

Selective synthesis of indene by liquid-phase dehydration of 1-indanol

Nicolás M. Bertero, Germán D. Bustos, Carlos R. Apesteeguía, Alberto J. Marchi*
 GICIC (Catalysis Science and Engineering Research Group), INCAPE (UNL-CONICET),
 Santiago del Estero 2654, (3000) Santa Fe (Argentina)
 *amarchi@fiq.unl.edu.ar

Introduction

Indene (ENE) is widely used in chemical industry for the production of resins, functionalized materials, pharmaceuticals, agrochemicals and catalysts for olefin polymerization [1]. However, the commercial process for obtaining high purity indene from oil heavy cuts is quite complex. In fact, an indene-rich fraction containing about 80 wt% is initially obtained by fractional distillation of coal tar. Then, this fraction is purified in order to separate benzonitrile, alkyl pyridines, alkyl benzenes, and phenol through either different acid and basic washing steps or crystallization at temperatures lower than 263 K [2]. It is desirable then to develop a simpler and more direct indene synthesis process. In this sense, the selective liquid-phase dehydration of 1-indanol (NOL) appears as an interesting technological alternative since a similar dehydration reaction has been successfully used to produce valuable olefins [3]. Over acid catalysts NOL may be converted into ENE via intramolecular dehydration and also into di-indanyl ether (ETH) via intermolecular dehydration (Fig. 1). Both products can be consecutively form heavy products (HP). Very few papers deal with the liquid-phase dehydration of NOL [4]. Precisely, in this work, the liquid-phase dehydration of NOL over SiO₂-Al₂O₃, HZSM5, HBEA and HMOR zeolites was studied under mild conditions.

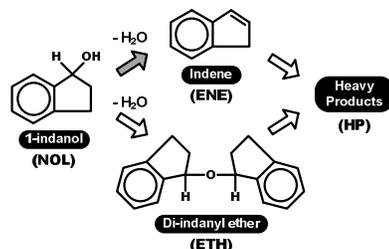


Figure 1. Reaction network of 1-indanol (NOL) conversion over acid catalysts.

Materials and Methods

Commercial SiO₂-Al₂O₃ (Ketjen), HZSM5 (Zeocat PZ), HBEA (Zeocat PB) and HMOR (Zeocat HZM-980) samples were used. Previous to their use the solids were calcined in air flow at 773 K for 2 h. Sample characterization was performed by using XRD, atomic absorption spectroscopy (AAS), N₂ physisorption at 77 K, TPD of NH₃ and IR of pyridine (Table 1). Liquid-phase NOL dehydration was carried out in a 600 ml autoclave, at 363 K and 2 bar, using 0.5 g of catalyst, 2.5x10⁻² mol of NOL, 150 ml of cyclohexane as solvent and a stirring rate of 600 RPM. Reaction products were analyzed ex-situ by gas chromatography.

Results and Discussion

Characterization results are shown in Table 1. It was verified by XRD that the crystalline structure of the zeolites was not modified after calcination. The microporous samples showed a specific surface area between 350 and 650 m².g⁻¹ and mesoporous SiO₂-Al₂O₃ showed an intermediate value of 460 m².g⁻¹. The Si/Al ratio for SiO₂-Al₂O₃ and HBEA was about 12, whereas for HZSM5 and HMOR was equal to 20 and 80, respectively. SiO₂-Al₂O₃ and HBEA exhibited an asymmetric NH₃ desorption band between 400 and 800 K with

the maximum at 500 K. In contrast, HMOR and HZSM5 showed two desorption bands that appeared in the 400-600 K and 600-900 K ranges, respectively. The acid site density determined from the NH₃ TPD profiles followed the order: HZSM5 > HBEA > SiO₂-Al₂O₃ > HMOR. Regarding Lewis (L) and Brønsted (B) acid sites, the pattern for the L/(L+B) ratio was: SiO₂-Al₂O₃ > HBEA ≈ HZSM5 > HMOR.

Table 1. Sample characterization and catalytic results.

Catalyst	Sg (m ² .g ⁻¹)	TPD NH ₃ (μmol.g ⁻¹)	IR pyr L/(L+B)	r ⁰ _{NOL} x10 ³ (mol.min ⁻¹ .g ⁻¹)	S ⁰ _{ENE} (%)	η _i (%) (X _{NOL} =90%)			η ^F _{ENE} (%)
						ENE	ETH	HP	
SiO ₂ -Al ₂ O ₃	460	280	0.75	2.13	45	31	10	5	47
HBEA	560	500	0.55	6.75	99	46	0	0	54
HMOR	650	101	0.11	2.84	99	53	0	0	90
HZSM5	350	770	0.50	0.69	97	61	1	0	94

Reaction conditions: W_C=0.5 g; T=363 K; p=2 bar (N₂); C⁰_{NOL}=0.16 M; stirring rate=600 RPM.

Initial NOL dehydration rates (r⁰_{NOL}), initial selectivity to ENE (S⁰_{ENE}), product yields at X_{NOL}=90% (η_i) and ENE yield at the end of reaction (η^F_{ENE}) are shown in Table 1. All the samples reached total NOL conversion in less than 2 hours. HBEA was the most active catalyst and the r⁰_{NOL} value for HBEA was in fact 2-3 times higher than HMOR and SiO₂-Al₂O₃ and one order of magnitude higher than HZSM5.

SiO₂-Al₂O₃ containing mostly L acid sites dehydrated initially NOL into both ENE and ETH (S⁰_{ENE}=45%), but with the progress of the reaction both products were converted to HP, giving a final ENE yield lower than 50%. In contrast, the zeolites with L/(L+B) ≤ 0.55 were very selective to ENE from the beginning of the reaction (S⁰_{ENE} > 97%). However, with HBEA a final ENE yield of only 54% was obtained, whereas with HMOR and HZSM5 η^F_{ENE} values higher than 90% were reached. For all the catalysts a considerable carbon imbalance was observed at X_{NOL} < 90%. This C atom imbalance diminished at total NOL conversion with HMOR and HZSM5 but not in the case of HBEA. The results presented here strongly suggest that a L/(L+B) ratio lower than 0.55 markedly promotes the initial olefin selectivity. Microporous structure and acid site density play an important role avoiding HP formation at high X_{NOL}. Differences between NOL consumption rate and product formation rates can be explained by a strong reactant adsorption and diffusional problems.

Significance

Indene yields higher than 90% were achieved in the liquid-phase dehydration of 1-indanol on HMOR and HZSM5 zeolites. This reveals the potential of this catalytic process for replacing the traditional complex process where the valuable indene is obtained from coal tar.

References

- Alt, H.G, Koppl, A. *Chem. Rev.* 100, 1205 (2000).
- Takigawa, Y., Nakaoka, H. *US Patent* 6291735 (2001).
- Bertero, N.M., Apesteeguía, C.R., Marchi, A.J. *Catal. Commun.* 10, 261 (2008).
- Tarlani, A., Riahi, A., Abedini, M., Amino, M.M., Muzart, J. J. *Mol. Catal. A: Chem.* 260, 187 (2006).