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Microporous and Mesoporous Materials

Short communication

Template assisted synthesis of porous carbons revisited — Where does the porosity come from?

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ABSTRACT

The template assisted synthesis of porous carbons using hard templates has been described for the first time in the 80s of the last century. Especially during the last two decades there was a huge increase in publications on that topic. A long standing issue under discussion has been the role of the template in the pore formation process. This contribution represents a comparative study of template assisted synthesis routes regarding the origin of the carbon replica porosity. For that, data obtained in our own lab and reported in thirteen different publications, respectively, have been evaluated and compared with each other. The interplay of different parameters such as textural properties of the template, carbon precursor and synthesis method, respectively, has been discussed.

1. Introduction

Since the 1980s the template assisted synthesis of porous carbons has been described as a powerful tool to obtain carbons with defined properties [1—7]. The general principle of these routes consists in the use of a porous material such as zeolites [2—5] or mesoporous silica [6] as a template. The template pores are filled with a carbon precursor, e.g. sucrose or furfuryl alcohol. After the carbonization of the precursor within the template pores and the subsequent removal of the template a negative carbon replica of the template is obtained. The conversion of gaseous precursors like propylene via the chemical vapor deposition (CVD) within the template pores has been described as an alternative route [3,4].

Provided that the template pores are filled by carbon completely, the properties of the carbon replica are determined by the template in the following ways:

- the internal surface area corresponds to those of the template because the template and the formed carbon network have a common interface;

- the pore size distribution is determined by the thickness of the template pore walls [4,8,9];
- the pore volume is determined by the skeleton volume of the template [9];
- the geometrical shape of the template particle will be transferred to the replica [4].

This scenario will here be termed as the direct template effect. However, besides the direct template effect additional factors have to be considered such as.

- the template pore filling degree, because very often template pores are not filled completely and unfilled template pore volume can remain as pore volume in the replica [9,10];
- the carbon distribution within the template particle which can result in local gradients of the pore filling degree and consequently in regions of different carbon network stability;
- the inherent carbon porosity caused by the chemical conversion of the precursor [4,10,11].

These factors can influence the quality of the synthesized products significantly. As an example, replicas obtained by the carbonization of sucrose in silica [12] possesses BET surface areas which are up to 10 times larger than it was expected by a direct template effect. So, additional effects, here caused by the

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incomplete template pore filling and the inherent carbon porosity have to be considered.

During the last two decades several groups have investigated numerous systems of templates and carbon precursors [3–22]. The variation of the used templates covers the pore size distribution over the whole range including micropores (zeolites), mesopores (silica) and macropores (porous concrete) as well. Many efforts have been undertaken to explain the development of the pores in the carbon replica for each individual system precursor − template. In this contribution, the data obtained that way shall now be compared and evaluated comprehensively regarding the question whether the textural properties of the replicas are dominated by the template effect or whether additional effects play a significant role. As far as possible, the contribution of the direct template effect shall be estimated in a quantitative way.

2. Experimental

The synthesis of the materials presented here has been reported previously in the literature. Table 1 gives a brief survey of the applied synthesis procedures, the template materials, the carbon precursors and the according reference, respectively.

3. Results and discussion

To compare the measured textural properties (i.e. pore volume and, respectively, BET surface area) of the carbons with those which could be predicted from a direct template effect we assume the following:

- the carbon-template-composites should contain only two kinds of pores and pore segments, respectively: those, which are completely filled by carbon and those, which are totally empty;
- there is no significant shrinking of the template;
- the carbon should not possess any inherent porosity.

Any deviations of the measured values from the predicted values will be discussed in terms of scenarios, which differ from those of the here presented assumptions.
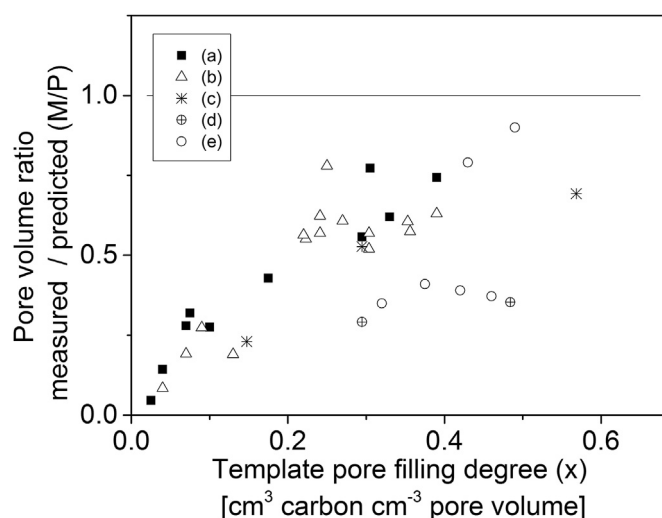
3.1. Development of the carbon pore volume

If the infiltrated carbon doesn't have any inherent porosity and the shape and the size of the template particle will be transferred to the replica particle, the value of the replica pore volume $V_{pore\ predict}$ (given in cm^3 per g carbon) can be predicted from the template skeleton volume and the volume of the unfilled template pores:

$$V_{pore\ predict} = \frac{V_{skel\ template} + V_{pore\ template} - x \cdot V_{pore\ template}}{m_{carbon\ infil}}$$

(1)

Fig. 1. Dependence of the ratio of measured and predicted pore volume M/P on the template pore filling degree x of carbons obtained from mesoporous templates but different precursor systems: silica-sucrose (a), silica-polymer (b), silica-CVD (c), silica-pitch (d), and porous concrete-sucrose (e). References, textural properties and synthesis parameters are given in S.2 (supplementary material).

where $V_{skel\ template}$ is the template skeleton volume in cm^3 per g template; $V_{pore\ template}$ is the template pore volume in cm^3 per g template, and x is the template pore filling degree expressed as the fraction of the carbon filled template pore volume in cm^3 carbon per cm^3 pore volume. The mass fraction of infiltrated carbon $m_{carbon\ infil}$ is given in g carbon per g template. Further details are given in the Supplementary section.

In trying to understand the development of the replica pore volume the ratio of the measured pore volume V_{pore} and the predicted pore volume $V_{pore\ predict}$ M/P according Eq. (1) has now been calculated. A replica mainly formed by a direct template effect will have a ratio near one. In general there is a dependence of that ratio from the template pore filling degree (Fig. 1). The higher the pore filling the closer the ratio M/P approaches a value of one. However, it does not achieve nor even exceed that value. There are different explanations for deviations from the value one:

(i) Carbon replica particles could get broken after dissolution of the template which has to be expected if a significant part of the template pores remains non-filled by carbon. As mentioned above, non-filled template pore volume contributes to the replica porosity. However, if the particle got broken these regions would now occur as external surface instead of internal pores and the measured value of the pore volume would be (considerably) lower than the predicted value. This explanation is supported by the trend shown in Fig. 1 because with increasing carbon loading of the template the probability of the particle breaking will be decreased

Table 1
Template, carbon precursor and template loading method of the presented materials.

Template	Carbon precursor	Method	Ref.
Mesoporous silica	Sucrose	Impregnation	[10,12–15]
Mesoporous silica	Fufuryl alcohol, Phenolic resin, pitch	Impregnation	[9,10,16,17]
Mesoporous silica	propene	CVD	[10]
Zeolite	ethene	Adsorption under pressure	[18]
Zeolite	Propene	CVD	[3,4,19]
	Furfuryl alcohol	Impregnation	
Porous concrete	Sucrose	Impregnation	[20]