A New MAS NMR Probe for *in situ* Investigations of Hydrocarbon Conversion on Solid Catalysts Under Continuous-flow Conditions

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The design and first application of a MAS NMR probe that allows the injection of gaseous educt compounds into the MAS rotor during NMR experiments is described.

Conversions of hydrocarbons on solid catalysts are arguably the most important reactions in petrochemistry. In a number of investigations NMR spectroscopy was applied to study adsorption and conversion of hydrocarbons inside the zeolite pores and cavities.[1] In all of these studies, samples sealed in glass ampoules or in airtight MAS rotors were applied. However, investigations of the equilibrium state of heterogeneously catalysed reactions require continuous-flow conditions. In this paper a new solid-state MAS NMR probe is described that allows the continuous flow of gaseous educt compounds through the solid catalyst in the MAS rotor during the NMR experiment.

Fig. 1 shows the *in situ* MAS NMR probe built on the basis of a commercial Bruker double-bearing 7 mm MAS probe. A glass tube (1.8 mm o.d. and 0.8 mm i.d.) is placed in the axis of the MAS NMR rotor through an axial hole (diameter of 2.5 mm) in the rotor cap [Fig. 1(*a*)]. The rotor ejection block on top of the MAS turbine is replaced by a support which fixes the injection tube [Fig. 1(*b*)]. A saturator is used to load the carrier gas with educt compounds. The flow rate of the carrier gas is adjusted by a capillary flow controller or a rotameter. The saturator is cooled to T = 285 K, whereas the tube connecting the saturator to the NMR probe is at room temp. The carrier gas and educt compounds are injected into the MAS rotor *via* the injection tube. The gas stream flows inside the rotor from the bottom to the rotor cap [Fig. 1(*a*)] and leaves the MAS rotor through the axial hole in the rotor cap. Prior to the NMR experiments, 300 mg of dehydrated catalyst powder were filled into the MAS rotor under dry nitrogen gas in a glove box. For *in situ* dehydration a respective amount of hydrated catalyst is used. With a special hollowborer an axial hole of 2.5 mm diameter is carefully bored into the powder material. This forms a cylindrical catalyst bed at the inner rotor wall [Fig. 1(*a*)]. Before transferring the rotor from the glove box to the MAS NMR probe the hole in the rotor cap is closed by a plug. This plug is removed after inserting the rotor into the MAS NMR turbine. During the careful insertion of the injection tube into the MAS rotor, rehydration of the calcined catalyst is prevented by a stream of dry nitrogen gas (8 ml s^{-1}). The spinning rotor and catalyst are heated by the bearing gas. The carrier gas and educt compounds are preheated by a heat-exchanger which consists of a spiral of stainless steel tube with 0.2 mm inner diameter and 420 mm length. The heat-exchanger is placed in the upper part of the MAS NMR probe which is covered by a glass bell.

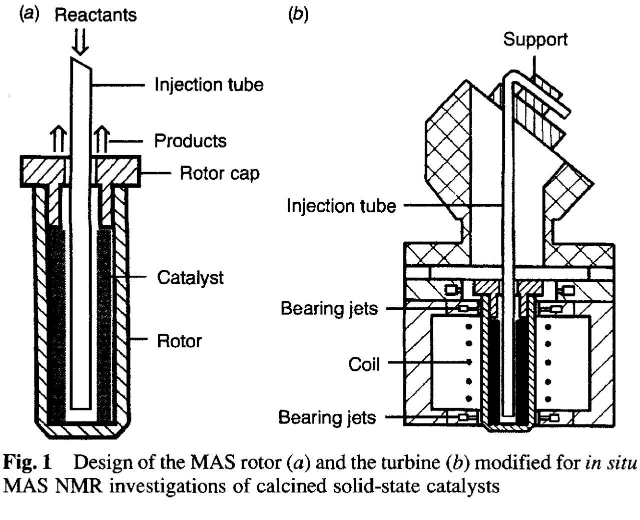

Fig. 1 Design of the MAS rotor (*a*) and the turbine (*b*) modified for *in situ* MAS NMR investigations of calcined solid-state catalysts

Using the above-described NMR probe *in situ* MAS NMR investigations at normal pressure and up to T = 423 K and the MAS rate of 3 kHz were carried out. Dry nitrogen was used as bearing and driving gas for MAS. The temperature inside the MAS rotor was calibrated using the ^{207}Pb MAS NMR shift of $Pb(NO_3)_2$ as an internal thermometer.[2] The temperature gradient, ΔT, over the whole sample room inside the MAS rotor was determined by the line broadening of the ^{207}Pb MAS NMR signal to maximum ΔT = 6 K at T = 423 K.

In situ MAS NMR sorption experiments of ammonia on H-form zeolites were carried out to study the homogeneous diffusion of guest molecules through the whole sample. As known from previous solid-state NMR investigations,[3,4] reammoniation of dehydrated zeolite HY leads to the formation of ammonium ions with a ^{1}H MAS NMR signal at *ca.* δ 7. To investigate the reammoniation of dehydrated zeolite HY under continuous-flow conditions a commercial zeolite Y (Union Carbide, NY) with a framework n_{Si}/n_{Al} ratio of 2.6 was used with a Na^+/NH_4^+ exchange degree of 88%. The calcination of this sample was performed for 12 h under vacuum at 673 K. For the reammoniation an ammonia stream with a modified residence time of W/F_{NH_3} = 75 g h mol^{-1} was injected into the MAS rotor, *i.e.* 300 mg dehydrated zeolite HY and an ammonia flow of 4 mmol h^{-1} were used. After 20 min the centre of gravity of the ^{1}H MAS NMR signal was shifted to *ca.* δ 7, which indicates the reammoniation of all accessible bridging OH groups.[3,4] The immediate decrease of the ^{1}H MAS NMR sideband pattern of all bridging OH groups after starting the ammonia flow, caused by an increase in the mobility of all Brønsted sites,[4,5] and the low-field shift of the whole central line to δ 7 indicates a homogeneous interaction of the ammonia molecules with all acidic hydroxy protons under continuous-flow conditions.

The dehydration of propan-2-ol is a well established reaction to characterize the Brønsted acidity of solid-state catalysts such as zeolite Y.[6–8] Therefore, this reaction was chosen for first *in situ* MAS NMR investigations of heterogeneous catalysis under continuous-flow conditions. 60% Lanthanum-exchanged zeolite LaNaY dehydrated for 12 h under vacuum at 523 K was used. The ^{1}H MAS NMR spectrum at the top of Fig. 2 shows an intense ^{1}H MAS NMR sideband pattern of zeolite OH groups marked by asterisks. At t = 0 a continuous flow of propan-2-ol with a modified residence time of $W/F_{2\text{-}p}$ = 450 g h mol^{-1} was led through the sample. After a propan-2-ol stream of 20 min, signals appear at δ 1.8, 4.5 and 8.5. Whereas the first two signals were assigned to Me and CH groups,[9] respectively, of propan-2-ol, the signal at δ 8.5 originates from the hydroxy protons or water[4,5] formed by propan-2-ol dehydration. At $t \geqslant 40$ min additional signals at δ 1.5, 2.0 and 3.0 appear which were assigned to methyl groups of different products and alkoxy species,[9] low-field shifted in result of adsorption in the zeolite cavities. The ^{1}H MAS NMR signals of CH and $=CH_2$ groups of these products overlap with the broad signal of reaction water shifted to *ca.* δ 6. However, by a decomposition of the methyl signals of propan-2-ol, propene and diisopropyl ether by computer simulation of the ^{1}H MAS NMR spectra permits the

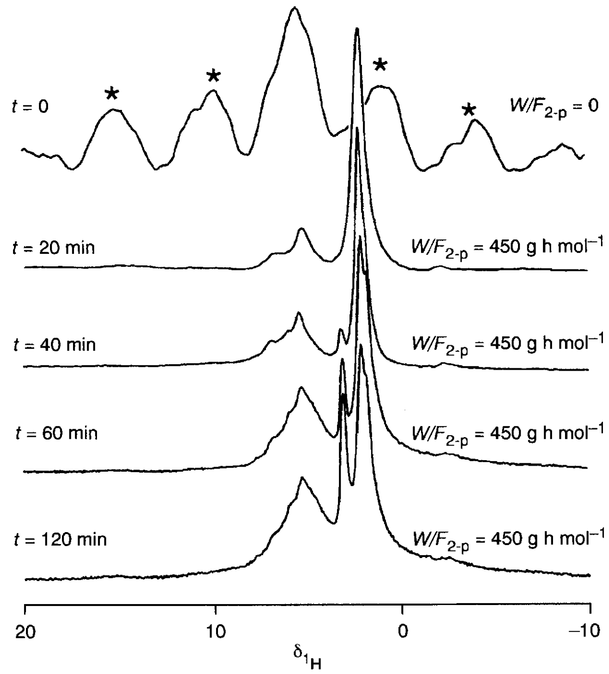

Fig. 2 ^{1}H MAS NMR spectra of dehydrated zeolite LaNaY recorded at the resonance frequency of 400.13 MHz, with the MAS rate of 3 kHz and at T = 403 K. The spectrum at the top shows the signals of the unloaded samples (* = MAS sidebands). Starting at the time t = 0 a propan-2-ol stream with a modified residence time of $W/F_{2\text{-p}}$ = 450 g h mol^{-1} was injected into the MAS rotor. The amplitudes of the spectra are not scaled.

quantitative determination of the relative concentrations of these reactants as a function of time on stream. For $t \leqslant 40$ min more diisopropyl ether than propene was found in the zeolite cavities, whereas for $t \geqslant 40$ min propene is the dominant reaction product.

In situ ^{13}C MAS NMR investigations of alcohol dehydration under continuous-flow conditions were carried out using propan-2-ol without isotopic ^{13}C enrichment. Fig. 3 shows the ^{13}C MAS NMR spectra (4000 scans) of zeolite LaNaY under a propan-2-ol flow with a modified residence time of $W/F_{2\text{-p}}$ = 50 g h mol^{-1}. The spectrum recorded at T = 353 K consists of signals at *ca.* δ 24 and 65 [Fig. 3(*a*)] originating from propan-2-ol and diisopropyl ether.[10] In the ^{13}C MAS NMR spectrum recorded at T 403 K signals appear at δ 19 and in the shift range between δ 110 and 145 indicating the formation of propene[10] [Fig. 3(*b*)]. Additional ^{13}C MAS NMR signals observed in the shift range between δ 34 and 42 point to the formation of small amounts of branched C_6 alkanes and alkenes. After stopping the propan-2-ol stream, desorption of all organic reactants from the zeolite catalyst was observed in the ^{1}H MAS NMR spectra recorded at 403 K, while the reaction water remained in the zeolite cavities.

The present investigation has demonstrated that the *in situ* MAS NMR probe depicted in Fig. 1 is a useful piece of equipment for the study of alcohol conversion on solid catalyst under continuous-flow conditions. The combination of ^{1}H and ^{13}C MAS NMR spectroscopy allows the characterization of active centres and the distribution of educts, reaction intermediates and reaction products inside the zeolite pores and cavities as a function of time on stream.

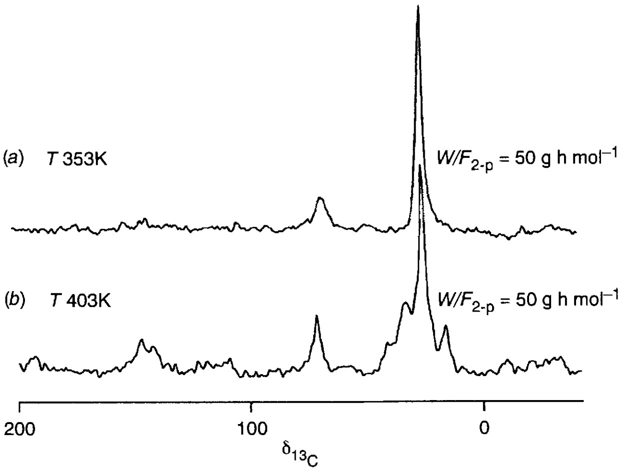

Fig. 3 ^{13}C MAS NMR spectra of dehydrated zeolite LaNaY under a propan-2-ol flow with $W/F_{2-\text{p}}$ = 50 g h mol^{-1} and recorded at a resonance frequency of 100.58 MHz, with a MAS rate of 3 kHz at T = 353 K (*a*) and T = 403 K (*b*)

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