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^{1}H NMR relaxation and diffusion studies of cyclohexane and cyclopentane confined in MCM-41

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Abstract

The rotational and translational dynamics of cyclohexane and cyclopentane confined in a MCM-41 solid have been studied as a function of temperature by measuring the T_1 and T_2 relaxation times and diffusivities, and the results are compared with values obtained for the bulk substances. Filling degrees of 60%, 80% and 104% were used when investigating the confined samples. The T_1 behaviour is remarkably similar for confined cyclohexane and cyclopentane although we compare compounds exhibiting different bulk phases at corresponding temperatures. T_1 and T_2 increase clearly with increasing pore filling, presumable as a result of a reduced contribution from surface relaxation. The self-diffusion rate of confined cyclopentane, however, decreases markedly with increasing pore filling in contrast to the situation for cyclohexane. In the former case, however, the diffusion experiment detects the diffusivity of all the liquid in the pores, while in the latter case only the diffusivity of the surface layer is monitored below the depressed melting point. The thickness of the surface layer inside the pores is approximately one molecular layer for both adsorbates, i.e., 0.65 and 0.52 nm for cyclohexane and cyclopentane, respectively.

Keywords: MCM-41; Cyclohexane; Cyclopentane; Dynamic NMR; Self-diffusion; Relaxation

1. Introduction

About 12 years ago scientists at the Mobil Research and Development Corporation learned how mesoporous materials with controlled and uniform pore sizes and large surface areas could be tailor-made, the so-called M41S materials [1,2]. These materials possess either a one-dimensional hexagonal pore structure (MCM-41), a three-dimensional cubic pore structure (MCM-48) or an unstable lamellar structure (MCM-50). The preparation technique requires an expertise within hydrothermal synthesis and surfactant chemistry. The pore size of these materials is in the range 1.5–10 nm, and the size of the crystallites varies, in the way of synthesis, from less than 1 μm to over 10 μm. The uniform mesoporous materials, unlike the microporous zeolites, have amorphous pore walls and the relatively large pore dimensions allow processing of considerably larger molecules, both with respect to catalysis and adsorption. Depending on the desired catalytic approach or application as adsorbents, the pore surface can be modified by various post-synthesis treatments.

The selectivity and activity of porous materials used in catalytic processes can depend critically on the diffusion properties. The widely used uptake and membrane techniques are sensitive to macroscopic transport processes of organic probe molecules [3], while NMR has become an increasingly important method for investigating microscopic motions [4]. The spin–lattice (T_1) and spin–spin (T_2) relaxation times are very sensitive to changes in the molecular mobility and environment. By

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applying the pulsed field gradient (PFG) NMR technique, direct information on microscopic transport phenomena can be obtained. By using a bipolar variation of the PFG sequence [5], the deteriorating effect of internal field gradients can be largely eliminated. A feature of the PFG technique is that it measures diffusion over distances of the order of a few micrometers [6]. If this is less than the size of the crystallites only intracrystalline self-diffusion is observed without complications from boundary or interparticle effects [6]. In practice, however, it is very often difficult to prepare mesoporous crystallites of sufficiently large size (~10 μm).

After having mainly used non-crystalline mesoporous materials in our previous dynamic NMR work [7–11], we now want to employ mesoporous materials of the M41S family in our investigations. Synthesis of MCM-48 only produced crystallites of approximately 1 μm in size, far too small for our intended investigations. However, preparation of MCM-41 under acidic conditions led to crystal sizes in the excess of 10 μm. The mesoporous MCM-41 solids are ideal model systems for fundamental adsorption studies due to their regular and well-defined pore geometry.

In the last decade, several workers have used cryogenic NMR to study the freezing/melting behaviour of water [12–17] and some organic compounds [15,18–20] confined in mesoporous MCM-41 solids and related materials. The gained information was in most cases used to determine the depressed freezing/melting points and the pore size distributions in the investigated porous materials. In three recent papers [21–23], the diffusion behaviour of *n*-hexane confined in mesoporous MCM-41 materials was studied at room temperature by the PFG NMR technique. A dynamic NMR study of cyclohexane confined in a MCM-41 solid has also been reported [24].

In the present work, the reorientational and translational dynamics of cyclohexane and cyclopentane confined within a newly prepared mesoporous MCM-41 solid are studied by high-field (9.4 T) NMR, and the results are discussed with reference to the bulk substances. These compounds are expected to have a non-specific and weak interaction with the amorphous pore walls. It is interesting to compare the effect of confinement on cyclohexane and cyclopentane since the former and latter compounds exhibit plastic and liquid bulk phases, respectively, throughout most of the investigated temperature region. On the time-scale of the NMR experiment, the molecules at the pore walls and at the interior of the pore might be in fast exchange, in particular for cyclopentane that remains in the liquid state at practically all the temperatures investigated.

Bulk cyclohexane exists in a face-centred cubic plastic phase between the transition point at 186 K and the melting point at 280 K [25]. Below the melting point, confined cyclohexane crystallizes only partially. Thus, a two-phase system, consisting of a highly mobile surface layer and a plastically crystalline solid at the centre of the pore, might be formed at least in pores exceeding ≈4 nm in size. Bulk cyclopentane solidifies into a hexagonal plastic phase at 179 K [26]. It is a suitable probe compound owing to its compact shape and large liquid range (179–322 K). To our knowledge, the molecular mobility of cyclopentane in confined geometries has not been investigated by NMR before.

2. Experimental

2.1. Sample preparation

The preparation of MCM-41 was performed under acidic, rather than alkaline, conditions in order to obtain crystal sizes of appropriate size (⩾10 μm) for the study of diffusion phenomena of confined fluids by PFG NMR. Consequently, the crystalline MCM-41 material was prepared according to the method of Karlsson et al. [27], using the following general gel composition (molar ratios):

$$0.24 \times \mathrm{C_{16}H_{33}TMABr} : 1 \times \mathrm{TEOS} : 9.2 \times \mathrm{HCl} : 130 \times \mathrm{H_2O}$$

where TEOS and TMA are short-hand notations for tetraethyl orthosilicate and trimethylammonium, respectively.

Before application, the mesoporous material was calcined by heating the sample at a rate of 3 K/min, first to 473 K (standby for 2 h) and subsequently to 823 K (standby for 4 h). During the entire calcination procedure, the mesoporous product was flushed with air at a flow rate of ≈100 ml/min.

The purely siliceous material was characterized by X-ray powder diffraction (XRD), high-resolution electron microscopy (HREM) and nitrogen adsorption/desorption isotherms at 77 K. The XRD shows uniquely that there is long-range hexagonal ordering. The crystallites were in excess of 10 μm. The pore size *R*, the specific surface area *S* and the specific pore volume *V* were determined to be 3.2 nm, 835 $m^2 g^{-1}$ and 0.90 $cm^3 g^{-1}$, respectively.

The cyclohexane (99.99%) and cyclopentane (⩾99%), obtained from Fisions Scientific Equipment and Fluka, respectively, were dried over molecular sieves before use. The six test samples, prepared in 5 mm o.d. NMR tubes, were each filled to a height of approximately 10 mm with the mesoporous material and dried at 423 K for at least12 h. The probe substance was then added to obtain a filling degree of approximately 60%, 80% and 104%. The quantity to be added was calculated from the known specific pore volume of the MCM-41 material. Vortex plugs were inserted into the NMR tubes before carefully sealing the tubes with polyethyl-