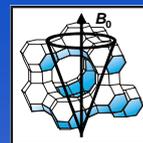




# In Situ Solid-State NMR Investigations of the Mechanisms of Hydrogenation Reactions on Noble Metal-Containing Zeolites

M. Dyballa, H. Henning, M. Scheibe, E. Klemm, M. Hunger,

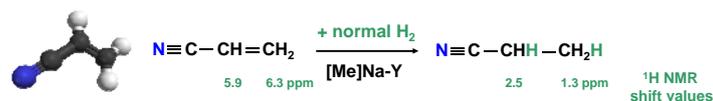
Institute of Chemical Technology, University of Stuttgart, 70550 Stuttgart, Germany



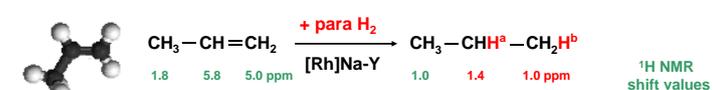
## INTRODUCTION

*In situ* MAS NMR spectroscopy was utilized for studying the hydrogenation of acrylonitrile and propene on noble metal-containing zeolite Y during continuous injection of hydrogen into *in situ* MAS NMR rotors utilized as microreactors. With this approach, the hydrogenation velocity of acrylonitrile on different noble metals (Pt and Rh) without an influence of olefin diffusion on the apparent reaction rate could be studied. In the case of propene hydrogenation, the pairwise incorporation of hydrogen could be demonstrated by hydrogenation with para-enriched hydrogen. In contrast to orthohydrogen with the total nuclear spin  $I = 1$ , parahydrogen has no total nuclear spin and thus no  $^1\text{H}$  NMR signal is caused. By the pairwise incorporation of the two H atoms of a parahydrogen molecule into another molecule, the symmetry of the parahydrogen is broken and the initial spin order is converted into a very large nonequilibrium spin polarization, called hyperpolarization.  $^1\text{H}$  MAS NMR signals due to a pairwise incorporation of para-enriched hydrogen into reactants are characterized by a typical antiphase shape.

## Hydrogenation of acrylonitrile with normal $\text{H}_2$



## Hydrogenation of propene with para-enriched $\text{H}_2$



## EXPERIMENTAL SECTION

Zeolite Na-Y ( $n_{\text{Si}}/n_{\text{Al}} = 2.7$ ) was exchanged with calculated amounts of tetraamineplatinum(II) chloride hydrate ( $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2 \times \text{H}_2\text{O}$ ) and rhodium(III) chloride hydrate ( $\text{RhCl}_3 \times \text{H}_2\text{O}$ ) for preparing zeolite 0.9[Pt]Na-Y with 0.9 wt% Pt and zeolite 0.4[Rh]Na-Y with 0.4 wt% Rh, respectively. These metal-exchanged zeolites were reduced in flowing hydrogen (100 ml/min) at 653 K for 2 h. For the *in situ*  $^1\text{H}$  MAS NMR experiments under continuous flow (CF) conditions, a Bruker 7 mm MAS NMR probe, modified with a gas injection system as described elsewhere [1], with a sample spinning rate of ca. 3 kHz was used. The spectra were recorded upon single pulse  $\pi/2$  excitation at a Bruker Avance III 400WB spectrometer with a  $^1\text{H}$  resonance frequency of 400 MHz. Para-enriched hydrogen was obtained by cooling normal hydrogen at the temperature of liquid nitrogen in the presence of FeO(OH) as ortho-para interconversion catalyst (Fig. 1). For performing hydrogenation experiments with para-enriched and normal hydrogen, the hydrogen flowed via a tube filled with FeO(OH) or via a by-pass to the *in situ* MAS NMR probe, respectively.

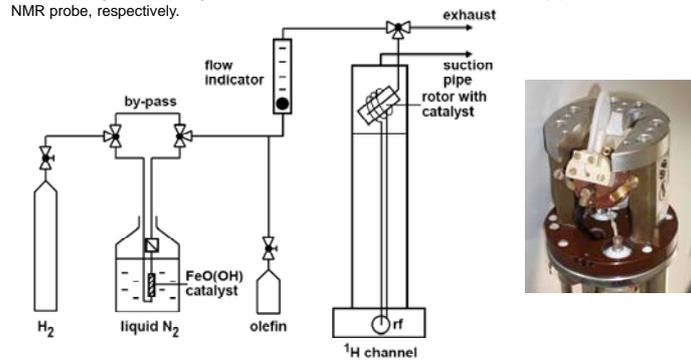


Fig. 1 Set-up for *in situ* MAS NMR experiments on the heterogeneously catalyzed hydrogenation of olefins under continuous flow (CF) conditions by normal hydrogen using the by-pass (top way) and by para-enriched hydrogen formed on the FeO(OH) catalyst in the liquid nitrogen bath (bottom way). On the right-hand side, the injection system on top of the MAS turbine is shown.

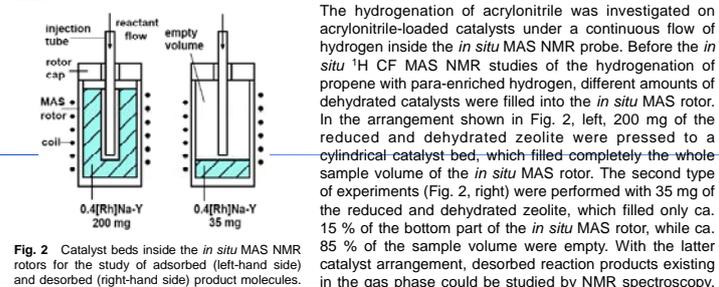


Fig. 2 Catalyst beds inside the *in situ* MAS NMR rotors for the study of adsorbed (left-hand side) and desorbed (right-hand side) product molecules.

The hydrogenation of acrylonitrile was investigated on acrylonitrile-loaded catalysts under a continuous flow of hydrogen inside the *in situ* MAS NMR probe. Before the *in situ*  $^1\text{H}$  CF MAS NMR studies of the hydrogenation of propene with para-enriched hydrogen, different amounts of dehydrated catalysts were filled into the *in situ* MAS rotor. In the arrangement shown in Fig. 2, left, 200 mg of the reduced and dehydrated zeolite were pressed to a cylindrical catalyst bed, which filled completely the whole sample volume of the *in situ* MAS rotor. The second type of experiments (Fig. 2, right) were performed with 35 mg of the reduced and dehydrated zeolite, which filled only ca. 15 % of the bottom part of the *in situ* MAS rotor, while ca. 85 % of the sample volume were empty. With the latter catalyst arrangement, desorbed reaction products existing in the gas phase could be studied by NMR spectroscopy.

## REFERENCES

- [1] M. Hunger, *Prog. Nucl. Magn. Reson. Spectroscopy* **53** (2008) 105-127
- [2] H. Henning, M. Dornbach, M. Scheibe, E. Klemm, M. Hunger, *Microporous Mesoporous Mater.* **164** (2012) 104-110.
- [3] H. Henning, M. Dyballa, M. Scheibe, E. Klemm, M. Hunger, *Chem. Phys. Lett.*, in press.

## ACKNOWLEDGEMENTS

Financial support by Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie is gratefully acknowledged. Furthermore, we thank Jens Weitkamp (Stuttgart) and Igor V. Koptuyug (Novosibirsk) for helpful discussions and experimental hints.

## RESULTS AND DISCUSSION

### Hydrogenation of acrylonitrile with normal $\text{H}_2$

In the *in situ*  $^1\text{H}$  CF MAS NMR spectra of zeolites 0.9[Pt]Na-Y and 0.4[Rh]Na-Y recorded during the hydrogenation of acrylonitrile, signals at 5.9 and 6.3 ppm due to acrylonitrile and at 1.3 and 2.5 ppm caused by the reaction product propionitrile (Scheme on the left-hand side) could be observed (Fig. 3). The complete hydrogenation of acrylonitrile over zeolites 0.9[Pt]Na-Y and 0.4[Rh]Na-Y was reached after very different reaction times,  $t$ . While this final reaction state is reached after  $t = 288$  s for the Pt-containing zeolite, a complete hydrogenation of acrylonitrile on zeolite 0.4[Rh]Na-Y was observed already after  $t = 48$  s. Furthermore, the  $^1\text{H}$  MAS NMR signals of reactants on zeolites 0.9[Pt]Na-Y and 0.4[Rh]Na-Y shown characteristic differences in their line widths (Figs. 3a and 3b). In addition, the  $^1\text{H}$  MAS NMR signals of the reaction product propionitrile are strongly broadened in the spectra of 0.9[Pt]Na-Y (Fig. 3a), while they are well-resolved in the spectra of zeolite 0.4[Rh]Na-Y (Fig. 3b). These different  $^1\text{H}$  MAS NMR properties of acrylonitrile and propionitrile on zeolites 0.9[Pt]Na-Y and 0.4[Rh]Na-Y hint to a higher mobility of the adsorbate molecules adsorbed on the latter material.  $^1\text{H}$  NMR studies of hydrogen gas injected into the empty *in situ* MAS NMR rotor gave a weak signal at 4.3 ppm.

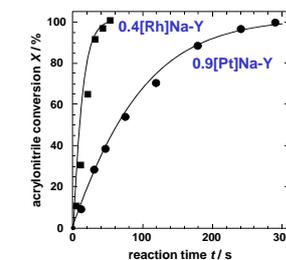


Fig. 4 Conversion of acrylonitrile over reduced zeolites 0.9[Pt]Na-Y and 0.4[Rh]Na-Y plotted as a function of the hydrogenation time under semi-batch conditions.

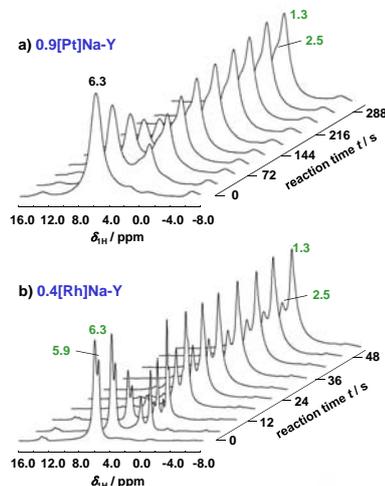


Fig. 3 Stack plot of *in situ*  $^1\text{H}$  CF MAS NMR spectra recorded during the hydrogenation of acrylonitrile over zeolites 0.9[Pt]Na-Y (a) and 0.4[Rh]Na-Y (b) at the reaction temperature of 295 K.

The quantitative evaluation of the intensity decrease of the acrylonitrile signals (Fig. 4) gave an apparent reaction velocity for the hydrogenation over zeolite 0.4[Rh]Na-Y ( $7.0 \times 10^{-3}$  mmol/s) been more than a factor six higher in comparison with that observed for zeolite 0.9[Pt]Na-Y ( $1.1 \times 10^{-3}$  mmol/s). During the initial period of the acrylonitrile hydrogenation on zeolite 0.4[Rh]Na-Y ( $t = 12$  to 24 s), weak and temporary  $^1\text{H}$  MAS NMR signals occurred, which might be due to half-hydrogenated intermediates with short lifetime (weak signals at 1.1, 1.9, and 2.9 ppm) [2].

### Hydrogenation of propene with para-enriched $\text{H}_2$

Initial *in situ* CF MAS NMR experiments of the hydrogenation of olefins with parahydrogen were performed with MAS rotors completely filled with the noble metal-containing zeolite Y (200 mg), i.e. according to the arrangement in Fig. 2, left. In Fig. 5, the *in situ*  $^1\text{H}$  CF MAS NMR spectra recorded during hydrogenation of propene on zeolite 0.4[Rh]Na-Y using normal hydrogen (a) and para-enriched hydrogen (b) as reactant are shown. According to the  $^1\text{H}$  NMR shift values of the reactants summarized in the Scheme on the left-hand side, the weak signals at 5.0 and 5.8 ppm are due to the  $\text{CH}_2$  and CH groups of propene, respectively. The  $\text{CH}_3$  group of propene is responsible for the weak shoulder at 1.8 ppm. The reaction product propane causes  $\text{CH}_3$  and  $\text{CH}_2$  signals at 1.0 and 1.4 ppm, respectively. The difference spectrum of the above-mentioned spectra (Fig. 5c) consists of two weak antiphase signals at 1.0 and 1.4 ppm assigned to  $\text{H}^{\text{b}}$  and  $\text{H}^{\text{a}}$  atoms in the  $\text{CH}_3$  and  $\text{CH}_2$  groups, respectively, of propane. The appearance of these signals indicates a pairwise incorporation of the hydrogen atoms of the parahydrogen into the propene molecules.

### 0.4[Rh]Na-Y (200 mg) + propene

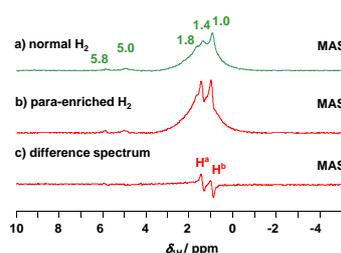


Fig. 5 *In situ*  $^1\text{H}$  CF MAS NMR spectra recorded during continuous hydrogenation of propene on zeolite 0.4[Rh]Na-Y (200 mg according to Fig. 2, left) at 295 K and using normal (a) and para-enriched hydrogen (b). The spectrum (c) is the difference spectrum of (b) and (a).

The line shapes of the propane signals at 1.0 and 1.4 ppm in the  $^1\text{H}$  MAS NMR spectra in Figs. 5a and 5b occur as an overlap of broad and narrow signals at same resonance positions. Upon decreasing the amount of catalyst inside the *in situ* MAS rotor, the  $^1\text{H}$  CF MAS NMR spectra shown in Fig. 6 were recorded. After switching the reactant flow to para-enriched hydrogen, the narrow signals at 1.0 and 1.4 ppm are enhanced and show an antiphase shape. These antiphase signals, which are more pronounced in the difference spectrum in Fig. 6c, indicate the presence of pairwise incorporated  $\text{H}^{\text{b}}$  and  $\text{H}^{\text{a}}$  atoms (see Scheme on left-hand side) in mobile and, therefore, desorbed propane molecules in the gas phase inside the partially empty MAS NMR rotor. This finding indicates that the hyperpolarization of the pairwise incorporated  $\text{H}^{\text{b}}$  and  $\text{H}^{\text{a}}$  atoms is involved in a rapidly relaxation and, therefore, intensity decrease for propane molecules, which are adsorbed in cages and pores of zeolite 0.4[Rh]Na-Y. Rapid desorption of the hyperpolarized reaction products from zeolite 0.4[Rh]Na-Y particles improves their detection.

### 0.4[Rh]Na-Y (35 mg) + propene

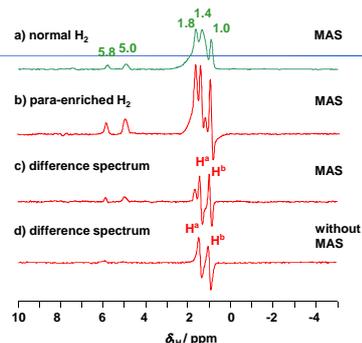


Fig. 6 *In situ*  $^1\text{H}$  CF MAS NMR spectra recorded during the continuous hydrogenation of propene on zeolite 0.4[Rh]Na-Y (35 mg according to Fig. 2, right) at 295 K and using normal (a) and para-enriched hydrogen (b). The spectrum (c) is the difference spectrum of (b) and (a). The spectrum (d) is the difference spectrum of two spectra recorded during continuous hydrogenation using normal and para-enriched hydrogen as before, but without application of MAS.