TEXTURE AND ACIDITY REQUIREMENTS FOR THE SELECTIVE LIQUID-PHASE INTRAMOLECULAR DEHYDRATION OF 1-PHENYLETHANOL

Nicolás M. Bertero, Carlos R. Apesteguía* and Alberto J. Marchi

Catalysis Science and Engineering Research Group (GICIC), INCAPE (UNL-CONICET), Santiago del Estero 2654, (3000) Santa Fe, Argentina. Email: <u>capesteg@fiq.unl.edu.ar</u>

Introduction

Commercial processes for liquid-phase dehydration of alcohols use strong mineral acid catalysts, such as H_2SO_4 or p-toluensulfonic acid, which pose serious environmental concerns. There is, therefore, increasing interest for developing suitable and recyclable solid catalysts for this process. In particular, 15 % of the worldwide production of styrene is obtained via the dehydration of 1-phenylethanol (PhE), a byproduct in the propylene oxide

Figure 1: Reaction network for PhE conversion



synthesis process. 1-PhE dehydration is also a useful test 1-PhE reaction because 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-PhE [2]. Figure 1 shows the reaction pathways

involved in 1-PhE conversion reactions. 1-PhE 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-PhE 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.

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 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 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

Sample	Sg	TPD NH ₃	IR pyridine	$r_{\rm eve}^0 \ge 10^3$	Selectivities		
_				PhE	$(X_{PhE} = 90\%)$		
	(m^2/g)	(µmol/g)	L/(L+B)	(mol/min g)	S	AME	HP
HPA/SiO ₂	205	163	0.20	8.1	18	62	20
SiO ₂ /Al ₂ O ₃	460	280	0.75	1.8	8	90	2
Al-MCM41	925	340	0.81	0.7	6	94	0
ZnO/SiO ₂	125	2240	1.00	0.4	1	99	0
HBEA	560	500	0.50	10.8	67	27	6
HZSM5	350	770	0.50	2.8	94	5	1

Table 1: Sample properties and catalytic results of PhE dehydration

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

1. R. Roesky, J. Weiguny, H. Bestgen, U. Dingerdissen, Appl. Catal. A: Gen. 176 (1999) 213.

2. J. Lange, V. Otten, J. Catal. 238 (2006) 6.