

Selective liquid-phase intramolecular dehydration of 1-phenylethanol over solid acids

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Introduction

The liquid-phase dehydration of alcohols is widely used in chemical industry because it forms valuable unsaturated organic molecules. Commercial processes for this reaction use strong mineral acid catalysts, such as H_2SO_4 , KHSO_4 or p-toluenesulfonic acid that entail concerns related to high toxicity, corrosion, and material disposal. 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. 1-Phenylethanol 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 produce indenes [1]. However, very few papers deal with the liquid-phase dehydration of 1-phenylethanol [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 1-phenylethanol conversion reactions. 1-Phenylethanol may be converted by intramolecular dehydration to styrene (S) but also may simultaneously form alpha-methylbenzene ether (AME) via an intermolecular dehydration/condensation reaction. Both products are consecutively converted to heavy products (HP). In this work, we studied the liquid-phase conversion of 1-phenylethanol on samples containing only either strong Brønsted (HPA/SiO₂) or Lewis (ZnO/SiO₂) acid sites, and catalysts containing both Lewis and Brønsted acid sites of either strong (zeolites HZSM5 and HBEA) or moderate (SiO₂-Al₂O₃, Al-MCM-41) strength.

Materials and Methods

Commercial SiO₂-Al₂O₃ (Ketjen), HZSM5 (Zeocat PZ), HBEA (Zeocat PB) and SiO₂ (Grace G62) samples were used. HPA(28%)/SiO₂, ZnO(20%)/SiO₂ and Al-MCM-41 were prepared in laboratory. Sample characterization was performed by employing XRD, N₂ physisorption at 77 K, TPD of NH₃, and IR of pyridine techniques (Table 1). 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. Batch catalytic run lengths were between 4 and 8 h.

Results and Discussion

Initial PhE dehydration rates (r_{PhE}^0) and selectivities at 90% PhE conversion (X_{PhE}) are shown in Table 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, that contains only Lewis (L) acid sites, showed a high selectivity for the intermolecular dehydration reaction, yielding 99% AME. Samples containing mainly Lewis

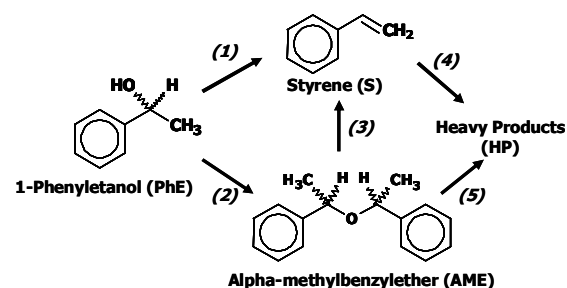


Figure 1. Reaction network of PhE conversion

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. However, the yield to S was never higher than 70% on HBEA because S was consecutively converted to HP for high PhE conversions. The density and strength of acid sites were higher

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 higher 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

Table 1: Sample properties and catalytic results of PhE dehydration

Sample	Sg (m ² /g)	Si/Al	TPD NH ₃ (μmol/g)	IR pyridine L/(L+B)	$r_{\text{PhE}}^0 \times 10^3$ (mol/min g)	Selectivities ($X_{\text{PhE}} = 90\%$)		
						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

on zeolite HZSM5 than on HBEA, but r_{PhE}^0 was lower on HZSM5 revealing diffusional constraints. Zeolite HZSM5 was almost completely selective to the formation of S reaching 95% S yield after 2 h of reaction. This is due to shape selectivity because the narrow channels of HZSM5 hinder the formation of bulky intermediates leading from S to AME and HP.

Significance

1-Phenylethanol is selectively converted in liquid phase to styrene on HZSM5 revealing the potential of this zeolite for producing fine chemicals via alcohol dehydration reactions.

References

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