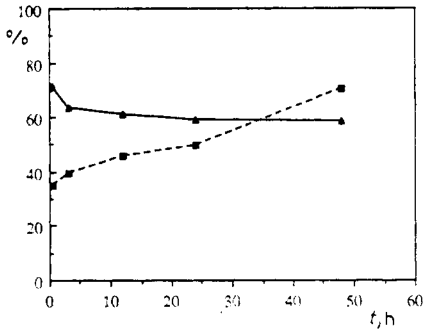


FIG. 1

Batch reaction (180°C) with zeolite Beta: ▲ selectivity, ■ conversion

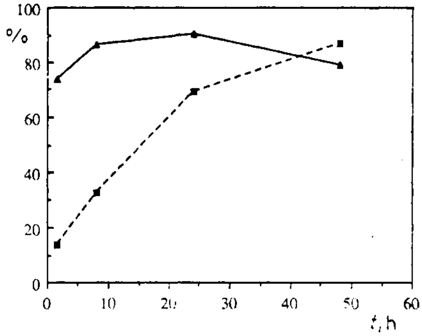


FIG. 2

Batch reaction (180°C) with zeolite ZSM-5: ▲ selectivity, ■ conversion

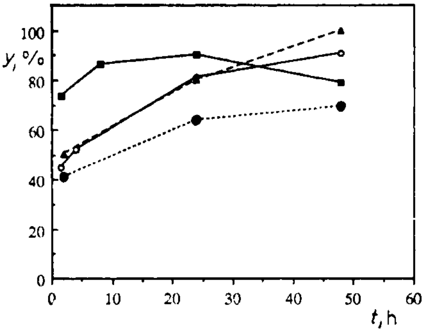


FIG. 3

Effect of Si/Al ratio on selectivity (y) in batch reaction (180°C): ■ Si/Al = 20, ▲ Si/Al = 83, ○ Si/Al = 120, ● Si/Al = 250

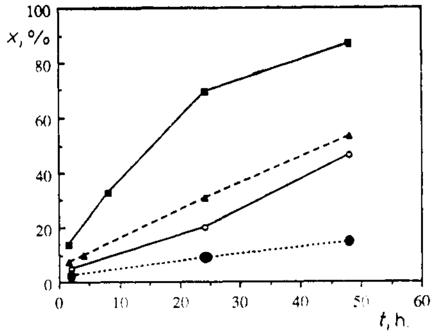


FIG. 4

Effect of Si/Al ratio on conversion (x) in batch reaction (180°C): ■ Si/Al = 20, ▲ Si/Al = 83, ○ Si/Al = 120, ● Si/Al = 250

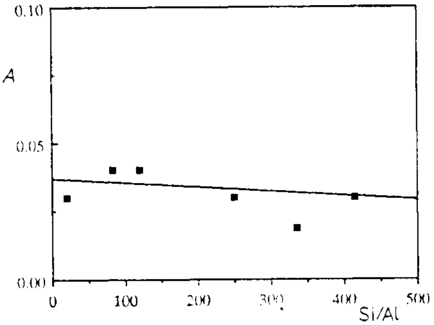


FIG. 5

Activity [mol $\min^{-1}$ (mol Al)$^{-1}$]

The formation of o-AcPhOH + p-AcPhOH + p-AcPhOAc in mol min^{-1} per Al atom appears to be more or less constant for the various catalysts (Fig. 5). This implies that for the Fries rearrangement of phenyl acetate, either all acid sites are equally active or that a constant fraction of the total number of sites in each catalyst determines its activity. Diffusion of the reaction components in the various catalysts is supposed not to be a variable.

Continuous Liquid and Gas Phase Experiments

Continuous liquid phase reactions offer the possibility to improve selectivity by limiting side reactions due to the prolonged contact time between the catalyst and reaction products encountered in batch reactions. Our results confirm the expected higher selectivity and it was also shown that catalyst performance (activity, stability and selectivity) improves upon increasing the reaction temperature from 180 to 200°C (Figs 6 and 7). After 20 h on stream at 200°C, a more or less stable conversion of about 10% is found, while after 20 h at 180°C, the conversion is close to zero.

In contrast to the continuous liquid phase experiments, the results in continuous gas phase show a deactivation within 7 h on stream, presumably due to the rapid formation of coke on the catalyst. The selectivity of the gas phase reaction with ZSM-5 increases considerably, however, by decreasing the reaction temperature from 420°C to 250°C (Figs 8 and 9).

The reason for this clear temperature effect is the enhanced formation of phenol at higher temperatures probably due to thermal decomposition and deacylation reactions. The strong dependence of phenol formation on the reaction temperature

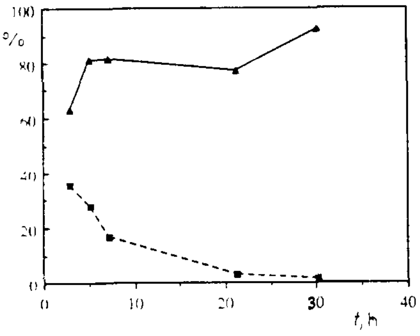


FIG. 6

Continuous liquid phase reactions at 180°C: ▲ % selectivity, ■ % conversion

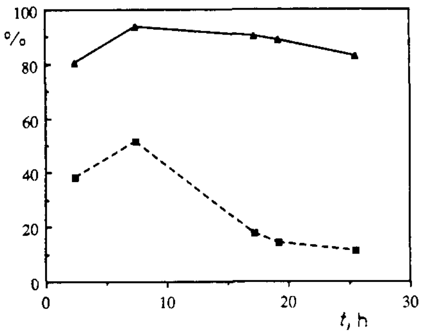


FIG. 7

Continuous liquid phase reactions at 200°C: ▲ % selectivity, ■ % conversion is illustrated in Fig. 10 and for gas phase Fries rearrangement, a temperature of 250°C is clearly to be preferred.

Reaction Mechanism

Using ZSM-5 based catalysts in batch reactions at 180°C a product composition as shown in Table II is normally obtained. It is interesting to note that *p*-AcPhOAc is apparently an intermediate product and that the *p*-AcPhOH/*o*-AcPOH ratio is not constant. The underlying reaction path is not clear and accordingly we have separately investigated the reactivity of the various products formed during the Fries rearrangement of phenyl acetate using ZSM-5 based catalysts. Batch experiments were performed at 180°C using sulfolane as a solvent. Results obtained with

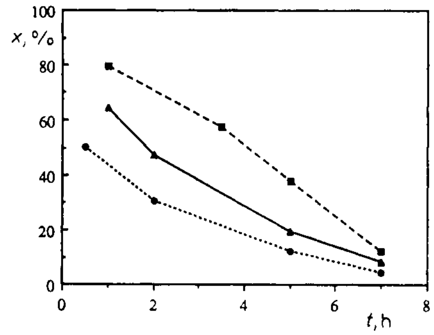


FIG. 8

Conversion (x) in continuous gas phase reactions with ZSM-5 at ● 250°C, ▲ 300°C, ■ 420°C

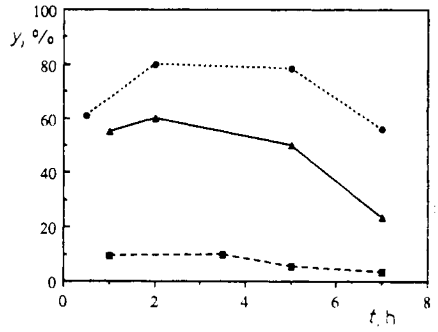


FIG. 9

Selectivity (y) in continuous gas phase reactions with ZSM-5 at ● 250°C, ▲ 300°C, ■ 420°C

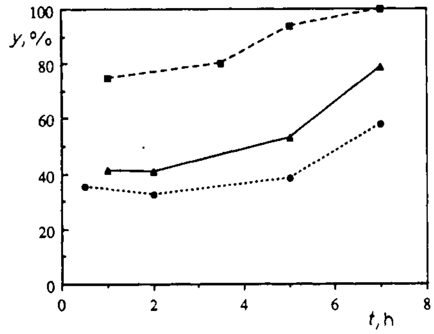
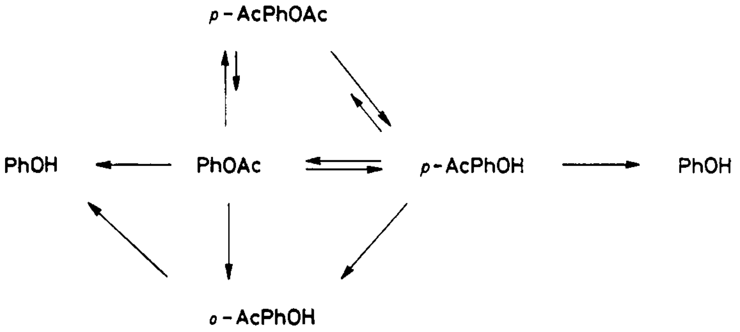


FIG. 10

Effect of temperature on phenol selectivity (y) at ■ 420°C, ▲ 300°C, ● 250°C phenyl acetate dissolved in sulfolane are given in Table III. It appears that the use of sulfolane as a solvent lowers the reaction rate of the phenyl acetate and that especially *o*-AcPOH formation is suppressed while phenol formation is increased.

When *o*-AcPhOH was used as reactant it had a low reactivity and phenol was the single product (Fig. 11). An experiment with *p*-AcPhOH as reactant showed that its reactivity is higher than that of derivative (Fig. 12) and that the products are phenol, *o*-AcPhOH, *p*-AcPhOAc and phenyl acetate. Also here *p*-AcPhOH seems to be an intermediate product. The reactivity of *p*-AcPhOH is lower than that of *p*-AcPhOH (Fig. 13). The products are *p*-AcPhOH and phenyl acetate.



SCHEME 2

These observations point to the reaction path given in Scheme 2 for the Fries rearrangement in sulfolane using ZSM-5 based catalysts. Phenol and *o*-AcPhOH are end products, *p*-AcPhOH and *p*-AcPhOAc are intermediates. *o*-AcPhOH is presumably stabilized by formation of an hydrogen bridge (*A*). Under the conditions applied here acylation–deacylation reactions play an important role in the Fries rearrangement and result in a strong intermolecular acylation activity. The acylium ions are presumably stabilized by the ion-stabilizing properties of

TABLE II

Product distribution in batch reaction at 180°C

t, h	PhOAc	PhOH	*o*-AcPhOH	*p*-AcPhOH	*p*-AcPhOAc	*p*/*o* ratio
1·5	86·5	6·9	1·9	1·7	3·2	0·8
8	67·4	12·8	6·7	6·5	7·5	1·0
24	30·6	18·4	17·1	25·5	9·9	1·5
48	13·1	22·3	33·8	28·1	3·3	0·8

TABLE III

Product distribution in batch reaction at 180°C using sulfolane

t, h	PhOAc	PhOH	*o*-AcPhOH	*p*-AcPhOH	*p*-AcPhOAc	*p*/*o* ratio
1·2	87·9	6·4	0·4	2·8	2·6	6·7
7	78·3	10·3	1·9	4·6	5·4	2·4
24	55·5	17·2	7·7	12·0	9·1	1·6
48	35·3	24·9	11·4	21·0	9·5	1·8
72	21·9	33·3	11·2	29·5	5·7	2·6

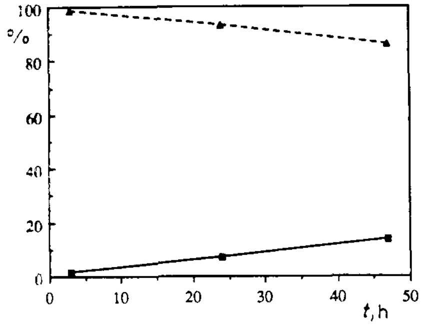


FIG. 11

o-Acetyphenol (*o*-AcPhOH) as reactant in batchl reaction (180° C): ▲ *o*-AcPhOH, ■ PhOH

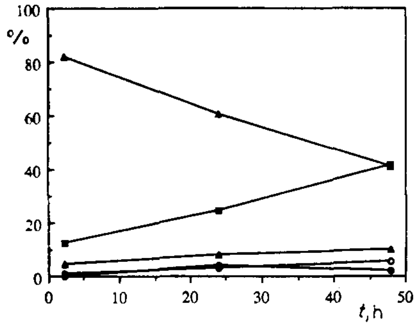


FIG. 12

p-Acetylphenol (*p*-AcPhOH) as reactant in batch reaction (180°C): ▲ *p*-AcPhOH, ■ PhOH, △ PhOAc, ○ *o*-AcPhOH, ● *p*-AcPhOAc

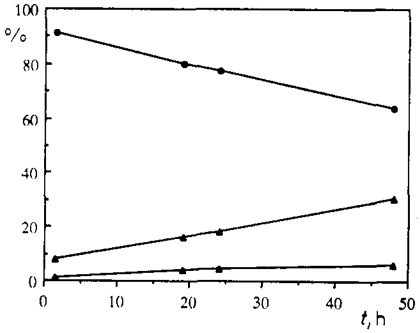


FIG. 13

p-Acetylphenyl acetate (*p*-AcPhOAc) as reactant in batch reaction (180°C): ● *p*-AcPh.OAc, ▲ *p*-AcPhOH, △ PhOAc sulfolane. Intermolecular acylation is also observed upon addition of toluene to the reaction mixture. The reaction mechanism will be more fully discussed elsewhere in combination with results obtained using 12-ring zeolites.

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