

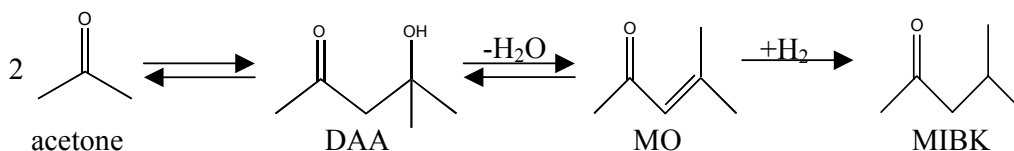
# SINGLE-STAGE LIQUID-PHASE SYNTHESIS OF MIBK OVER A COMBINATION OF ACTIVATED HYDROTALCITES AND PALLADIUM ON CARBON NANOFIBERS

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## Introduction

Methyl isobutyl ketone (MIBK) is an industrially important chemical, mainly used as a coating solvent. It is the third largest tonnage product obtained from acetone. The synthesis of MIBK from acetone and H<sub>2</sub> is mainly produced via a conventional three-step process (see scheme). The condensation of acetone to form diacetone alcohol (DAA) and the dehydration of DAA to mesityl oxide (MO) are base and acid catalyzed reactions, respectively. The selective hydrogenation of the C=C bond of MO to form MIBK is generally catalyzed by supported noble metals.



However, the yield and selectivity to MIBK in the conventional process are low and process conditions severe. In a single-stage liquid-phase process under mild conditions, thermodynamic limitations of the first and second step can be dealt with and side reactions starting from mesityl oxide (MO) can be avoided [1]. Performing the process in the liquid-phase at low temperature and moderate hydrogen pressure requires considerably more active and selective catalysts than those presented in literature. In our study we investigated specially activated Mg/Al hydrotalcites (HT) as solid base catalyst, which exhibits high activity in condensation reactions at low temperatures and show dehydration functionality [2]. For hydrogenation of  $\alpha,\beta$ -unsaturated ketones and aldehydes, palladium-based catalysts, especially Pd/C catalysts, exhibit the best performance in the hydrogenation of the olefinic bond [3,4]. As a promising alternative for activated carbon we used carbon nanofibers (CNF) as the support material.

## Experimental

Fishbone carbon nanofibers (CNF) were grown out of a 57 wt% Ni/SiO<sub>2</sub> catalyst at 773 K from syngas. To remove the growth catalyst, CNF was refluxed in KOH and treated in boiling concentrated nitric acid, respectively. Palladium (1 wt%) was deposited on CNF via an ion adsorption method, earlier applied by Hoogenraad *et al.* [5]. The catalyst precursor was reduced in hydrogen flow at 523 K for 2 hours.

Catalysts were characterized with SEM, TEM, ICP, H<sub>2</sub> chemisorption and N<sub>2</sub> physisorption. A Mg/Al hydrotalcite (HT) was prepared via co-precipitation at 333 K [6]. HT was activated (HT<sub>act</sub>) using the procedure of Roelofs *et al.* [2], involving a controlled heat treatment up to 723 K and rehydration in decarbonated water. Samples were characterized with SEM, XRD, volumetric CO<sub>2</sub> adsorption and N<sub>2</sub> physisorption. Hydrogenation experiments were performed in the liquid-phase at 313 K and moderate H<sub>2</sub> pressures (1-20 bar) in acetone and ethanol. The single-stage synthesis of MIBK starting from acetone and H<sub>2</sub> was performed at 331 K and 1.2 bar H<sub>2</sub>.

## Results and discussion

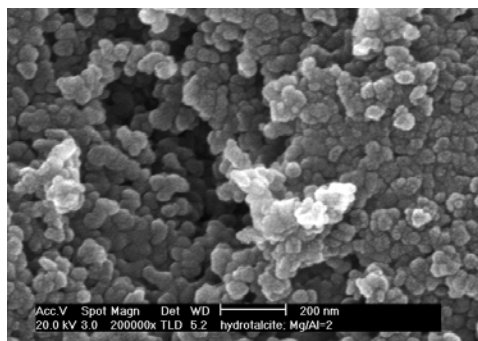


Figure 1. SEM image of HT.

In Figure 1 an SEM image of HT is displayed, showing the regular hexagonally shaped structure. A highly active catalyst for the condensation and dehydration was obtained after applying the activation procedure [2]. TEM examination of Pd/CNF (Figure 2) reveals palladium particles on the fibers of about 1-4 nm, which is confirmed with H<sub>2</sub>-chemisorption. The fibers are tightly interwoven and the skeins of the fibers form a porous structure. We have found with XPS and TEM studies (especially with TEM tilt series) that a considerable amount

of Pd particles is situated in the inner core of these fishbone type carbon nanofibers (10-15%). Treatment of CNF in nitric acid resulted in opening of the inner tubes with a diameter of 4-9 nm and the creation of anchoring sites for the metal precursor.

Pd/CNF was investigated for the liquid-phase hydrogenation of MO at 313 K and moderate H<sub>2</sub> pressures (1-20 bar) for application in the single-stage liquid-phase production of MIBK. From a comparison to other catalysts, i.e., Pd on graphite, Pd on SiO<sub>2</sub> and Pt on CNF, it was found that Pd/CNF exhibits the highest specific activity in the hydrogenation of MO performed in ethanol at 1.2 bar H<sub>2</sub>. All Pd catalysts showed higher selectivities to MIBK than the Pt catalyst, i.e., >99% and 94%, respectively.

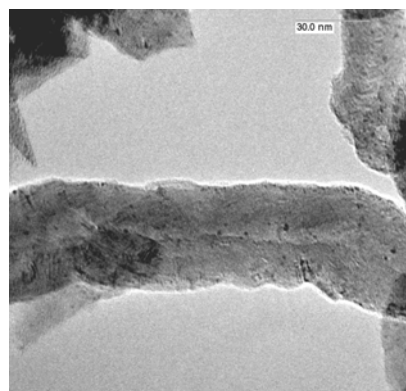


Figure 2. TEM image of Pd/CNF.

Hydrogenation of MO at 1.2 bar H<sub>2</sub> suffers from severe mass transfer limitations in H<sub>2</sub> due to which at relatively high MO concentrations, i.e., 5 wt% in ethanol and 1 wt% in acetone, (polymerization) products of MO rapidly deactivate the metal sites. A high excess of MO near the active sites could occur if hydrogen, with its low solubility in ethanol and acetone, is rapidly depleted in the catalyst particles due to a high rate of hydrogenation in combination with internal diffusion limitations in hydrogen at 1.2 bar. By utilizing low MO concentrations or higher H<sub>2</sub> pressures (~10 bar) deactivation can be suppressed. The catalyst is highly selective to MIBK. No acetone hydrogenation was found up to 20 bar over Pd/CNF.

The results obtained with a catalyst mixture of HT<sub>act</sub> as solid base and Pd/CNF in the single-stage liquid-phase synthesis of MIBK at 331 K will be presented and discussed (Figure 3).

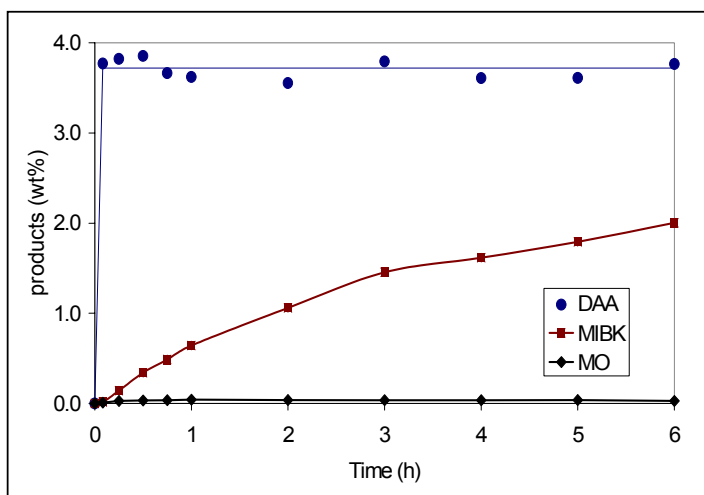


Figure 3. Product formation in the single-stage synthesis of MIBK from acetone and H<sub>2</sub> over HT<sub>act</sub> and Pd/CNF at 331 K.

With this catalyst system acetone and H<sub>2</sub> are selectively converted into MIBK. Due to the balance between the formation rate and the rate of hydrogenation, from the start the steady-state concentration of MO is low and remains low, even at a H<sub>2</sub> pressure of 1.2 bar, due to which deactivating MO polymers are not formed. It was found that under the conditions used the dehydration reaction is the rate-determining step.

### Conclusions

Results obtained with the HT<sub>act</sub> – Pd/CNF catalyst mixture demonstrates the suitability of the catalyst system for the single-stage synthesis of MIBK starting from acetone and hydrogen under mild conditions. The catalysts are stable over several hours due to the low steady-state concentration of MO. Further work will focus on enhancing the dehydration rate of diacetone alcohol over HT.

### References

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