

Effects of surface modifications on molecular diffusion in mesoporous catalytic materials

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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 (Al_2O_3) surfaces and passivation of titania (TiO_2) surfaces with alkyl chains, on the diffusion pattern.

Diffusion of binary mixtures acetone/chloroform inside Al_2O_3 and $\text{Pd}/\text{Al}_2\text{O}_3$ is investigated. The deposition of Pd nanoparticles onto the Al_2O_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 TiO_2 with octyl aliphatic chains, is also assessed by using primary alcohols, in the range C_1 - C_8 . The experiments show that in the bare 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.^{1,2} Removal and replacement of $-\text{OH}$ surface groups in bare 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 C_1 - 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.

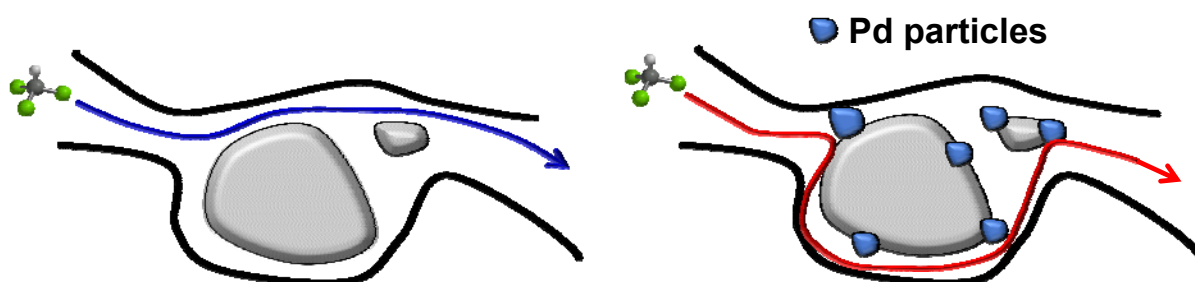


Figure 1: Schematic of diffusion path in (left) Al_2O_3 and (right) $\text{Pd}/\text{Al}_2\text{O}_3$ of a chloroform molecule. Pd particle deposition might influence the diffusion path and hence the tortuosity of the structure.

References

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