



Properties of CMK-8 carbon replicas obtained from KIT-6 and pyrrole at various contents of ferric catalyst

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ABSTRACT

The CMK-8 carbons were synthesised using two KIT-6 silica matrices exhibiting well-ordered structures. With increasing synthesis temperature, the BET surface area and micropore volume diminished while the average size of mesopores increased. Among the replicas of KIT-6(1 2 0), the one synthesised using the largest amount of FeCl₃ (2.00 g/g silica) showed the best structure ordering. The opposite trend was observed for carbons derived from KIT-6(1 0 0): the replica prepared with use of 0.75 g FeCl₃/g silica exhibited the best structure ordering, reflected in the narrowest pore size distribution (centred at 4.3 nm), $a_0 = 20.54$ nm, and $S_{\text{BET}} = 1313$ m²/g. This was due to an appropriate geometric relationship between the pore size and wall thickness of the matrix. The replicas of KIT-6(1 2 0) appeared to have a more homogenous pseudo-graphitic character. All the replicas exhibited high catalytic activity in oxidation of SO₂ in a liquid phase. The catalytic activity process does not directly correlate with the total nitrogen content; it relates to nitrogen of the quaternary type and depends on external surface areas of the samples studied.

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1. Introduction

The CMK-8 carbons are replicas prepared from pyrrole similarly to the CMK-3 carbons [1]. Simultaneous presence of carbon, nitrogen, and iron in catalysts is beneficial for generating active sites appropriate for oxygen reduction [2]. For example, carbons prepared by pyrolysis of a furan resin mixed with phthalocyanine, containing nitrogen atoms in particular chemical environments, exhibit an enhanced activity in the oxygen reduction [3]. Formation of such active sites during the carbon synthesis via pyrrole polymerisation and subsequent carbonisation is possible as well.

A number of papers on preparation of carbons from polypyrrole have been published by now [4]. This precursor has also been used to synthesise replicas of micro/mesoporous matrices [5–8]. Most of these replicas were obtained from the SBA-15 matrix [5,6,8]. However, there are no reports on the synthesis of CMK-8 type carbons from polypyrrole.

The CMK-8 materials are the carbons synthesised using the KIT-6 silica matrix. KIT-6 as well as MCM-48 belong to the cubic system and to the same *Im3d* space group. This three-dimensional (3D) structure facilitates the mass transfer kinetics in adsorption-based

applications [9] and is beneficial for obtaining the carbon replicas. The diameter of the MCM-48 main pores is usually narrower than that of KIT-6. The other difference between these two structures is that KIT-6 exhibits an additional pore system connecting the main pores. Due to that, formation of a stable faithful replica of KIT-6 should be possible, as it is in the case of the materials pair SBA-15/CMK-3. Lack of such a porous system in MCM-48 results in a less-ordered replica structure (*I4₁32*) obtained after removal of silica [10]. The 3D ordered mesoporous silica applied as a matrix in the synthesis of the carbon replicas seems to provide sufficient accessibility to FeCl₃ used as a catalyst for the pyrrole polymerisation.

In the presented method for the replica synthesis with use of controlled amounts of FeCl₃, carbon materials of various pore sizes, pore volumes, and surface areas were obtained. After carbonisation of the carbon–silica composites, the samples were washed with the HF and HCl solutions and with water to remove silica and residual Fe.

The aim of this study was to estimate the influence of (i) the amount of introduced FeCl₃ as the catalyst for pyrrole polymerisation and (ii) use of two matrices of different pore diameters (7.4 and 8.4 nm, BJH_{des}) on sorption properties of the CMK-8 replicas. It is known from the literature, that nitrogen-containing carbons are active in the SO₂ oxidation [11–14]. However, the results about the effect of the total nitrogen content and of the contents of particular nitrogen forms on the catalytic activity of the carbon materials are

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inconsistent. Thus, catalytic properties of the obtained carbons were tested in the reaction of the SO_2 oxidation performed in an aqueous solution. The influences of the ordering of the carbon pore structure and of the nitrogen content on the rate of the SO_2 oxidation process were also studied.

2. Experimental

The KIT-6 parent materials were obtained after a slightly modified procedure reported by Kim et al. [15]. According to this, the gel of the following molar composition: 0.017 P123:1.2 TEOS:1.31 BuOH:1.83 HCl:195 H_2O was applied. Two matrices, KIT-6(1 0 0) and KIT-6(1 2 0), were synthesised at 373 and 393 K, respectively. The CMK-8 replicas were prepared similarly as CMK-3 [8], using pyrrole and FeCl_3 as the polymerisation catalyst. They were also similarly washed with solutions of HF and HCl and with deionised water. The carbons are denoted as $\text{C}_x\text{NKIT-6}(1\ 0\ 0)$ and $\text{C}_x\text{NKIT-6}(1\ 2\ 0)$, where x is the number of g FeCl_3 (0.75, 1.25, and 2.00) per 1 g of KIT-6. The matrices and replicas were characterised by XRD, nitrogen adsorption, thermal analysis, and TEM with EDX. Sorption isotherms were determined with a Micromeritics ASAP 2010 volumetric analyser. Structure properties were examined using a Philips X'Pert PRO System. TGA and DTA profiles were recorded with a TA Instruments SDT 2960 apparatus. The catalytic activity was measured at 294 K using a batch reactor in an aqueous phase with a SO_2 solution of 1.65×10^{-3} M SO_2 and O_2 concentration kept constant by continuous air bubbling inside the reactor ($3\ \text{dm}^3/\text{h}$, $[\text{O}_2] > 10^{-3}$ M). The SO_2 conversion was monitored by conductometry [12,13]. Catalytic activities of CMK-3 free of nitrogen and of CMK-3N1.25 discussed elsewhere [1] are taken into account for comparison.

3. Results and discussion

The XRD powder patterns of KIT-6(1 0 0) and KIT-6(1 2 0), being the materials with a cubic symmetry, exhibit features characteristic of the $Ia3d$ structure (Fig. 1). The most intense peak (at $2\theta = 0.94^\circ$) of the KIT-6(1 0 0) pattern corresponds to the interplanar distance of $d_{2\ 1\ 1} = 9.45$ nm. The interplanar distance of KIT-6(1 2 0) is somewhat larger: $d_{2\ 1\ 1} = 10.08$ nm, as derived from the peak located at $2\theta = 0.88^\circ$. This indicates that the unit cell constant, a_0 , of KIT-6 increases as the synthesis temperature rises.

The nitrogen sorption isotherms for the KIT-6 materials (Fig. 2) are of type IV, each with a hysteresis loop of type H_1 occurring at $p/p_s = 0.65$ – 0.80 . Filling the pores of KIT-6(1 2 0) begins at $p/p_s = 0.75$, compared to $p/p_s = 0.70$ for KIT-6(1 0 0). The hysteresis loop for KIT-6(1 2 0) appears at higher values of p/p_s (0.75–0.80) in relation to that for KIT-6(1 0 0), which suggests that pore diameters of the former material are larger. Structural parameters derived from the α_s plots (Table 1) indicate that the micropore volume of KIT-6(1 0 0) is larger ($0.06\ \text{cm}^3/\text{g}$) and the mesopore volume is smaller ($0.98\ \text{cm}^3/\text{g}$) as compared to KIT-6(1 2 0) (0.01 and $1.08\ \text{cm}^3/\text{g}$, respectively). The BET surface areas are 781 and $698\ \text{m}^2/\text{g}$ for KIT-6(1 0 0) and KIT-6(1 2 0), correspondingly. The pore diameters, calculated by the BJH method from the adsorption branches of the isotherms, are 8.91 and 9.77 nm (Fig. 3) while those derived from the desorption branches, 7.35 and 8.39 nm for KIT-6(1 0 0) and KIT-6(1 2 0), respectively. One can conclude that the volume and average diameter of mesopores increase while the volume of micropores slightly decreases as the synthesis temperature rises.

After impregnation with FeCl_3 , sorption capacity of KIT-6 decreases, although the isotherm shape (type IV) and position of the hysteresis loop are preserved (Fig. 2b). This indicates that a fraction of pores is blocked, some pores remaining unfilled.

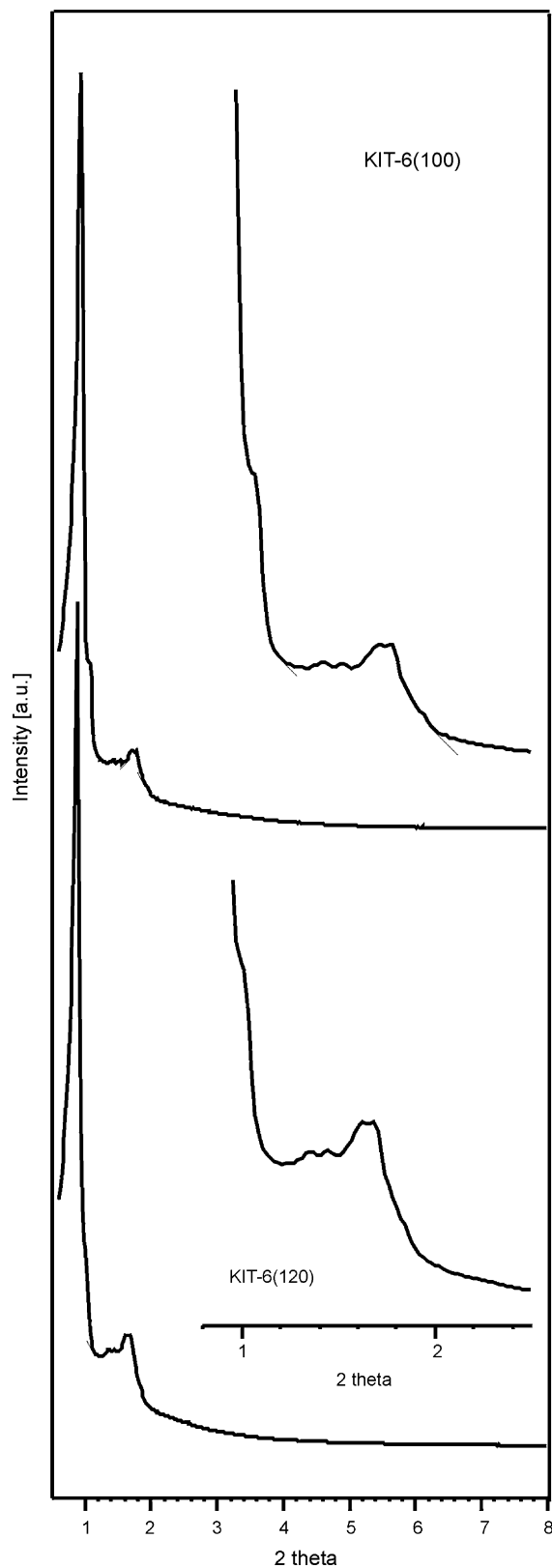


Fig. 1. XRD powder patterns of KIT-6(1 0 0) and KIT-6(1 2 0) matrices.

The prepared mesoporous carbons exhibit different structure ordering. Lack of peaks within the 2θ range of 0.6 – 7.5° in the XRD patterns of $\text{C}_{0.75}\text{NKIT-6}(1\ 2\ 0)$ and $\text{C}_{1.25}\text{NKIT-6}(1\ 2\ 0)$ does not unequivocally prove that an ordered mesoporous phase is absent in these materials (Fig. 4a). It is possible that a broad peak

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