



Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

Structuring zeolite bodies for enhanced heat-transfer properties



Lars Borchardt^a, Nina-Luisa Michels^a, Torsten Nowak^b, Sharon Mitchell^a,
Javier Pérez-Ramírez^{a,*}

^a Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir-Prelog-Weg 1, CH-8093 Zürich, Switzerland

^b Fraunhofer Institute for Reliability and Microintegration, Department of Environmental and Reliability Engineering, Gustav-Meyer-Allee 25, D-13355 Berlin, Germany

ARTICLE INFO

Article history:

Received 20 November 2014

Accepted 19 January 2015

Available online 11 February 2015

Keywords:

Zeolites
Thermal conductivity
Additives
Shaping
Thermography

ABSTRACT

The predominantly insulating nature of zeolites, as many classes of porous catalysts, can severely impair heat transfer and hence their performance in industrial processes. Strategies developed to engineer the thermophysical properties of technical zeolites for fixed-bed applications comprise the use of conductive secondary phases as structured catalyst supports or as inert diluents. However, the impact of integrating conductive additives into composite zeolite bodies (pellets, extrudates, or granules) has not been widely explored. Here, using a transient hot-plate technique to decouple the distinct contributions of porosity, sample hydration, and temperature, we quantify the impact of metallic (copper), ceramic (silicon carbide, aluminum nitride, boron nitride), and carbonaceous (graphite, carbon nanotubes) phases on the thermal conductivity of shaped zeolites at the body and packed-bed scales. The decisive role of particle morphology, dominating over the intrinsic conductivity of an additive, is corroborated through the three-dimensional reconstruction of data acquired by focused ion beam-scanning electron microscopy and X-ray microtomography coupled with in-situ thermographic studies. In particular, the order-of-magnitude improvement evidenced on application of graphite sheets stems from the extended paths of low thermal resistance created in the millimeter-sized catalyst ensemble. Through the identification of structure-property relations, our approach provides new insights into the rational design of composite porous materials with enhanced heat-transfer properties.

© 2015 Elsevier Inc. All rights reserved.

1. Introduction

The performance of heterogeneously-catalyzed processes is inextricably linked with transport phenomena. Compared to the major progress witnessed in the engineering of catalytic solids with enhanced mass-transfer properties through nanostructuring or the design of hierarchical pore networks [1–4], strategies to optimize their thermophysical properties have received much less attention. In an industrial reactor (Fig. 1a), thermal regulation is a multi-scale task encompassing both axial and radial profiles within the catalyst bed and local gradients within individual catalyst bodies (ensembles) [5,6]. Often, solutions for heat management remain heavily reliant on improving the efficiency of exchange at the reactor level, through the choice of reactor technology and/or process conditions

[7–10]. Aside from potentially catastrophic risks as thermal runaway, inefficient heat exchange can accelerate catalyst deactivation due to increased coking or irreversible degradation of the active phase, increase energy demands, and restrict space-time yields [11,12], bringing major economic and environmental incentives to optimize the thermal control by other means.

Of the basic modes of heat transfer [13,14], conduction via microscopic diffusion presents a wide window for improved control by materials design. As highly conductive materials, the application of metals as copper [15], ceramics as silicon carbide [16,7], boron nitride [17] or aluminum nitride [18], and carbons as graphite [19], carbon nanotubes [20,21] or graphene [22], has been considered for the thermal engineering of materials. In catalysis, their use as structured catalyst supports (monoliths, foams, etc.) attracts great interest to avoid the development of local temperature gradients within catalysts when applied in highly exo-/endothermic reactions as the partial oxidation of methane [23], steam cracking/reforming [24], Fischer-Tropsch

* Corresponding author.

E-mail address: jpr@chem.ethz.ch (J. Pérez-Ramírez).

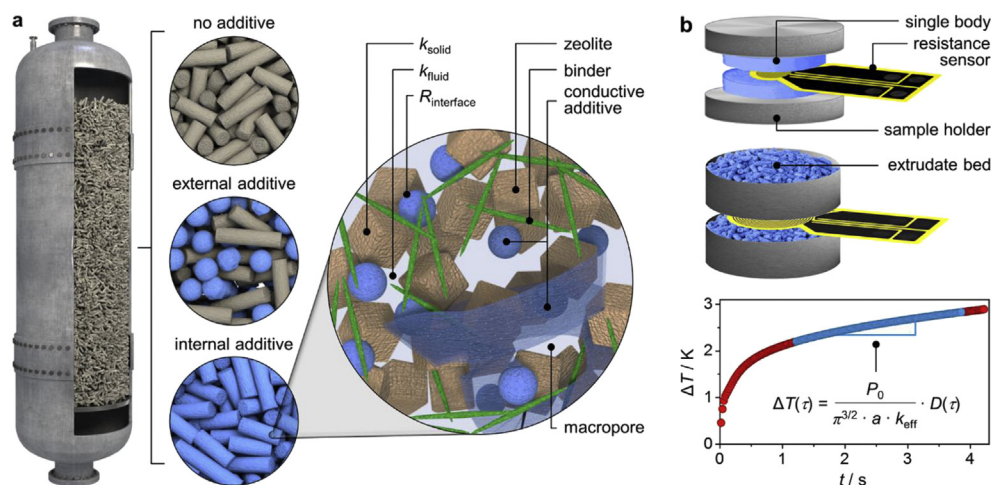


Fig. 1. a) Temperature regulation in industrial reactors is a multiscale task encompassing both radial and axial gradients across the packed bed and those localized within individual catalyst bodies. Heat transfer could be improved through the application of conductive additives, either external to, or within, the catalyst ensemble. The effective thermal conductivity of the latter, here illustrated for a zeolite catalyst, depends on the type and organization of the component phases and on the surrounding fluid medium. b) A versatile transient hot-plate method is used to determine the impact of diverse additives on the thermal conductivity of catalyst bodies and beds, which is derived from the temperature change (ΔT) in relation to the total power output (P_0) and the radius of the resistance sensor (a) as a function of time $D(\tau)$.

synthesis [25], and methanol-to-hydrocarbons [26], as well as during subsequent oxidative regeneration (coke burn off) [23,24]. However, although effective, this strategy often results in an unacceptably low catalyst loading per unit reactor volume. On the other hand, only exceptional works have considered the application of conductive additives to enhance the thermophysical properties of more widely applied structured zeolite geometries as pellets, extrudates, or granules [8,9]. In this regard, it is worth emphasizing that it is not uncommon for technical zeolite catalysts to contain high additive contents (e.g. up to 90%), offering significant room for modification of the formulation [27]. Furthermore, the enhanced thermophysical properties, where quantified, have not been rationalized in relation to the structural organization. Since the increased thermal resistivity imposed by grain boundaries (due to phonon-interface scattering) and interstitial fluids can severely penalize the effective thermal conductivity, the intrinsic properties of the additive cannot be directly extrapolated to a composite body [28].

Zeolites are arguably the most successful heterogeneous catalysts, widely exploited in refinery and petrochemical applications [27,29]. Building on continued efforts to improve fundamental understanding in the scale up of zeolite catalysts [30–32], we

explore the impact of well-known conductive additives of distinct type and particle properties on the thermophysical properties of these insulating materials. A transient hot-plate method is selected to quantify the thermal conductivity since, unlike steady-state or membrane/thin film-specific measurements, it enables the convenient assessment over a wide range of length scales and shapes (Fig. 1b). Binary and ternary systems, the latter additionally incorporating a binder, are shaped by different methods to decouple the contribution of catalyst geometry, while comparative measurements across a catalyst beds demonstrate that superior heat-transfer properties are retained even when the fluid phase becomes more influential. Visualization of the spatial integration of the additive, and in particular the three-dimensional insights gained by micro-computed X-ray tomography and focused ion beam-scanning electron microscopy, reveals the decisive role of phase connectivity in the up to one order of magnitude enhancements achieved. Thermographic profiling provides additional spatiotemporal resolution, confirming the enhanced heat-transfer properties of the catalyst ensembles. The findings are expected to be of wide relevance for catalysis and other fields of application in which inefficient heat transfer hampers the performance such as sorbents, electrochemical, and energy storage.

Table 1
Structural and thermophysical characteristics of the additives studied.

Additive	Supplier	d_{additive}^a [μm]	k_{eff}^b [$\text{W m}^{-1} \text{K}^{-1}$]	k_{in}^c [$\text{W m}^{-1} \text{K}^{-1}$]
Silicon carbide, SiC_n	Aldrich	<0.1	0.37	270 [33]
Silicon carbide, SiC_n	Aldrich	<0.1	0.65	–
Silicon carbide, SiC_n	Alfa Aesar	~400	– ^d	–
Aluminum nitride, AlN	Aldrich	~10	1.2	320 [33]
Copper spherical, Cu_s	Aldrich	<75	5.5	400 [33]
Copper fiber, Cu_f	Homemade	$50 \times 1,000$	5.5	–
Carbon nanotubes, CNT	Strem	0.1×10	–	<10,000 [21]
Boron nitride sheets, BN_n	Aldrich	<1	1.7	~2,000 [17]
Boron nitride sheets, BN_n	Alfa Aesar	~44	10	–
Graphite sheets, gr	Aldrich	<20	10	~2,000 [19]

^a Average particle diameter according to supplier's specifications.

^b Effective thermal conductivity of the single-phase body.

^c Literature values of the intrinsic thermal conductivity.

^d Shaped body not attained.

Download English Version:

<https://daneshyari.com/en/article/72644>

Download Persian Version:

<https://daneshyari.com/article/72644>

[Daneshyari.com](https://daneshyari.com)