Chemical Engineering Journal 288 (2016) 223–227

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Short communication

Fabrication and pressure drop behavior of novel monolithic structures with zeolitic architectures

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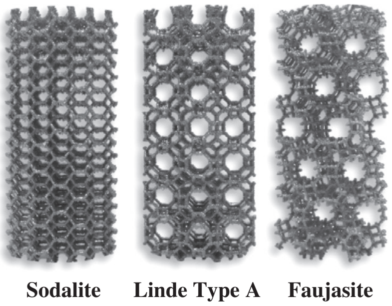
HIGHLIGHTS

- Fabrication of novel monolithic structures with zeolitic architectures by SEBM.
- Monolithic structures having well-defined pores, cages and channels.
- Monolithic structures with desired porosities and pressure drop characteristics.
- Design and development of innovative structured supports and/or reactors.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 25 September 2015
Received in revised form 28 November 2015
Accepted 30 November 2015
Available online 11 December 2015

Keywords:
Monoliths
Zeolitic architecture
Structured supports/reactors
Pressure drop
SEBM

ABSTRACT

Novel monolithic structures with zeolitic [sodalite (SOD), Linde-Type A (LTA) and faujasite (FAU)-type] architectures having well-defined pores, cages and channels are successfully fabricated by selective electron beam melting (SEBM) using Ti–6Al–4V powder. The open porosities of the monoliths are 92.87% (SOD), 94.64% (LTA) and 95.67% (FAU), respectively. Although the porosity of the FAU monolith is relatively higher than the other two monoliths (SOD and LTA), but exhibits higher normalized pressure drop due to its inherent pore tortuosity (supercages interconnected by 12-ring channels in all three dimensions). This represents a significant step forward for the design and development of innovative structured supports and/or reactors with desired porosities and pressure drop characteristics.

1. Introduction

Zeolites are microporous crystalline aluminosilicates with well-defined pores, cages and channels of molecular dimensions [1]. Owing to their unique combination of properties, such as high ion-exchange capacities, high acidities, high surface areas and shape selectivity characteristics, they have found widespread use as ion-exchangers, adsorbents and catalysts in many industrially important catalytic processes [2]. Among the zeolite structures, sodalite (SOD), Linde-Type A (LTA) and faujasite (FAU)-type zeolites are well-known to share certain common characteristics, such as crystal structure (cubic) and the structural building units (sodalite and/or β cages). In zeolite SOD [3], each β-cage (6-ring pore system) is connected to six nearest neighboring β-cages through common T4-rings; whereas, zeolite LTA framework is built by

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http://dx.doi.org/10.1016/j.cej.2015.11.104

bridging β-cages through double T4-rings (D4R), thus forming the α-cages (8-ring pore system) [4]. In contrast, the zeolite FAU framework is composed of β-cages, which are linked through double T6-rings (D6R), thus forming the super cages (12-ring pore system) [5].

Monolithic honeycomb structures are mainly used in emission control technologies, such as automotive exhaust gas catalytic converters, particulate filters and selective catalytic reduction (SCR) systems in thermal power plants [6]. Cordierite monoliths are traditionally produced by extrusion molding of the dough containing synthetic cordierite or kaolin (clay) and polymeric binders, followed by various pre- and post-treatment procedures. Such monolithic honeycomb structures offer several advantages including low-pressure drop, high porosity and high geometric surface areas, etc. They have also been successfully tested as structured supports and/or reactors in combination with active catalytic coatings for many catalytic applications [7]. Most importantly, they have shown significant performance enhancements especially for catalytic reactions with very low residence times and high space velocities. However, the concept of the monolithic honeycomb structures as catalyst supports and/or as structured reactors is not without problems, for instance, lack of radial mixing and poor heat/mass transfer, etc.

Three-dimensional monolithic ceramic structures of Al_2O_3 [8,9] and SiC [10] have also been fabricated by robocasting (moldless fabrication technique) using colloidal precursors. In addition, open cellular ceramic foams with interconnected porosities are a new class of monolithic structures with complex pore architectures [11]. In particular, ceramic foams offer solutions to the problems associated with conventional monolithic honeycomb structures, since they provide both radial mixing and better heat/mass transfer characteristics. However, their complex pore architectures are generally characterized by representative geometries (cubic, dodecahedral, tetrakaidecahedra, Weaire–Phelan and hollow spheres as well) [12–14]. Therefore, monolithic structures with zeolitic architectures (well-defined pores, cages, and channels) would be highly advantageous for the development of novel structured supports/reactors. Although the preparations of honeycomb monoliths with square or hexagonal channels using zeolite powders (e.g. 5A and ZSM-5) [15,16] and inorganic binders (e.g. bentonite, kaolin and colloidal silica) via extrusion techniques have been reported in the literature, but there are no reports dealing with the fabrication of monolithic structures with zeolitic architectures.

Selective electron beam melting (SEBM) is a versatile powder-based additive manufacturing method, which allows the translation of 3D-CAD (3-dimensional computer aided design) geometric models into real 3D metal components [17]. SEBM offers a high level of design freedom for the fabrication of various customized biomedical [18] and dental [19] implants. In addition, SEBM process has opened up possibilities for the fabrication of various Ti–6Al–4V lattice structures (cubic [20], dodecahedron [21], tetrakaidecahedron [22], diamond [23] and auxetic [24]). Nevertheless, they do not possess the inherent zeolitic architectures, including different pore shapes (circular elliptical and teardrop), channel dimensions (1-D, 2-D and 3-D) and cages.

For the first time, we present the fabrication of novel monolithic structures with zeolitic (SOD, LTA and FAU) architectures having well-defined pores, cages and channels by SEBM using Ti–6Al–4V powder. All the three monolithic structures were tested for their pressure drop behavior.

2. Experimental

First, the zeolite structural models were built using the Avogadro's software based on the crystallographic data available for zeolites, such as SOD, LTA and FAU, respectively, in order to obtain the lists of *XYZ* coordinates for all the T-atoms in each zeolite unit cells. Those *XYZ* coordinates were used for generating the 3-D computer-aided design (CAD) models of zeolites using the CAD software. CAD models of zeolites were then sliced into layers with a nominal layer thickness of 50 μm.

Monolithic structures with zeolitic (SOD, LTA and FAU) architectures were additively fabricated using an *Arcam AB S12* SEBM system (scanning speed: $400\,mm\,s^{-1}$; accelerating voltage: 60 kV; process temperature: ~750 °C; He pressure: 2×10^{-3} mbar). The SEBM method comprises of four steps: raking of the powder onto the process platform, preheating of the applied powder layer using a strongly defocused beam, melting the selected areas using a focused beam in accordance with instructions from a 3-D CAD program and lowering of the process platform by one layer thickness. This procedure is repeated until the desired monolithic structure with zeolitic architecture (∅ = ~3.0 cm and *L* = ~6.7 cm) is achieved. The time needed for building such monolithic structures with zeolitic architectures was ca. 22 h. In the present study, spherical Ti–6Al–4V powder (TLS Technik GmbH, Bitterfeld, Germany) in the particle size range of 45–100 μm was used as the precursor for the fabrication of those monolithic structures.

The surface and microstructural characteristics of the monolithic structures were studied using an environmental scanning electron microscope *FEI Quanta 200* equipped with an EDX detector *INCA Energy 200* from *Oxford Instruments Analytical Ltd*. The cross-section of the strut was prepared by embedding the strut in epoxy resin, cutting with a diamond saw, polishing and sputtering with gold. The density measurements of the monoliths were carried out at room temperature (20 °C) using a home-made water–buoyancy apparatus along with a microbalance (Sartorius).

A home-built tubular flow-through reactor (∅ = 3.2 cm and *L* = 95 cm) equipped with a gas flow distributor was used for the pressure drop measurements as a function of superficial air velocities at room temperature. The superficial velocity of air and the

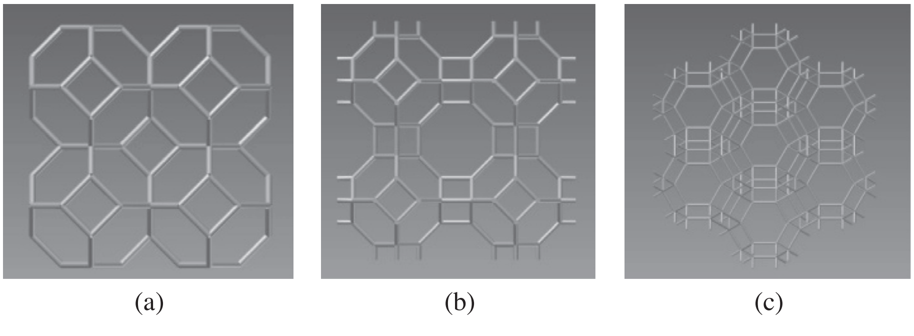

Fig. 1. CAD models of zeolites: (a) sodalite (SOD), (b) Linde-Type A (LTA) and (c) faujasite (FAU).