A Strategy for the Simultaneous Synthesis of Methallyl Alcohol and Diethyl Acetal with Sn-β

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Introduction

Methallyl alcohol (Mol) is an important chemical that is widely used as a raw material for various applications. The conventional method to prepare Mol is hydrolysis of methylallyl chloride, which requires the use of alkali, an organic solvent, as well as high temperature and pressure. Alternatively, Shimasaki et al. proposed vapor phase hydrogen transferred between methacrolein (Mal) and ethanol, catalyzed by a less expensive and heterogeneous catalyst modified MgO [1]. However, this process is suffered from a low conversion of Mal even under high temperature, and the catalyst stability was also an issue as well. Therefore, the development of an effective but environmentally benign procedure for Mol synthesis is still needed. Diethyl acetal (Dal) is also an important chemical, widely used as an oxygenated additive for diesel fuel to reduce the emission of particles and nitrous oxides, and a precursor for pharmaceuticals and perfumes [2]. However, the direct use of acetaldehyde to synthesize suffers from its low boiling point (294 K), toxicity, and instability.

Herein, we report a facile strategy for the simultaneous synthesis of Mol and Dal in high yields at low temperature with post-synthesized Sn-β, which is modified by various treatments to manipulate the acid properties, showing fantastic activity in Meerwein–Ponndorf–Verley reduction between Mal and primary alcohols. The correlation of the catalyst properties with reaction activity is especially emphasized.

Materials and Methods

The dealuminated zeolite (deAl-β) was ground with the tin (II) acetate. Sn-β was prepared by calcining under air flow at 823 K for 3 h. Sn-β-Ar was pre-calcined in the flow of Ar (3 h). Sn-β-Ar-Na was prepared by soaking Sn-β-Ar into a 1.0m $NaNO_3$ solution and stirred at 353 K for 12 h. The solid sample was recovered by filtration with distilled water [3].

The methacrolein and the ethanol were introduced in the flask with catalysts. The mixture was heated to 350 K and reacted for a defined time. Small aliquots were withdrawn at different intervals.

Results and Discussion

The acid properties of the catalysts were characterized by FTIR with pyridine adsorption (Figure 1a). After dealumination, Lewis and Brønsted bands almost disappear with the appearance of typical hydroxyl groups owing to the formation of silanol nests. The subsequent incorporation of Sn enhanced the Lewis acidity. With the treatment of calcined in Ar, the Lewis acidity was further increasing. With catalysts exchanged with Na, the medium Brønsted acidity decreased, indicating that Na was changed with protons of hydroxyl groups.

As shown in Figure 1b, with the treatment of calcined in Ar and exchanged with Na, the yield of Mol is increasing while the yield of side product C6 addition is gradually decreasing, which result from the enhanced Lewis acidity and reduced medium Brønsted acidity that derived from the hydroxyl groups.

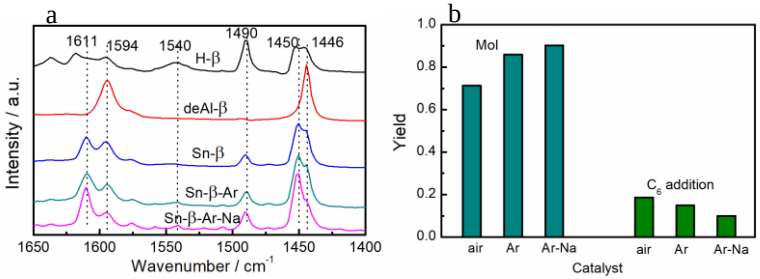
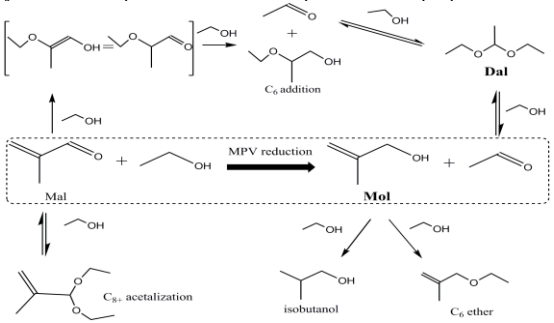


Figure 1. (a) FTIR spectra of catalysts with pyridine adsorption, (b) Comparison of the catalytic results of three Sn-β catalysts. Reaction conditions: reflux, 350 K, 0.9 mmol Mal, 80 mmol ethanol and 0.5 g catalysts.

After a detailed investigation by using different substrates as reactants, the possible reaction pathways with a complex network of side products was proposed in Scheme 1.



Scheme 1. Proposed reaction pathways involved in the reaction of Mal in ethanol over Sn-β.

Significance

We have developed an approach to simultaneously synthesize the Mol and Dal at low temperature with high yields, which is significant to understand and manipulate the complex reactions between α,β-unsaturated aldehydes and primary alcohols. Acid properties of post-synthetic Sn-β zeolite can be fine-tuned through simple treatments.

References

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