

Synthesis of styrene and indene by liquid-phase catalytic dehydration

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Introduction

The liquid-phase dehydration of alcohols is widely used in chemical industry for the production of valuable olefins. Commercial processes employ strong mineral acid catalysts, such as H₂SO₄, or p-toluensulfonic acid that entail concerns related to high toxicity, corrosion, and material disposal [1]. Some novel processes based on solid acid catalysts have been reported and the influence of the acidic properties on the olefin selectivity and yield is currently matter of study [2].

In particular, the intramolecular dehydration of 1-phenylethanol (PHE) is of industrial interest in order to produce styrene (STY), which is used in the production of a wide variety of polymeric products [2]. PHE may be converted by intramolecular dehydration into STY but also may simultaneously form α -methylbenzylether (AME) via intermolecular dehydration mechanism (Fig. 1.a). Indene (INE) is another valuable olefin extensively employed for the production of resins, functionalized materials, pharmaceuticals, agrochemicals, etc. [2]. Indene is mainly obtained from coal tar, but the process requires many unit operations in order to separate benzonitrile, alkyl pyridines, alkyl benzenes, etc. Thus, the intramolecular dehydration of 1-indanol (IND) appears as an attractive alternative to obtain INE if the competitive intermolecular IND dehydration to di-1-indanyl ether (DIE) may be prevented (Fig. 1.b). The olefin and the ether, in both PHE and IND dehydrations, can be then converted to heavy products (HP). In this work, the liquid-phase dehydration of PHE and IND to selectively obtain STY and INE was studied over HBEA, HMOR and HZSM5 zeolites.

Materials and Methods

Commercial samples of HBEA, HMOR and HZSM5 zeolites were calcined in air flow at 773 K for 2 h previous to their use. 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 dehydrations were carried out in a 600 ml autoclave, at 363 K and 2 bar (N₂), using 0.5 g of catalyst, 2.5x10⁻² mol of reactant (NOL), 150 ml of cyclohexane as solvent and a stirring rate of 600 RPM. Reaction products were analyzed ex-situ by GC.

Results and Discussion

Zeolite characterization results are shown in Table 1. The Si/Al ratios for HBEA, HZSM5 and HMOR were 12.5, 20 and 80, respectively. The zeolite surface areas were between 350 and 650 m².g⁻¹. HBEA exhibited an asymmetric NH₃ desorption band between 400 and 800 K (maximum at 500 K). In contrast, HMOR and HZSM5 showed two desorption

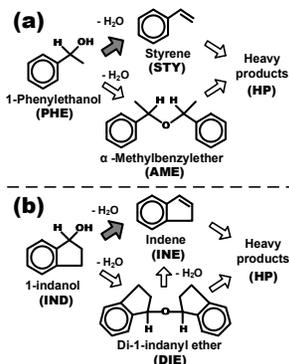


Figure 1. Dehydration of: (a) 1-phenylethanol and (b) 1-indanol.

bands in the 400-600 K and 600-900 K ranges. The acid site density (n_a) followed: HZSM5 > HBEA > HMOR, while Brønsted/Lewis ratio (B/L) followed: HMOR > HZSM5 > HBEA.

Table 1. Sample characterization and catalytic results.

Sample	Sg (m ² .g ⁻¹)	TPD NH ₃		IR pyr B/L	PHE dehydration		IND dehydration	
		n_a (μmol.g ⁻¹)	T ^{MAX} (K)		$r_{PHE}^0 \times 10^3$ (mol.min ⁻¹ .g ⁻¹)	S ⁰ _{STY} (%)	$r_{IND}^0 \times 10^3$ (mol.min ⁻¹ .g ⁻¹)	S ⁰ _{INE} (%)
HBEA	560	500	500	0.8	3.04	96.4	6.75	99.2
HMOR	650	101	460 / 790	8.3	2.33	50.3	2.84	99.1
HZSM5	350	770	520 / 730	1.0	1.90	94.2	0.69	97.3

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

The pattern for the initial dehydration rate was the same for both reactions: HBEA > HMOR > HZSM5 (Table 1). For catalysts with similar pore size (HBEA and HMOR) the r_{NOL}^0 increased with the acid site density (n_a). HZSM5 with higher n_a but smaller pores showed the lowest activity due to important diffusion limitations. In the PHE dehydration, HBEA and HZSM-5 were initially very selective to the olefin (S⁰>90%) but HMOR was not (S⁰≈50%). Thus, the S⁰_{STY} strongly depended on the B/L ratio. Instead, S⁰_{INE} was higher than 97% for all the zeolites. This is explained by transition state shape selectivity in the IND dehydration that avoids DIE formation. Except for HMOR in PHE dehydration, in all the cases an important lack of C balance (>25%) was observed (Fig. 2) at X_{NOL}=90%. The increase in olefin yield observed after total NOL conversion indicates that this is a consequence of strong diffusional restrictions. These may be due to: (a) strong interaction of olefins with acid sites; (b) kinetic diameter vs. pore size and (c) presence of cavities of 13Å inside HBEA structure. The maximum olefin yields were obtained with HMOR and HZSM5 (Fig. 2).

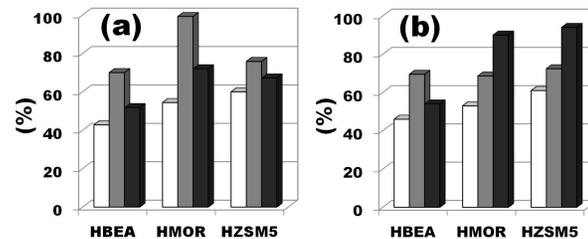


Figure 2. Olefin yield (□) and C balance (■) (both at X_{NOL}=90%) and maximum olefin yield (■) in the dehydration of: (a) PHE and (b) IND.

Significance

Indene yields of up to 94% are obtained from the liquid-phase dehydration of 1-indanol on HMOR and HZSM5 zeolites, while a maximum styrene yield of 70% is achieved on HZSM5 via 1-phenylethanol dehydration.

References

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