

## Synergy in bimetallic Al-Zr-TUD-1

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### Introduction

Reduction of the amount of waste generated in chemical synthesis can be achieved by employing heterogeneous catalysts such as zeolites and mesoporous silicates instead of classical mineral acids. As zeolites are microporous crystalline solids the pore size might cause diffusion limitations. To overcome this mesoporous materials with similar acidity as zeolites have been developed. TUD-1[1] is such a mesoporous material. TUD-1 possesses an amorphous sponge-like 3D structure, leading to less diffusion limitations, while at the same time being highly stable and straightforward to prepare.

Many different transition metals have been incorporated into the TUD-1 structure such as Al and Zr. Al-TUD-1 having Brønsted as well as Lewis acid sites has been successfully employed in alkylation of phenol with *tert*-butyl alcohol while Zr-TUD-1, a purely Lewis acid catalyst has been applied in the Meerwein-Ponndorf-Verley reduction and the Prins reaction.[2,3]

In the synthesis of TUD-1 triethanolamine is employed as complexing agent for Si, Al and Zr, leading to incorporation of the metals Al and Zr as isolated species. It even enabled combining both metals into the TUD-1 structure with different Al/Zr ratios to study the synergy between the Brønsted and Lewis acid sites. This bimetallic Al-Zr-TUD-1 was tested in MPV reduction of 4-*tert*-butyl cyclohexanone and the Prins cyclisation of citronellal. No synergy between Brønsted acid sites and Lewis acid sites was detected in Lewis acid catalyzed MPV reaction. However, the opposite was true for Brønsted as well as Lewis acid catalyzed Prins cyclisation of citronellal: Here synergy between the different types of acid sites improved the reaction. [4] This constitutes a major breakthrough in the area of heterogeneous acid catalyzed catalysis.

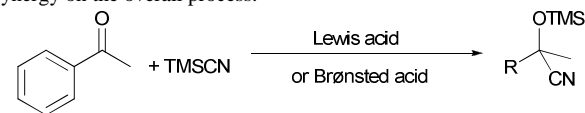
### Materials and Methods

All chemicals were purchased from Aldrich, Janssen or Acros. For the catalytic experiments anhydrous solvents were used and solids were used as received, all the other liquids were distilled prior to use. Catalysts were either dried at 100 °C or activated in the presence of air up to 600 °C at a temperature ramp of 1 K/min and subsequent heating at 600 °C for 10 hr. The experiments were performed in dried glassware under a nitrogen atmosphere.

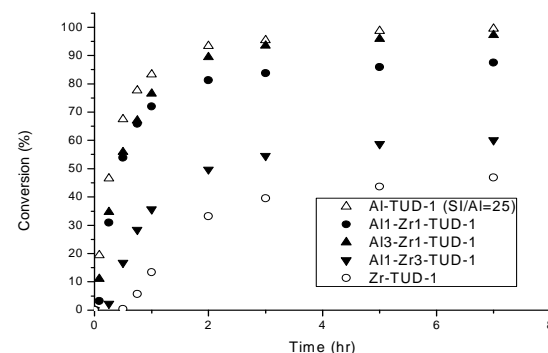
### Results and Discussion

To further explore the synergy observed in the Prins cyclisation of citronellal employing bimetallic Al-Zr-TUD-1 other reactions are investigated. Currently we are focusing on the cyanosilylation of acetophenone with trimethylsilylcyanide (TMSCN) a reaction that can be catalyzed by both Brønsted as well as Lewis acid catalysts (see scheme 1). From our

preliminary results (see figure 1), the reaction seems to follow a reaction pathway that is more complex than initially expected. In the first stage of the reaction the TMSCN reacts with silanol groups on the surface of the catalyst, modifying it. Although unexpected this enables detailed mechanistical insight. We will report on the parameters governing these reactions and the influence of synergy on the overall process.



**Scheme 1** Cyanosilylation of acetophenone with trimethylsilylcyanide



**Figure 1** Cyanosilylation of Acetophenone with TMSCN employing different catalysts

These results will be also supplemented with the results from spectroscopic measurements.

### Significance

Synergy found in Al-Zr-TUD-1 leading to higher activities will further encourage the use of heterogeneous instead of homogeneous catalysts in chemical synthesis. It will potentially allow reductions in energy consumption in all acid catalysed industrial processes.

### References

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