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Tuning the activity by controlling the wettability of MOF eggshell catalysts: A quantitative structure–activity study

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ABSTRACT

In this work, we report a quantitative structure-activity relationship of functionalized ZIF-type materials (SIM, Substituted Imidazolate Material). Keeping the catalytic center unmodified, post-synthetic modification allows an efficient control of the hydrophilic–hydrophobic balance which drives the competitive adsorption of reactants and products. Hence, we attribute the increase in the reaction rate of Knoevenagel condensation (up to seven times) to the modification of the environment of catalytic sites through the creation of hydrophobic environment surrounding the catalytic sites. Surface tension properties are monitored by measuring the contact angle with a water droplet on a SIM thin film grown on a flat support. We show that the contact angle is directly correlated to the catalytic activity of Knoevenagel condensation. Hence, we propose that the contact angle of a catalyst thin layer with water can be a quantitative descriptor of direct relevance for catalytic processes which produces water and/or for catalysts that are poisoned with water. Finally, we measured the intrinsic reaction rate free of external and internal diffusion limitations by controlling the thickness of the SIM shell on SIM/alumina beads. Insights on the localization of the active sites (surface vs. bulk) are provided.

1. Introduction

Metal-organic frameworks (MOFs) are a new class of hybrid porous materials that are very attractive to design new type of catalysts [1–8]. Their catalytic properties arise from structural features already present on their frameworks such as open metal centers [9–13], acid bridging hydroxyl [14] or accessible N-bases on the organic linkers [15,16]. Because of their well-defined structure and site isolation, MOFs are found to be a very appropriate class of model solid catalysts. Indeed, it is possible in practice to change one particular feature without affecting the others, which is usually a challenge for other porous inorganic catalysts. For example, it is possible to control the pore size by selecting longer ligands, everything else remaining the same. It is also possible, to a certain extent, to synthesize isomorphous structures with different cations; MIL-53 compounds can be obtained by a wide range of metal cations such as Al^{3+}, Ga^{3}, Fe^{3+} or Cr^{3+} others, and eventually mixture of thereof [17]. With the purpose of getting more sophisticated MOF catalysts, post-synthetic modification (PSM) methods have been recently developed [18–20]. It consists in the chemical modification of the solid after formation of the parent crystalline structure by grafting organic or organometallic species onto the parent MOF host without significant modification of the initial structure [14,21–25]. Despite these advantages for the design of model catalysts, in order to carry out fundamental investigations on catalytic mechanisms, studies of structural–activity relationship are still rarely found [26,27].

Furthermore, it shall be noticed that crystalline defects present on MOF-5 and ZIF-8 (zeolite imidazolate frameworks) are likely responsible for catalyzing some acid–base reactions [14,28]. Concerning ZIF-8, Chizallet et al. have reported its outstanding catalytic activity in transesterification reaction of vegetable oil with various alcohols [29]. From experimental and molecular modeling results, they have found that Zn(II) and Zn(III) species, which are Lewis acid sites, are located at the external surface and/or are bulk defects of ZIF-8. Moreover, the N^{-} at the extremity of monocoordinated imidazolate ligands as well as NH groups can participate as Brønsted bases.

On the other hand, water poisoning is an often encountered issue in catalysis [30–32]. Indeed, catalytic reactions can be hindered or just limited due to poisoning effects originating from moisture in the air or from the water formed as the product of reaction. Water molecules are irreversibly adsorbed on the catalytic sites, leading to catalyst deactivation. This motivates the design and engineering of catalytic materials with hydrophobic features – such as the hydrophobic outer shell of enzymes – in order to prevent water-induced catalyst poisoning. Cohen has reported hydrophobization of amino-containing MOF powders by post-synthetic modification, through amide coupling, using alkyl anhydrides [33]. In his study, the best results are obtained with an alkyl chain of 6 carbons and a minimum PSM yield of 17% to create a superhydrophobic MOF.

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A key challenge for industrial use of MOFs is to deliver them in a shape suitable for applications [34,35]. Superhydrophobic properties of thin films used against biofouling are originated from a combined engineering at molecular level (low-surface-energy coatings such as perfluorinated compounds) and at macroscopic levels (rough surfaces) [36]. These studies are mainly based on nonporous materials, like silica wafers [37], polymer coatings [38,39] and metals [40–43]. Very few studies report superhydrophobic properties of microporous films [44].

Our team have already reported post-synthetic modification of a porous substituted imidazolate material, SIM-1. It belongs to the class of ZIF materials [45]. Zinc imidazolate SIM-1 is isostructural to ZIF-8 (SOD), which is commercialized under the name Basolite Z-1200 [46,47]. SIM-1 solid consists of Zn–N_4 tetrahedra linked by carboxyimidazolates. We have already reported that creating a hydrophobic environment by post-synthetic modification on SIM-1 powder can enhance the catalytic activity by an order of magnitude factor [48]. We have also described earlier the preparation of supported thin films of SIM on different alumina supports [49–53].

In this work, we report for the first time a quantitative structure–activity relationship of a functionalized MOF. Hydrophilic–hydrophobic balance of SIM, which drives the adsorption of water, is controlled by functionalization of the material by grafting C_{12} alkyl chains onto the framework. Surface tension properties are monitored by measuring the contact angle with a water droplet on SIM thin film grown on a flat support. We show that the contact angle is directly correlated to the catalytic activity of Knoevenagel condensation. Hence, we propose that the contact angle of a catalyst thin layer with water can be a quantitative descriptor of direct relevance for catalytic processes which produces water and/or for catalysts that are poisoned by water. We provide general principles and methodologies that can be applied to other type of porous materials such as zeolites or ordered mesoporous materials. Finally, we measured the intrinsic reaction rate free of external and internal diffusion limitations by controlling the thickness of SIM shell on SIM/alumina beads. Insights on the localization of the active sites (surface vs. bulk) are provided.

2. Materials and methods

2.1. Film preparation and characterization

All reactions are carried out in anhydrous solvents as received. All other reagents were commercially available and were used without further purification.

Hydrophobic features are quantified by measuring the contact angle of a water drop deposited on the dry material surface. For this measurement, supported SIM-1 thin films on flat alumina disks are synthesized following a general method already reported [51,53]. We used symmetric anodic alumina disks (13 mm diameter, 60 μm thickness, pore size 200 nm, supplied by Whatman, Fig. 1). The disk is immersed into a solution of $Zn(NO_3)_2 \cdot 4H_2O$ (0136 M) and 4-methyl-5-imidazolecarboxaldehyde (0,55 M). After a solvothermal treatment at 358 K for 48 h, the resulting supported material is washed with ethanol to remove the unreacted precursors and the fine SIM-1 unsupported particles. Supported SIM-1 on disk is then dried at room temperature.

Catalytic tests are carried out on eggshell type catalysts. Alumina beads are coated with SIM-1 layer following the synthesis procedure described above. Beads are α-alumina beads (1.5 mm diameter, BET area 2 $m^2\,g^{-1}$, supplied by Saint-Gobain Norpro, Fig. 1). In order to control the thickness of the films in SIM-1/α-alumina beads composites, synthesis time varies between 8, 24 and 48 h.

Thickness and homogeneity of SIM-1 films on α-alumina beads are characterized by SEM using a JSM 5800LV (JEOL). Tension range is 0.3–30 kV, and effective resolution is 0.5 nm at 30 kV.

Characterization of hydrophobic surfaces is usually performed by contact angle measurement with water. When the apparent water contact angle is lower than 90°, the surface is hydrophilic; when it is higher than 90°, the surface is hydrophobic; and when the contact angle is higher than 150°, the surface is coined as superhydrophobic [36]. Thus, hydrophobic properties of SIM materials are determined from contact angle of a water drop with SIM thin film on anodic alumina disk, a flat support being required. In practice, a drop of deionized water is deposited using a syringe on the surface of the sample, and the contact angle is determined from pictures made using a CCD camera [54]. The values are an average of three independent experiments.

Structure integrity of SIM layers is checked by Powder X-ray Diffraction (PXRD) directly on SIM/alumina flat disk or by crushing the SIM/alumina beads into fine powder with a mortar, and the data are collected at room temperature using a Bruker D5005 Diffractometer equipped with a secondary graphite monochromator (Cu Kα radiation, wavelengths $\lambda = 0.154178$ nm) and a scintillation counter.

2.2. Post-synthetic modification (PSM) procedure

Post-synthetic modification procedure is applied on both SIM-1/flat disk layer and eggshell SIM-1. SIM-1/alumina composites (one disk or 20 beads) are immersed in a solution of 7 mL of anhy-

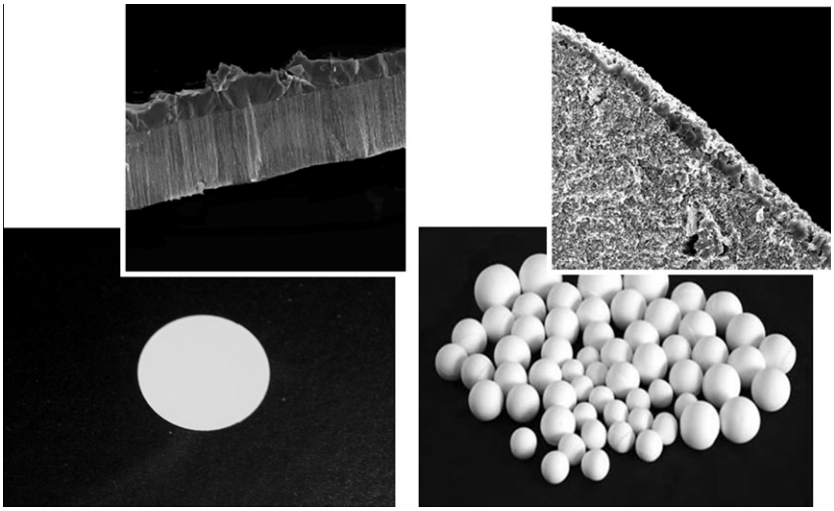

Fig. 1. Representative photographs of alumina supports, disk (left) and beads (right). Upper pictures show SIM/alumina cross-sections as observed by SEM.