Research Article

SURFACE and INTERFACE ANALYSIS

Received: 10 February 2009 Revised: 11 March 2009 Accepted: 28 April 2009

(www.interscience.wiley.com) DOI 10.1002/sia.3080

# Adsorption and separation of light alkane hydrocarbons by porous hexacyanocobaltates (III)

G. Autie-Castro,[a] M. Autie,[a] E. Reguera,[a,b]* J. Santamaría-González,[c] R. Moreno-Tost,[c] E. Rodríguez-Castellón,[c] and A. Jiménez-López[c]

**The adsorption and separation of light *n*-alkane hydrocarbons (propane, butane, pentane, hexane and heptane) by zinc and cadmium hexacyanocobaltates (III) were studied from inverse gas chromatographic data. These two solids are representative of the porous frameworks found for transition metals hexacyanometallates. For cadmium, the porous framework is related to the presence of systematic vacancies for the building block, [Co(CN)$_6$], while for Zn it is a consequence of a tetrahedral coordination for the Zn atom. These linear light hydrocarbons (paraffins) are effectively separated by these two porous frameworks. The involved differential adsorption heats and the related separation coefficients were estimated from the recorded chromatographic data. No significant differences for the separation ability of light *n*-alkane hydrocarbons by the evaluated materials were observed. Copyright © 2009 John Wiley & Sons, Ltd.**

*Supporting information may be found in the online version of this article.*

**Keywords:** porous solids; *n*-alkane separation; inverse gas chromatography; *n*-alkane adsorption

## Introduction

Transition metals hexacyanometallates have received a renewed attention in the last few years mainly due to their role as prototype of porous solids for the hydrogen storage.[1–11] This series of porous solids results from the assembling of the anionic building block, $[M^{n+}(CN)_6]^{n-6}$, through a second transition metal, $T^{m+}$, which links neighboring blocks through their N ends. When the T metal adopts an octahedral coordination solids, with a cubic unit cell are obtained. In this case the porosity is related to the existence of systematic vacancies for the building block due to the required material charge neutrality.[1,9,11,12] The resulting porous framework is formed by spherical cavities of *ca* 8.5 Å diameter, which remain communicated by windows of about 4.5 Å. For zinc also, the tetrahedral coordination is possible and a zeolite-like porous solid free of vacancies results.[7,10,12] In this case, the available free volume results from ellipsoidal cavities of *ca* 12 × 9 × 8 Å, which remain communicated by elliptical windows of about 5 Å of larger diameter.[13] In addition to hydrogen, the porous frameworks of this series of coordination compounds have also been evaluated from $H_2O$, $CO_2$, $N_2$, and Xe adsorption data,[7,10–14] but remain poorly characterized for larger adsorbates like light alkane hydrocarbons. For some combinations of adsorbent and adsorbate coordination, interaction could be present.[15] However, *n*-alkanes have no ability to form coordination bond with metals.

Inverse gas chromatography (IGC) is a well-established technique for the materials surface characterization,[16,17] particularly using the zero surface coverage method where the role of the adsorbate–absorbate interactions is minimized. The necessary equipment is a standard gas chromatograph, equipped with a short packed column containing the material to be studied. IGC can be used to explore the material surface for a wide temperature range using different probe species and an appropriate gas carrier. The obtained data provide information on the adsorption isotherm, the involved adsorption heats, and on the material surface partition coefficients for the components of a gaseous mixture. The study of adsorption and separation of light alkane hydrocarbons using ICG has been reported for a wide diversity of materials.[18] However, as far as we know, within porous hexacyanometallates, this technique has only been used to evaluate the surface properties of nickel and copper hexacyanoferrates.[19] In this contribution we are reporting the results of an IGC study on the adsorption and separation of light *n*-alkane hydrocarbons (propane, butane, pentane, hexane and heptane) in representative porous frameworks of hexacyanometallates, particularly, in cadmium and zinc hexacyanocobaltates (III).

## Experimental

The materials under study were prepared mixing aqueous hot (60 °C) solutions (0.01 M) of $K_3[Co(CN)_6]$ and of sulfate of the involved metals ($Zn^{2+}$ and $Cd^{2+}$). The resulting precipitates were aged for 24 h within the mother liqueur at the precipitation

---

* Correspondence to: E. Reguera, Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada del IPN, Unidad Legaría, DF, México. E-mail: ereguera@yahoo.com

a Instituto de Ciencia y Tecnología de Materiales, Universidad de La Habana, Cuba

b Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada del IPN, Unidad Legaría, DF, México

c Departamento de Química Inorgánica, Cristalografía y Mineralogía, Facultad de Ciencias, Universidad de Málaga, España