

EFFECT OF THE ZEOLITE STRUCTURE TYPE ON THE PROPERTIES OF CARBONS REPLICAS MADE BY A NANOCASTING PROCESS.

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Introduction

In recent years, novel microporous carbons have been obtained from zeolite templates (mainly from commercial Y zeolite (FAU-structure type)) using the nanocasting technique [1]. We studied the nanocasting of 13 non commercial zeolites. They were chosen for their large pore aperture (at least one opening formed by 8 or more TO4 tetrahedra (T=Si, Al, Ge)). In the light of the results, the zeolites were divided in 4 categories: Group A consists of three zeolites with a three-dimensional porous network with large openings: beta (*BEA-structure type), faujasite Y (FAU-structure type) and EMC-2 (EMT-structure type). Group B consists of zeolites of structural groups: AFI, OFF, IFR. Zeolites ITQ-4 (IFR-structure type) and AIPO4-5 (AFI- structure type) have a one-dimensional porous network with large openings. The porous network of offretite (OFF structure type) is three-dimensional but has two types of channels. The first one is two-dimensional with a low opening diameter while the second is one-dimensional with large openings. Group C consists of zeolites of structural groups: MTW, STT, MWW, MOR, MEL, and MFI. These zeolites present one-, two- or three-dimensional porous networks but the diameter of openings is relatively small. Group D consist of the zeolite IM-12 (UTL-structure type). This silico-germanate presents a two-dimensional porous network with very large openings. Its calcined form is very sensitive to damp, which could cause the collapse of the structure [2].

Experimental

The CVD process used was derived from reference [3]. The chemical vapor deposition is performed at 650°C for 5 h and is followed by a heat treatment at 900°C during 4h. The matrix was etched by using an excess of hydrofluoric acid (40%). Hereafter, the samples are named with the 3 letters of the zeolite structure type. The letter C is added for the carbon replica. The samples were characterized by X-ray diffraction, nitrogen physisorption at 77K, scanning and transmission electron microscopies.

Results and discussion

The XRD patterns of the carbon replicas of the group A display at least one peak in the same angular range as the parent zeolites (Figure 1).

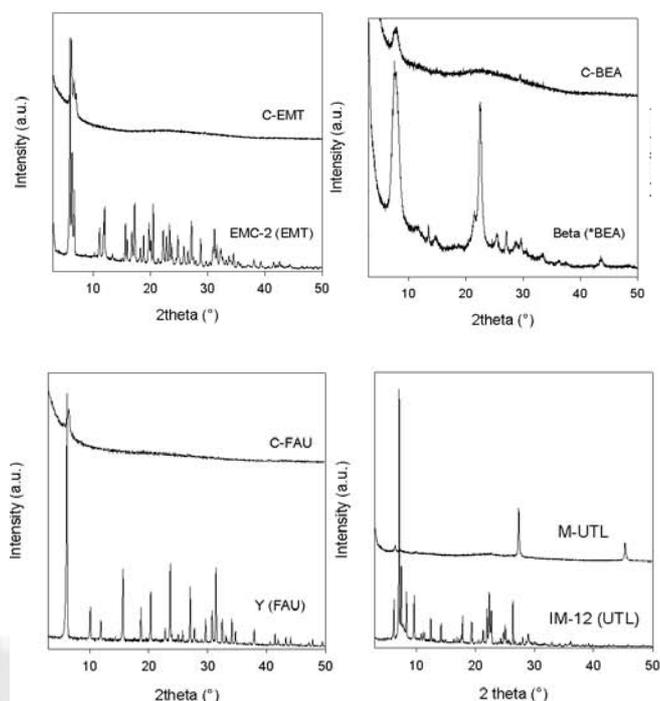


Fig. 1 XRD patterns (Cu K α radiation) of zeolites EMC-2 (EMT), beta (*BEA), Y (FAU) and IM-12 (UTL), carbon replicas C-EMT, C-BEA and C-FAU and carbon/zeolite composite M-UTL.

Also, these carbons show the same symmetry as their host material. The pore volumes and specific surface areas are large due mainly to the microporous character of the samples (Table 1). The pore size distribution (PSD) curves of these carbon replicas show three pore diameter maxima. The first one is attributed to adsorption on localized site. These sites can be defects inside carbon walls or ultramicropores formed by nanographenes stacking. The second is due to the zeolite wall dissolution. The third maximum arises from the incomplete filling of the zeolite template. No diffraction peak is detected for the carbon replicas of groups B and C. The one-dimensional structure or pore aperture is too small to get a proper infiltration of the carbon precursor and therefore the amount of carbon in the composite zeolite/carbon remains low. The pore volumes and specific surfaces are low (Table 1). The PSD curves of these carbon replicas do not display pore diameters attributed to the zeolite wall dissolution. The macroscopic morphologies observed on SEM and TEM images for the replicas are similar to those of the zeolite template. The carbon coating on the surface of zeolite crystals allows keeping the morphology of the mould. The zeolite IM-12 (UTL) collapses during the chemical vapor deposition. Indeed, the powder XRD pattern of composite M-UTL

displays the peaks (111) and (220) of germanium (Figure 1). Germanium oxide is therefore reduced by the decomposition products of acetylene (C and H₂, for example).

Table 1. Carbon Fractions in the Carbon/Zeolite Cocomposites, Specific surface Areas and Pore Volumes of the Carbon Replicas.

Group	Mould	Amount of carbon (%)	Apparent surface area BET (m ² /g)	Total Pore Volume (cm ³ /g)	Microporous Pore Volume (cm ³ /g)
A	Beta (*BEA)	29	1600	0.90	0.69
	faujasite Y (FAU)	20	2700	1.32	1.09
	EMC-2 (EMT)	23	3200	1.44	1.41
B	ITQ-4 (IFR)	8	370	0.20	0.14
	AlPO-5 (AFI)	4	340	0.34	0.13
	Offetite (OFF)	15	530	0.30	0.21
C	ZSM-12 (MTW)	14	290	0.57	0.10
	silicalite-2 (MEL)	7	110	0.16	0.04
	ZSM-5 (MFI)	5	150	0.11	0.06
	SSZ-23 (STT)	7	180	0.17	0.07
	MCM-22 (MWW)	17	310	0.48	0.12
	Mordenite (MOR)	6	290	0.42	0.11
D	IM-12 (UTL)	2	390	0.34	0.15

Conclusions

The zeolites with a three-dimensional channel system having a large aperture allow the infiltration of high amounts of carbon. Thus, faithful carbon replicas with ordered nanoporosity are obtained. Other types of zeolites, with lower dimensionality of the pore network or with a lower aperture do not appear as suitable candidates for the nanocasting process.

References

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