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

Spectroscopic background: The investigation of reaction mechanisms is an important task in the research field of heterogeneous catalysis. Due to the duration of *in situ* solid-state NMR experiments, this method is not suitable for studies of transition states of reactions. However, *in situ* solid-state NMR allows the observation of stable intermediates on the catalyst surface, which are not possible to detect in their desorbed state, e.g., by gas chromatography or mass spectrometry. Therefore, *in situ* solid-state NMR is a helpful tool for clarifying reaction mechanisms in heterogeneous catalysis. *In situ* solid-state NMR under batch conditions is able to observe the results of the conversion of reactants loaded on activated catalysts to intermediates or reaction products, but not to study the steady state of a reaction (compare with *in situ* solid-state NMR under flow conditions).

In situ solid-state NMR experiments under batch conditions are performed with sealed samples of activated solid catalysts loaded with reactants (see Fig. 1 and Section "sample tube system 4", accessible via link "*In Situ* Solid-State NMR Techniques").



Fig. 1

In the most cases, the conversion of the adsorbed reactants is started by heating the catalyst samples in an external oven. Another approach is the heating of the sealed samples inside a high-temperature MAS NMR probe, followed by a NMR measurement at room temperature. Often, both experimental procedures are named *in situ*. With these experimental procedures, the **reactants have an infinite contact time** with the active surface sites of the catalyst.

The most often utilized isotopes of reactants investigated by *in situ* solid-state NMR are ¹³C nuclei (spin I = 1/2, relative sensitivity of 1.7 x 10⁻⁴, see Section "method 4")

and ¹⁵N nuclei (spin *I* = 1/2, relative sensitivity of 3.8 x 10⁻⁶, see Section "method 5"). ¹H nuclei are mainly used for studies of H/D exchange reactions. Batch experiments have the advantage that **only few amounts of very expensive** ¹³C- and ¹⁵N**enriched reactants are necessary**. Therefore, a broad variety of reactants and their reaction mechanisms on solid catalysts are available for *in situ* solid-state NMR under batch conditions. By this method, the catalyst samples are sealed in **gas-tight MAS rotors** or in symmetrical **glass ampoules**, which fit into MAS rotors (see Section "sample tube system 4", accessible via link "In situ Solid-State NMR Techniques"). Another possibility is the application of a special reactant adsorption apparatus, such as the **CAVERN equipment** (see Section "sample tube system 5 (CAVERN system)", accessible via link "*In situ* Solid-State NMR Techniques" and Ref. [1]), which allows the direct preparation of catalyst samples in gas-tight MAS rotors. Further experimental details of the *in situ* solid-state NMR spectroscopy under batch conditions are described in Refs. [2] to [6].

In chemical industry, ε -caprolactam is an important reactant for the production of Polyamid 6 (Perlon). To replace the conventional method for synthesizing ε -caprolactam in concentrated sulfuric acid or oleum, the vapor-phase **Beckmann** rearrangement of cyclohexanone oxime to ε -caprolactam on solid catalysts is interesting as an environmentally benign process. It was found that high-silica zeolites, such as the silicalite-1 (structure type MFI), are suitable catalysts for this reaction. First industrial applications [7, 8] required deeper understanding of the mechanism of the vapor-phase Beckmann rearrangement of cyclohexanone oxime on zeolite catalysts and the effect of additives, such as methanol [9-12].

Utilizing ¹⁵N-cyclohexanone oxime and ¹³C-enriched methanol, *in situ* solid-state NMR studies of the above-mentioned reaction on MFI-type zeolites and mesoporous SBA-15 materials were performed [11, 12]. **Scheme 1** gives an overview on the suggested reaction mechanism as well as experimentally observed (without parenthesis [11, 12]) and calculated (in parenthesis [13]) ¹⁵N chemical shifts [11]. In **Fig. 2**, ¹⁵N CPMAS NMR spectra, and in **Fig. 3**, ¹³C CPMAS NMR spectra, recorded upon conversion of pure and mixtures ¹⁵N-cyclohexanone oxime and methanol on silicalite-1, are shown [12].

The first steps of the Beckmann rearrangement of cyclohexanone oxime on zeolites are the adsorption of the reactants via hydrogen bonding at SiOH groups in silicalite-1 (**A**) or the N-protonation of the reactant by hydroxyl groups in zeolites H-ZSM-5 and https://michael-hunger.de



Scheme 1

H-[B]ZSM-5 (**B**). On strong acid sites, a 1,2-H shift leading to O-protonated cyclohexanone oxime **C** is followed by the formation of carbenium ions **D** as intermediates. A more stable state of this intermediate is the nitrilium ion **E**. The calculated ¹⁵N chemical shift of $\delta_{15N} = -224$ ppm for this intermediate indicates that species **E** may be responsible for ¹⁵N NMR signals at $\delta_{15N} = -237$ ppm. The further conversion of species **E**, which should be accompanied with a decrease of the signal at $\delta_{15N} = -237$ ppm, leads to the formation of non-protonated and protonated ε -caprolactam (**F** and **G**, respectively) causing ¹⁵N NMR signals at $\delta_{15N} = -260$ ppm and $\delta_{15N} = -347$ ppm, respectively [12].

In the ¹⁵N CPMAS NMR spectrum of cyclohexanone oxime on silicalite-1, recorded upon heating at T = 393 K, signals of pure cyclohexanone oxime at $\delta_{15N} =$ -55 ppm and of species **A** at $\delta_{15N} = -46$ ppm occur (**Fig. 2a**), also in the presence of methanol (**Fig. 2d**). Upon heating at T = 523 K for 20 and 60 min (**Figs. 2b and 2c**, respectively), ¹⁵N CPMAS NMR signals at $\delta_{15N} = -260$ ppm, -269 ppm, and -387ppm indicate the formation of ε -caprolactam **F**, hydroxylamine, and amines, respectively. A small peak in the chemical shift range of $\delta_{15N} = -237$ to -243 ppm has been attributed to nitrilium ions E or to O-protonated ε-caprolactam F [11, 13].



The ¹³C CPMAS NMR spectra recorded in the presence of ¹³C-methanol and upon heating at T = 523 K for 20 and 60 min (**Figs. 3e and 3f**, respectively [12]) indicate a lower catalyst reactivity. This could be due to the coverage of silanol groups by methanol and a partial conversion of methanol into surface methoxy groups.

The ¹³C CPMAS NMR spectra of the additive ¹³C-methanol in **Figs. 3a to 3c** [12] were recorded under identical conditions like used for the spectra in Figs. 2d to 2f. This spectra consist of signals at $\delta_{13C} = 49$ ppm (**Fig. 3a**), due to pure ¹³C-methanol, and at $\delta_{13C} = 25$ ppm, 28 ppm, and 42 ppm (**Figs. 3b and 3c**), indicating the conversion of methanol to hydrocarbons (e.g. isobutane) and alkylamines (e.g. isopropylamine). Isopropylamine ($\delta_{13C} = 42$ ppm) may be formed via the reaction of isobutane with hydroxylamine, which is formed as a by-product of the Beckmann rearrangement. No formation of amines with methanol as an additive was observed by *in situ* solid-state NMR, which is a positive aspect for an industrial application of this reaction.

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Fig. 3

The *in situ* batch solid-state NMR technique using glass inserts for MAS rotors is utilized in a broad manner for the investigation of the mechanisms of heterogeneously catalyzed reactions. Refs. [4] to [6], [14], and [15] give a survey on the most important studies in this research field.

A significantly other experimental technique, than the glass ampoule method, is utilized for investigations of the synthesis and crystallization of solid materials by *in situ* NMR spectroscopy. For these applications, no preparation of samples at a vacuum line is required, but the MAS NMR technique must be suitable for studies under high-pressure (HP) and high-temperature (HT) conditions. Often, the MAS NMR technique utilized for these applications is based on MAS rotors with sealing screws and O-rings at the top. In some cases, the MAS rotors have a cylindrical pencil shape with a conical bottom containing notches for the driving gas (spin tip). Refs. [16] and [17] give a survey on different HPHT MAS NMR techniques and introduce in characteristic applications.

Catalyst preparation: Before the *in situ* solid-state NMR measurements, the catalyst samples were dehydrated inside a "sample tube system 1" at "vacuum line 1", both accessible via link "*In Situ* Solid-State NMR Techniques". The dehydration starts with an evacuation at room temperature for ca. 10 minutes followed by a temperature https://michael-hunger.de

ramp from room temperature to T = 393 K within 2 hours. At this temperature, the sample was dehydrated for 2 hours. Subsequently, the temperature was increased up to T = 723 K within 3 hours and the sample was evacuated at this temperature for 12 hours. After this treatment, the sample tube system was closed via the vacuum valve and disconnected from the vacuum line (after this line was ventilated with air). Mixtures of ¹⁵N-cyclohexanone oxime and dehydrated silicalite-1 were prepared as follows. First, 20 mg of ¹⁵N-cyclohexanone oxime was evacuated at room temperature and mixed with ca. 300 mg of dehydrated zeolite in a mini glove box (see Section "mini glove box", accessible via link "In Situ Solid-State NMR Techniques"), purged with dry nitrogen gas. Subsequently, the catalyst loaded with ¹⁵N-cyclohexanone oxime was filled into an MAS NMR glass ampoule (see Section "sample tube system 4", accessible via link "In Situ Solid-State NMR Techniques"), evacuated at room temperature at "vacuum line 2" (see Section "vacuum line 2", accessible via link "In Situ Solid-State NMR Techniques"), and, finally, sealed. In the case of studying reactant mixtures, commercial ¹³C-methanol was adsorbed on the catalyst loaded with ¹⁵N-cyclohexanone oxime inside the "sample tube system 4"

at a partial pressure of p = 70 mbar using "vacuum line 2". Finally, the sample inside the MAS NMR glass ampoule was sealed and this ampoule was inserted into the MAS rotor. Heating of the sealed catalyst samples was performed in an external oven.

In situ solid-state NMR studies: The ¹⁵N and ¹³C CPMAS NMR spectra of the catalyst loaded with reactants were recorded at a Bruker MSL 400WB spectrometer at resonance frequencies of $v_0 = 40.53$ MHz and 100.58 MHz, respectively, and using a 7 mm Bruker MAS NMR probe with sample spinning rates of $v_{rot} = 3.5$ to 4.7 kHz. The CPMAS NMR spectra were obtained with a contact time of $\tau = 5$ ms and a recycle delay of 2 s. The ¹⁵N and ¹³C CPMAS NMR spectra were referenced to nitromethane ($\delta_{15N} = 0.0$ ppm) and tetramethylsilane ($\delta_{13C} = 0.0$ ppm), respectively.

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