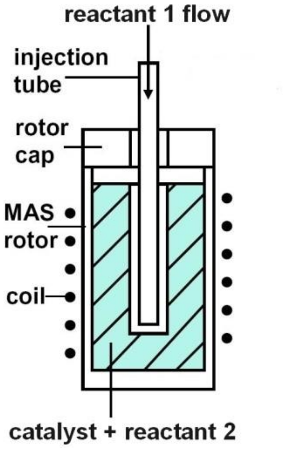
In situ solid-state NMR studies of heterogeneously catalyzed reactions under semi-batch conditions

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 Refs. [5] and [6] and Topic "3" of the link "*In Situ* Solid-State NMR Techniques"), semi-batch experiments by utilizing solid-state NMR spectroscopy became 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 inject continuously a gaseous reactant into an MAS rotor filled with the activated catalyst, which is was loaded with a second non-volatile reactant before starting the experiment.



Scheme 1

In the following example, the **hydrogenation (hydrogen is reactant 1) of preloaded acrylonitrile (reactant 2)** on noble metal-containing catalysts was studied under semi-batch conditions (**Fig. 1**). This method allows the **exclusion of an effect of reactant diffusion and catalyst deactivation on the experimentally observed**

reaction rates since the reactant acrylonitrile is 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.

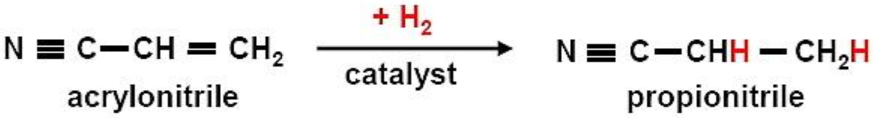


Fig. 1

In situ ^{1}H MAS NMR spectroscopy of the hydrogenation of acrylonitrile under semi-batch 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 (ϕ_{pore} = 4.5 nm), mesoporous SBA-15 (ϕ_{pore} = 3.4 nm), and dealuminated zeolite DeA-Y (ϕ_{pore} = 0.7 nm), with similar noble metal loadings were studied. For comparison, also a noble metal-containing aluminum-rich zeolite H,Na-Y ($n_{\text{Si}}/n_{\text{Al}}$ = 2.7) was utilized as support material. Before the *in situ* ^{1}H semi-batch MAS NMR experiments, the reduced and non-hydrated catalysts were loaded with acrylonitrile according to column 2 of Table 1 [8]. Subsequently, the acrylonitrile-loaded samples were transferred without contact to air into the MAS rotor and the NMR probe. The hydrogenation was observed after starting the hydrogen flow at the temperature of T = 298 ± 1 K as a function of time.

The kinetics of the acrylonitrile hydrogenation was determined via the time-dependent change of the ^{1}H MAS NMR signals of the CH_2 ($\delta_{1\text{H}}$ = 6.1 ± 0.2 ppm) and CH groups ($\delta_{1\text{H}}$ = 5.7± 0.2 ppm) of acrylonitrile and the CH_3 ($\delta_{1\text{H}}$ = 1.0 ± 0.3 ppm) and CH_2 groups ($\delta_{1\text{H}}$ = 2.2 ± 0.2 ppm) of the reaction product propionitrile (see **Fig. 1**). As an example, **Fig. 2** shows the stack plot of *in situ* ^{1}H 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 ^{1}H MAS NMR signals of acrylonitrile were evaluated by a quantitative simulation of the recorded spectra. Subsequently, the negative logarithms of the intensities $I(t)$, related to the intensity I_0 of the ^{1}H 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].

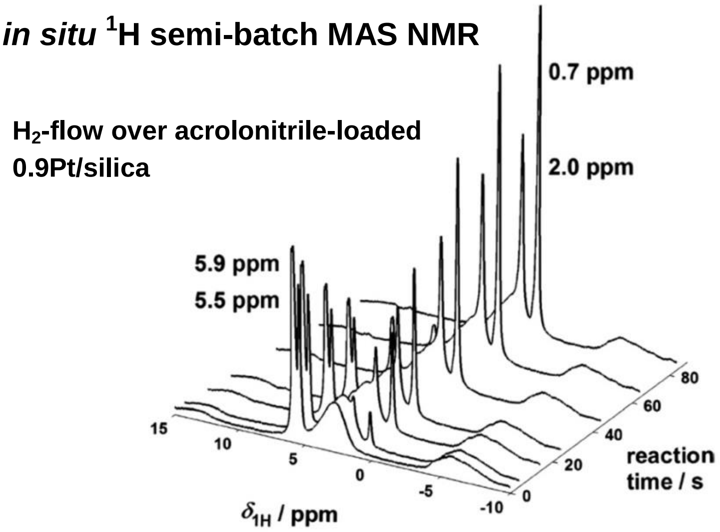


Fig. 2

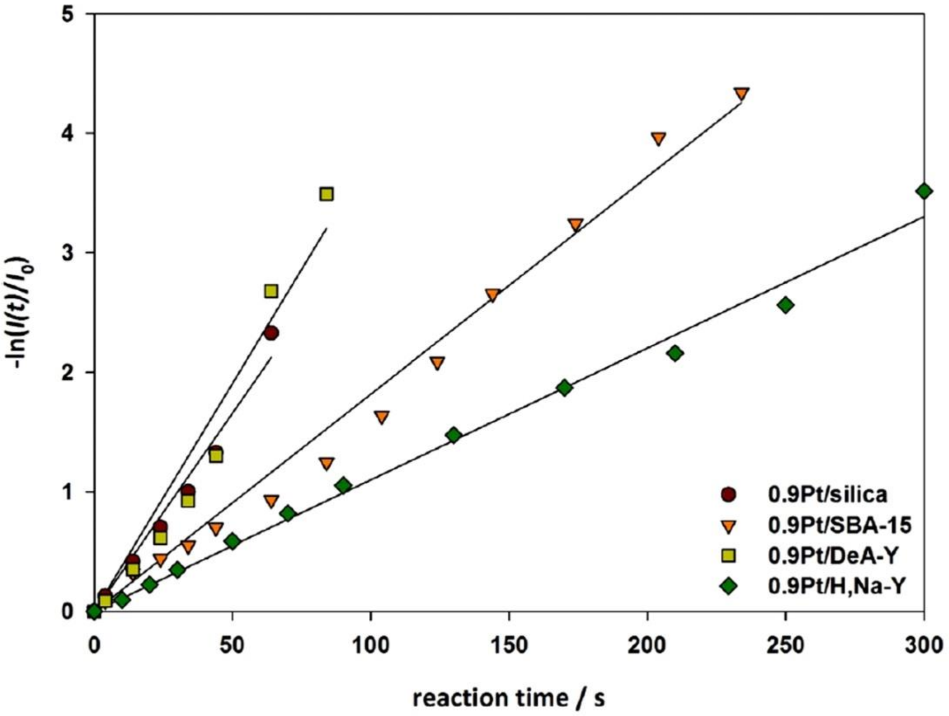
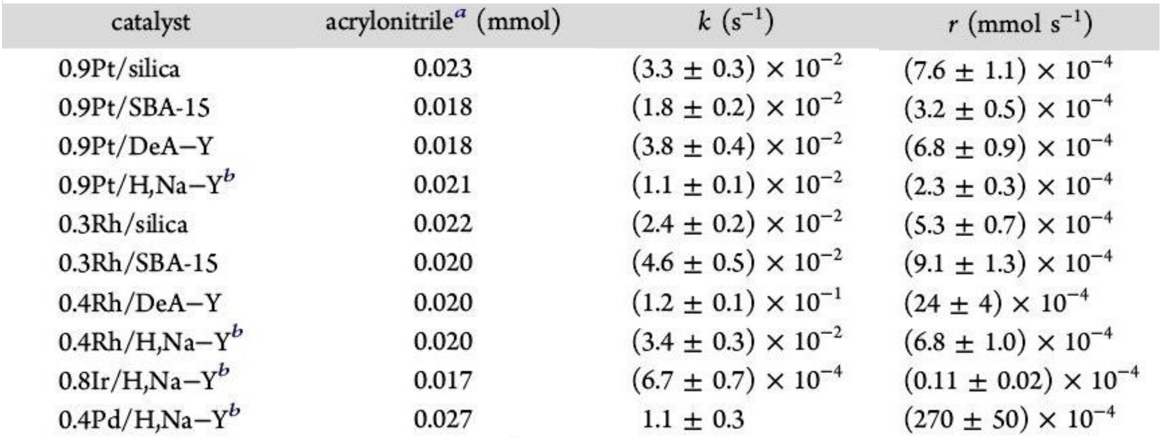


Fig. 3

The obtained *k* values, determined by the slope of a linear regression (least-squares fitted) passing through the coordinate origin, are summarized in column 3 of **Table 1**, lines 2 to 5. With the same procedure, also the *in situ* ^{1}H 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



catalyst	acrylonitrile[a] (mmol)	k (s^{-1})	r ($mmol\ s^{-1}$)
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 ^{1}H MAS NMR; *b*) data taken from Ref. [7]

Table 1

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 indicate that the intrinsic hydrogenation rates of 0.9 wt.-% Pt or 0.3 to 0.4 wt.-% Rh on silica, SBA-15, and zeolite DeA-Y are almost independent of the different pore sizes of their support materials. Furthermore, also the zeolites DeA-Y (n_{Si}/n_{Al} = 93) and H,Na-Y (n_{Si}/n_{Al} = 2.7) with same pore size and 0.9 wt.-% Pt or 0.4 wt.-% Rh show intrinsic hydrogenation rates in a narrow range of $r = 2 \times 10^{-4}$ to 7×10^{-4} mmol s^{-1} and $r = 7 \times 10^{-4}$ to 24×10^{-4} mmol s^{-1}, respectively. Hence, also the effect of the different aluminum contents (n_{Si}/n_{Al} ratios) of these microporous catalysts on their hydrogenation activity was found to be weak.

Catalyst preparation: The noble metal-loaded catalysts were calcined 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 glass tubes inside a glove box purged with dry nitrogen gas (see Section “mini glove box” via link “*In Situ* Solid-State NMR Techniques”), and subsequently evacuated ($p < 10^{-2}$ Pa) at T = 298 K for 12 h. The transfer of the sample material into the 4 mm MAS rotors was performed in a glove box purged with dry nitrogen gas (*vide supra*). For further details, see Refs. [7] and [8].

In situ solid-state NMR studies: The *in situ* ^{1}H 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”.

Before the *in situ* experiments, 50 ± 5 mg of the reduced and non-hydrated catalysts, filled into a 4 mm Bruker MAS NMR rotor, were loaded with acrylonitrile (natural abundance) at a vacuum line (see “vacuum line 2”, accessible via link “*In Situ* Solid-State NMR Technique”). To remove physisorbed acrylonitrile, the samples were evacuated at T = 298 K for 10 min. Subsequently, the rotors containing the acrylonitrile-loaded catalysts were sealed with a common gas-tight cap to measure the acrylonitrile loadings. The amounts of the adsorbed acrylonitrile were determined by ^{1}H MAS NMR spectroscopy using $\pi/2$ single-pulse excitation and a repetition time of 20 s.

After insertion of the MAS rotor into the probe, the glass tube for the injection of the hydrogen was inserted into the rotor via the hole in the cap and under purging with dry nitrogen. After starting the sample spinning and the stabilization of the temperature at T = 298 K, the first single-scan ^{1}H MAS NMR spectrum was recorded at the resonance frequency of ν_0 = 400.13 MHz and 4 s after starting the hydrogen injection with a flow rate of 300 mL/min into the rotor. The sample spinning rate was ν_{rot} = 4 kHz, while single-scan spectra were recorded every 10 s. The signal intensities were evaluated 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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