Novel zeolite composites and consequences for rapid sorption processes

Alfons Brandt · Martin Bülow · Anna Deryło-Marczewska · Jacek Goworek · Jens Schmeißer · Wolfgang Schöps · Baldur Unger

Received: 25 April 2007 / Revised: 30 June 2007 / Accepted: 11 July 2007 / Published online: 14 September 2007
© Springer Science+Business Media, LLC 2007

Abstract Novel sorbents for rapid dynamic sorption processes based on the concept of sorption-active shell/sorption-inert core composite granules are presented. Tailoring such composites to a technical sorption process is exemplified by NaX and LiLSX zeolites as sorption-active components. Composite granules are characterized by various techniques specifically by oxygen-VPSA pilot-scale tests and liquid-phase sorption experiments. The composite sorbents exhibit excellent potential for efficiency enhancement of existing processes by lowering investment and operating costs.

Keywords Gas-phase and liquid-phase sorption · Oxygen · VPSA · Mixtures of non-electrolytes · Cu²⁺-ion kinetics · Zeolites NaX and LiLSX · Zeolite-sorbent shapes · Composites · Sorption-inert cores · Granulation

1 Introduction

During the past three decades considerable progress has been achieved in cyclic ad-/desorption processes for production of oxygen, O₂, together with remarkable development of related sorbents (MacKee 1964; Chao 1989; Coe et al. 1993; Reiß 1994; Fitch et al. 1995; Kumar 1996). Such pressure-swing adsorption, PSA, and vacuum-pressure-swing adsorption, VPSA, processes are of specific interest from an efficiency point of view for small-to-medium output O₂ generators (1 ~ 15 tons p.d. (PSA), 10 ~ 150 tons p.d. (VPSA) at 90 ~ 93 (95)% O₂ purity) (Atkinson et al. 1995). In parallel to improvement of technical processes and their engineering, much attention has been paid to the invention, manufacture and utilization of novel types of sorbents including their enhanced interaction properties with nitrogen, N₂, and industrial procedures to create the best-possible shaped materials for those technologies.

In the case of zeolites for sorption-equilibrium processes, the entire volume of sorption-active particles is used, as a rule, since there is no relevant time limitation to the sorption process. A different picture exists in case of fast dynamic sorption processes. If separation of molecules of different types proceeds by rapid swing between ad- and desorption steps, the molecular-transport rate within a sorbent particle may restrict the specific particle-volume faction, which really participates in the process. Usually, only partial utilization of sorption-active phase takes place. The molecular-transport time from the particle’s surface into its volume (and back) may limit the possible cycle time, and, in many cases, the efficiency of the entire technical process. Since diffusion of O₂ and N₂ within typical O₂-VPSA zeolite-sorbent crystals is rather fast (Bülow et al. 1996; Bülow and Shen 1998), intraparticle transfer rate of sorbing species may mainly be limited by the “effectiveness” of...
the related meso-/macroporous transport system (Bülow and Shen 2004). These considerations lead to the idea of novel material composites for rapid sorption processes that this paper will deal with.

2 Background and formulation of the problem

Technical sorbents and adsorbers for a given process are optimized inter alia with respect to their particle shape and size to meet the requirements for sorption, mechanical properties and pressure-drop behavior. In rapid dynamic processes improvement can be achieved, if the time for molecular transfer within a sorbent particle of certain shape is decreased, e.g., by reducing the diffusion-path length or the transport resistance. This can be done by reducing the particle size and/or providing transport pores within the particle to be sufficient in amount and size. Although size reduction of sorbent granules allows for cycle-time reduction that leads to higher productivity per units of volume and time on one and the same amount of sorbent or size of adsorber, this approach is connected with pressure-drop increase and, thus, restricted by a specific particle-size limit.

As well known, in many rapid cycle processes only the outer shell of a given sorbent particle participates in the sorption process while the core remains practically unused during the operation. This suggests a way towards sorbent-performance enhancement, viz., a decrease in the molecular-transport paths can be achieved by using of composite granules comprising a sorption-inert core and a sorption-active shell material (Lü and Bülow 2000; Lü et al. 2001a, 2001b; Monereau et al. 2000; Tang et al. 2001). Identical sorption-kinetic behavior exists for a sorption-active shell/sorption-inert core composite particle and a sorption-active shell/hollow core particle—if their other parameters remain equal (Lü and Bülow 2000). To visualize this approach to materials, an electron micrograph showing a sectional profile of an EPS-polymer-core bead with FAU-zeolite shell to provide a hollow zeolite bead by thermal removal of the organic core is shown in Fig. 1. The corresponding hollow bead can be made by thermal removal of the polymeric core.

A performance enhancement by reducing diffusion resistance within sorbent particles of certain shapes requires the existence of transport (meso- and macro) pores therein that have to be sufficient in amount and size. The diameter of said pores should be at least in the range of the mean free path length of the molecules to be ad-/desorbed. Ways were exemplified (Hirano et al. 1990; Brandt et al. 2004) towards appropriate transport pores in FAU-zeolite sorbent particles, which consist of subsequent kneading, shaping and rounding of sorbent bodies. Addition of suitable additives such as fibrous clay (Kawamoto et al. 1999) or thermally degradable spacers (Chao and Pontonio 1999) is possible if the treated material is resistant with regard to thermal/hydrothermal stress. The “spacing ability” of several selected materials is illustrated by electron micrographs seen in Fig. 2, cf. also Table 1.

Considering the need for secondary pores within a range of at least (200–500) nm, fibrous as well as granule-shaped thermally removable organic materials within the lower µm-size range would meet this requirement, cf. Table 1. A LiLSX zeolite was beaded by using attapulgite clay as binder, and, for comparison, 5 wt-% of two different spacers (either Arbocel BE 600-30 for a short-length cellulose fiber type material, or Cellotin ZZ 8/1 for a long-length cellulose fiber type) were added to the granulation mix. As a result, volume and mean sizes of secondary pores are increased but bulk density is lowered, i.e., a larger porosity with a higher amount of transport pores of the desired size is generated. Different spacers may influence the final bead properties differently, e.g., a longer fiber may cause an even higher porosity with transport pores of larger diameter. Suitable thermally removable spacers allow for tailoring the transport-pore system in sorbent particles.

On the other hand, shaping principles/conditions are specific with regard to the shape type, particular properties of products shaped and their yields. Table 2 gives a summary of commonly used shaping procedures. Having in mind formation of sorption-active shell/sorption-inert core composite granules, suitable plating/coating procedures should be considered, in which a core/seed is used as the base, onto which the sorption-active material is deposited layer by layer. The so-called “rotor-coating” principle often used in the making