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Diffusion in Hierarchically Structured Zirconia Spheres

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1. Introduction

Porous transition metal oxides are a very important group of materials for applications in heterogeneous catalysis, either as an active catalyst or as a support for catalytically active components. A major aspect of current research is the control of a well-defined particle morphology and a high specific surface area in combination with a defined porosity. For the latter, a hierarchically structured pore system is desired, because transport limitations, especially for bulky molecules can be suppressed [1].

Zirconia is known to be an effective material for a wide range of applications. For instance, it is mainly used as catalyst support for high temperature conversions [2]. A contemporary challenge is the tuning of the textural properties of zirconia [3], e.g., by the use of exo-templating [4]. In this study, the self-diffusivity of cyclohexane in porous zirconia spheres was studied. The influence of a hierarchically structured pore system, by introducing additional mesoporosity with a tri-block copolymer was also investigated.

2. Experimental section

In the presented study, polymer-based spherical activated carbon (PBSAC provided by Blücher GmbH, $A_{BET} = 1748$ m^2 g^{-1}) and templated ZrO_2-spheres were used for the experiments. The characterization with N_2-sorption, XRD and SEM from the ZrO_2-spheres and the presence of a hierarchically structured pore system was discussed in a recent publication [4].

All diffusion measurements were performed on an NMR spectrometer equipped with a pulsed-field gradient unit which produces a maximal gradient strength about 35 T/m [5], using a 13-interval stimulated-echo pulse sequence [6]. The NMR tube containing the porous materials, was connected to a reservoir with the vapor of cyclohexane [7]. All ZrO_2 materials except of the ZrO_2 powder were used with particle diameters in the range of 0.20-0.40 mm. The amount of adsorbed molecules in the samples was determined from the intensity of the free induction decay (FID) signal following a single 90°-pulse.

3. Results and Discussion

For ZrO_2, the presence of a hierarchically structured pore system was discussed in a recent publication [4]. In Figure 1 (left part) the SEM micrograph of a hierarchically structured ZrO_2 sphere is shown. Results from N_2-sorption show that the ZrO_2-spheres contain larger mesopores with diameters of 10-20 nm. Additional pores with 3 nm diameter are present in the case of hierarchically structured ZrO_2. The amount of small mesopores can be adjusted by the amount of tri-block copolymer to zirconium (n_{TBC}/n_{Zr}) in the synthesis gel [4].

In Figure 1 (right part), the effective self-diffusivities D_{eff} against the relative pore filling θ with cyclohexane is shown. On decreasing the concentration, the obtained functions $D_{eff}(\theta)$ pass a maximum. This observation was discussed in a recent paper [7], explaining the existence of the maximum with a two-phase exchange model between an adsorbed and gaseous phases. Below $\theta < 0.2$, corresponding to less than one monolayer, D_{eff} decreases with decreasing coverage, as it is mostly determined by the surface diffusion with respect to the gas phase molecules. For porous ZrO_2, D_{eff} increases, if templates are used, in contrast to the non-templated powder. This can be attributed to the more open pore system resulting from the template removal. Furthermore, D_{eff} increases after introducing additional mesopores with 3 nm diameter. This effect could result from the existence of a liquid phase in the small pores and a gaseous phase in the larger pores.

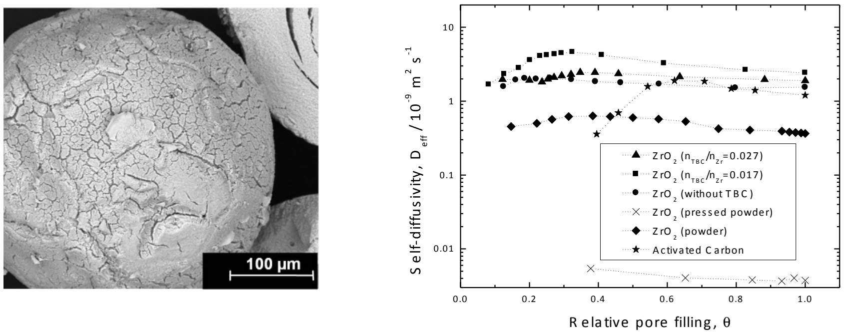

Fig. 1. SEM micrograph of a hierarchically structured ZrO_2-sphere (left part) and the effective self-diffusivity of cyclohexane in porous ZrO_2 with particle diameter of 0.20-0.40 mm, at 297 K on desorption from PFG NMR (right part).

4. Conclusion

Zirconia with pores of 10-20 nm diameter prepared by exo-templating with polymer-based, spherical activated carbon exhibits a self-diffusivity of cyclohexane that is higher by one order of magnitude than the powder from conventional synthesis. A further increase in self-diffusivity can be obtained after introducing smaller mesopores with 3 nm diameter additionally to the pores at 10-20 nm. Thus, the mesoporous ZrO_2-spheres reported here are attractive candidates as supports or catalysts for the conversion of bulky molecules.

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