Phenol Acylation: Unexpected Improvement of the Selectivity to *o*-Hydroxyacetophenone by Passivation of the External Acid Sites of HZSM5

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The acylation of phenol by acetic acid on zeolite ZSM5 is unexpectedly oriented towards *o*-hydroxyacetophenone by dealumination of the outer surface of the crystallites, which can be ascribed to the existence of two different pathways for the formation of *o*- and *p*-hydroxyacetophenones.

Medium-pore zeolites such as ZSM5 are well adapted to the selective synthesis of the smallest isomer (*i.e.* the *para* isomer) of disubstituted benzenic hydrocarbons.[1–3] However secondary reactions on the non-selective sites of the crystallite outer surface can significantly affect the *para* selectivity. Thus, because of very rapid secondary isomerization, an equilibrium mixture of xylenes is obtained in toluene disproportionation with non-modified HZSM5 zeolites.[3] Various ways have been developed for reducing the activity of the external sites: increasing the zeolite crystallite size, impregnation with phosphorus, boron, magnesium or silicon compounds, deposition of coke,[4–6] selective dealumination of the outer surface[7,8] *etc.* By such means a significant improvement in the *para* selectivity of hydrocarbon synthesis is obtained, this improvement being due not only to the deactivation of the external acid sites but also to an increase in the sieving effect. We show here that unexpectedly the *para* selectivity of the acylation of phenol with acetic acid decreases by dealumination (with ammonium hexafluorosilicate) of the outer surface of ZSM5 zeolite.

Zeolite HZSM5 ($Na_{0.15}H_{2.1}Al_{2.25}O_{192}Si_{93.75}$) was synthesized according to the method of Guth and Caullet.[9] The method for dealuminating zeolites with ammonium hexafluorosilicate has been previously described.[10] Two dealuminated ZSM5 samples were prepared under conditions differing only by the ratio *R* between the number of silicium atoms in $(NH_4)_2SiF_6$ and the total number of aluminium atoms of the zeolite ($R = 1$ for HZSM5 D1 and $R = 4$ for HZSM5 D4). The total ratio Si:Al changed from 41.8:1 with non-modified HZSM5 to 42.4:1 with HZSM5 D1 and to 43.8:1 with HZSM5 D4. Dealumination had practically no effect on the capacity of the zeolite for adsorption of *n*-hexane at 0°C. While only a slight decrease in the activity of *m*-xylene isomerization could be observed, the *para*:*ortho* ratio at 30% conversion increased from 1.5:1 with the non modified sample to 1.7:1 with the dealuminated one.

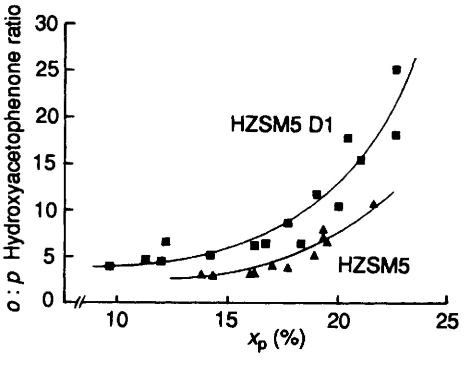
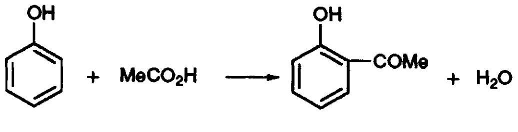


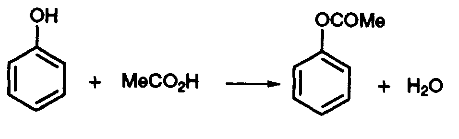
Fig. 1 Hydroxyacetophenone ratio (*o*:*p*) on HZSM5 and HZSM5 D1 as a function of the conversion of phenol X_p



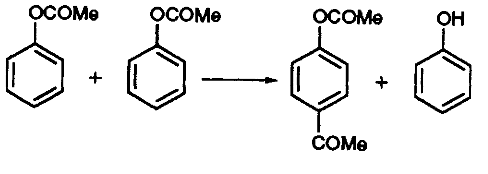
(1)

The acylation of phenol with acetic acid was carried out under the following conditions: flow reactor, temperature 533 K, 100 mg of zeolite, pressures of phenol and acetic acid of 0.05 bar, pressure of nitrogen of 0.9 bar, flow rates of phenol and of acetic acid varying from 3.5 to 34.5 mol h^{-1} so as to obtain various conversion levels. Dealumination had practically no effect on the zeolite activity and for any sample the deactivation was very slow. The main reaction products were phenylacetate resulting from phenol *O*-acylation and *o*-hydroxyacetophenone resulting from phenol *C*-acylation. Lower amounts of *p*-hydroxyacetophenone and traces of heavier products: *p*-acetoxyacetophenone, 4-acetoxy-6-methyl 2-pyrone and 2-methylchromone were also observed. The dealumination caused a strong increase in the *o*- to *p*-hydroxyacetophenone ratio (*o*:*p*). This is shown in Fig. 1 which compares the *ortho*:*para* ratio on HZSM5 D1 and on the non-modified sample. The effect was still more pronounced with HZSM5 D4. On this catalyst the *para* isomer, initially formed in low amounts (o:p = 30:1), disappeared after 2 h of reaction. It must be underlined that this was also the case for *p*-acetoxyacetophenone. The same results were found with a HZSM5 sample modified by deposition of tetramethoxysilane.

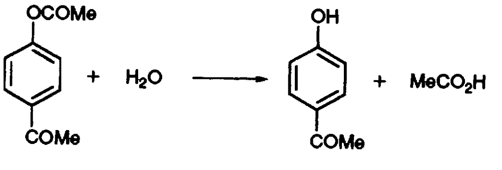
This unexpected increase in the *o*:*p* ratio can only be explained by postulating that the *ortho* and *para* isomers of hydroxyacetophenones result from different pathways. That leading to the *ortho* isomer would occur mainly in the pores of the ZSM5 zeolite and the path leading to the *para* isomer occurs only on the external acid sites. A kinetic study of phenol acylation with acetic acid has recently shown that *o*-



(2)



(3)



(4)

hydroxyacetophenone (but not *p*-hydroxyacetophenone) was formed through *C*-acylation of phenol with acetic acid, eqn (1).[11] The selectivity to the *ortho* isomer would be due to a pronounced stabilization of the transition state.

The formation of the *para* isomer would occur through a complex pathway involving three successive reaction steps: *O*-acylation of phenol, eqn. (2), the autoacylation (disproportionation) of the phenylacetate produced with formation of *p*-acetoxyacetophenone, eqn. (3), and finally the hydrolysis of *p*-acetoxyacetophenone, eqn. (4), the limiting step being the phenylacetate autoacylation.

The decrease in the *para* selectivity observed in this work could indicate that at least one of these steps occurs on the external acid sites. This would probably be the reaction of eqn. (3) which involves a bulky transition state and leads to relatively bulky products. If this proposal is correct the question arises as to why only *p*-acetoxyacetophenone is formed. A possible answer is that there is a steric hindrance to the approach of the acetyl group to the *ortho* position of phenylacetate (to lead to *o*-acetoxyacetophenone). In agreement with this hypothesis a high *p*- to *o*-acetoxyacetophenone ratio (about 20:1 at 400°C) was found for phenylacetate autoacylation on Y zeolite.[11]

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References

1 N. Y. Chen, W. E. Garwood and F. G. Dwyer, *Shape Selective Catalysis in Industrial Applications*, Chemical Industries, M. Dekker, New York, Basel, 1989, vol. 36.

2 E. G. Derouane, *Zeolites: Science and Technology*, ed. F. R. Ribeiro, A. E. Rodrigues, L. D. Rollmann and C. Naccache, NATO ASI Series, Martinus Nijhoff Publishers, The Hague, Boston, Lancaster, Series E: Applied Sciences, no. 80, 1984, p. 347.

3 D. H. Olson and W. O. Haag, *ACS Symp. Ser.* 1984, **248**, 275.

4 W. W. Kaeding, C. Chu, L. B. Young, B. Weinstein and S. A. Butter, *J. Catal.*, 1981, **67**, 157.

5 W. W. Kaeding, C. Chu, L. B. Young and S. A. Butter, *J. Catal.*, 1981, **69**, 392.

6 L. B. Young, S. A. Butter and W. W. Kaeding, *J. Catal.*, 1982, **76**, 418.

7 M. S. Rigutto, H. J. A. de Vries, S. R. Magill, A. J. Hoefnagel and H. van Bekkum, *Heterogeneous Catalysis and Fine Chemicals III*, ed. M. Guisnet, J. Barbier, J. Barrault, C. Bouchoule, D. Duprez, G. Pérot and C. Montassier, *Studies in Surface Science and Catalysis*, Elsevier, Amsterdam, Oxford, New York, 1993, vol. 78, p. 661.

8 J. M. Silva, M. F. Ribeiro, F. R. Ribeiro, N. S. Gnep, M. Guisnet and E. Benazzi, unpublished work.

9 J. L. Guth and P. Caullet, *J. Chim. Phys.*, 1986, **83**, 155.

10 Q. L. Wang, M. Torrealba, G. Giannetto, M. Guisnet, G. Pérot, M. Cahoreau and J. Caisso, *Zeolites*, 1990, **10**, 703.

11 I. Neves, unpublished work.