

Colloidal Processing and CO₂-Capture Performance of Hierarchically Porous Al₂O₃-Zeolite 13X Composites

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Abstract

Hierarchically porous composites for CO₂-capture have been produced by coating the inner walls of foam-like macroporous alumina monoliths, produced by templated synthesis, with microporous zeolite 13X particles. Homogeneous and dense coatings of the particulate adsorbent were obtained when the impregnation process was performed at a pH above 9. At this pH-level the colloidal stable suspensions of the negatively charged zeolite 13X particles could fill all the voids of the highly connected pore space of the alumina supports and attach to the monolith walls, which had been pre-coated with poly(ethylene imine). A CO₂-uptake as high as 5 mmol CO₂/g zeolite 13X was achieved for alumina-zeolite 13X composites through minimisation of the added inorganic binder, kaolin, to only 3.0 wt% with respect to zeolite content, and through optimisation of the thermal treatment.

Keywords: CO₂-uptake, adsorption, colloids, alumina, macroporous

I. Introduction

Carbon capture and storage (CCS) has the potential to substantially reduce the combustion-related emission of CO₂ into the atmosphere¹. Current commercial post-combustion technologies for capture and separation of CO₂, for instance absorption in amine-based liquids, are, however, energy extensive and expensive². Recent work has suggested that adsorption-driven gas separation processes could offer a more energy- and cost-efficient separation of CO₂ from flue gases³.

Pressure swing adsorption (PSA) and temperature swing adsorption (TSA) are commonly used technologies for low-cost gas separation using solid adsorbents^{1,3}. The solid adsorbents used for CO₂-adsorption are characterised by a high surface area and include e.g. activated carbon⁴, zeolites^{4,5}, metal organic frameworks⁶, and aluminophosphates (ALPO)⁷. The zeolite 13X, a sodium aluminosilicate with a pore diameter of 10 Å, has attracted significant interest for CO₂-capture as this low-cost adsorbent has a high CO₂-uptake capacity^{4,8,9}.

Swing adsorption processes (PSA/TSA) typically employ packed beds of pellets or granules of a suitable adsorbent material¹⁰. Packed beds exhibit low mass transport coefficients and large pressure drop across the adsorbent bed resulting in long cycle time and low efficiency, making them less suitable for CO₂-separation from large point sources¹¹. Recent work by Webley *et al.* has suggested that hierarchically porous adsorbents can overcome the limitations of packed adsorbent beds to allow rapid swing adsorption processes¹². Tailoring the con-

nectivity of micro/meso/macro-pores in a hierarchically structured adsorbent can achieve high mass transfer coefficients through the macropores while maintaining a large surface area¹³.

Today, pellets or other simple adsorbent shapes are formed by extruding the adsorbent powders together with a clay binder which provides the necessary strength¹⁰. However, an inactive binder does not take part in the adsorption process and thus reduces the volumetric efficiency of the structured adsorbent and can cause clogging of the microporous particle surface, leading to low mass transfer rates^{10,14}. We have previously shown how binderless hierarchically porous zeolite 13X monoliths with a CO₂-adsorption capacity of 6 mmol/g can be produced by means of colloidal processing followed by slip-casting and thermal treatment¹⁵.

Two main routes for producing hierarchically porous ceramic components of zeolitic materials can be identified: assembling micro-/mesoporous particles or precursors into components also possessing macroporosity; and, adding micro-/mesoporous particles or precursors to macroporous ceramic monoliths¹⁶. Macropores can be introduced and shaped in microporous powder bodies by extrusion¹⁴, templating¹⁷, or foaming of colloidal suspensions¹⁸, and by (partial) sintering of powders¹⁵. Nucleation and *in-situ* growth of zeolites on macroporous sacrificial templates, such as polymer foams¹⁹ and biological specimens²⁰, result in hierarchically porous materials with a well-defined macropore structure and a high specific strength. Nucleation and *in-situ* growth is, however, associated with long processing times.

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Micro- and mesoporosity can also be introduced to macroporous ceramic supports by slurry-coating^{5,21}, chemical or physical vapour deposition²² or by the use of preceramic polymers²³. The volume fraction of the adsorbent is lower in these types of composite materials, but high mass transfer coefficients, short diffusion distances and rapid cycling can be achieved. Slurry-coating on ceramic foams results in composite materials with relatively high mechanical strengths, low pressure drops¹³ and high accessibility to the active adsorption sites in the porous particulate coatings²¹. The high tortuosity of foams also favours mixing and distribution of flue gases to the adsorption sites¹³.

In this study, we have developed a colloidal process route to coat the walls of a foam-like macroporous alumina support with a zeolite 13X particulate film. The colloidal stability and rheological properties of the aqueous zeolite suspensions have been related to the homogeneity of the deposited zeolite particulate coatings and the fraction of accessible surface area in the deposited zeolite 13X coatings. We show that a very low amount of kaolin (3.0 wt%) and optimised thermal treatment can yield zeolite 13X particulate coatings with a high CO₂-uptake, which are firmly attached to the alumina support walls.

II. Experimental

(1) Materials

We produced the macroporous alumina supports by means of a previously described procedure^{24,25} that involves gel casting an alumina suspension with thermally expandable polymeric microspheres (EPS) (ON316WUX, Expancel, Sweden) as a sacrificial templating agent for the macropores. The organic materials were removed at 600 °C prior to sintering of the macroporous alumina to full density at 1500 °C.

The poly(ethylene imine) (ammonium salt, 99 % purity, Mw = 10 000), abbreviated to PEI (Polysciences, Inc., U.S.A.) was used as-received. The commercially available zeolite 13X (Luoyang Jianlong Chemical Industrial Co., LTD. Yanshi, Henan, China) had a particle size of 3–5 µm. The inorganic binder, kaolin, was obtained from Sigma-Aldrich (Sigma-Aldrich, Chemie GmbH, Germany). The kaolin particles have an irregular morphology and a particle size distribution in the range of 0.1–1.0 µm. The pH of the particulate suspensions was adjusted with HCl (aq).

(2) Procedure

The surfaces of the macroporous alumina supports were pre-coated with a cationic polyelectrolyte by immersing the sintered monolith in a 2 wt% solution of PEI at pH 7.0. The excess of PEI was rinsed off and the pre-coated monoliths were dried. Aqueous suspensions containing 20 wt% zeolite 13X and varying amounts of kaolin (3.0, 4.0 and 6.5 wt% with respect to zeolite 13X dry weight basis (dwb)) were gently ball-milled for 24 h to break up large agglomerates of the zeolite 13X and kaolin powders. The aqueous powder suspensions were ball-milled at three different pH-values: pH 7.0, 8.0 and 9.6. The macroporous alumina supports, pre-coated with PEI, were immersed in the zeolite 13X/kaolin suspensions for three hours. The

impregnation process was facilitated by applying a vacuum of 5 mbar during the first 30 min and gentle shaking for 2.5 h. The coated supports were thereafter washed with deionised water and dried in a climate chamber (KBF 115, Binder GmbH, Germany) at 40 °C and 30 % relative humidity. For double-coated supports a second layer of zeolite 13X and kaolin particles was applied by repeating the coating process after drying (pre-coating with PEI followed by immersion in the zeolite 13X/kaolin suspensions and drying). After drying, the coated supports were heated to 780 °C at a heating rate of 1 K/minute in a muffle furnace (Nabertherm GmbH, Germany).

(3) Characterisation

The total porosity of the sintered macroporous alumina supports was evaluated using water as immersion liquid. Macroporous bodies, which had been dried to a constant weight at 120 °C and then cooled to room temperature in a desiccator, were weighed in air and then evacuated and infiltrated with distilled water. The weight of the water-filled porous ceramics was determined, which allowed the pore volume to be estimated. The solids content of zeolite 13X/kaolin was evaluated by weighing the dry macroporous alumina supports before and after the impregnation.

The zeta potential of dilute (0.01–0.10 wt%) suspensions of zeolite, kaolin and alumina particles, respectively, were measured as a function of pH with a Zetasizer Nano ZS instrument (Malvern Instruments Inc., London, UK). Prior to measurement, the suspensions were deagglomerated by ultrasonication and the pH was adjusted by adding HCl (aq) and NaOH (aq). The scanning electron microscopy (SEM) was performed with a field-emission gun scanning electron microscope (FEG-SEM) JSM-7000F (JEOL, Japan) operating at an acceleration voltage of 3.0 kV.

Powder X-ray diffraction (PXRD) patterns were recorded with a PANalytical X'pert PRO MP diffractometer using CuK_{α1}-radiation. The powders were placed on zero-reflection Si-plates and measured using a 20-mm beam mask and an automatic divergence slit that constantly irradiated a length of 20 mm of the sample. A range from 7 to 100° 2θ was scanned in 1 h. Known amounts of zeolite 4A (Luoyang Jianlong Chemical Industrial Co., LTD. Yanshi, Henan, China) were added as an internal standard to the powders of the alumina/zeolite 13X materials for quantitative phase analysis of zeolite 13X, which has a similar mass-absorption coefficient to zeolite 4A. The obtained patterns were quantified by Rietveld-refinement for the three observed phases: Al₂O₃, zeolite 13X and zeolite 4A.

We evaluated the specific surface area (SSA) of the alumina-zeolite 13X composites by analysis of nitrogen isotherms using an ASAP 2020 analyzer (Micromeritics, U.S.A.). The alumina-zeolite 13X composites were degassed at 300 °C for 10 h prior to measurement. The specific surface area was calculated using the BET model within the 0.05–0.15 p/p₀ relative pressure region. The fraction of accessible surface area of the zeolite 13X-coatings was calculated by normalising the SSA of the alumina-zeolite 13X composites to the SSA of the unprocessed zeolite 13X-powder. The CO₂-uptake measurements were

performed on a Gemini 2375 (Micromeritics, U.S.A.) at 0 °C within a relative pressure region of 0.05–0.998 p/p₀. Prior to measurement, the as-received powder and thermally treated alumina-zeolite 13X composites were pre-treated under a flow of dry N₂ gas at a temperature of 350 °C for 8–10 h.

III. Results and Discussion

(1) Coating the inner walls of macroporous alumina supports with zeolite 13X particles

Macroporous alumina supports were functionalised with the microporous CO₂-adsorbent zeolite 13X, using kaolin as a binder, by means of a vacuum-driven impregnation process (Fig. 1). The coating of the alumina supports was performed with suspensions of zeolite 13X and kaolin at three different pH-values: 7.0, 8.0 and 9.6, respectively. The alumina supports were produced with a previously reported sacrificial templating process that results in spherically shaped macropores connected by open windows, also called throats. These throats, with a mean size of 20 μm (± 13 μm)²⁵, provide gateways for the colloidal suspension of zeolite 13X and kaolin to enter into the internal macropores of the alumina supports. The open macroporosity of the alumina supports was 65 % ± 3, prior to impregnation. Previous characterisation by X-ray tomography on macroporous alumina monoliths with similar porosities suggests that > 97 % of the pores are interconnected by one or more throats into a percolating network of macropores²⁴.

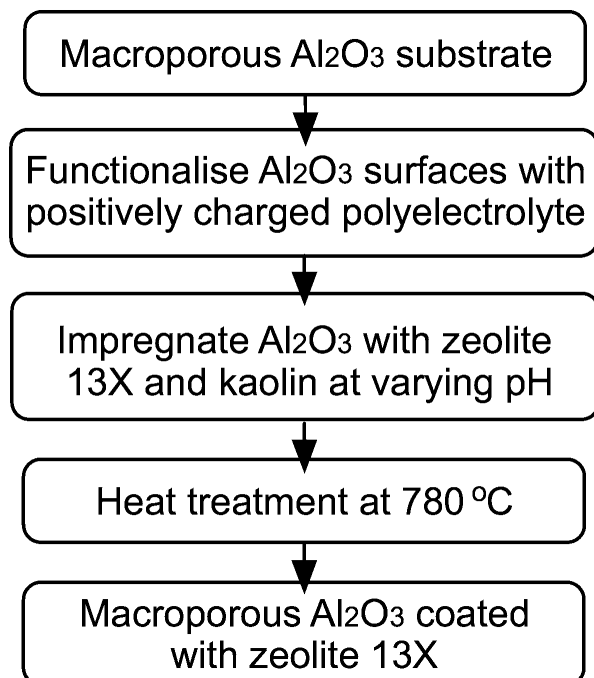
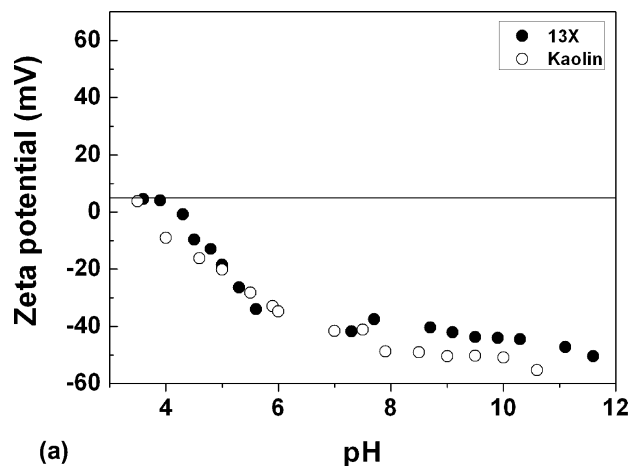


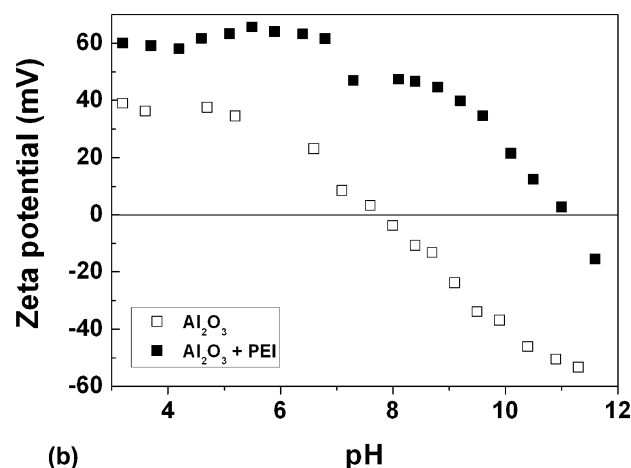
Fig. 1: Flow chart for producing alumina-zeolite 13X composites by coating macroporous alumina supports.

The electrokinetic data in Fig. 2a shows that both zeolite 13X and kaolin display a significant negative surface charge at pH-values above 5. The zeta potential data confirm previous findings that the surfaces of both the aluminosilicate zeolite (13X) and the aluminosilicate clay (kaolin) are dominated by acidic silanol groups with a pH-

dependent dissociation behaviour^{26,27}. The zeta potential data suggests that colloidally stable suspensions of mixtures of kaolin and zeolite 13X can be prepared above pH 5. Alumina on the other hand is an amphoteric oxide with an intrinsic point of zero charge (PZC) around pH 8–9 (Fig. 2b). Adsorption of the cationic polyelectrolyte poly(ethylene imine) (PEI) increases the PZC of alumina to pH 11 and renders the alumina particles highly positively charged (> +30 mV) up to pH 9.6 (Fig. 2b).



(a)



(b)

Fig. 2: Zeta potential of: (a) kaolin and zeolite 13X; (b) pure alumina, and alumina with 2 wt% dry weight basis (dwb) of poly(ethylene imine) (PEI).

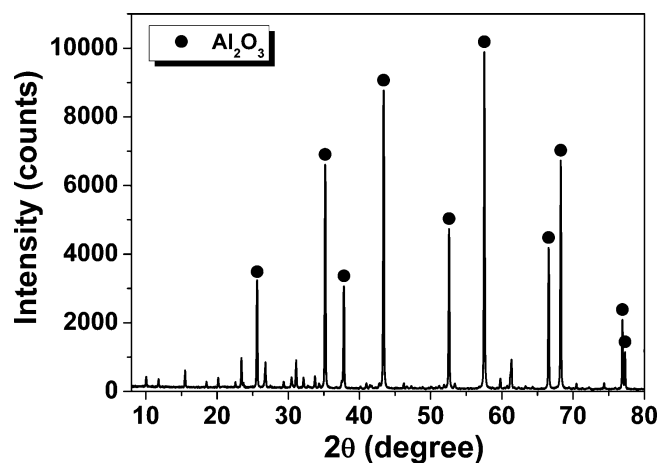


Fig. 3: Powder X-ray diffraction pattern of alumina coated with zeolite 13X and kaolin. The characteristic peaks of alumina (Al₂O₃) are indicated.

Table 1: Amount of zeolite 13X in the coated alumina supports after single and double coating (comparison of gravimetric determination and quantification of powder X-ray diffraction (PXRD) analysis), BET specific surface area and the accessible surface area of the deposited zeolite 13X

Material label ^{a)}	13X content (wt%) ^{b)}			SSA ^{c)} (m ² /g) after double coating	Accessible surface area of the deposited 13X (%) ^{d)}
	Single coating Gravimetric	Double coating Gravimetric	Double coating PXRD		
pH7.0/K3.0	7 (±1.0)	9 (±1.0)	-	57 (±1)	98
pH7.0/K4.0	8 (±1.0)	10 (±1.0)	-	57 (±1)	89
pH7.0/K6.5	7 (±1.0)	9 (±1.0)	10 (±1.0)	45 (±1)	83
pH8.0/K3.0	6 (±0.5)	9 (±1.0)	-	59 (±1)	91
pH8.0/K4.0	6 (±1.0)	8 (±1.5)	-	54 (±1)	88
pH8.0/K6.5	8 (±0.5)	13 (±2.5)	13 (±1.5)	47 (±1)	56
pH9.6/K3.0	8 (±0.5)	9 (±1.0)	-	58 (±1)	96
pH9.6/K4.0	9 (±0.5)	10 (±1.0)	13 (±2.0)	-	-
pH9.6/K6.5	8 (±1.0)	11 (±1.0)	-	55 (±1)	73

a) The material label refers to the pH of the zeolite 13X/kaolin suspension during the coating process, and to the kaolin (K) content in suspension in wt% dry weight basis.

b) Weight of zeolite 13X relative to weight of alumina support.

c) BET specific surface area (SSA)

d) Given a specific surface area of 658 m²/g of the zeolite 13X powder¹⁵.

Fig. 3 shows a PXRD pattern of an alumina-zeolite 13X composite, with the characteristic peaks of zeolite 13X and alumina indicated. The PXRD analysis confirmed that the crystallinity of the zeolite 13X was preserved and no additional phase was formed after the heat treatment up to 780 °C of the zeolite 13X-coated macroporous alumina supports.

The macroporous alumina supports, pre-coated with PEI, were immersed in the zeolite 13X/kaolin suspensions at pH-values where the negatively charged particles are electrostatically attracted to the positively charged pore walls. The coating procedure was repeated once. Table 1 shows that the alumina supports contained 7–9 wt% zeolite 13X already after the first coating step. After the second coating step, the amount of zeolite 13X in the alumina supports increased by an average of 30 wt% (relative to the first coating). This increase in weight indicates that the first coating step did not significantly block the throats between the macropores in the alumina supports.

We also evaluated the amount of deposited zeolite 13X in the composites after coating and thermal treatment by quantitative powder X-ray diffraction (PXRD) analysis, for a few supports. The PXRD analysis in Table 1 confirms the gravimetric quantification of zeolite 13X in the coated alumina supports.

The SEM images in Fig. 4a and 4b show that the alumina pore walls were evenly coated with zeolite 13X without bare patches, which indicates that the zeolite 13X/kaolin suspensions penetrated the macropores of the alumina monoliths. The thermal treatment resulted in a particulate film that adhered firmly to the alumina, exemplified in Fig. 4d which shows a dense alumina pore wall coated with tightly packed zeolite 13X particles on each side. Fig. 4c shows that the throats remained open after the coating process. This is essential for the performance of the composite as a gas adsorbent in which all the coated macropores should be accessible for the flowing gas.

(2) Surface area and CO₂-uptake of the hierarchically porous alumina-zeolite 13X composites

The fraction of accessible surface area of the zeolite 13X in the coated alumina supports depended on the kaolin content in the coatings (Table 1). The zeolite 13X-coated alumina supports with the lowest amount of kaolin (3.0 wt%) recorded the highest BET specific surface area (58 m²/g (±2)) as well as the highest fraction of accessible surface area (> 90 %). The specific surface area values in Table 1 suggest that the zeolite 13X particles are more easily accessible in the coatings containing 3.0 wt% of kaolin, compared to the coated materials containing a higher amount of kaolin (6.5 wt%).

The highest specific CO₂-uptake, with respect to the amount of zeolite 13X, was recorded for the alumina-zeolite 13X composites for which the zeolite 13X suspension had a pH of 9.6 during the coating process (Fig. 5a): 5.8 mmol CO₂/g 13X. The specific CO₂-uptake of alumina supports coated with zeolite 13X decreased as a function of decreasing pH of the coating process, as seen in Fig. 5a. The reduced CO₂-uptake for the materials prepared at a lower pH is related to the lower surface area of these materials, as seen in Table 1. As recently shown by Akhtar *et al.*¹⁵, the pH of a zeolite 13X suspension has a notable effect on its flow properties; the lowest viscosity of a zeolite 13X suspension was recorded for a pH of 9.6 and the viscosity increased below pH 9.6. This suggests that the higher viscosity of the particle suspensions at pH-values below 9.6 reduced the ability of the zeolite 13X suspension to penetrate all pores of the macroporous alumina supports and to coat the available inner surfaces during the coating process.

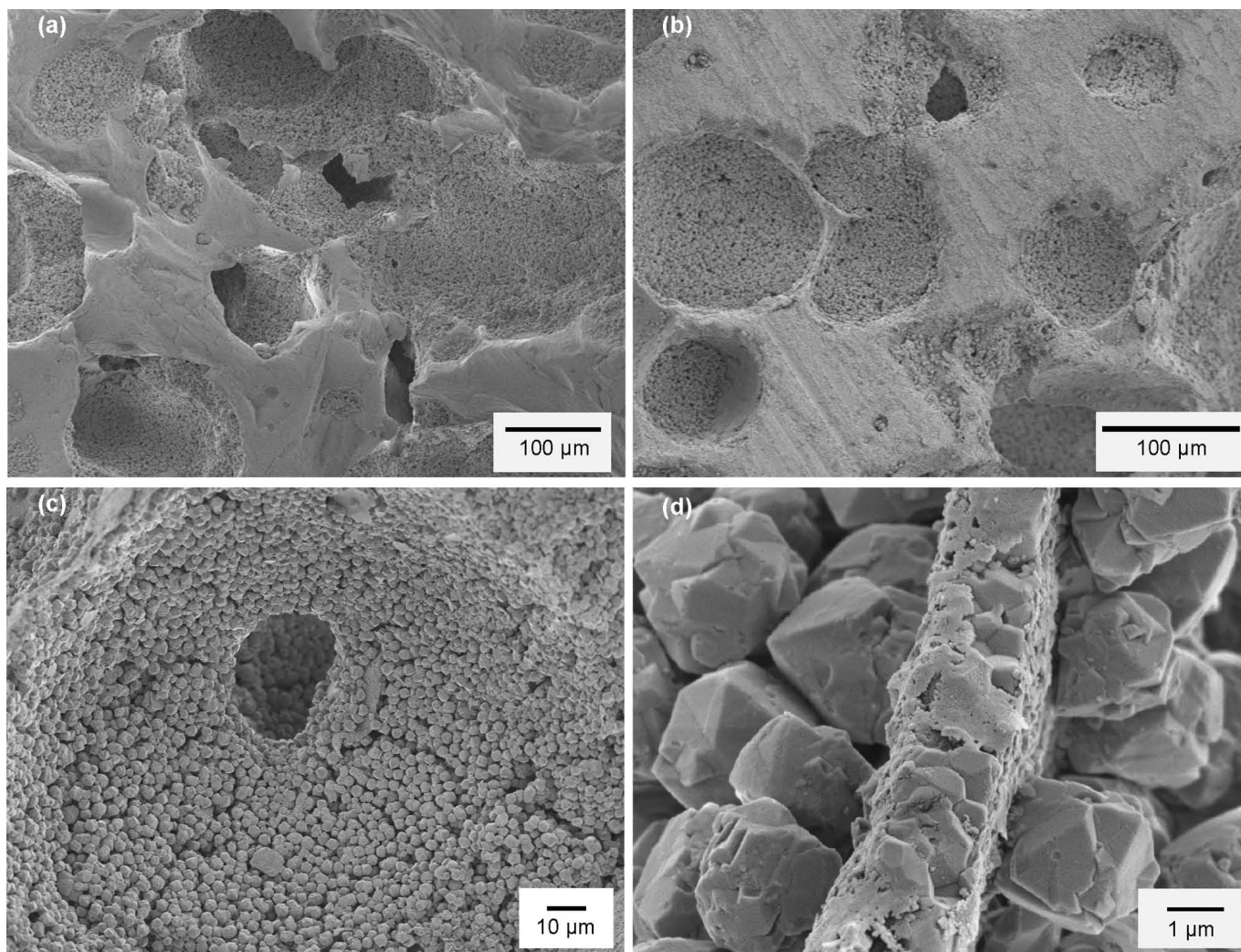


Fig. 4: Scanning electron microscopy images of fracture surfaces showing the zeolite 13X/kaolin coatings in macroporous alumina supports: An alumina support with (a) a double coating and (b) with a single coating, (c) a throat connecting two coated macropores and (d) a dense alumina wall separating two pores coated with zeolite 13X particles.

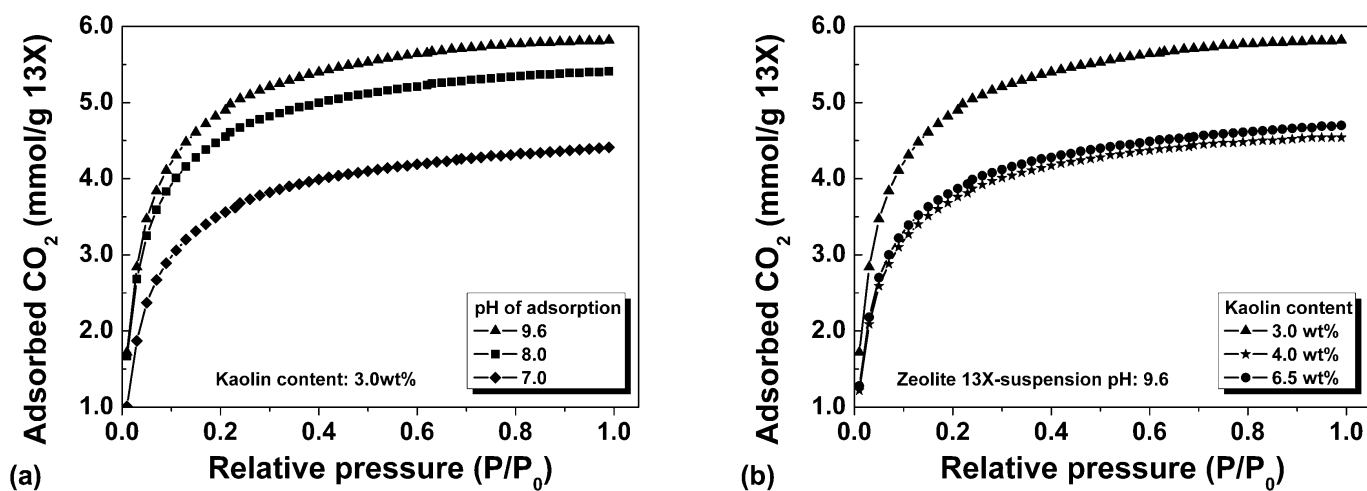


Fig. 5: CO₂-adsorption isotherms at 273 K as a function of relative pressure of macroporous alumina coated with zeolite 13X and kaolin: (a) CO₂-uptake curves for macroporous alumina double-coated with zeolite 13X and 3.0 wt% kaolin (with respect to zeolite 13X) at pH 9.6, pH 8.0 and pH 7.0, respectively; (b) CO₂-uptake curves for macroporous alumina double-coated at pH 9.6 with zeolite 13X and 3.0 wt%, 4.0 wt% and 6.5 wt% kaolin (with respect to zeolite 13X), respectively.

The results shown in Fig. 5b suggest that the relative amount of kaolin also has an influence on the specific CO₂-uptake. The materials that contain zeolite 13X coatings with 3.0 wt% kaolin showed a higher specific CO₂-uptake compared to coatings with 4.0 wt% and 6.5 wt% kaolin. This effect of increasing kaolin content on the decreasing CO₂-adsorption is supported by the decreasing fraction of accessible surface area in the coated supports as a function of (increasing) kaolin content (Table 1). The results suggest that the kaolin particles blocked the access of the CO₂-gas to the microporous zeolite 13X particles and thus negatively affected the CO₂-uptake.

IV. Conclusions

We show that coatings of zeolite 13X can be applied onto the inner walls of foam-like macroporous alumina supports using a very low amount of kaolin as a binder: 3.0 wt% with respect to zeolite 13X content. Homogeneously distributed coatings of zeolite 13X in the highly cellular macroporous alumina supports could be obtained from colloidal zeolite 13X/kaolin suspensions by means of a vacuum-driven impregnation process. The specific CO₂-uptake (with respect to zeolite 13X content) and the surface area were the highest for coatings deposited from colloidal suspensions of zeolite 13X and kaolin at pH 9.6: 5.8 mmol CO₂/g 13X. At pH-values below pH 9.6 the viscosity of the colloidal suspensions increases, which inhibits the penetration of particles into the macroporous alumina.

The amount of zeolite and kaolin incorporated into the macroporous alumina materials, as evaluated by gravimetric measurements and corroborated by quantitative powder X-ray diffraction analysis, reached 10–13 wt% after a second coating step. The addition of a small but homogeneously distributed amount of kaolin resulted in stable coatings, after heat treatment at 780 °C. We show with powder X-ray diffraction that the zeolite 13X preserved its crystallinity and microporosity after heat treatment.

The pores of the coated macroporous alumina supports remained connected also after the second coating step, which granted accessibility of a flowing gas to the microporous zeolite 13X particles and its adsorption sites.

The specific CO₂-uptake was the highest when the coatings had been produced at pH 9.6 and a minimal amount of kaolin, 3.0 wt% with respect to zeolite 13X content, was used as an inorganic binder. The uptake of adsorbed CO₂ in the coated macroporous alumina increased from 4 mmol CO₂/g 13X to 5 mmol CO₂/g zeolite 13X, when the kaolin content decreased from 4.0 wt% to 3.0 wt%. The hierarchically porous alumina-zeolite 13X composites thus had a specific capture performance close to that of binderless hierarchically porous zeolite 13X monoliths (6 mmol CO₂/g zeolite 13X)¹⁵.

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