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Modeling the MOF mediated synthesis

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Highlights

- The stability of Cu-BTC, Fe-BTC and ZIF-67 (Co) is key for their use in catalysis
- Temperature effect is different for Cu, Fe and Co size evolution in the MOFMS
- Avrami's nucleation model describes best the MOFMS of Cu-BTC, Fe-BTC and ZIF-67(Co)

1. Introduction

Metal organic frameworks (MOFs) are crystalline compounds consisting of metal ions or clusters coordinated to organic molecules to form one- two-, or three-dimensional pore structures [1]. Frequently, the main constraint of MOFs in catalysis is their limited thermal stability. Otherwise, the thermal decomposition of MOFs, also called MOF-mediated synthesis (MOFMS), is used to synthesize highly stable catalysts. Starting with a very regular, defined and well-dispersed system, the pyrolysis of a MOF in inert atmosphere delivers metal/metal oxides/metal carbide nanoparticles embedded in a porous carbon matrix (NP@C) with outstanding catalytic properties in terms of both activity and stability for different reactions [2-4]. After all, the MOFMS is expanding rapidly among the research community these days. Understanding the crystal growth evolution of the NPs in the MOFMS is of the utmost importance in order to gain control on this technique. In view thereof, this work quantitatively analyzes the decomposition of MOFs, thus the MOFMS process, and the crystal growth evolution of the MOF derived NPs, in the attempt to provide a powerful tool for future work on this topic. To this purpose, three broadly studied MOFs ZIF-67(Co), Fe-BTC and Cu-BTC have been selected in this study.

2. Methods

Commercial Fe-BTC (Basolite F300) and Cu-BTC (Basolite C300) were supplied by BASF. ZIF-67(Co) was prepared according to the method reported by Xia *et al.*[5] The stability of MOFs was addressed by thermogravimetric analysis (TGA) in N_2 from 30-800 °C at different heating rates (2, 5 and 10 K/min) providing the experimental data for the modelling and parameter estimation of the solid conversion rate $d\alpha/dt$ (Eq.1) using different solid conversion models ($f(\alpha)$. The parameter estimation has been carried out in MATLAB by minimizing the sum of squared residuals (*SSR*) between the model and the experimental conversion data and using Friedman´s approach[6] as a first estimation of the E_a and k_0 parameter values as a function of the conversion level. Among different solid conversion models, the Avrami nucleation model (Eq. 2) has been analyzed.

$$\frac{d\alpha}{dt} = k(T)f(\alpha)f_2(pi) = k_0 \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \qquad \textbf{(1)}$$

$$f(\alpha) = N(1-\alpha)\left(-ln(1-\alpha)\right)^{(N-1)/N} \qquad \textbf{(2)}$$

After the collapse of the framework, the evolution of the metal crystallite size has been measured continuously by *in situ* Powder X-Ray Diffraction (PXRD) from 30 to 800 °C in steps of 50 or 100 °C following 5 K/min and 15 min dwelling time for measuring.

3. Results and discussion

According to parameter estimation and model discrimination, the *two- (N2) or three-dimensional (N3) growth of nuclei* model by Avrami [7] describes best the decomposition of these MOFs in inert atmosphere. The Avrami model assumes that i) nucleation occurs randomly and homogeneously over the entire untransformed portion of the material, ii) the growth rate does not depend on the extent of transformation and iii) the growth occurs at the same rate in all directions. Moreover, Table 1 shows the estimated parameter values for the three MOFs after SSR minimization. The *N2 growth of nuclei* describes best the decomposition of ZIF-67 (Co) and Fe-BTC whereas the *N3 growth of nuclei* applies to the Cu-BTC. According to the parameter estimation, ZIF-67 (Co) has the highest Ea (260 kJ mol^{-1}), followed by Cu-BTC (230 kJ mol^{-1}) and Fe-BTC (185 kJ mol^{-1}). According to thermodynamics [4], these three MOFs tend to form metallic nanoparticles (NP) in inert atmosphere at high temperature, as confirmed by PXRD. The average Cu, Co and Fe crystallite sizes have been calculated using the Scherrer equation. Results in Figure 1 show for Cu-BTC, an increase in the Cu crystal size ranges from 24 to 33 nm starting from 623 K up to 1173 K. For ZIF-67, increase in the Co crystal size ranges from 5 to 55 nm starting from 773 K up to 1173 K. For Fe-BTC, the increase in the Cu crystal size ranges from 4 to 40 nm starting from 723 K up to 1173 K.

Table 1. Estimated parameter values for Avrami's *N*-dimensional growth of nuclei model for ZIF-67, MIL-100, HKUST-1 decomposition

	Ea kJmol^{-1}	**k_0 s^{-1}**	**mean-SSR**
ZIF-67 (N2)	260	$7.6\cdot10^{15}$	$1.5\cdot10^{-2}$
Fe-BTC (N2)	185	$2.1\cdot10^{12}$	$2.8\cdot10^{-2}$
Cu-BTC (N3)	230	$8.3\cdot10^{18}$	$1.4\cdot10^{-2}$

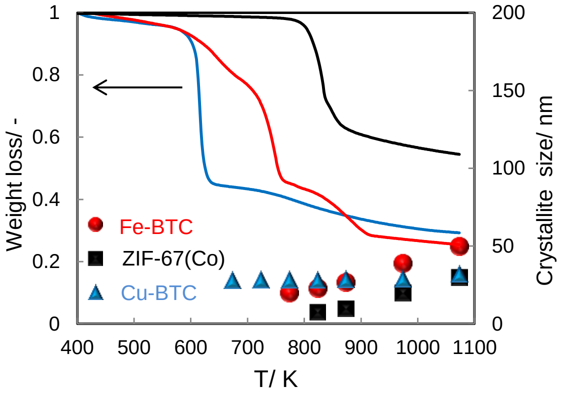

Figure 1. Evolution of metal NP size during pyrolysis of ZIF-67, Fe-BTC and Cu-BTC at 5 K/min

4. Conclusions

The decomposition process of Cu-BTC, Fe-BTC and ZIF-67 (Co) is well described by the Avrami nucleation models. Regarding the crystallite size evolution of the NPs, Cu is hardly affected by the pyrolysis temperature, whereas for both Co and Fe the increase in size follows a similar trend, although the Fe nanoparticles are considerably bigger than the Co nanoparticles from ZIF-67.

Keywords
Metal Organic Frameworks; Decomposition; Crystal growth; Modelling

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