

Multi-technique approaches to study diffusion phenomena in vacuum gas oil hydrotreating

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Abstract

The aim of this work is to quantify mass transfer limitations in hydrodesulfurization (HDS) of Vacuum Gas Oil (VGO). Inverse chromatography experiments were performed for different mesoporous aluminas with similar porosity. By varying the molecular size of the probe, it was shown that the diffusional regime is molecular diffusion. Hindered diffusion was not observed even for a C₃₀ molecule like squalane. Using appropriate modeling tools, the apparent tortuosities of each alumina are estimated. Even though the diffusion regime is molecular diffusion, the apparent tortuosity is smaller for aluminas with higher mean pore diameters. These results will be useful for the design of innovative HDT catalysts.

Keywords

Hydrotreating, Vacuum Gas Oil, Internal diffusional limitation, Inverse chromatography

Introduction

By studying the HDS of a VGO model molecule in a batch reactor under representative operating conditions, mass transfer limitations have been clearly identified. In this work, we want to link the physical properties of porous solids and their impact on internal diffusional limitations. To characterize these internal diffusion limitations, breakthrough curves with two different molecules were practiced on various hydrotreating supports. For the smaller molecule, the diffusion regime is clearly molecular diffusion, which allows to calculate a tortuosity coefficient for each solid. Afterwards, by increasing the size of the probe molecule, the possible impact on the diffusion regime and the tortuosity was studied. These results will be used to link the tortuosity factor to the properties of the porous supports.

Experimental setup

Five different aluminas, representative of hydrotreating catalysts, were studied in this work. Their main properties are summarized in Table 1 and Figure 1. The chosen catalyst supports are of the same porosity, but their pore size distributions are quite different. Support D has the smallest pores.

Table 1. Textural properties of the aluminas

	Pore volume (cm ³ .g ⁻¹)	Porosity	BET surface area (m ² .g ⁻¹)	Vol. BJH desorption mean pore radius (nm)
A	0.74	0.71	270	10
B	0.78	0.72	290	9
C	0.72	0.70	300	8
D	0.71	0.72	340	7
E	0.77	0.73	160	18

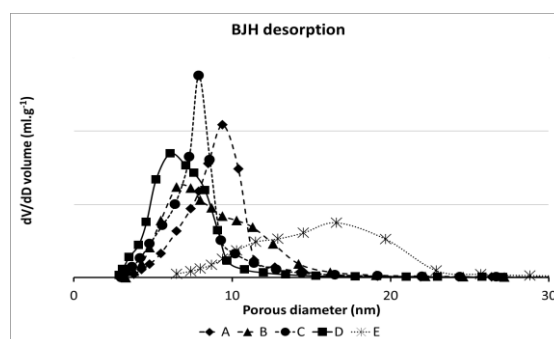


Figure 1. Pore size distribution

Breakthrough curves were used for pore characterization of porous chromatography stationary phases. For the five aluminas, columns of 50 cm were filled with crushed and sieved alumina particles. The particle radius was measured by means of laser granulometry. The breakthrough experiments were performed with different particle

sizes to evaluate external mass transfer. It was found that the mass transfer limitations were entirely due to internal diffusion limitations.

Binary solutions of methyl cyclohexane (MCH), a 7 carbon naphthene, and squalane (SQ), a 30 carbon paraffin, in n-heptane (C7) were prepared at a concentration of 3wt%. For practical convenience, the solute samples were introduced by a step change and the outlet concentration measured by a refractometer. Experiments were carried out at 35°C in the liquid phase at various volumetric flows.

Intra-granular diffusion coefficients D_p were estimated from the dispersion of the breakthrough curves using the plate theory of chromatography (Ruthven).

If the regime is molecular diffusion then:

$$D_p = \frac{D_m \cdot \varepsilon_p}{\tau} \quad (1)$$

The molecular diffusion coefficients D_m were estimated from the Haduk and Minhas correlation (Hayduk and Minhas). For hindrance diffusion, equation (1) is not valid and D_p will depend on the size of the molecule.

Results and discussion

The Van Deemter curves for MCH/C7 and SQ/C7 mixtures in alumina D are shown in Figure 2.

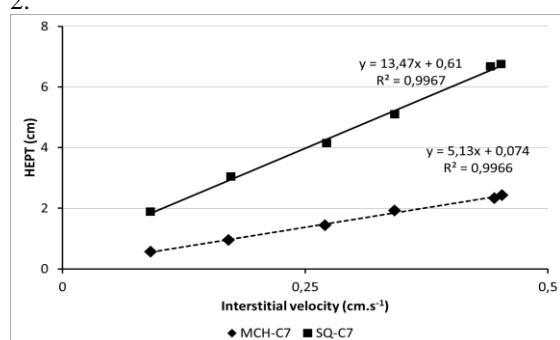


Figure 2. Van Deemter curves for alumina D

The experimental HETP data varies linearly with the interstitial velocity, in agreement with the chromatography theory. The values of D_p evaluated from the slope of the curves and the corresponding tortuosity values are listed in Table 2.

Table 2. Estimated tortuosity τ for alumina D.

Probe	Slope (s ⁻¹)	D_p (cm ² .s ⁻¹)	D_m (cm ² .s ⁻¹)	τ
MCH-C7	5.13	$8.10 \cdot 10^{-6}$	$4.1 \cdot 10^{-5}$	3.57
SQ-C7	13.47	$3.10 \cdot 10^{-6}$	$1.6 \cdot 10^{-6}$	3.65

The tortuosity values for MCH and SQ are very close. The probe size does not impact the diffusion

regime, which is therefore governed by molecular diffusion for both compounds.

The same IC experiments were performed with both probes for all the alumina samples. The resulting tortuosity values can be seen on Table 3.

Table 3. Tortuosity value for the various aluminas

	MCH-C7 τ	SQ-C7 τ
A	2.70	2.73
B	2.91	2.91
C	3.34	3.31
D	3.60	3.59
E	2.38	2.41

The order of magnitude of the tortuosity values is much higher than expected by correlations based on ideal systems (random packing of uniform spheres or cylinders) still in agreement with other works on catalysis supports (Shen and Chen).

Tortuosity does not vary with molecular size, showing that the diffusion regime is molecular for all samples. Hence, tortuosity should not depend on the mean pore size of the solid. Surprisingly, the tortuosity varies significantly from one sample to another, in the order of magnitude of the mean pore size.

Conclusion

Breakthrough experiments show that for methyl cyclohexane and squalane in n-heptane, the diffusional regime in porous media is governed by molecular diffusion.

Still, the tortuosity values obtained with different solids with similar porosity show a surprising effect of the pore size. The mean pore size and the organization of the pore network may both be impacted by other parameters, such as the nanoparticles morphology. A more thorough characterization of the solids will be conducted and should provide more information.

References

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