Electronic Supplementary Information (ESI)

Diffusion of Methyl Oleate in Hierarchical Micro-/Mesoporous TS-1-Based Catalysts Probed by PFG NMR Spectroscopy

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1. Sample preparation and details of PFG NMR experimentation

Diffusion studies were performed by ^{1}H NMR using a wide-bore 9.4 T Bruker BioSpin spectrometer. It is equipped with a home-built gradient unit producing ultra-high *z*-gradients of up to 35 T m^{-1} in a 7 mm o.d. NMR sample compartment.

Before loading materials into the NMR tubes, the powders were pressed into discs using 110 MPa pressure in a hydraulic press (Perkin Elmer, 25 T) for pelletizing. The discs were subsequently milled and sieved in order to obtain pellets of 300–1000 μm in diameter. This was done to prevent fleeting of the powder into the vacuum pump during the sample activation step. Such pelletization results in appearance of inter-particle pore spaces. Thus, three characteristic pore spaces should be considered: i.) micro- and/or mesopores within the crystallites, ii.) large mesopores or macropores between the crystallites within the pellet, and iii.) large macropores between the pellets themselves (bulk phase). Fig. S1 demonstrates SEM image of the pellets after milling and their surfaces.
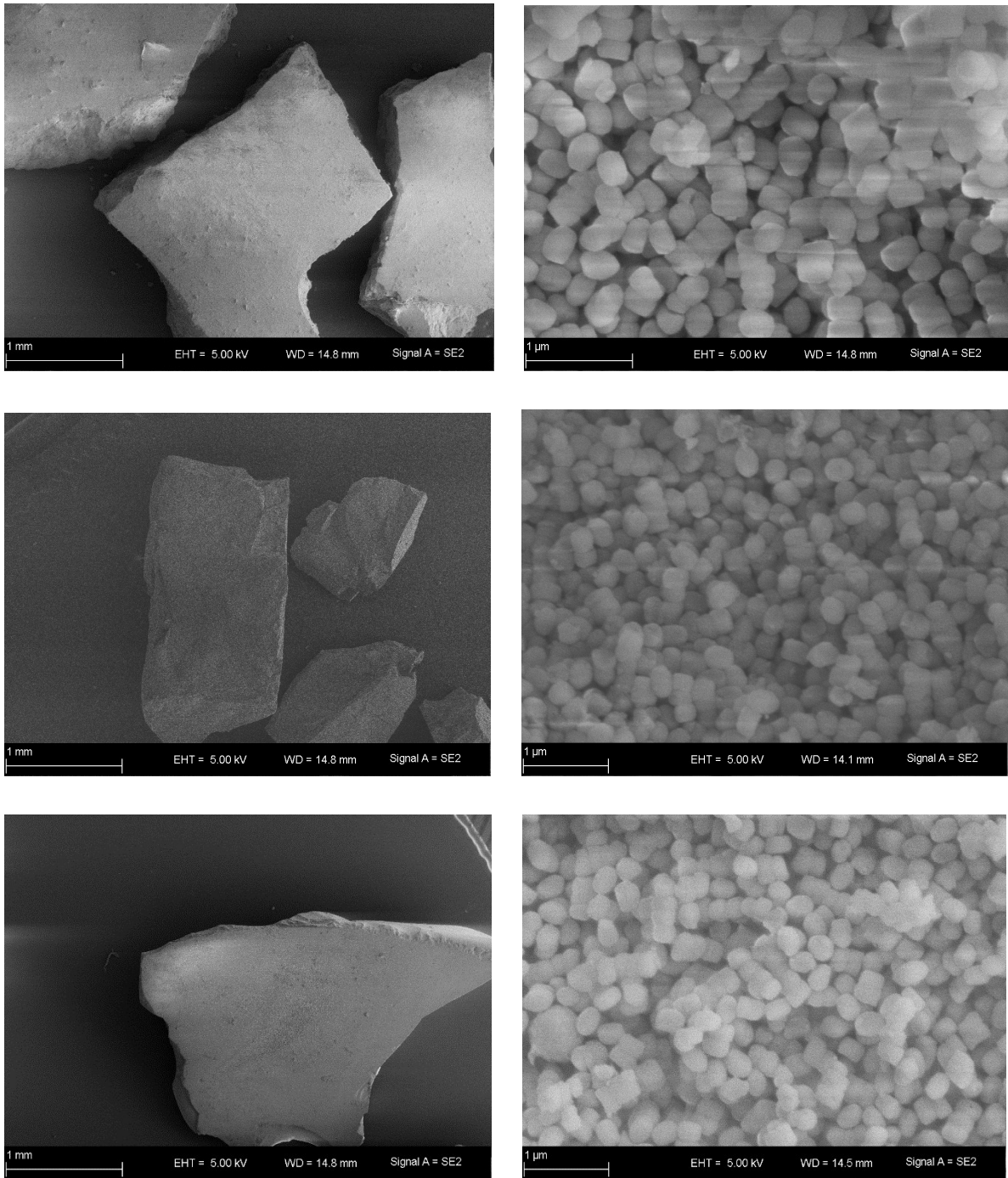
Fig. S1: SEM images of pelletized materials (TS-1_ns70 – top, D_NH$_3$/TPAOH – middle, R-_D_NH$_3$/TPAOH – bottom) taken with lower (left) and higher (right) magnifications to see entire pellets and their surface, respectively.

NMR samples were prepared in 7 mm o.d. glass tubes. Around 150 mg of each pre-dried sample (TS-1_ns70, D_NH$_3$/TPAOH and R_D_NH$_3$/TPAOH) was placed within the NMR tube. Each NMR tube was then connected to a custom-built vacuum system, and samples were activated under high vacuum (10^{-5} – 10^{-4} mbar) at around 400 K for overnight. After cooling them to room temperature, each of the samples was saturated under vacuum by injection of MO (99%, Sigma Aldrich) and acetonitrile (99.8%, Sigma Aldrich) separately. The amount of liquids was chosen to be sufficient to cover the particles of the samples completely. This was done to ensure that all micropores (when acetonitrile is used) and mesopores (for acetonitrile and MO) were completely filled. After loading, the NMR tubes were detached from the vacuum system by flame sealing. This method of the sample saturation implies that in addition to the molecules in the micro- and mesopores, there will always be a fraction of molecules that is outside the porous particles, which will contribute to the observed NMR signals, too.

A stimulated echo (STE) pulse sequence[1] was applied with the following parameters of the pulse sequence: τ = 2 ms, δ = 0.5 ms, and Δ = 8, 18, 40 and 160 ms. Here, τ is the spacing between the first two ($\pi/2$) pulses, δ is the effective duration of the gradient pulses, and Δ is the gradient pulses separation. The signal accumulation was performed with a repetition time of 5 times of T_1, where T_1 is the nuclear magnetic spin-lattice relaxation time of the component having the longest relaxation in the system (bulk MO, T_1=1.1 s). Additionally, selected diffusion experiments were carried out using the 13-interval pulse sequence[2] with the same values of diffusion times and gradient amplitudes used in experiments with STE. This serves to estimate a possible effect of the internal magnetic fields originating from the susceptibility differences between the fluid and the porous material and effects of undesirable eddy current effects. A small difference within the range of experimental uncertainty was observed (Fig. S2). These experiments were conducted for two different times Δ – 8 ms and 18 ms.
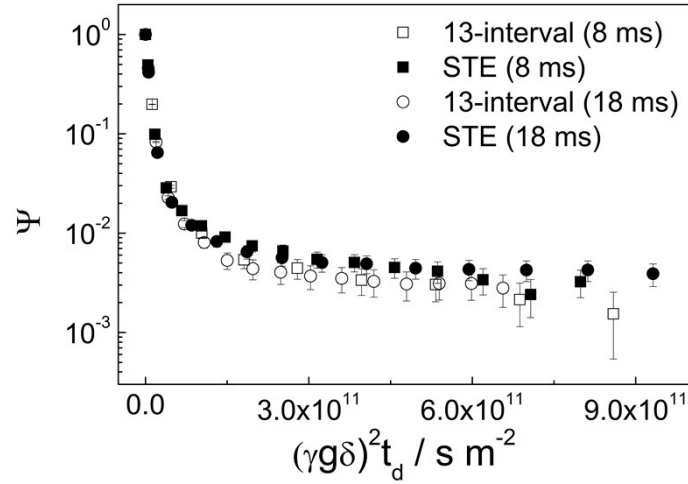
Fig. S2: ^{1}H PFG NMR diffusion attenuation curves measured for R_D_NH$_3$/TPAOH material oversaturated with MO at 298 K. The data obtained by 13-interval and STE pulse sequences are represented by open and solid symbols, respectively. The presence of an additional pair of gradient pulses in the 13-interval pulse sequence was taken into account plotting values of $(\gamma g\delta)^2 t_d$.

Generally, the decrease of the measured NMR signal (ψ) caused by diffusion for a system containing molecular ensembles (p_i) with different diffusion coefficients (D_i), and being in the slow (compared to the time of the experiment) diffusion exchange can be presented in the form:

$$\psi(g\delta,t_d) = \sum_i p_i \cdot exp\left(-D_i\gamma^2 g^2\delta^2 t_d\right) \tag{S1}$$

where γ is the gyromagnetic ratio of the nucleus that is observed, g and δ are the amplitude and the duration of the gradient pulses, respectively, t_d is the effective diffusion time ($[\Delta - \delta/3]$ in case of STE and $[\Delta - \delta/6 - \tau/2]$ in case of the 13-interval pulse sequence). In the conducted experiments, due to relatively short δ-values (0.5 ms), one may assume that $t_d \cong \Delta$. Under conditions of a fast diffusion exchange, Eq. (1) transforms into:

$$\psi_{fast}(g\delta,t_d) = exp\left(-D\gamma^2 g^2\delta^2 t_d\right) \tag{S2}$$

in which $D = \sum_i p_i D_i$ is the time-averaged diffusion coefficient of the exchanging ensembles. For $i > 1$, Eq. (1) gives a poly-exponential decay of the observed NMR signal, while Eq. (2) results in a mono-exponential decay.

2. Textural properties of the materials

As reported in Ref.[3], it is suggested that the material after alkaline treatment possesses a mesopore systems with pore openings considerably smaller than the diameter of the inner pores, e.g. ink-bottle shaped pores or partially constricted interconnected porous systems. More uniform mesopores in the range of 3-10 nm are present in the pseudomorphically transformed material R_D_NH$_3$/TPAOH (V$_{3\text{-}10nm}$, R_D_NH$_3$/TPAOH $=$ 0.13 cm^{3}g^{-1} vs. V$_{3\text{-}10nm}$, D_NH$_3$/TPAOH 0.04 cm^{3}g^{-1}) exhibiting a specific BET surface area of 483 m^2 g^{-1}, i.e., 130 m^2 g^{-1} higher than that of the alkaline treated material. In addition, 235 m^2 g^{-1} is contributed from the "external" surface (cf. Tab. 1).

Table S1. Specific surface area A$_{BET}$, micropore area V$_{micro}$, external surface area A$_{ext}$ and specific volume of micropores V$_{micro}$, pores in the range of 3-10 nm V$_{3\text{-}10nm}$ as well as 10-40 nm V$_{10\text{-}40nm}$ and titanium content ω_{Ti} of TS-1_ns70, D_NH$_3$/TPAOH and R_D_NH$_3$/TPAOH catalysts (adapted from Ref.[3])

	ω_{Ti}[a]/ wt.%	V$_{micro}$[b]/ cm^{3}g^{-1}	V$_{3\text{-}10nm}$[c]/ cm^{3}g^{-1}	V$_{10\text{-}40nm}$[c] / cm^{3}g^{-1}	A$_{micro}$[b] / m^{2}g^{-1}	A$_{ext}$[b]/ m^{2}g^{-1}	A$_{S,BET}$[d]/ m^{2}g^{-1}
TS-1_ns70	0.90	0.20	n.d.	n.d.	420	13	433
D_NH$_3$/TPAOH	1.00	0.13	0.04	0.11	280	78	358
R_D_NH$_3$/TPAOH	1.10	0.13	0.13	0.05	248	235	483

[a] ICP-OES; [b] t-plot-DeBoer; [c] BJH; [d] BET; n.d. - not determined.

References

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