

Diffusion of light gases in nanoporous gold by pulsed field gradient NMR at high field

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Nanoporous gold with pores in the mesopore range has recently attracted attention of the scientific community due to its potential applications in catalysis. Simple fabrication of nanoporous gold along with high specific area, tunable framework and chemical flexibility has led to its attractiveness as a catalyst [1,2]. As one specific example, nanoporous gold has shown to be a promising candidate for catalytic oxidation of carbon monoxide (CO) to carbon dioxide (CO₂) [1-3]. Fundamental understanding of molecular diffusion in nanoporous gold is of crucial importance for its potential applications in catalysis.

¹³C pulsed field gradient (PFG) NMR at 17.6 T was used to study self-diffusion of CO, CH₄ and CO₂ in a bed of nanoporous gold particles at 296 K. Additional measurements were done to study self-diffusion of CH₄ in the same sample using ¹H PFG NMR at same magnetic field to confirm the absence of any measurement artifacts. The measurements were performed for a broad range of the root mean square displacements (root MSDs) that were smaller and larger than the mean particle size (~250 μm). For root MSDs smaller than the particle size the following two ensembles are expected for each type of gas: (1) molecules that diffuse inside the particle, and (2) molecules that diffuse in the gas phase of the sample outside the particles. The following equation was used to fit the measured PFG NMR attenuation curves

$$\Psi = \frac{S(g)}{S(g=0)} = p_1 \exp(-D_1 q^2 t) + p_2 \exp(-D_2 q^2 t), \quad (1)$$

where constants p_1 and p_2 are the phase fractions and D_1 and D_2 are the corresponding diffusivities of the respective ensembles. Figure 1 shows examples of the measured PFG NMR attenuation curves along with the best fit curves using Eq. 1 and the corresponding best fit parameters. While for the diffusion times of 6 and 10 ms two molecular ensembles were observed, only one ensemble was observed for the diffusion time of 30 ms. The latter time is sufficiently large to lead to a fast exchange of diffusing molecules between the particles and the surrounding gas phase.

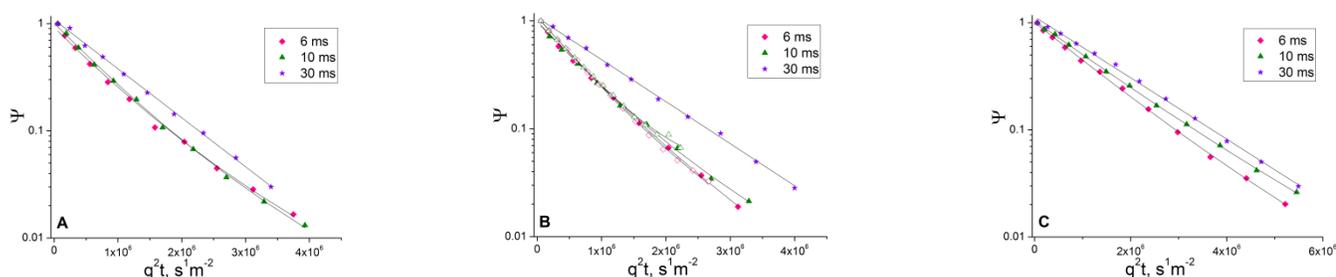


Figure 1. ¹³C PFG NMR attenuation curves measured for a bed of porous gold particles equilibrated with 15 bar of CO (A), 15 bar of CH₄ (B, filled) and 15 bar of CO₂ (C) at 296 K. Also shown for comparison are the corresponding data obtained for CH₄ diffusion using ¹H PFG NMR (B, hollow). The solid lines represent the results of least-square fitting using Eq. 1.

Diffusion inside particles of nanoporous gold can be characterized by a tortuosity factor, which can be defined as the ratio between the diffusivity D_0 in a well-defined reference system (bulk gas phase) and the corresponding diffusivity D in nanoporous gold

$$\tau = \frac{D_0}{D}. \quad (2)$$

The diffusivities D_1 and D_2 (Fig. 1) obtained from fitting the PFG NMR attenuation curves using Eq. 1 were used, respectively, as D and D_0 . The resulting tortuosity factors were found to be the same for all three gases (Table 1).

Table 1. Average tortuosity factors for each sorbate loaded into the nanoporous gold sample

Sorbate Loading Pressure	Average Tortuosity Factor
15 Bar CO ₂	1.8 ± 0.29
15 Bar CH ₄	2.2 ± 0.26
15 Bar CO	2.1 ± 0.35

References

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