

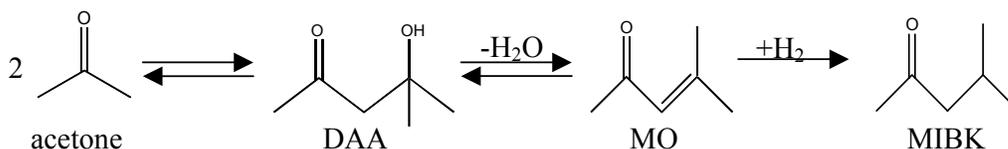
SINGLE-STAGE LIQUID-PHASE SYNTHESIS OF MIBK OVER A COMBINATION OF ACTIVATED HYDROTALCITES AND PALLADIUM ON CARBON NANOFIBERS

Ferry Winter, A. Jos van Dillen, Krijn P. de Jong
Department of Inorganic Chemistry and Catalysis, Debye Institute, Utrecht University
Sorbonnelaan 16, 3584 CA Utrecht, The Netherlands

e-mail address: f.winter@chem.uu.nl

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 H₂ 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 α,β -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/SiO₂ 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, H₂ chemisorption and N₂ physisorption. A Mg/Al hydrotalcite (HT) was prepared via co-precipitation at 333 K [6]. HT was activated (HT_{act}) 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 CO₂ adsorption and N₂ physisorption. Hydrogenation experiments were performed in the liquid-phase at 313 K and moderate H₂ pressures (1-20 bar) in acetone and ethanol. The single-stage synthesis of MIBK starting from acetone and H₂ was performed at 331 K and 1.2 bar H₂.

Results and discussion

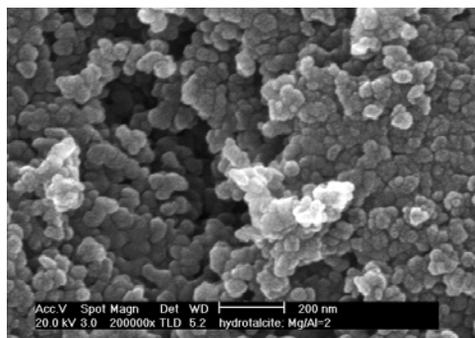


Figure 1. SEM image of HT.

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 H₂-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 H₂ 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 SiO₂ 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 H₂. All Pd catalysts showed higher selectivities to MIBK than the Pt catalyst, i.e., >99% and 94%, respectively.

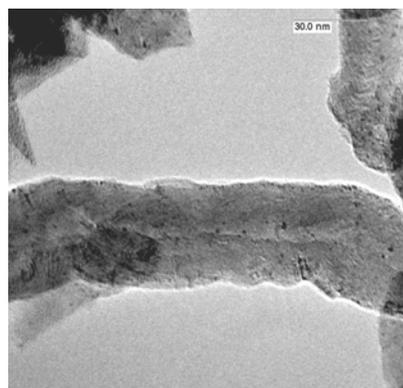


Figure 2. TEM image of Pd/CNF.

Hydrogenation of MO at 1.2 bar H₂ suffers from severe mass transfer limitations in H₂ 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 H₂ 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_{act} 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).

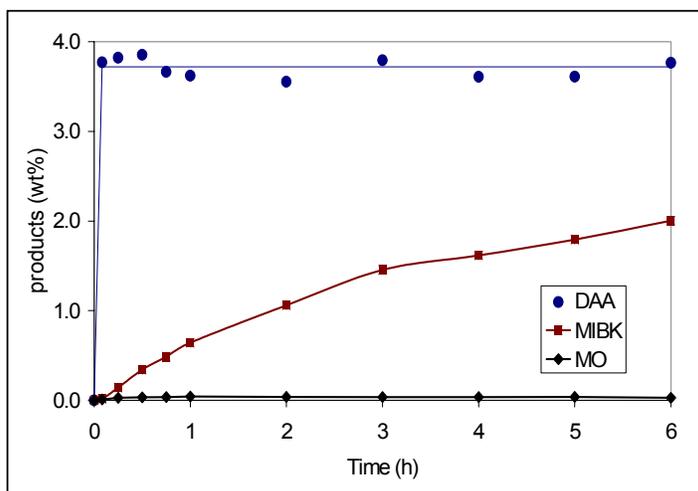


Figure 3. Product formation in the single-stage synthesis of MIBK from acetone and H₂ over HT_{act} and Pd/CNF at 331 K.

With this catalyst system acetone and H₂ 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 H₂ 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_{act} – 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

- [1] Salvapati GS, Ramanamurty KV, Janardanarao M. Selective catalytic self-condensation of acetone. *J. Mol. Catal.* 1989; 54:9-30.
- [2] Roelofs JCAA, van Dillen AJ, de Jong KP. Condensation of citral and ketones using activated hydrotalcite catalysts. *Catal. Lett.* 2001; 74(1-2):91-94.
- [3] Nikolopoulos AA, Howe GB, Jang BW-L, Subramanian R., Spivey JJ, Olsen DJ, Devon TJ, Culp RD., Novel Noble-metal-based catalysts for liquid-phase acetone condensation. In: Ford ME, editor. *Chemical Industries 82, Catalysis of organic reactions*, New York, 2001:533-543.
- [4] Ponec V. On the role of promoters in hydrogenations on metals; α,β -unsaturated aldehydes and ketones. *Appl. Catal. A* 1997; 149:27-48.
- [5] Hoogenraad MS. Growth and utilization of carbon fibrils. Utrecht University the Netherlands, PhD thesis, 1995.
- [6] Miyata S, Kumura T. Synthesis of new hydrotalcite-like compounds and their physico-chemical properties. *Chem. Lett.* 1973:843-848.