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Direct and Indirect Observation of Coke Deposits on HZSM-5 by ^{1}H NMR Imaging

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The location of coke deposits in industrial HZSM-5 pellets contained in a fixed-bed reactor was revealed in two different ways by ^{1}H NMR imaging (MRI). In the first way, coke depositions in the reactor were detected directly by using the SPRITE technique, a special MRI sequence for detecting materials with short T_2 relaxation times. In the second, indirect way, carbonaceous residues were visualized by applying spin-echo sequences to a coked catalyst sample loaded with propane. Because the behavior of adsorbed gases depends on their interaction with the catalyst it was possible to distinguish between fresh and coked zeolitic areas within the bed. The application of MRI for coke-concentration profiling in fixed-bed reactors and catalyst pellets is discussed.

Key Words: **HZSM-5; coke; MRI; SPRITE.**

INTRODUCTION

Hydrogen-deficient carbonaceous residues are commonly responsible for catalyst deactivation during the course of organic reactions. A wide variety of spectroscopic techniques, including infrared (IR), ultraviolet–visible, electron spin resonance, and nuclear magnetic resonance (NMR), have been applied to the problem of determining the chemical structure of the coke species formed on zeolite catalysts (1, 2). The location of the coke deposits within a reactor can be considered at both macroscopic and microscopic scales. At the macroscopic level one requires information on the axial and radial distribution of carbonaceous residues (coke) throughout the fixed-bed reactor, as well as the distribution within the individual porous catalyst pellet. At the microscopic level (nanometer scale), especially for zeolite catalysts, the coke distribution within the intracrystallite pore system and on the surface of the zeolite crystallites must also be considered.

Sorption studies with quite different probe molecules (e.g., *n*-butane) indicate that where the size of the reactants allows them to enter the intracrystallites pores, coking takes place inside the zeolite crystallites (3). The PFG NMR technique with methane and propane as the adsorbed molecules revealed that the intracrystalline self-diffusion coefficient is affected only by carbonaceous deposits within the zeolitic pore system and not by external coke layers (4). In addition, the ^{129}Xe NMR technique provides evidence that coke formation occurs preferentially inside the channel system of HZSM-5 up to about 8 wt% coke (5). In addition, coke deposits inside the zeolite crystallites and on their external surface can be made visible by transmission electron microscopy (6, 7), but various complications hinder the suitability of this approach for the characterization of coke. For example, the necessity of using ultrahigh vacuum may result in migration of the coke species, and in any case such a technique does not allow the observation of carbonaceous deposits in a real zeolite bed.

Positron emission tomography (PET) using ^{11}C-labeled compounds has been applied to adsorption studies and axial concentration profiling within chemical reactors (8). In principal, PET is capable of generating *in situ* 3D images of carbonaceous deposits with a resolution of about 3 mm. However this method is relatively expensive, because a cyclotron is required to generate the short-lived isotope ^{11}C ($t_{1/2} = 20.4$ min). The use of such short-lived isotopes limits application to relatively rapid processes, whereas deactivation due to coke deposition is generally slow.

^{1}H magnetic resonance imaging (MRI) has been successfully applied to visualize internal structures and to observe dynamic processes in a wide range of nonmedical systems. The first application of MRI to zeolite research dates from 1978 (9). However, the investigation of adsorption processes in commercial zeolites was restricted to processes with relatively long time scales (hours, days). The reason was that high accumulation rates are required due to the small spin concentrations and short relaxation times of the adsorbates (10–15). Only recently have observations of adsorption and desorption processes of alkanes and water in various zeolite beds with process lifetimes shorter than 15 min (16, 17) been successfully undertaken.

Coke deposits in catalyst beds can be made visible by MRI in two different ways. In the direct way, the small

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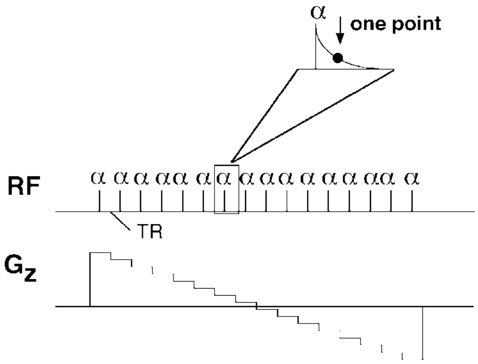

FIG. 1. One-dimensional schematic SPRITE sequence. The radio frequency pulse (RF) and the primary phase encoding gradient in z direction (G_z) are shown. The gradient is stepped with a broadband RF pulse (repetition time, TR) applied at each gradient level. Only one point of the magnetization is sampled after each small flip angle (α) excitation.

amount of hydrogen present in the coke species might be detected in an activated, dehydrated zeolite sample. However spin–spin relaxation times under 100 μs and the low-spin density of hydrogen in the carbonaceous residues are major obstacles to the direct visualization of coke species. In the indirect way, the dehydrated zeolite was preloaded with the adsorbate (e.g., hydrocarbons or water). By taking advantage of the difference in the relaxation times of the adsorbed molecules and the different adsorption affinities of the fresh and coked zeolite surfaces, the macroscopic distribution of coke within a zeolite pellet and catalyst bed have been observed (10–12). It is nevertheless true that short relaxation times severely limit the study of coke distribution by MRI.

The difficulty of using MRI for this purpose (i.e., the short spin–spin relaxation time T_2) has been substantially overcome by the development of a new imaging technique: single point ramped imaging with T_1 enhancement—SPRITE (18). SPRITE is a modified version of the SPI (single point imaging) pulse sequence technique with broadband RF excitation. This technique is a pure phase encoding technique with a stepped or ramped primary encoding gradient. Single points of the signal are collected at each gradient step, as indicated in Fig. 1. Due to the short relaxation times, in general only one acquisition point can be acquired at each gradient value. However, the application of a ramped-phase gradient with RF-pulse excitation at every gradient level permits imaging with relatively high speed, so that the acquisition time of the SPRITE method is in principle not much larger than the acquisition time of traditional spin-echo methods.

EXPERIMENTAL

The HZSM-5 catalyst (Si/Al = 80, mean crystallite size 2–5 μm, 5-mm pellets with 20 wt% γ-Al_2O_3 as binder) was supplied by KataLeuna GmbH (GER). The long time stability of the zeolite catalyst during methanol-to-gasoline conversion was studied in a pilot-scale fixed-bed reactor with gas recirculation at 693 K, feed of 0.9–2.0 $g_{methanol}/(g_{cat} \cdot h)$, and pressure of 1.0–3.0 MPa (19). After 850 h onstream the sample had converted more than 1500 $g_{methanol}/g_{cat}$. The spent sample (20.5 wt% coke) was characterized by temperature-programmed oxidation (TPO) and ^{13}C CP MAS NMR (20). For TPO, samples were heated in a Netzsch TG 209 thermobalance at 10°C/min up to 900°C in a flow of synthetic air of 10 ml/min. Solid-state ^{13}C MAS NMR measurements were carried out using a Bruker MSL 300 spectrometer. Magic-angle spinning (MAS) was performed at a 5-kHz spinning rate. The contact time in the ^{13}C CP studies was 3 ms. The FTIR measurements were performed on an IFS 66 spectrometer (Bruker, GER) equipped with a MCT detector and coupled with a praying mantis DRIFT attachment (Harrick, UK). A resolution of 2 cm^{-1} was chosen.

The imaging measurements were performed on a Nalorac (Martinez, Ca) 2.35-T horizontal bore superconducting magnet (32 cm i.d.) working at a proton frequency of 100 MHz. A water-cooled 7.5-cm-i.d. gradient set (maximum gradient, 1 T/m) was employed, driven by Techron (Elkhardt, In) 7780 amplifiers. A homebuilt RF probe was used, driven by a 2-kW AMT (Brea, Ca) 3445 amplifier. The experiments were performed with a Tecmag (Houston, Tex) Libra S-16 console at ambient temperature.

In a customized sample fresh and spent HZSM-5 pellets were arranged in such a way that in a cylinder (3 cm i.d.), two layers (each 3.3 cm thick) of coked pellets were separated by a layer (also 3.3 cm) of fresh pellets (see Fig. 2). This special sample was employed in all the MRI experiments discussed here. Due to the radial symmetry of the sample only one-dimensional axial profiles were measured. In principle, extension to two-dimensional profiles is possible.

To visualize the coke deposits directly we had to apply the SPRITE technique and to remove most of the adsorbed

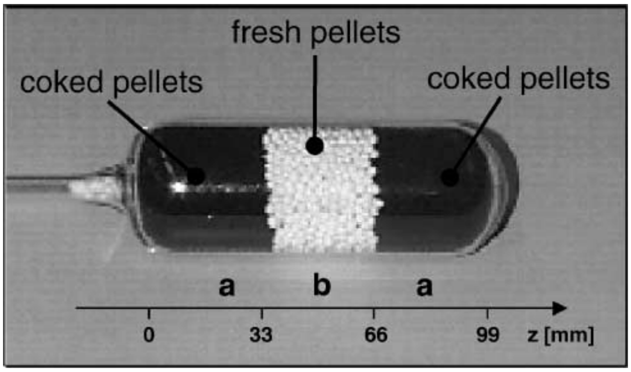

FIG. 2. Photograph of the sample used for the study. Two layers of coked HZSM-5 (areas a) were separated by a layer of fresh HZSM-5 (area b). Each layer was about 3.3 cm in length.

molecules from the sample. The dehydration of the zeolites was carried out at 400°C over 24 h with a pressure below 10 Pa. To detect the coke deposits indirectly by visualizing the different adsorption behaviors and the different relaxation times in the sample we loaded the dehydrated sample with a fixed amount of propane (2 molecules per channel intersection) as an adsorbate. Propane instead of water was used as tracer compound, because the possibility cannot be excluded that the penetration of water into each coke-reduced zeolitic pore may be hindered due to the hydrophilic character of water. Spin-echo MRI methods were possible in this case because T_2 for propane in the zeolite was significantly larger than T_2 for the unloaded coke deposits in the sample.

RESULTS AND DISCUSSION

To meet practical demands for characterization techniques to optimize the shape and size of catalyst pellets, ^{1}H NMR imaging was applied to samples of spent industrial catalysts. As pointed out the low-spin density of hydrogen in carbonaceous residues hinders their direct visualization. In order to demonstrate the potential of the SPRITE technique we used coked HZSM-5, deactivated under industrial conditions.

With regard to infrared spectroscopy studies of coke formation the regions between 1300 and 1700 cm^{-1} are suitable. IR measurements of spent HZSM-5 pellets showed broad bands near 1580 cm^{-1}. These bands are commonly assigned to the C–C stretchings of highly condensed species, whereas bands between 1500 and 1540 cm^{-1} have been assigned to alkylnaphthalenes. The C–H bending modes of paraffinic species yield bands at 1360–1390 cm^{-1} and 1420–1490 cm^{-1} (1). The IR spectrum of the spent HZSM-5 sample (Fig. 3) reveals the highly unsaturated nature of the coke species. Compared to the intense bands at 1585 cm^{-1}, the signals at 1375 cm^{-1} and 1440–1470 cm^{-1} are weak. The low hydrogen content of carbonaceous residues (H/C ratio of 0.5) has been confirmed by elemental analysis. Therefore, it was expected that this sample would not be usable for conventional MRI measurements but would prove suitable as a test sample for SPRITE methods.

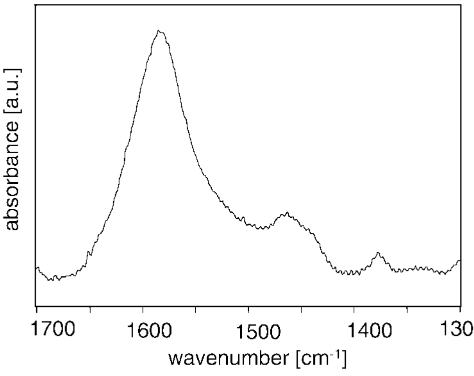

FIG. 3. IR spectrum of coke on HZSM-5 (20 wt%, H/C ratio = 0.5). The intense band at 1585 cm^{-1} and the weak signals at 1375 and 1455 cm^{-1} indicate the high content of carbon and the low content of hydrogen, thus revealing the highly unsaturated nature of the coked species.

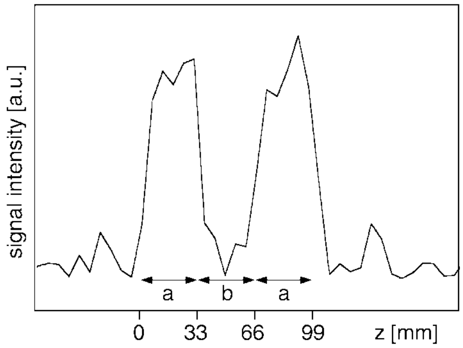

FIG. 4. One-dimensional SPRITE profile for the dehydrated HZSM-5 sample shown in Fig. 2. Encoding time, 50 μs; repetition time, 1.2 ms; FOV, 36 cm. Some 5000 accumulations were carried out in 15 min. The a areas indicate the spin concentration of hydrogen at the dehydrated, coked zeolites; the b area shows the low hydrogen spin density of the dehydrated, fresh HZSM-5 zeolites. The profile reflects clearly the coke distribution of the sample.

To visualize the coke deposits directly it was necessary to apply the SPRITE technique, because T_2 for the dehydrated H-ZSM5 sample with fresh and coked arrays inside was only 65 μs. By using a short encoding time of 50 μs and a repetition time of 1.2 ms, a 1D SPRITE profile of the coke distribution of the sample was obtained in 15 min (Fig. 4). The spatial resolution of the image obtained with a field of view (FOV) of 33 cm was only 0.5 cm. This relatively coarse spatial resolution was determined by the minimal, and short-lived, signal of the sample. Since the sample was dehydrated at 400°C over 24 h with a pressure below 10 Pa, most adsorbed molecules should have been removed from the sample. The signal corresponding to the small residual concentration of adsorbed molecules remaining in the zeolite can be seen in the center of Fig. 4, which is equivalent to the uncoked part of the sample. The larger amount of the signal related to the coked regions, shown right and left of the center in our profile, were caused by the hydrogen-containing compounds forming the coke. In order to visualize this tiny signal, the background signal of the probe head had to be subtracted. Nevertheless, in future, it seems possible that with specially made MRI probe heads, and by using newer special SPRITE sequences, the direct observation of coke will become easier and the spatial resolution will be improved. In addition the acquisition time could be further reduced by using newer developments in SPRITE technique (multipoint acquisition, centric k-space sampling (21)). Therefore, the SPRITE technique seems to be a powerful tool for studying coke distributions in catalyst beds.

If the zeolites are dehydrated and loaded with different gases, the MRI profiles will reflect the adsorption behavior of the loaded gases. Compared to the large NMR signal caused by the adsorbed molecules, the tiny NMR signal of the coke deposits will be negligible. For further experiments we loaded the dehydrated sample at room temperature with propane until equilibrium (2 molecules of propane per channel intersection). Figure 5 shows a 1D profile of the propane-loaded sample obtained in 16 s and detected by a $\pi/2$–π spin echo sequence with an observation time of 1.1 ms, an encoding time of 0.8 ms, a repetition time of 0.5 s, and a FOV of 36 cm.

Figure 5 suggests that the fresh zeolite adsorbs a larger amount of propane than the coked pellets of the sample. Spin-echo sequences are, however, sensitive to the spin–spin relaxation time T_2. Due to the different adsorption strengths of propane on fresh and coked HZSM-5, T_2 varies over the sample and the different regions of the zeolite bed can be distinguished. Because the SPRITE technique is not so sensitive to T_2 variations, SPRITE images of the propane-loaded sample showed that the spin density is in fact uniform over the sample.

By choosing different values of parameters for the sequences and/or using different spin-echo sequences, it is possible to suppress the NMR signals of different regions inside the sample, depending on the coke content of these regions. Spin-lattice relaxation time (T_1) measurements showed that T_1 of propane in the coked part of this sample was equal to 21 ms, in comparison to 65 ms in the fresh part. By using an inversion-recovery π–τ–$\pi/2$–π spin-echo sequence we were able to show the effect of suppressing the different coked parts of the sample (Fig. 6). The signal from the coked parts of the sample could be suppressed at a value of $\tau = 15$ ms for the characteristic time constant. In contrast, at $\tau = 45$ ms, the respective signal of the fresh part of the sample could be suppressed, too.

In a typical catalyst bed an irregular distribution of coke deposits will exist within the bed and this will lead to a distribution of relaxation times for the adsorbed molecules. Under these conditions it is difficult to suppress the fresh or coked regions of the sample only by applying a simple inversion recovery experiment. Other complications can also appear if more then one compound is adsorbed on the zeolite, because the relaxation times of the different compounds may overlap each other. Nevertheless, by using T_1-mapping SPRITE and spin-echo sequences, it is still possible to locate the coke deposits.

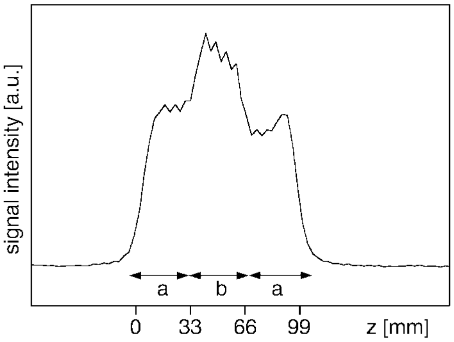

FIG. 5. One-dimensional spin-echo profile of the propane-loaded HZSM-5 sample. Observation time, 1.1 ms; encoding time, 0.8 ms; repetition time, 0.5 s; FOV, 36 cm. Some 32 accumulations were carried out in 16 s. The profile reflects the different adsorption behavior of propane in the different coked arrays of the sample. The a areas show the spin concentration of propane at the coked zeolites; the b area indicates the higher spin density of propane at the fresh HZSM-5 zeolites.

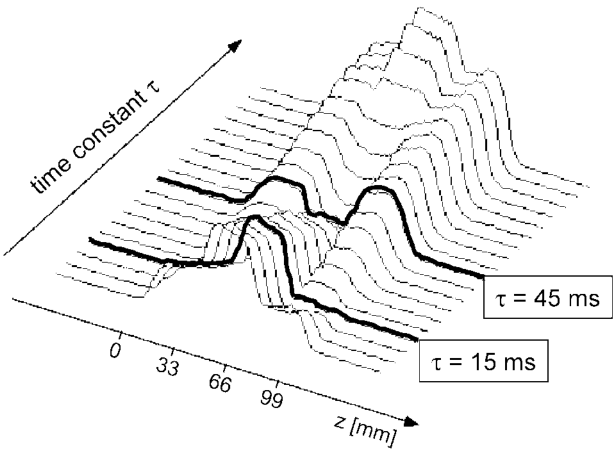

FIG. 6. One-dimensional inversion recovery π–τ–$\pi/2$–π spin-echo profiles of the propane-loaded HZSM-5 sample measured under conditions similar to those of the experiments shown in Fig. 5 for different values of the characteristic time constant τ. The FOV was 20 cm. At values of $\tau = 15$ ms the signal of the coked section and at $\tau = 45$ ms the signal of the fresh sample region could be suppressed.

The spatial resolution of the images obtained is an important argument for the assessment of MRI as a method for studying coke formations in catalyst beds. We used a SPRITE sequence with a spatial resolution of 0.5 cm (Fig. 4) and spin-echo sequences with spatial resolutions of 0.34 (Fig. 5) and 0.14 cm (Fig. 6). It seems that high resolution is possible if spin-echo sequences are used. For single pellets, with lengths of about 1 cm, a spatial resolution of 0.15 mm was recently achieved (16). Thus, ^{1}H NMR imaging enables nondestructive axial and radial concentration profiling at both the macro- and micrometer scale. Furthermore, due to the spectrometric background it is possible to trace different signals, e.g., aliphatic or aromatic hydrogen. From the industrial point of view, the potential of MRI using the SPRITE technique can be applied to optimize the effectiveness factor of different shapes of catalyst pellets.

CONCLUSIONS

^{1}H NMR imaging is a powerful tool for visualization of the macroscopic distribution of coke in fixed-bed reactors. The direct NMR location of carbonaceous residues was realized by the SPRITE technique. Furthermore, it is possible to distinguish between fresh and coked areas by the different behavior of adsorbed hydrocarbons on the zeolites surface. Using the SPRITE technique the time needed to obtain MRI profiles and images seems to be short enough to allow the effects of catalyst shape and size on the effectiveness factor, coke formation, and other dynamic processes to be studied in industrial pelleted catalysts.

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