In situ solid-state NMR studies of heterogeneously catalyzed reactions under semi-batch conditions

Spectroscopic background: The heterogeneously catalyzed hydrogenation of hydrocarbons on metal catalysts plays an important role in petrochemistry and refining, such as for the elimination of alkynes in gas streams of alkenes, the purification of feedstocks for polymerization reactions from polyenes, which are poisoning the polymerization catalysts, or the selective conversion of double- and triple-bond-containing organic compounds with and without functional groups into desired industrial products [1-4]. With the development and introduction of *in situ* flow MAS NMR probes (see Topic 3 of link "In Situ Solid-State NMR Techniques" and Refs. [5] and [6]), solid-state NMR studies of heterogeneously catalyzed reactions under semi-batch conditions were possible. Generally, a **reaction under semi-batch** conditions is a variation of a reaction under batch condition, where one reactant (reactant 1 in Scheme 1) is continuously added to another reactant (reactant 2 in Scheme 1) contained in the reactor right from the start. In the case of an *in situ* semi-batch solid-state NMR experiment, a flow MAS NMR probe is utilized to continuously inject a gaseous reactant into an MAS rotor filled with the activated catalyst, which was loaded with a second non-volatile reactant before starting the experiment.



Scheme 1

In the subsequently described experiment (Fig. 1), the hydrogenation (hydrogen is reactant 1) of acrylonitrile (reactant 2) on noble metal-containing catalysts was studied under semi-batch conditions. This method allows the exclusion of an effect

of reactant diffusion and catalyst deactivation on the experimentally observed reaction rates since the reactant acrylonitrile was already adsorbed inside the catalyst pores at the beginning of the *in situ* semi-batch solid-state NMR experiment, i.e. before starting the hydrogen flow.



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In situ ¹H MAS NMR spectroscopy of the hydrogenation of acrylonitrile under semibatch conditions was performed for investigating the intrinsic hydrogenation activity of homologous series of noble metal-containing solid catalysts with different porosities [7, 8]. For this purpose, three siliceous supports, i.e. silica ($\phi_{pore} = 4.5$ nm), mesoporous SBA-15 ($\phi_{pore} = 3.4$ nm), and dealuminated zeolite DeA-Y ($\phi_{pore} = 0.7$ nm), with similar noble metal loadings were studied. For comparison, also a noble metal-containing aluminum-rich zeolite H,Na-Y ($n_{Si}/n_{AI} = 2.7$) was utilized as support material. Before the *in situ* ¹H semi-batch MAS NMR experiments, the reduced and non-hydrated catalysts were loaded with amounts of acrylonitrile according to **column 2 of Table 1** [8]. Subsequently, the acrylonitrile-loaded samples were transferred without air contact into an MAS rotor, in a glove box, purged with dry nitrogen, and put into an *in situ* flow MAS NMR probe. The hydrogenation was observed after starting the hydrogen flow at the temperature of $T = 298 \pm 1$ K as a function of time.

The kinetics of the acrylonitrile hydrogenation was determined via the timedependent change of the ¹H MAS NMR signals of the CH₂ ($\delta_{1H} = 6.1 \pm 0.2$ ppm) and CH groups ($\delta_{1H} = 5.7 \pm 0.2$ ppm) of acrylonitrile and the CH₃ ($\delta_{1H} = 1.0 \pm 0.3$ ppm) and CH₂ groups ($\delta_{1H} = 2.2 \pm 0.2$ ppm) of the reaction product propionitrile (see **Fig. 1**). As an example, **Fig. 2** shows the stack plot of *in situ* ¹H MAS NMR spectra recorded during the hydrogenation of acrylonitrile on 0.9Pt/silica up to the reaction time of 84 s [8]. For determining the velocity rate constants *k* of the acrylonitrile hydrogenation, the time-dependent intensities *I*(*t*) of the ¹H MAS NMR signals of acrylonitrile were evaluated by a quantitative simulation of the spectra. Subsequently, the negative logarithms of the intensities *I*(*t*), related to the intensity *I*₀ of the ¹H MAS NMR signals of acrylonitrile before starting the hydrogen flow, were plotted as a function of the reaction time *t*. **Fig. 3** shows the plots of the $-\ln(I(t)/I_0)$ values as a function of the reaction time for the acrylonitrile hydrogenation on 0.9Pt/silica, 0.9Pt/SBA-15, 0.9Pt/DeA-Y, and 0.9Pt/H,Na-Y under semi-batch conditions [8].



Fig. 2



Fig. 3

The obtained *k* values, determined by the slope of a linear regression (least-squares fit), passing through the coordinate origin, are summarized in **column 3 of Table 1**,

catalyst	acrylonitrile ^a (mmol)	$k (s^{-1})$	$r \pmod{s^{-1}}$
0.9Pt/silica	0.023	$(3.3 \pm 0.3) \times 10^{-2}$	$(7.6 \pm 1.1) \times 10^{-4}$
0.9Pt/SBA-15	0.018	$(1.8 \pm 0.2) \times 10^{-2}$	$(3.2 \pm 0.5) \times 10^{-4}$
0.9Pt/DeA-Y	0.018	$(3.8 \pm 0.4) \times 10^{-2}$	$(6.8 \pm 0.9) \times 10^{-4}$
0.9Pt/H,Na-Y ^b	0.021	$(1.1 \pm 0.1) \times 10^{-2}$	$(2.3 \pm 0.3) \times 10^{-4}$
0.3Rh/silica	0.022	$(2.4 \pm 0.2) \times 10^{-2}$	$(5.3 \pm 0.7) \times 10^{-4}$
0.3Rh/SBA-15	0.020	$(4.6 \pm 0.5) \times 10^{-2}$	$(9.1 \pm 1.3) \times 10^{-4}$
0.4Rh/DeA-Y	0.020	$(1.2 \pm 0.1) \times 10^{-1}$	$(24 \pm 4) \times 10^{-4}$
0.4Rh/H,Na-Y ^b	0.020	$(3.4 \pm 0.3) \times 10^{-2}$	$(6.8 \pm 1.0) \times 10^{-4}$
0.8Ir/H,Na-Y ^b	0.017	$(6.7 \pm 0.7) \times 10^{-4}$	$(0.11 \pm 0.02) \times 10^{-4}$
0.4Pd/H,Na-Y ^b	0.027	1.1 ± 0.3	$(270 \pm 50) \times 10^{-4}$

a) determined by ¹H MAS NMR; *b*) data taken from Ref. [7]

Table 1

With the same procedure, also the *in situ* ¹H MAS NMR spectra recorded during the hydrogenation of acrylonitrile on the Rh-, Ir-, and Pd-containing catalysts were evaluated. Using the acrylonitrile loadings given in **column 2 of Table 1**, the reaction rates *r* summarized in **column 4** were calculated. The reaction rates of all Pt- and Rh-containing siliceous catalysts are in the range of $r = 3 \times 10^{-4}$ to 8×10^{-4} mmol s⁻¹ and $r = 5 \times 10^{-4}$ to 24×10^{-4} mmol s⁻¹, respectively. These values do not depend on the different pore sizes of their support materials in a systematic manner. Comparing the reaction rates *k* for zeolites DeA-Y ($n_{Si}/n_{AI} = 93$) and H,Na-Y ($n_{Si}/n_{AI} = 2.7$) with same pore size, allways the support material with the higher aluminum content (H,Na-Y) shows a lower intrinsic hydrogenation rate. The most significant differences in the reaction rates *k* were found for Ir- and Pd-containing zeolites H,Na-Y, showing very low and very high hydrogenation rates, respectively, in comparison to the abovementioned Pt- and Rh-containing catalysts (last two lines of **Table 1**), which indicate the specific hydrogenation properties of these two metal compounds (Ir and Pd).

Catalyst preparation: The noble metal-loaded catalysts were activated in synthetic air (750 mL/min) by heating with a rate of 2 K/min up to T = 573 K, at this temperature for 3 h, and sealed in gas-tight bottles. Before the hydrogenation experiments, these samples were reduced in flowing hydrogen (100 mL/min) at T =

623 K for 2 h, transferred without air contact into a "sample tube system 1" inside a mini glove box (see Sections "sample tube system 1" and "mini glove box", both accessible via link "*In Situ* Solid-State NMR Techniques"), purged with dry nitrogen gas, and, subsequently, evacuated ($p < 10^{-2}$ Pa) at T = 298 K for 12 h.

Before an *in situ* experiment, 50 ± 5 mg of the sample material was transferred into a 4 mm MAS rotor without air contact in a mini glove box, purged with dry nitrogen gas. This reduced and non-hydrated catalyst was loaded with acrylonitrile (natural abundance) at "vacuum line 2" (see "vacuum line 2", accessible via link "*In Situ* Solid-State NMR Technique"). For this purpose, the 4mm MAS rotor with the catalyst was put into a "sample tube system 1". For the removal of surplus acrylonitrile, the catalyst sample was evacuated at T = 298 K for 10 min. Subsequently, the rotor with the acrylonitrile loading was determined by ¹H MAS NMR. For further details, see Refs. [7] and [8].

In situ solid-state NMR studies: The *in situ* ¹H semi-batch MAS NMR spectra in Fig. 2 were recorded using a 4 mm Bruker MAS NMR probe, modified as described in Section "flow probe 2", accessible via link "*In Situ* Solid-State NMR Technique". Inside a mini glove box, purged with dry nitrogen, the common MAS rotor cap was replaced by a cap with a hole (see Section "flow probe 2"). After the insertion of the MAS rotor into the probe, the glass tube used for the injection of the hydrogen gas was inserted into the rotor via the hole in the cap. After starting the sample spinning and stabilization of the temperature at *T* = 298 K, the hydrogen injection into the rotor was started with a flow rate of 300 mL/min. The ¹H MAS NMR spectra were recorded at a Bruker Avance III 400WB spectrometer with a resonance frequency of v_0 = 400.13 MHz, a sample spinning rate of v_{rot} = 4 kHz, and in a single-scan mode with a repetition time of 10 s. The signal intensities were determined by comparing with an external intensity standard (dehydrated zeolite 35H,Na-Y) after the *in situ* experiments and by simulating the spectra using the Bruker software WinFit [7, 8].

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