Carbon Dioxide Transport in a Samaria Aerogel Catalyst by High Field Diffusion NMR

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Introduction

Development of transport-optimized catalysts requires fundamental understanding of diffusion in catalytic materials. In this project, we applied some of the approaches and ideas which were originally developed for zeolitic materials to describe self-diffusion of carbon dioxide in alumina supported samaria aerogel catalyst. Aerogels are sol-gel derived porous materials featuring high porosity (>95% by volume) and high surface area (102-103 m^2g^{-1} or higher) which can be easily prepared in the form of both monoliths and powders and are interesting for a number of catalytic applications. In the case of samaria aerogels, the oxidative coupling of methane (OCM) is an interesting reaction. Apart from the desired reaction products, ethane and ethylene, total oxidation to CO_2 is an important side reaction. In order to get first insight into the transport properties of such aerogels, we chose CO_2 as a probe molecule for self-diffusion studies by pulsed field gradient (PFG) NMR.

Experimental

Samples of alumina stabilized samaria aerogels were formed in the laboratory of Prof. Bäumer following the epoxide addition sol-gel method. Diffusion data were obtained by C-13 PFG NMR using a wide-bore 17.6 T Bruker BioSpin spectrometer located at AMRIS, University of Florida. Magnetic field gradients with the amplitude of up to 30 T/m were generated using diff60 diffusion probe and Great60 gradient amplifier (Bruker BioSpin).

Results and Discussion

Fig. 1 shows PFG NMR attenuation curves for CO_2 diffusion in the alumina stabilized samaria aerogel catalyst for both monolith and powder bed preparations.[1] It is seen in Fig. 1 that the attenuation curves for the monolith catalyst sample are mono-exponential and diffusion time independent. This behavior corresponds to normal (Fickian) diffusion with a constant self-diffusivity for the range of the effective diffusion times used in the measurements. Using the Einstein relation, the corresponding range of the root mean square displacements (RMSDs) is found to be between ~60 and ~200 µm, i.e. much smaller in comparison to the smallest dimension of the monolith particles which is on the order of 2-3 mm. The PFG NMR attenuation curves for the powder bed in Fig. 1 are not mono-exponential and also depend upon the effective diffusion time. The observed behavior indicates a transition of the diffusion process from the intraparticle to long-range regimes as diffusion time increases. In the former regime sorbate displacements are smaller than or comparable with the particle sizes, while in the latter regime these displacements are larger than the particle sizes.[1,2]

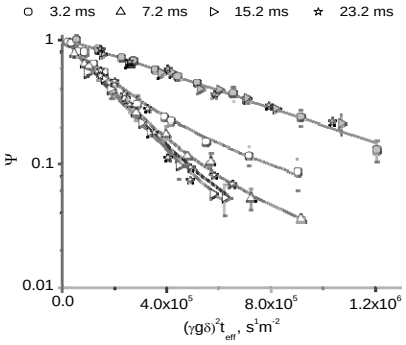

Fig. 1. PFG NMR attenuation curves for CO_2 diffusion at different diffusion times in samaria alumina aerogel catalyst prepared as a monolith (filled symbols) and as a powder bed of 100-280 µm sized particles (unfilled symbols) at 297 K.

Conclusions

PFG NMR employing a high magnetic field of 17.6 T was used to study self-diffusion of carbon dioxide in alumina stabilized samaria aerogel, a promising porous catalyst for gas-phase reactions.

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References

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[2] Mueller, R., *et al*., Chemie Ingenieur Technik **85**, 1749-1754 (2013).