Hydrolysis of Water-insoluble Esters by Octadecyl Immobilized H-ZSM-5 Catalyst in a Water–Toluene System

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In the hydrolysis of water-insoluble esters in a water–toluene system octadecyltrichlorosilane-treated ZSM-5, which floated at the interface of the two liquids, was observed to be a solid interface catalyst.

Zeolites have many uses in organic synthesis, for example photolysis of alkanophenones[1] and dibenzyl ketone,[2] and the ring-opening reaction of 2,3-epoxy alcohols,[3] in which the substrate molecules orientate in the cavity or channel with suppression of translational movement. ZSM-5 zeolite is the strongest solid acid in aqueous solution[4] and is expected to have a high activity as a catalyst.

It is well known that esters are hydrolysed by saponification followed by neutralization, or by refluxing them in the presence of water and a protic acid. In the latter case, the acidic catalyst must be separated from the product. The application of a solid acid as a catalyst will make the separation easy, and Namba *et al.* have reported[4] the hydrolysis of ethyl acetate in aqueous solution. The method is, however, limited to the water-soluble esters. Treatment with alkyl silyl reagents gave ZSM-5 lipophilicity with the hope that the alkyl group and hydrophobic esters would then interact.

H-ZSM-5-70Na was prepared from ZSM-5-70Na by a conventional cation exchange procedure using 1 mol dm^{-3} NH_4Cl aqueous solution, followed by calcination in air at 500 °C. An octadecyl immobilized H-ZSM-5-70Na (abbreviated as H-ZSM-5-70Na-C_{18}) was prepared by treating H-ZSM-5-70Na with octadecyltrichlorosilane.[5] Hydrolysis of water-insoluble octyl acetate by H-ZSM-5-70Na-C_{18} was attempted. H-ZSM-5-70Na-C_{18} (40 mg) and octyl acetate (0.13 mmol, 22.4 mg) were added to a toluene (5.0 ml) and water (5.0 ml) mixture, and the suspension was refluxed. H-ZSM-5-70Na-C_{18} catalyst floated on the toluene–water interface while the non-alkylated H-ZSM-5 was in suspension in the water. After 48 h, the octyl acetate was consumed and octyl alcohol was produced quantitatively in the toluene phase concomitant with the formation of acetic acid, while only 30%

Table 1. The hydrolysis of octyl acetate under various zeolites.[a]

Zeolite[b] (Type)	R_i[c]/10^{-4} mol g-cat^{-1} h^{-1}
—	0.00
H-A-C_{18} (3A type)	0.07
H-F-C_{18} (Faujasite type)	0.04
H-Z-Y4.8-C_{18} (Y type)	0.24
H-Z-HM15-C_{18}[d] (Mordenite type)	0.59
H-Z-HM20-C_{18}[e] (Mordenite type)	0.33
H-ZSM-5-70Na[f]	0.43
H-ZSM-5-70Na-C_{18}[f]	5.62
H-ZSM-5-1000H-C_{18}[g]	0.36

[a] Octyl acetate (2.5 mmol; 429 mg) and zeolite (40 mg) were used. Other conditions as in the main text. [b] Zeolite-C_{18} represents the zeolite treated with octadecyltrichlorosilane. [c] Initial rates of the formation of octanol. [d,e,f,g] The Si : Al atomic ratios are 7.5, 10.1, 39.0, and 543.3, respectively.

Table 2. Effect of octadecyltrichlorosilane treatment on the hydrolysis of esters.[a]

RC(=O)OR′			R_i[b]/10^{-4} mol g-cat^{-1} h^{-1}			
R	R′	Amount/ mmol	H-ZSM-5-70Na-C_{18}	H-ZSM-5-70Na	None[c]	E[d]
CH_3	CH_3	6.2	21.26	21.81	0.01	1.0
CH_3	C_2H_5	5.1	13.71	12.69	0.00	1.1
CH_3	C_4H_9	3.1	5.45	5.50	0.00	1.0
CH_3	C_6H_{13}	2.5	9.99	5.07	0.00	2.0
CH_3	C_8H_{17}	2.5	5.62	0.36	0.00	15.6
C_3H_7	C_4H_9	2.5	30.66	2.48	0.00	12.4
C_5H_{11}	CH_3	2.5	17.51	7.92	0.00	2.2
C_5H_{11}	C_2H_5	2.5	12.22	4.98	0.00	2.5
C_9H_{19}	CH_3	2.5	7.05	1.74	0.00	4.1

[a] Conditions as in the text. [b] Initial rates of the formation of the corresponding alcohols. [c] Blank test without catalyst. [d] $E = R_i$(H-ZSM-5-70Na-C_{18})/R_i(H-ZSM-5-70Na).

of octyl acetate was consumed with H-ZSM-5-70Na. No reaction other than hydrolysis was observed. H-ZSM-5-70Na-C_{18} is seen to be an effective solid catalyst for the hydrolysis of water-insoluble esters.

Other zeolites and esters were studied and the results are summarized in Tables 1 and 2. Table 1 shows that the H-ZSM-5 series exhibited higher activity, H-ZSM-5-70Na-C_{18} especially had the highest activity. Table 2 shows the effect of octadecylsilane treatment. The reaction rates of water-soluble esters such as methyl, ethyl, and butyl acetate were the same when silane treated or non-treated ZSM-5s are used, and consequently the effect was low. In contrast, the reaction rates of water-insoluble esters such as octyl acetate, butyl butyrate, and methyl decanoate increased by silane treated ZSM-5. The most pronounced effect was found in the case of octyl acetate, *i.e. ca.* 16 times. Thus, alkyl-silane-treated ZSM-5 catalyst show a new type of interface catalysis.

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