



Impact of solvents and surfactants on the self-assembly of nanostructured amine functionalized silica spheres for CO₂ capture[☆]

Edith Berger^a, Maximilian W. Hahn^a, Thomas Przybilla^b, Benjamin Winter^b, Erdmann Spiecker^b, Andreas Jentys^{a,*}, Johannes A. Lercher^a

^a Department of Chemistry and Catalysis Research Center, Technische Universität München Lichtenbergstraße 4, 85747 Garching, Germany

^b Center for Nanoanalysis and Electron Microscopy (CENEM) & Institute of Micro- and Nanostructure Research, Friedrich-Alexander-Universität Erlangen-Nürnberg, Cauerstraße 6, 91058 Erlangen, Germany

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ABSTRACT

Macroscopic SiO₂ spheres with a homogeneous amine distribution were synthesized by a one-step emulsion based synthesis approach in a flow column reactor. The CO₂ adsorption capacity of the nanostructured amine-functionalized silica spheres was studied in absence and presence of H₂O. The structural properties were adjusted by varying solvents and surfactants during the synthesis and, at constant amine loadings, were found to be the main factor for influencing the CO₂ sorption capacities. Under water-free conditions CO₂ is bound to the amino groups via the formation of carbamates, which require two neighboring amino groups to adsorb one CO₂ molecule. At constant amine concentrations sorbents with lower surface area allow to establish a higher amine density on the surface, which enhances the CO₂ uptake capacities under dry conditions. In presence of H₂O the CO₂ adsorption changes to 1:1 stoichiometry due to stabilization of carbamates by protonation of H₂O and formation of further species such as bicarbonates, which should in principle double the adsorption capacities. Low concentrations of physisorbed H₂O (0.3 mmol/g) did not impair the adsorption capacity of the adsorbents for CO₂, while at higher water uptakes (0.6 and 1.1 mmol/g) the CO₂ uptake is reduced, which could be attributed to capillary condensation of H₂O or formation of bulky reaction products blocking inner pores and access to active sites.

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1. Introduction

The development of concepts for the decrease of the emission of greenhouse gases is an eminent task for the 21st century [1–3]. Particularly in the economically fast growing countries in Asia, the necessity of cheap and abundant sources of energy leads to a large number of newly built coal-fired power plants, representing the largest stationary emitters of greenhouse gases [4,5]. As CO₂ constitutes the main component of the greenhouse gases in the flue gas streams of conventional coal-fired power with a concentration

of approximately 10%–15% [6,7], it will become exceedingly important to equip coal fired power plants with CO₂ capture units to limit further changes for the climate worldwide [2,8,9].

The principle of aqueous phase, amine based absorption units, was developed in the early 1930s by the oil industry for separation of CO₂ from natural gas [10]. However, the high energy demand for the thermal regeneration of the aqueous systems led to recent investigations into solid amine functionalized sorbents that possess a significantly lower heat capacity compared to the aqueous phase and based processes [11]. Amine-impregnated, silica supported adsorbents are among the most studied systems [11]. A well-structured porosity and large pore volumes are the most important characteristics of an efficient support making SBA-15 or MCM-41 the materials of choice [12,13]. High molecular weight amines that contain primary, secondary or tertiary amino groups, i.e., tetraethylenepentamine (TEPA) or polyethyleneimine (PEI), which are loaded by impregnation onto high surface area carrier materials, are mostly employed for binding CO₂ [14–19]. However, these materials suffer from degradation and desorption of amines at higher temperatures or under vacuum conditions [15,20,21].

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* Corresponding author. Tel: +49 8928913540; Fax: +49 8928913544.

E-mail addresses: jentys@mytum.de (A. Jentys), johannes.lercher@mytum.de (J.A. Lercher).

Mechanistic investigations of the adsorption process are mainly limited to surface bound single amino groups, such as grafted aminosilanes, which are also applicable for long term gas separation processes due to their higher stability [11,22–24]. CO₂ adsorption on solid amine functionalized sorbents at low CO₂ partial pressures has been intensively investigated over the last decade [11,14,16,25–30]. In the absence of H₂O, it is widely agreed that CO₂ adsorption is a cooperative reaction requiring two vicinal amino groups [25] and, therefore, studies on materials with low amine densities or even isolated amino groups, can yield unrealistic energetic and thermodynamic results for the CO₂ adsorption [27,31]. Impregnation and grafting methods of highly mesoporous ordered supports with amines or aminosilanes allow to achieve high densities of active adsorption sites on the outer surface and the pore entrances, while a homogenous distribution of amines over the entire porous oxide structure is difficult to accomplish [32,33].

In order to overcome local concentration gradients of the amino groups along the pores we developed a one-step synthesis yielding sorbents with homogeneously distributed amino groups within the porous nano-structured network. The sorbents were functionalized directly during the synthesis with secondary aminosilanes to achieve effective CO₂ sorption at low partial pressures in combination with high cycle stability, resulting from a marginal degeneration of the amines during the regeneration step [20,34]. The one step synthesis of the amine functionalized nano-structured spheres was based on an emulsion based condensation process, previously applied by our group to synthesize hierarchically-structured spherical adsorbents for high pressure CO₂ adsorption [35]. In this contribution, we report the role of the solvents and surfactants on the structure and surface properties of the amine functionalized spherical adsorbents. This kind of material is suitable for low temperature CO₂ capture applications and diluted CO₂ streams, such as flue gases from energy plants, due to the selective interaction of the amino groups with CO₂ [36,37]. While keeping the amine loading constant, the role of the surface area and pore structure on the amine spacing and mechanistic restrictions was investigated and

the influence of H₂O, typically present in flue gas, on the uptake capacity of the sorbents in relation to their structural properties is discussed.

2. Experimental

2.1. Synthesis

Macroscopic SiO₂ spheres with hierarchically ordered pores were synthesized by an oil-in-water emulsion based synthesis [35], where a two component water immiscible precursor solution was injected dropwise into the aqueous phase. In this approach each droplet acts as a micro-reactor for the condensation of the silica phase. The use of organosilanes allows a direct functionalization of the spheres. The first component of the precursor solution consisted of solvent and surfactant and was prepared by mixing 2.7 g of the surfactant, Pluronic RPE 1720 ((PO)₁₃(EO)₁₆(PO)₁₃; BASF) or 25R4 ((PO)₁₈(EO)₄₅(PO)₁₈; BASF) and 3.0 g of the solvent benzyl alcohol (>99%, Sigma-Aldrich) or γ -valerolactone (99%, Aldrich) under stirring for 15 min at room temperature (the components used for the synthesis are shown in Fig. 1). The second component, an Si rich precursor solution containing 3.0 g tetraethyl orthosilicate (TEOS; TES40, Wacker Silicones), 2.2 g of phenyltrimethoxysilane (PTMS; 97%, Aldrich) and 3.3 g of trimethoxy [3-(methylamino)propyl] silane (MAPS; 97%, Aldrich) was separately prepared by stirring for 15 min. Both solutions were merged and mixed for 10 min prior to injection into the water-filled reactor column at 60 °C (length 3 m) [35]. The spheres were directly formed by micelle formation and base catalyzed condensation [35]. Their size, typically in the millimeter range, depends on composition and injection rate. After the condensation, the spheres were aged in deionized (DI) water for 48 h and washed with DI water and ethanol. The SiO₂ spheres were dried overnight to remove residual solvents and Soxhlet extraction in ethanol was performed for 24 h under reflux to remove the

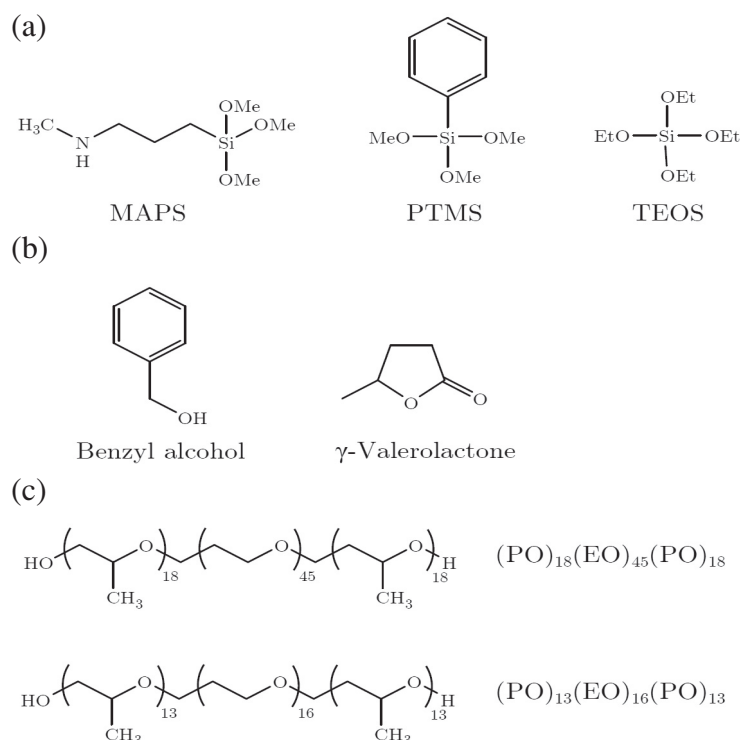


Fig. 1. Components of the precursor mixture. (a) Structure directing compounds, (b) solvents and (c) surfactants.

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