

***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 the transition state of reactions. However, *in situ* solid-state NMR allows to 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 an one-time 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).

Generally, ***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”).

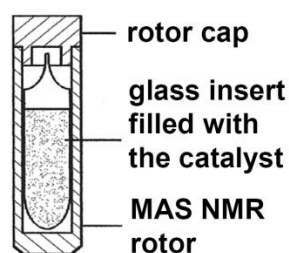


Fig. 1

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 solid catalyst.

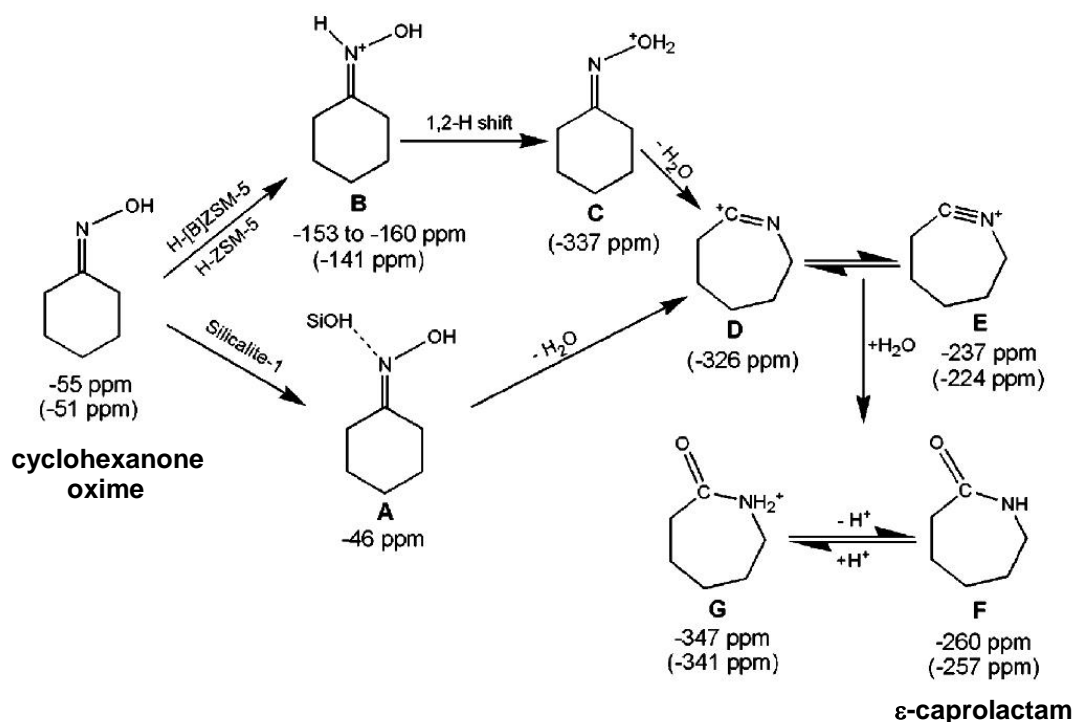
The most often utilized isotopes of reactants investigated by *in situ* solid-state NMR are ^{13}C nuclei (spin $I = 1/2$, relative sensitivity of 1.7×10^{-4}) and ^{15}N nuclei (spin $I =$

1/2, relative sensitivity of 3.8×10^{-6}). ^1H nuclei are mainly used for studies of H/D exchange reactions. Batch experiments have the advantage that **only few amounts of very expensive ^{13}C - and ^{15}N -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 in MAS rotors (see Section “sample tube system 4” via link “*In situ* Solid-State NMR Techniques”). Another possibility is the application of a special loading apparatus, such as a **CAVERN equipment** (see Section “sample tube system 5 (CAVERN system)” via link “*In situ* Solid-State NMR Techniques” and Ref. [1]), which allows the direct preparation of catalyst samples in gas-tight MAS rotors. For reviews on *in situ* solid-state NMR under batch conditions, see Refs. [2-6].

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** 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 ^{15}N -cyclohexanone oxime and commercial ^{13}C -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]) ^{15}N chemical shifts [11]. In **Fig. 2**, ^{15}N CPMAS NMR spectra, and in **Fig. 3**, ^{13}C CPMAS NMR spectra recorded upon conversion of pure and mixtures ^{15}N -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 H-[B]ZSM-5 (**B**). On strong acid sites, a 1,2-H shift leading to



Scheme 1

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 ^{15}N chemical shift of $\delta_{15\text{N}} = -224$ ppm for this intermediate indicates that species **E** may be responsible for ^{15}N NMR signals at $\delta_{15\text{N}} = -237$ ppm. The further conversion of species **E**, which should be accompanied with a decrease of the signal at $\delta_{15\text{N}} = -237$ ppm, leads to the formation of non-protonated and protonated ϵ -caprolactam (**F** and **G**, respectively) causing ^{15}N NMR signals at $\delta_{15\text{N}} = -260$ ppm and $\delta_{15\text{N}} = -347$ ppm, respectively..

In the ^{15}N CPMAS NMR spectrum of cyclohexanone oxime on silicalite-1, recorded upon heating at $T = 393$ K, signals of pure cyclohexanone oxime at $\delta_{15\text{N}} = -55$ ppm and of species **A** at $\delta_{15\text{N}} = -46$ 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), ^{15}N CPMAS NMR signals at $\delta_{15\text{N}} = -260$ ppm, -269 ppm, and -387 ppm indicate the formation of ϵ -caprolactam (**F**), hydroxylamine, and amines, respectively. A small peak in the chemical shift range of $\delta_{15\text{N}} = -237$ to -243 ppm has been attributed to nitrilium ions (**E**) or to O-protonated ϵ -caprolactam [11, 13].

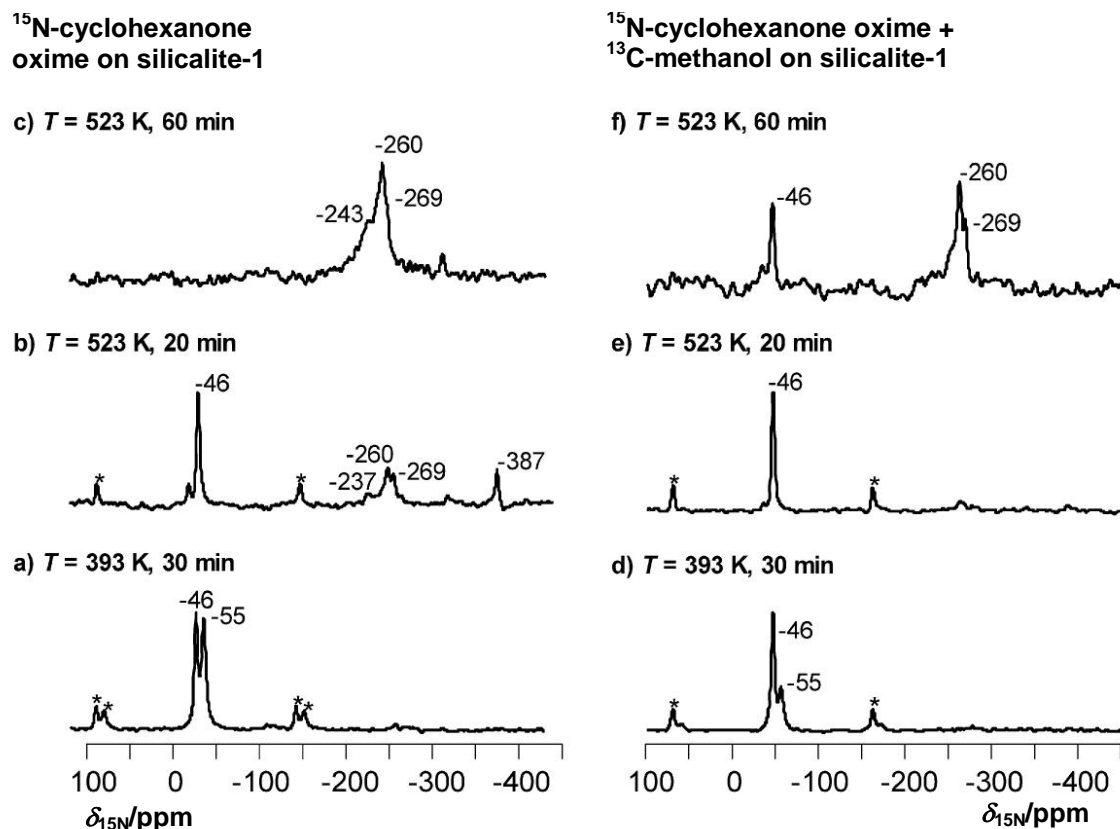
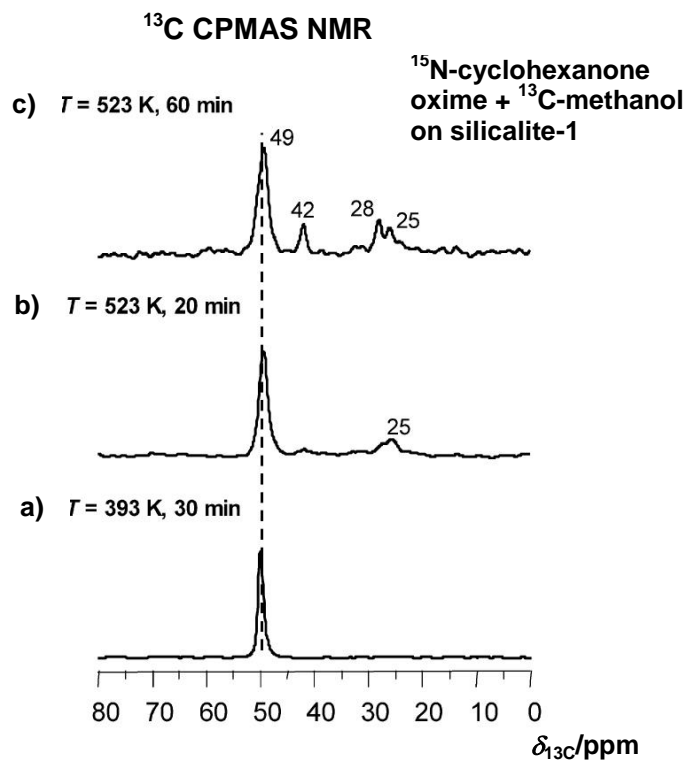
¹⁵N CPMAS NMR

Fig. 2

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) 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. Due to the presence of methanol as an additive, O-protonated ϵ -caprolactam ($\delta_{15\text{N}} = -237$ to -243 ppm) and the amines ($\delta_{15\text{N}} = -387$ ppm) are not observed. This observation indicates that the enhanced selectivity to ϵ -caprolactam in the vapor-phase Beckmann rearrangement of cyclohexanone oxime is caused by a decrease in the energy barrier for the product desorption step. No side reactions leading to the formation of amines occurred with methanol as an additive, which is a positive aspect for industrial application of this reaction.

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 $\delta_{13\text{C}} = 49$ ppm (**Fig. 3a**), due to pure ¹³C-methanol, and at $\delta_{13\text{C}} = 25$ 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 ($\delta_{^{13}\text{C}} = 42\text{ ppm}$) may be formed via the reaction of isobutane with hydroxylamine, which is formed as a by-product of the Beckmann rearrangement.

Catalyst preparation: Before the *in situ* solid-state NMR measurements, the catalyst samples were dehydrated inside a „sample tube system 1“ at the „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 ramp from room temperature to $T = 393\text{ K}$ within 2 hours. At this temperature, the sample is dehydrated for 2 hours. Subsequently, the temperature is increased up to $T = 723\text{ K}$ within 3 hours and evacuated at this temperature for 12 hours. After this treatment, the sample tube system is closed via the vacuum valve and disconnected from „vacuum line 1“ after this line was ventilated with air. Mixtures of ^{15}N -cyclohexanone oxime and dehydrated silicalite-1 were prepared as follows. First, 20 mg of ^{15}N -cyclohexanone oxime was evacuated at room temperature and mixed with ca. 300 mg of dehydrated zeolite in a mini glove box purged with dry nitrogen gas (see Section “mini glove box”, accessible via link [“In Situ Solid-State NMR Techniques”](#)). In the case of studying reactant mixtures, the commercial ^{13}C -<https://michael-hunger.de>

methanol was adsorbed on the catalyst loaded with ^{15}N -cyclohexanone oxime at a partial pressure of $p = 70$ mbar using “vacuum line 2”. Finally, the samples were sealed in glass ampoules and inserted into the MAS rotor (see Section “sample tube system 4”, accessible via link “*In Situ* Solid-State NMR Techniques”). The heating of the sealed catalyst samples was performed in an external oven.

In situ solid-state NMR studies: *In situ* ^{15}N and ^{13}C CPMAS NMR spectra of the reaction mixtures were recorded using a 7 mm Bruker MAS NMR probe at resonance frequencies of $\nu_0 = 40.53$ MHz and 100.58 MHz, respectively, and with sample spinning rates of $\nu_{\text{rot}} = 3.5$ to 4.7 kHz. The CPMAS NMR spectra were obtained with a contact period of $\tau = 5$ ms and a recycle delay of 2 s. ^{15}N and ^{13}C CPMAS NMR spectra were referenced to nitromethane ($\delta_{^{15}\text{N}} = 0.0$ ppm) and tetramethylsilane ($\delta_{^{13}\text{C}} = 0.0$ ppm), respectively.

References:

- [1] J.F. Haw, B.R. Richardson, I.S. Oshiro, N.D. Lazo, J.A. Speed, *Reactions of propene on zeolite HY catalyst studied by in situ variable temperature solid-state nuclear magnetic resonance spectroscopy*, J. Am. Chem. Soc. 111 (1989) 2052-2058, DOI: 10.1021/ja00188a016.
- [2] E.G. Derouane, H. He, S.B. Derouane-Abd Hamid, I.I. Ivanova, *In situ MAS NMR investigations of molecular sieves and zeolite-catalyzed reactions*, Catal. Lett. 58 (1999) 1–19, DOI: 10.1023/A:1019044926400.
- [3] M. Hunger, J. Weitkamp, *In situ Magnetic Resonance Techniques: Nuclear Magnetic Resonance*, in: B.M. Weckhuysen (ed.), *In situ Spectroscopy of Catalysts*, American Scientific Publishers, Stevenson Ranch, California, 2004, ISBN: 978-1-4020-9678-5, p. 177-218.
- [4] A.G. Stepanov, V.N. Parmon, D. Freude, *In situ NMR spectroscopy in heterogeneous catalysis: Kinetic study of hydrocarbon conversion mechanisms*, Kinetics and Catalysis 48 (2007) 521-534, DOI: 10.1134/S0023158407040088:
- [5] I.I. Ivanova, Y.G. Kolyagin, *Impact of in situ MAS NMR techniques to the understanding of the mechanisms of zeolite catalyzed reactions*, Chem. Soc. Rev. 39 (2010) 5018-5050; DOI: 10.1039/c0cs00011f.
- [6] A. Stepanov, *Results of NMR spectroscopic studies of hydrocarbon conversions on solid acid catalysts in the last 25 years*, Kinetics and Catalysis 51 (2010) 854-872, DOI: 10.1134/S0023158410060121.

- [7] H. Ichihashi, M. Ishida, A. Shiga, M. Kitamura, T. Suzuki, K. Suenobu, K. Sugita, *The catalysis of vapor-phase Beckmann rearrangement for the production of ϵ -caprolactam*, *Catal. Surv. Asia* 7 (2003) 261-270, DOI: 10.1023/B:CATS.0000008165.80991.05.
- [8] Y. Izumi, H. Ichihashi, Y. Shimazu, M. Kitamura, H. Sato, *Development and industrialization of the vapor-phase Beckmann rearrangement process*, *Bull. Chem. Soc. Jpn.* 80 (2007) 1280-1287, DOI: 10.1246/bcsj.80.1280.
- [9] A.B. Fernández, M. Boronat, T. Blasco, A. Corma, *Establishing a molecular mechanism for the Beckmann rearrangement of oximes over microporous molecular sieves*, *Angew. Chem. Int. Ed.* 44 (2005) 2370-2373, DOI: 10.1002/anie.200462737.
- [10] V.R. Reddy Marthala, Y. Jiang, J. Huang, W. Wang, R. Glaser, M. Hunger, *Beckmann rearrangement of ^{15}N -cyclohexanone oxime on zeolites silicalite-1, H-ZSM-5, and H-[B]ZSM-5 studied by solid-state NMR spectroscopy*, *J. Am. Chem. Soc.* 128 (2006) 14812-14813, DOI: 10.1021/ja066392c.
- [11] A.B. Fernández, I. Lezcano-Gonzalez, M. Boronat, T. Blasco, A. Corma, *NMR spectroscopy and theoretical calculations demonstrate the nature and location of active sites for the Beckmann rearrangement reaction in microporous materials*, *J. Catal.* 249 (2007) 116-119, DOI: 10.1016/j.jcat.2007.03.030.
- [12] V.R. Reddy Marthala, S. Rabl, J. Huang, B. Thomas, M. Hunger, *In situ solid-state NMR investigations of the vapor-phase Beckmann rearrangement of ^{15}N -cyclohexanone oxime on MFI-type zeolites and mesoporous SBA-15 materials in the absence and presence of the additive ^{13}C -methanol*, *J. Catal.* 257 (2008) 134-141, DOI: 10.1016/j.jcat.2008.04.014.
- [13] NNMR Predictor & dB 9.0, Advanced Chemistry Development, Inc.: Toronto, Ontario, Canada.