Quantitative electron tomography analysis of zeolites porosity

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1. INTRODUCTION

Hydrocracking catalysts are bifunctional, consisting of a metallic function supported on an acidic support. In order to achieve a high activity, the support is commonly prepared by shaping a USY zeolite in amorphous binder. However, the size and the tortuosity of the micropores/mesopores of the zeolite induce diffusionnal limits, restricting the middle distillates selectivity, target products of the hydrocracking process.

In order to generate new catalysts with higher selectivity, two design improvements are performed on zeolites : decreasing the size of the elementary zeolite crystals and controlling the mesoporous network.

Electron microscopy is a proper technique to characterize zeolites. By scanning electron microscopy, it is possible to observe the zeolites crystals and to quantify their size down to some dozens of nm ; by transmission electron microscopy, microporosity and mesoporosity can be observed and the mean size of pores can be measured. It is necessary to use electron tomography to visualize the 3D organization of mesoporosity.

In this study, we compared the crystals morphology and 3D mesoporous network of nanoagregates of zeolites prepared by an alternative synthesis to the reference USY commercial zeolite. Results of electron tomography on these zeolites are presented. In order to compare samples, advanced methods, based on morphological mathematics tools, were applied in order to provide quantitative data, such as porous volume, pore connectivity and accessibility.

2. RESULTS

2.1 Experimental conditions

The reference material used in this study is a commercial USY zeolite (Zeolyst, CBV712), a Y zeolite dealuminated by steaming to create a mesoporous network. Two alternative catalysts were characterized. The first one is the reference zeolite which was post-treated by an alkaline treatment inducing desilication. The second one is a nanoagregate of zeolite Y which was modified inducing dealumination and mesoporosity formation.

Electron tomography acquisitions were performed using a TEM JEOL 2100F operating at 200 kV. Tilted series were acquired in bright-field mode using Gatan Digital Micrograph routine. The tilt angles vary between about +/- 70° for all samples, the angle step is 1.5° in Saxton mode. Series were first aligned by cross-correlation and then by a fine alignment using gold fiducial markers. Filtered backprojection method is performed to reconstruct the volume. IMOD software [1, 2] was used for alignment and reconstruction. For each sample, at least 3 acquisitions were performed. After alignment and reconstruction, one representative object was selected for segmentation step and porosity quantification.

2.2 Method of segmentation and quantification of porosity

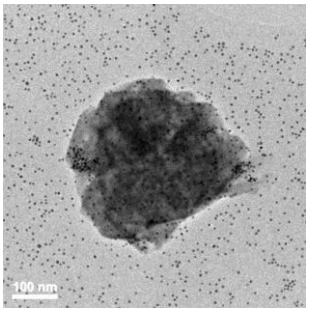
In order to facilitate segmentation, a 3D Flowing Bilateral Filter [3] was applied to the reconstructed object. This filter allows high quality and fast noise reduction preserving edges of the objects. Segmentation was completed in Avizo®. It was based on iterations of grey level thresholding, smoothing and islands removals. Quantification of mesoporous network was performed by applying mathematical morphology approach.

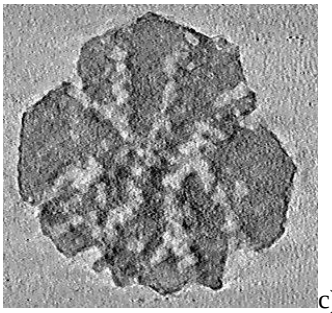
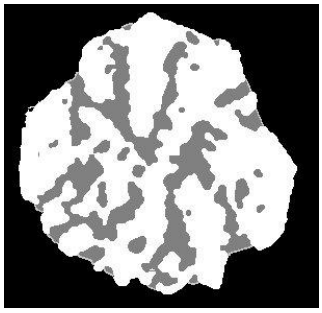
The same following image processing workflow was applied for all samples. It is illustrated on figure 1 :

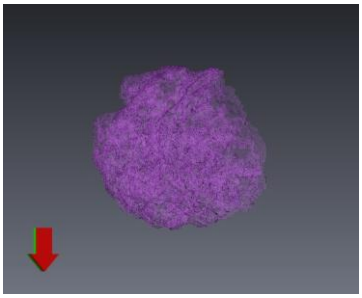
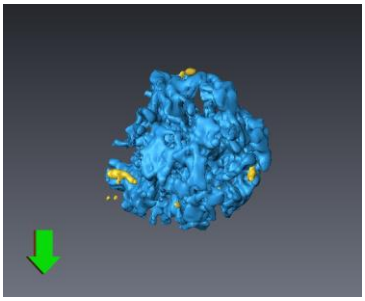
- A geodesic morphological closure [4] permits to “close” the zeolite crystal and extract mesoporous network
- Closed (non-accessible) and open (interconnected and connected to the outside of the crystal) porosity are visualized. The closed, open and total porosity are quantified, connectivity is defined

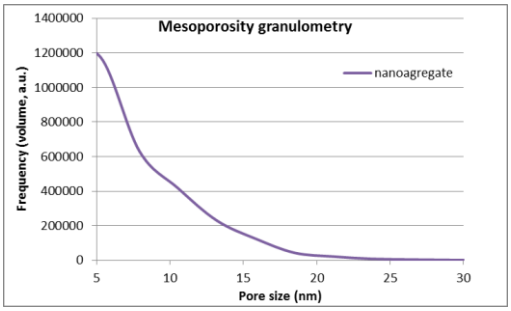
as the ratio of the open pores to the total mesoporosity. Tortuosity of pores is defined as the ratio of geodesic distance over euclidean distance [4].

- Granulometry of porosity is measured by morphological opening with spheres of increasing sizes. A fast algorithm using exact distance transform is used. Thus a characteristic pore size is calculated.

a) 

b) 
c) 

d) 
e) 

f) 

g)

	% total agregate volume
Mesoporous volume	28%
Closed porosity	< 1%

Figure 1. a) TEM image of a nanoagregate of zeolite ; b) slice of the reconstructed filtered volume ; c) segmentation and porosity extraction ; d and e) 3D model of zeolite and porous network (in yellow, closed porosity); f) granulometry analysis of porosity; g) Porosity quantification.

3. CONCLUSION

Electron tomography analysis was applied on three different mesoporous zeolites. A workflow of image analysis was developed in order to compare quantitatively mesoporosity. We will show that this method permits to outline differences in porosity accessibility and pore distribution.

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