

## Effects of surface modifications on molecular diffusion in mesoporous catalytic materials

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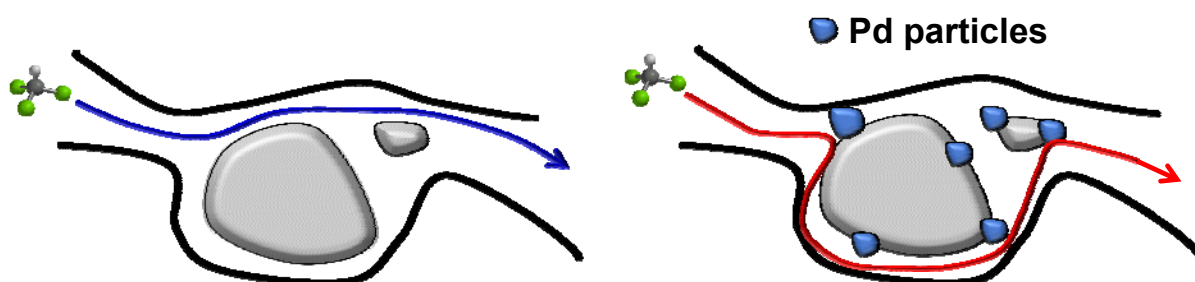
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In this work, we use pulsed-field gradient (PFG) NMR to probe molecular diffusion of liquids inside mesoporous structures and assess the influence of surface modifications, namely, deposition of palladium (Pd) nanoparticles over alumina ( $\text{Al}_2\text{O}_3$ ) surfaces and passivation of titania ( $\text{TiO}_2$ ) surfaces with alkyl chains, on the diffusion pattern.

Diffusion of binary mixtures acetone/chloroform inside  $\text{Al}_2\text{O}_3$  and  $\text{Pd}/\text{Al}_2\text{O}_3$  is investigated. The deposition of Pd nanoparticles onto the  $\text{Al}_2\text{O}_3$  surface leads to a reduction of the diffusion coefficient of guest molecules inside the pore network, suggesting that Pd particles obstruct some diffusion pathways, hence, increasing the average tortuosity of the pore network.

The effect of surface passivation, by replacing  $-\text{OH}$  surface groups of  $\text{TiO}_2$  with octyl aliphatic chains, is also assessed by using primary alcohols, in the range  $\text{C}_1$ - $\text{C}_8$ . The experiments show that in the bare  $\text{TiO}_2$  sample, higher alcohols show a behavior of enhanced diffusion, relative to the diffusion expected based on tortuosity values, which is attributed to a hydrogen bonding network disruption, which has been previously observed when studying diffusion of alcohols and polyols in mesoporous materials.<sup>1,2</sup> Removal and replacement of  $-\text{OH}$  surface groups in bare  $\text{TiO}_2$  by octyl chains leads to a diffusion behavior inside the pore space that is independent of alcohol chain length. In particular, the apparent tortuosity of all the  $\text{C}_1$ - $\text{C}_8$  alcohols becomes the same and equal to that measured using weakly-interacting molecules such as alkanes, the latter being considered the true estimate of the tortuosity of the pore structure. This shows that the presence of  $-\text{OH}$  groups over the surface, and hence the chemistry of the surface, is an important factor in affecting diffusion of alcohols inside the pore space.

In summary, the work shows that changes in surface properties change diffusion mass transport in pore networks, which may be a factor to consider when using such materials in catalytic applications.



**Figure 1:** Schematic of diffusion path in (left)  $\text{Al}_2\text{O}_3$  and (right)  $\text{Pd}/\text{Al}_2\text{O}_3$  of a chloroform molecule. Pd particle deposition might influence the diffusion path and hence the tortuosity of the structure.

### References

- [1] M. D. Mantle et al: *Pulsed-Field Gradient NMR Spectroscopic Studies of Alcohols in Supported Gold Catalysts*. The Journal of Physical Chemistry C **115**, 1073-1079 (2010).
- [2] C. D'Agostino, J. Mitchell, Lynn F. Gladden, Mick D. Mantle: *Hydrogen Bonding Network Disruption in Mesoporous Catalyst Supports Probed by PFG-NMR Diffusometry and NMR Relaxometry*. The Journal of Physical Chemistry C **116**, 8975-8982 (2012).