Microporous and Mesoporous Materials 248 (2017) 91–98

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Tortuosity of mesoporous alumina catalyst supports: Influence of the pore network organization

Svetan Kolitcheff [a], Elsa Jolimaitre [a], Antoine Hugon [a], Jan Verstraete [a], Pierre-Louis Carrette [a], Mélaz Tayakout-Fayolle [b,] *

[a] IFP Energies nouvelles, Rond-point de l'échangeur de Solaize, BP 3, 69360, Solaize, France
[b] Univ Lyon, Université Claude Bernard Lyon 1, CNRS, LAGEP UMR 5007, 43 boulevard du 11 novembre 1918, F-69100, Villeurbanne, France

ARTICLE INFO

Article history:
Received 14 December 2016
Received in revised form
31 March 2017
Accepted 7 April 2017
Available online 9 April 2017

Keywords:
Alumina support
Inverse liquid chromatography
Internal diffusional limitations
Tortuosity
Pore network
Pore size distribution

ABSTRACT

Inverse liquid chromatography experiments were performed on five mesoporous alumina catalyst supports with similar porosity and different pore size distributions. By varying the size of the molecular tracer, it was shown that the diffusion regime in our conditions is molecular diffusion. Hindered diffusion was not observed even for squalane, a C_{30} molecule. Using the slope of the Van Deemter equation, the tortuosity of each alumina support was determined. The results are in disagreement with literature correlations: although all alumina supports had similar total porosities, the measured tortuosity values are really different and much higher than those predicted by these theoretical models. This discrepancy has been resolved by assuming a two−level pore network organization, whose characteristics can be entirely estimated from a classical nitrogen adsorption isotherm. This simple methodology allows to evaluate the mass transfer in mesoporous alumina supports knowing their textural properties, which is an important issue for the design and optimization of numerous catalytic processes.

1. Introduction

γ-Aluminas are used as catalyst supports in a variety of chemical and refinery processes. It is particularly the case in the field of petroleum (and recently biomass-derived oil) hydrotreating. Different support characteristics have a direct impact on the final activity of the catalyst, amongst which are the surface area and chemistry, the mechanical strength and the mass transfer properties. Over the past decades, a large amount of research has been dedicated to the optimization of the catalyst active phase (i.e. maximization of the selectivity and of the chemical kinetic rate), whereas mass transfer properties have been essentially put aside. As the particle size of industrial catalysts is generally chosen to be large in order to limit the bed pressure drop, mass transfer in the catalyst pore network may now become the limiting step for the new generation of industrial hydrotreating catalysts, in particular for heavy liquid petroleum fractions such as vacuum distillates or biomass-derived pyrolysis oils. It is therefore necessary to improve the characterization of mass transfer of liquids in mesoporous alumina supports in order to better understand the relationship between the synthesis conditions, the textural properties and the mass transfer kinetics.

Over the years, many experimental techniques have been implemented to measure mass transfer kinetics in porous solids. Given the constraint of liquid phase diffusion, Pulsed Field Gradient Nuclear Magnetic Resonance (PFG-NMR) [1,2] and inverse chromatography [3] can be considered as the most adequate. Because it is simple to operate and gives access to transport parameters (against self-diffusion coefficients for PFG-NMR), inverse chromatography was selected for this study. Recently, Soukup et al. [4] evaluated diffusion coefficients in hydrotreating catalysts and supports by inverse chromatography. However, the experiments were operated in the gas phase and Knudsen diffusion was the predominant transport mechanism. Hence, the texture effects (for example the influence of the pore size distribution) cannot be extrapolated to the liquid phase. To the best of our knowledge, Inverse Liquid Chromatography (ILC) to study mesoporous alumina supports has never been reported in the literature so far. Nevertheless, the use of ILC to characterize transport properties of large molecule in silica has already been reported [5].

---

* Corresponding author.
E-mail address: melaz.tayakout-fayolle@univ-lyon1.fr (M. Tayakout-Fayolle).

http://dx.doi.org/10.1016/j.micromeso.2017.04.010
1387-1811/

Two major difficulties arise when studying mass transfer of high molecular weight hydrocarbons inside mesoporous alumina supports.

First of all, the porous structures of industrial alumina supports strongly depend on their synthesis conditions, are highly complex and still not well characterized. An alumina catalyst support (≈ 1 mm of diameter) is essentially the result of the stacking of millions of elementary alumina nanocrystals (≈ 10 nm of diameter) [6]. Given their tiny size, and their tendency to aggregate, the exact morphology of the nanocrystals and of the porous volume created in their vicinity is generally not accessible by microscopic techniques. The pore volume is therefore mostly characterized by mercury porosimetry and nitrogen adsorption analysis, yielding pore volumes and pore size distributions. Using different techniques, a recent study postulated that alumina catalyst supports are constituted of different scales of porosity [2].

The second difficulty is related to the diffusion mechanism, which in liquid phase can be either molecular diffusion (when intermolecular collisions are dominant, i.e. when the size of the molecule is small compared to that of the pore) or hindered diffusion (sometimes called surface diffusion, when the interactions between the molecule and the surface become predominant). For high molecular weight hydrocarbons in mesoporous pores, it is not clear which diffusion regime is rate-limiting, and this information has to be determined experimentally.

In the molecular diffusion regime, the conventional approach to account for the effect of the porous network is to introduce a correction of to the molecular diffusion coefficient D_m by two textural parameters, the particle porosity ε_p and the tortuosity τ in order to obtain the well-known effective diffusion coefficient:

$$D_{eff} = D_m \cdot \varepsilon_p / \tau. \tag{1}$$

The porosity represents the void fraction inside the porous particles and can easily be evaluated from classical porosimetry techniques. Evaluation of the tortuosity of a given porous system is, however, much more complicated. From a geometric point of view, the tortuosity represents the ratio between the total length of the diffusion path of the fluid in a porous medium and the corresponding straight-line distance. From a macroscopic point of view, equation (1) links two diffusion coefficients, with and without the presence of the porous medium, and defines the tortuosity as a correction factor that is necessary to account for the presence of the porous medium once the void fraction has been taken into account. The tortuosity factor therefore depends on the support porosity (i.e. the tortuosity decreases, if the void fraction increases) and the network structure, but, in the molecular diffusion regime, it does not depend on the size of the molecular tracer. Indeed, if molecules of strongly differing sizes are not able to follow the same paths in the porous network, the diffusion mechanism is surface hindered.

The simplest way to evaluate τ is to apply one of the numerous of theoretical or empirical relations between τ and ε_p that have been proposed in literature [7,8]. Unfortunately, to select an appropriate relation, a good knowledge of the geometric properties of the system (shape, size and size distribution of the elementary nanocrystals) is required, which is rarely available for most alumina supports. Moreover, "real" solids often differ significantly from ideal stacking systems considered in theoretical works. It is therefore often necessary to evaluate τ experimentally. To do so, the best solution is to measure the effective diffusion and use equation (1) to calculate the tortuosity factor.

In this work, five mesoporous γ-alumina supports of equal porosity and different pore size distributions were studied. To characterize their diffusional properties, inverse liquid chromatography (ILC) experiments were performed with two molecules of strongly different sizes: methylcyclohexane (C_7H_{14}) and squalane ($C_{30}H_{62}$). Both tracers were diluted in *n*-heptane to determine both the diffusion regime and the tortuosity values. Finally, a decomposition of the porosity into two different porous networks is proposed to explain the diffusion behavior inside the studied materials.

2. Experimental

2.1. Materials and texture analysis

Five boehmite γ-alumina supports, provided by IFPEN, were studied in this work. The γ-alumina supports are obtained by precipitation of aluminum salts in an aqueous solution. The boehmite precipitate was filtered and washed. Shaping involves the passage from a boehmite powder to support pellets. The extrudates are trilobal. Their diameter ranges from 1.2 to 2 mm and the lengths from 2 to 6 mm. A thermal treatment at high temperature (from 798 to 1248 K) was performed to obtain the final support. The aim of these thermal treatments is to optimize the particle size, which increases with temperature, the average pore diameter, the total pore volume, and the surface area. The final γ-alumina support has a purity >99% by weight. The added impurities, introduced during the precipitation in the aqueous solution, are P, Na, Cl and Mg elements. These impurity quantities have not effect on textural properties.

Textural properties were measured by physical nitrogen adsorption on an ASAP 2420 instrument and helium pycnometry on an Accupyc 1340 instrument. The BET surface area S_{BET}, the pore volume V_p and the microporous volume were evaluated form the nitrogen isotherm. Helium pycnometry provided the structural density ρ_s. The porosity ε_p of all the studied solids was determined according to the following expression:

$$\varepsilon_p = \frac{V_p}{V_p + \frac{1}{\rho_s}}. \tag{2}$$

The textural properties of all alumina supports are reported in Table 1. All studied alumina supports are strictly mesoporous. As the alumina supports were selected to have very similar porosities in order to focus on the tortuosity effect, the porous volume and structural density are very close for all samples. Only the BET surface varies significantly, meaning that the nanocrystals used for the alumina support synthesis display different surface/volume ratios. The BJH method was used to estimate the pore size distributions of the studied alumina supports reported in Fig. 1 from the nitrogen desorption branch. The pore size distributions of the different samples vary significantly. Alumina supports B and D seem to be almost mono-disperse, while the three others are at least bimodal. Besides, the maximum of the curve is around 5 nm for sample A and nearly 17 nm for sample E.

Table 1
Alumina supports textural properties.

Alumina support	S_{BET} ($m^2.g^{-1}$)	V_p ($cm^3.g^{-1}$)	ρ_s ($g.cm^{-3}$)	ε_p
A	340	0.71	3.3	0.72
B	300	0.72	3.3	0.70
C	290	0.78	3.3	0.72
D	270	0.74	3.3	0.71
E	160	0.77	3.5	0.73