Microporous and Mesoporous Materials 153 (2012) 236–246

Contents lists available at SciVerse ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Catalytic activity of HKUST-1 coated on ceramic foam

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ARTICLE INFO

Article history:
Received 5 September 2011
Received in revised form 19 December 2011
Accepted 29 December 2011
Available online 5 January 2012

Keywords:
Ceramic foam
HKUST-1
Hydroxyl radicals
Phenol oxidation
Tubular reactor

ABSTRACT

The *in situ* preparation of a Cu-bearing metal-organic framework material, HKUST-1, coated on an open-cell ceramic foam (CF) is presented. The material used as coating is a robust metal-organic framework with a micro-porous structure that is a reminiscent of the zeolite framework topology. In spite of relatively low thermal stability of HKUST-1 with respect to zeolites, this material has an interesting catalytic behavior in the formation of hydroxyl radicals. The synthesized HKUST-1 coated on CF (HKUST-1/CF) samples has been characterized and then used to carry out the preliminary hydroxyl radicals formation from hydrogen peroxide (HP) decomposition and the consecutive phenol oxidation tests. The maximum phenol abatement obtained is 95% after about 40 min, using a solution with an HP conversion of 70%. The HP kinetic data analysis has been done varying the reaction temperature in the range 60–80 °C. The hierarchical micro/macro-porous catalytic system has been used for more than 40 consecutive reaction runs, maintaining the catalytic activity and showing a negligible copper leaching.

1. Introduction

The metal-organic framework materials can be used as highly selective molecular sieves, sensors or catalysts [1]. The remarkable properties of these materials, such as high micro-pore volume, large pore sizes, high crystallinity and metal content, can be designed with more flexibility than in the case of zeolitic materials [2]. These properties make this class of porous materials very interesting as catalyst for low temperatures reactions, such as liquid phase transformations [3–10].

Open-cell ceramic foams (CF) are used primarily in applications where fluid transport in the microstructure is required (molten metal filtration, hot gas filtration, catalyst supports) [11]. The main characteristics that make the CF attractive in many research fields are low pressure drop, high surface area enhancing mass transport, radial mixing in the tortuous structure with improved heat transfer in highly endothermic and exothermic reactions [12]. The CF can be produced using various methods, including replication method, starch consolidation, foaming method and gel-casting of foam [13]. The use of the coating technique for the generation of a new reactor concept is gaining great interest [14–17].

The HKUST-1, as powder or as supported material, was recently used for applications in gas storage, molecular separation and gas adsorption. The Cu atoms in the HKUST-1 framework have a large affinity for water adsorption [18]. The adsorption properties of HKUST-1 material towards hydrogen [19–21], NO [20,22], CO_2, CO, N_2 [20,23], ammonia [22,23], CO_2/H_2O [24], CO_2/CH_4 and C_2H_4/C_2H_6 [23], pyridine [25], small aromatics (*o*-, *m*- and *p*-xylene) and polycyclic aromatic hydrocarbons (naphthalene, anthracene, phenanthrene) [26], methane [27], acetylene [28] are reported.

HKUST-1 was used as sorbent for liquid chromatography to carry out the selective separation of organic compounds including benzene, ethylbenzene, styrene and other aromatic species [29]. The heats of adsorption of Kr, Xe, N_2, CO_2, CH_4, n-C_4H_{10} and i-C_4H_{10} gases using HKUST-1 as sorbent material were evaluated [30].

HKUST-1 material was used as catalyst for the cyanosilylation of aldehydes and ketones [10], hydrosilylation of ketones [31], oxidation of hydroquinone to *p*-benzoquinone [32], oxidation of toluene, benzene and other aromatic substrates by H_2O_2 [33]. It was also used as highly selective Lewis acid catalyst for the isomerization of terpene derivatives [34].

In this work, the preparation of a new type of catalyst using a CF coated with the HKUST-1 material is presented. This metal-organic framework has been chosen because it possesses the advantageous catalytic properties of a structure with open metal sites. The catalytic activity has been evaluated for the production of hydroxyl radicals ($HO^{\cdot}$) from HP using a continuous process. Further, $HO^{\cdot}$ radicals has been used to obtain the decomposition of phenol. HP has been decomposed up to ca. 85%. The complete decomposition of phenol obtained confirmed the efficiency of the catalyst in the production of $HO^{\cdot}$ radicals.

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doi:10.1016/j.micromeso.2011.12.055

Nomenclature

HKUST-1	Cu-bearing metal-organic framework
CF	ceramic foam
HKUST-1/CF	HKUST-1 coated on CF
HKUST-1/P	HKUST-1 powder
HP	hydrogen peroxide, H_2O_2
$HO^{\cdot}$	hydroxyl radicals
PPI	pores per linear inch
HF	hydrofluoric acid
BTC	1, 3, 5-Benzene tri-carboxylic acid
XRD	X-ray diffraction
SEM	scanning electron microscopy
EDX	energy-dispersive X-ray analysis
TG	thermo-gravimetric analysis
DSC	differential scanning calorimetry
S_{BET}	Brunauer–Emmett–Teller surface area
HPLC	high-performance liquid chromatography
S_C	SBET of coated HKUST-1
S_P	SBET of powder HKUST-1
S_{CF}	SBET of as-made CF
m_{HK}	mass of coated HKUST-1 from porosimetric data
$V_{\mu p}$	micro-pore volume
d_p	micro-pore diameter
V_R	tubular reactor volume
V_{CF}	volume occupied by the CF in the tubular reactor
τ	residence time, min^{-1}
Q_{HP}	HP flow rate
X_{HP}	HP conversion
C_0^{HP}	HP concentration (M) at reaction time 0
C_t^{HP}	HP concentration (M) at reaction time t
T_{HP}	tubular reactor temperature
R_a	HP decomposition rate
k	kinetic constant, cm/min
E_a	activation energy
A	frequency factor
X_{Phenol}	phenol conversion
C_0^{Ph}	phenol concentration (M) at reaction time 0
C_t^{Ph}	phenol concentration (M) at reaction time t
T_{Ph}	semi-batch reactor temperature
V_0^{Ph}	volume of the starting phenol solution
η	global process efficiency
CAs	ring-opened low-molecular weight carboxylic acids
HQ	hydroquinone
o- and *p*-BQ	*o*- and *p*-Benzoquinone

2. Experimental section

2.1. Materials

The microcellular commercial CF (Fig. 1), model VUKOPOR A (nominal size (*d*) 25 mm × (*h*) 15 mm) purchased from Lanik (Czech Republic), obtained via the replication method with a cell density of 30 PPI (pores per linear inch), was used as support for the HKUST-1 deposition. The CF was kept in a dilute solution of hydrofluoric acid (HF 5%v/v in H_2O) for 6 h at room temperature [35], in order to remove the impurities present on the support surface. The mass loss observed during the HF washing was lower than 10 wt.%.

The coating was obtained using the *in situ* conventional one-step hydrothermal crystallization technique. The synthesis procedure for the preparation of HKUST-1 is a large-scale synthesis process [23], resulted from an optimization of a literature recipe [36]. For the coating of the CF, the synthesis mixture was prepared using the following recipe: 6.52 g of copper nitrate tri-hydrate ($Cu(NO_3)_2{\cdot}3H_2O$) were dissolved in 15 ml of distilled water (1.8 M Cu^{2+}) and 3.22 g of 1, 3, 5-benzene tri-carboxylic acid (BTC) were dissolved in 15 ml of ethanol (1 M BTC). These solutions were maintained under agitation for 30 min at 25 °C, then BTC solution was slowly added to Cu^{2+} solution. The obtained hydrogel was stirred for 1 h at 25 °C and than poured on the CF specimen, placed in a autoclave and heated under hydrothermal conditions (autogeneous pressure) up to the desired synthesis temperature for 18 h. Finally, the Teflon-lined reactor was rapidly cooled to room temperature and the coated ceramic foam (HKUST-1/CF) together with the turquoise powder (HKUST-1/P) were recovered, washed with distilled water and dried at 110 °C for 12 h. The synthesis temperatures were 110, 140 and 170 °C and the HKUST-1/CF samples obtained were named C1, C2 and C3, respectively. Another HKUST-1/CF sample, named C4, was obtained after two consecutive deposition cycles on the same CF support at the temperature of 110 °C.

Fig. 1. The ceramic foam support.

2.2. Physico-chemical characterization

The X-ray diffraction (XRD) powder patterns of the synthesized samples were obtained using a Philips PW 1710 diffractometer with CuKα radiation, $2\Theta = 5–50$. Scanning electron microscopy (SEM) was carried out using a Cambridge Stereoscan 360 SEM. The elemental composition of the samples was measured by means of the energy-dispersive X-ray analysis (EDX). Thermo-gravimetric (TG) analysis and differential scanning calorimetry (DSC) were performed on a Netzsch STA 409 instrument, in static air between 20 and 600 °C at a heating rate of 2 °C/min. The Brunauer–Emmett–Teller surface area (S_{BET}) of the samples were evaluated from the N_2 adsorption/desorption analysis at 77 K using an ASAP 2000 Micromeritics instrument, after 12 h activation in vacuum at 150 °C. The compressive strength was evaluated using an Instron 4464-H1884 instrument, with a cross-head speed of 0.5 mm/min.