

Tandem Hydrogenation-dehydration Reactions for the Synthesis of Olefins from Aromatic Ketones

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Introduction

The synthesis of fine chemicals usually involves several consecutive-parallel reaction steps that often employ as many batch reactors as chemical transformations are needed in the global synthesis. This methodology frequently allows the successful selective synthesis of the desired product, but involves high operative costs. Besides, the multi-step batch processes require large volumes of solvents, salts and acid or basic liquids thereby generating significant amount of wastes that need to be either recycled or removed. Thus, it is of environmental and economic interest to develop novel integrated methodologies allowing one-pot synthesis processes via the catalytic promotion of tandem reactions.

The two-steps conversion of aromatic ketones to aromatic olefins that involves consecutive hydrogenation-dehydration reactions has been studied using homogeneous catalysis for obtaining valuable products such as 2,6-dimethylnaphtalene and indenes. Here, we investigated the use of solid catalysts for the one-pot synthesis of aromatic olefins from aromatic ketones via tandem hydrogenation-dehydration reactions. Definitions of “tandem” process are not unanimous in the literature [1]. We used the concept of tandem consecutive reactions, wherein the first step is necessary but not sufficient for the tandem process, and changes in reaction conditions are also required to facilitate propagation. The conversion of acetophenone (AP) to styrene (STY) was used as model reaction (Figure 1). The AP hydrogenation and 1-phenylethanol (PHE) dehydration reactions were first studied separately in order to select the best catalysts for achieving high conversions and selectivities. Then, the selected catalysts were employed for investigating the one-pot synthesis of STY from AP.

Materials and Methods

Sample characterization was performed by employing XRD, TPR, N₂ physisorption at 77 K, H₂ chemisorption, TPD of NH₃, and IR of pyridine techniques. AP hydrogenation and PHE dehydration were carried out in liquid phase at 363 K, in a batch reactor, using cyclohexane as solvent. Reaction products were analyzed ex-situ by gas chromatography.

Results and Discussion

The AP conversion to PHE was studied at 10 bar (H₂) over Ni(8%), Co(8%), Cu(8%), Pd(0.5%) and Pt(0.5%) supported on SiO₂. The selectivity pattern towards PHE (S_{PHE}) was: Cu/SiO₂ > Pd/SiO₂ > Ni/SiO₂ > Co/SiO₂ > Pt/SiO₂. The PHE selectivity on Cu/SiO₂ was 100% during the complete catalytic run. The PHE dehydration to STY was investigated at 2 bar (N₂) over HPA(28%)/SiO₂, γ -Al₂O₃/SiO₂-Al₂O₃, Al-MCM-41 and zeolites HY, HZSM-5 and HBEA. Zeolites HY, HBEA and HZSM-5 contained similar Lewis/Bronsted acid sites ratios (between 0.5 and 0.6) and showed the highest initial selectivities to STY. However, zeolite HY was rapidly deactivated reaching only 20% of PHE conversion. The initial STY selectivity on

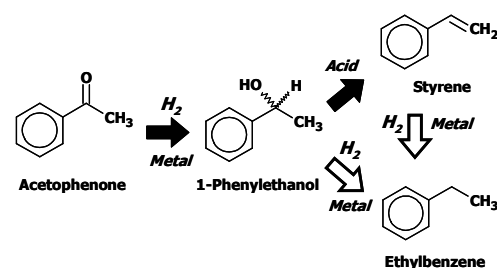


Figure 1: Conversion of acetophenone to styrene

The one-pot synthesis of STY from AP was studied using a mechanical mixture of Cu/SiO₂ and HZSM-5. Initially, we performed an exploratory catalytic run at 363 K and 10 bar (H₂), loading the reactor with AP and the catalyst mechanical mixture. The reaction formed significant amounts of ethylbenzene (EB), thereby indicating that PHE produced by AP

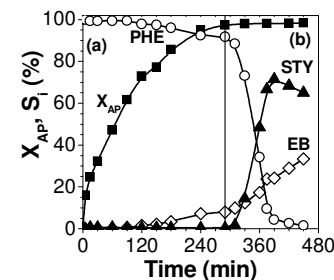


Figure 2: Tandem hydrogenation-dehydration reactions. a) P_{H₂}=20 bar, 333 K; b) P_{H₂}=1 bar, 353 K.

PHE dehydration on HZSM-5 against STY hydrogenation on Cu/SiO₂ (Figure 2.b). It is observed that the formation of STY rapidly increased in this second step; the selectivity to STY attained 70% when PHE was completely consumed.

Significance

The one-pot synthesis of styrene from acetophenone may be efficiently achieved via tandem consecutive hydrogenation-dehydration reactions. It is expected that the catalysts and reaction conditions employed here may be successfully extrapolated to promote the synthesis of valuable olefins from aromatic ketones of similar structure than acetophenone.

References

1. Denmark, S.E. and Thorarensen, A. *Chem. Rev.* 96, 137 (1996).

zeolite HBEA was 96%, but increasing amounts of heavy products were formed with the progress of the reaction. In contrast, zeolite HZSM-5 was very stable and selective to STY, yielding 96 % of STY. The superior selectivity and stability observed on zeolite HZSM-5 for PHE dehydration is explained by considering that the narrow channels of this zeolite avoid the formation of bulky products.