

Lewis/Brønsted balance as a key factor in the selective liquid-phase dehydration of 1-phenylethanol into styrene

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Introduction

The liquid-phase dehydration of alcohols is widely used to obtain olefins. Commercial processes for this reaction use strong mineral acid catalysts, such as H_2SO_4 , KHSO_4 or p-toluensulfonic acid, which are toxic and corrosive. New industrial strategies demand the replacement of liquid acids by solid catalysts. However, studies on alcohol dehydration over solid acids have been essentially performed in gas phase, at relatively high temperatures. In particular, 15 % of the worldwide production of styrene is obtained via the dehydration of 1-phenylethanol (PhE), a byproduct in the propylene oxide synthesis process. PhE dehydration is also a useful test reaction because 1-phenylethanol is structurally similar to much more expensive alcohols widely used in Fine Chemicals. One example is the dehydration of indanols to produces indenenes [1]. However, very few papers deal with the PhE liquid-phase dehydration [2] and knowledge on the exact requirements of density, nature and strength of surface acid sites for improving the styrene yield and selectivity on solid acids is lacking. Figure 1 shows the reaction pathways involved in PhE conversion reactions. PhE may be converted into styrene (S) but also may simultaneously form alpha-methylbenzene ether (AME). Both products can be consecutively converted to heavy products (HP). In this work, we studied the liquid-phase conversion of PhE on samples containing different strength and proportions of Brønsted and Lewis acid sites.

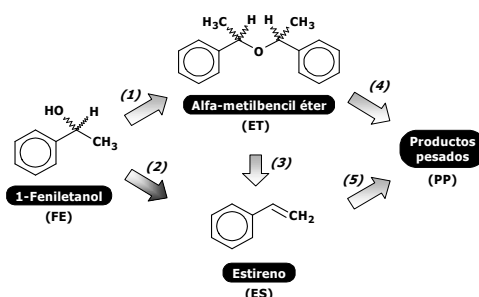


Figure 1: reaction scheme in the dehydration of 1-phenylethanol.

Experimental

Commercial $\text{SiO}_2\text{-Al}_2\text{O}_3$ (Ketjen), HZSM-5 (Zeocat PZ), HBEA (Zeocat PB) and SiO_2 (Grace G62) samples were used. HPA(28%)/ SiO_2 , ZnO(20%)/ SiO_2 and Al-MCM-41 were prepared in laboratory. Sample characterization was performed by employing XRD, N_2 physisorption at 77 K, TPD of NH_3 , and IR of pyridine techniques. Liquid-phase dehydration of PhE was carried out in a 600 ml autoclave, at 363 K, using 0.5 g of catalyst and cyclohexane as solvent.

Results and discusión

Initial PhE dehydration rates (r°_{PhE}) and selectivities are shown in Table 1.

Table I. textural, acid properties of the catalysts and catalytic activity results.

Sample	S _g (m ² /g)	Si/Al	TPD NH ₃ (μmol /g)	IR pyridine L/(L+B)	r _{PhE} ⁰ x 10 ³ (mol/min g)	Selectivities (X _{PhE} = 90%)		
						S	AME	HP
HPA/SiO ₂	205	-	163	0.20	8.1	18	62	20
SiO ₂ /Al ₂ O ₃	460	11.2	280	0.75	1.8	8	90	2
Al-MCM-41	925	20.0	340	0.81	0.7	6	94	0
ZnO/SiO ₂	125	-	2240	1.00	0.4	1	99	0
HBEA	560	12.5	500	0.50	10.8	67	27	6
HZSM5	350	20.0	770	0.50	2.8	94	5	1

HPA/SiO₂, which contains essentially strong Brønsted (B) acid sites, converted PhE at high rates forming initially mainly AME that was then converted to S and HP. ZnO/SiO₂, which contains only Lewis (L) acid sites, was poorly active but highly selective for the intermolecular dehydration reaction, yielding 99% AME. Samples containing mainly Lewis acid sites (SiO₂-Al₂O₃, Al-MCM-41) formed also only AME as primary product that was then converted to S and HP, in particular on SiO₂-Al₂O₃ because of its stronger acid strength. Zeolite HBEA exhibited similar density of Brønsted and Lewis acid sites and was the most active catalyst. The initial formation rates of S and AME were similar on HBEA, but then AME was converted to S. These results on HBEA showed that the selective formation of S is promoted by the presence of similar amounts of strong surface Lewis and Brønsted acid sites (see Figure 2). However, the yield to S was never higher than 70% on HBEA because S was consecutively converted to HP. The density and strength of acid sites were higher on zeolite HZSM-5 than on HBEA, but was lower on HZSM-5 revealing diffusional constraints. Zeolite HZSM-5 was almost completely selective to the formation of S reaching 95% S yield after 2 h of reaction. This is because by shape selectivity the narrow channels of HZSM-5 hinder the formation of bulky intermediates involved in AME and HP formation.

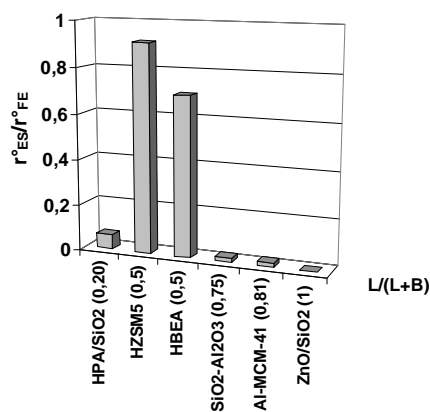


Figure 2: initial selectivity to styrene vs. balance of acid sites.

Conclusions

1-Phenylethanol is selectively converted in liquid phase to styrene on HZSM-5 revealing the potential of this zeolite for producing fine chemicals by dehydration.

References

- [1] Roesky, R., Weiguny, J., Bestgen, H. and Dingerdissen, U. *Appl. Catal. A: Gen.* 176 (1999) 213.
- [2] Lange, J. and Otten, V. *J. Catal.* 238 (2006) 6.