Dirk Otter

Adsorption on Metal-Organic Frameworks

From Material Characterization to CO_2/CH_4 Separation

SHAKER VERLAG

Adsorption on Metal-Organic Frameworks – From Material Characterization to CO_2/CH_4 Separation

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Preface

Due to my affinity for technology and natural sciences, I have always been fascinated by the underlying meachnisms and driving forces of material conversion and separation processes as they are found in the chemical industry as well as in biotechnology. Consequently, after finishing my studies of chemical and biological engineering it was my wish to gain more insights and make scientific contributions in this field.

The target groups of my research are the material sciences for the topological and morphological illumination of highly microporous solid particles and the separation sciences for the purification of carbon dioxide from biogas and natural gas by means of adsorption. Especially the latter is of great importance today in context of the reduction of the CO_2 footprint.

I would like to thank Prof. Dr. rer. nat. em. Hans-Juergen Holdt (former Head of Chair of Inorganic Chemistry, University Potsdam) and his colleagues Dr. rer. nat. Suvendu Mondal and Anas Alrefai as well as Dr.-Ing. Sebastian Ernst (at this time Fraunhofer ISE) for synthesizing and providing the porous materials that were subject of the research, and for the many stimulating discussions and inputs.

I would also like to take this opportunity to thank my many fellow - internal as well as external - PhD colleagues, who were always open to technical questions and interested in my work. In particular I would like to emphasize Dr.-Ing. Samer Alzyod (at this time TU Kaiserslautern) and Dr.-Ing. Christian Geitner (Fraunhofer UMSICHT) for their valuable inputs in terms of numerical simulations.

Since the topic was very interdisciplinary, there were intersections with almost all the chairs of our faculty. For this I would like to thank representatively the working groups of Prof. Dr.-Ing. Sergiy Antonyuk, Prof. Dr.-Ing. Hans Hasse, Prof. rer. nat. Roland Ulber, Prof. Dr.-Ing. Tilmann Beck, Prof. Dr.-Ing. Alois Schlarb, Dr.-Ing. Sandra Wolff, Prof. Dr.-Ing. Stefan Ernst and of course all my colleagues from Prof. Dipl.-Ing. Dr. techn. Hans-Joerg Bart.

I would also like to thank my many students, who contributed enormously to the success of my research with their work. Especially I would like to thank Nina Lonsdorf, Jonas Schneider, Max Dieler, Volker Daenekas, Pascal Duerrwang, Fanis Kargiozidis, Elena Koerner, and Tobias Recktenwald.

Finally, on a professional but also personal level, I would like to thank my supervisor Prof. Dipl.-Ing. Dr. techn. Hans-Joerg Bart, who placed his trust in me and gave me a great

deal of freedom to work independently, while always providing me with his professional support. My thanks also go to his loyal post-doc and companion of many years, Dr.-Ing. Lorenz Kraetz, who was always eager to join conversations and knew where to find information from the literature.

Credits also go to Prof. Dr.-Ing. Erik von Harbou for taking over the audit chair and to Prof. Dr.-Ing.em. Sigfried Ripperger for the reviewing of my thesis.

For the tireless moral support and proof reading, I would also like to thank my dear girlfriend, Kristin O'Donnell.

A big thank you is also due to my family, especially to my dearest little sister Henrike. You are the best!

Kurzfassung

Das Verfahren der Adsorption zur Trennung von Gasgemischen gewinnt in der Prozesstechnik immer mehr an Bedeutung, da es einigen konkurrierenden Verfahren, wie der kryogenen Destillation oder Absorption energetisch überlegen ist. Neuartige synthetische Materialien, wie beispielsweise Zeolithe oder insbesondere metal-organic frameworks (MOFs), bergen dabei ein enormes Potential, die Prozesseffizienz durch Selektivitätssteigerungen weiter zu optimieren.

In vorliegender Arbeit wird mit einer Sonderklasse der wasserbeständigen Zeolitic Imidazolate Frameworks (ZIF), den Imidazolate Frameworks Potsdam (IFPs), eine neuartige isostrukturelle MOF-Serie hinsichtlich ihrer adsorptiven Trenneigenschaften für Methan /Kohlenstoffdioxid-Gemische charakterisiert. Die verwendeten hochmikroporösen Materialien werden sowohl bezüglich ihrer morphologischen und strukturellen Eigenschaften in statischen Adsorptions-Screenings (Gleichgewichtsmessungen) als auch bezüglich ihres Trennverhaltens in dynamischen Adsorptionsprozessen im Festbett (Durchbruchskurven) analysiert. Dabei wird auch der Einfluss unterschiedlicher funktioneller Gruppen auf die physikochemischen Eigenschaften der isoretikulären IFP-Serie beleuchtet. Die mathematischen Modelle zur Beschreibung der statischen und dynamischen Adsorption werden vorgestellt und anhand experimenteller Daten validiert, darunter ein neues Modell zur Beschreibung von spezifischen, Hysterese aufweisenden Wasserdampf-Isothermen, sowie weitere Modelle zur Beschreibung von Adsorptions-gleichgewichten von Reinstoffen und Gemischen und insbesondere das Modell zur Simulation von Durchbruchkurven unter Berücksichtigung der Massen- und Energie-bilanzen. Unter Anwendung eines heterogenen Kinetikmodells werden detaillierte kinetische Analysen anhand der experimentellen Daten durchgeführt und die Bedeutung kinetisch induzierter Selektivitätssteigerungen aufgezeigt. Anhand der so gewonnen Erkenntnisse wird die Einführung eines kostengünstigen Komposit-Materials, aus mit kinetisch selektivem Ni-MOF-74 beschichteten preiswerten mesoporösen Aluminiumoxid-Trägern (Kern-Schale-Ansatz), zur Steigerung der Trenn- und Kapazitätseffizienz demonstriert.

Abstract

The process of adsorption for the separation of gas mixtures is becoming increasingly important in separation technology, as it is energetically superior to competing processes, such as cryogenic distillation or absorption. Novel synthetic materials, such as zeolites or in particular metal-organic frameworks (MOFs), offer enormous potential to further optimise process efficiency by increasing selectivity.

In the present work a novel isostructural MOF series called Imidazolate Frameworks Potsdam (IFPs) – which is a special subclass among the water resistant Zeolitic Imidazolate Frameworks (ZIF) – is characterised with respect to its adsorptive separation properties for methane/carbon dioxide mixtures. The highly microporous materials are analysed both in terms of their morphological and structural properties in static adsorption screenings (equilibrium measurements) as well as their separation behaviour in dynamic adsorption processes in fixed beds (breakthrough curves). In this context the influence of different functional groups on the physicochemical properties of the isoreticular IFP series is also highlighted. The mathematical models for describing static and dynamic adsorption are presented and validated on the basis of experimental data, including a new model for the description of hysteresis exhibiting water vapour isotherms, as well as for adsorption equilibria of pure substances and mixtures, and in particular a model for the simulation of breakthrough curves taking into account the mass and heat balances, respectively. By applying a heterogeneous kinetic model, detailed kinetic analyses are performed on the experimental data and the importance of kinetically induced selectivity enhancement is illuminated. On basis of thhis knowledge a composite material consisting of cheap mesoporous alumina carriers coated with more expensive but kinetically selective Ni-MOF-74 (core-shell approach) is used to demonstrate an increase in separation efficiency that will ultimately allow more economically viable processes.

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