DOI: 10.1002/zaac.201000227

# Methane Storage in Prussian Blue Analogues and Related Porous Solids: Nature of the Involved Adsorption Forces

**Blanca Zamora,[a] Jorge Roque,[a] Jorge Balmaseda,[b] and Edilso Reguera*[a,c]**

**Keywords:** Methane storage; Adsorption; Porous solids; Prussian blue; Zeolite analogues

**Abstract.** Methane adsorption is possible through three types of interactions: (1) dispersive forces (van der Waals type); (2) polarization of its electron cloud by a positive charge center; (3) induced quadrupole moment by perturbation of the molecule electron cloud through the polarization interaction. This induced quadrupole moment is able to interact with the local electric field gradient. Porous Prussian blue analogues and related zeolite-like zinc hexacyanometallates appear to have unique features for the evaluation of the relative importance of these adsorption forces for the methane storage in molecular porous materials. Methane adsorption isotherms for $T_3[Co(CN)_6]_2$ ($T$ = Mn, Co, Ni, Cu, Zn, Cd) and $Zn_3A_2[Fe(CN)_6]_2$ ($A$ = Na, K, Rb, Cs) were recorded and interpreted. From the obtained adsorption data information on the relative contribution of both electrostatic and dispersive interactions to the adsorption forces was obtained.

## Introduction

Methane is the main component of natural gas. It has the highest H/C ratio for a hydrocarbon and, in consequence, the minimum $CO_2$ production during the combustion reaction. In this reaction 55.48 kJ·g$^{-1}$ of energy are liberated, which is above the value obtained from gasoline (47.5 kJ·g$^{-1}$). These two features and the great worldwide availability of methane-containing natural gas deposits have stimulated its application not only as energy bearer for homes and business but also in mobile technologies and as source for hydrogen production. Methane can also be obtained by decomposition of organic wastes. In order to address the development of appropriate methods for methane storage to be applied in mobile applications, the U.S. Department of Energy (DOE) has set the target of 180 V(STP)/V (STP = equivalent of methane per volume of adsorbent material storage system), under 35 bar and near ambient temperature. This target allows to obtain an energy density of adsorbed methane, which is similar to that of current compressed natural gas systems [1, 2]. Up to date, that target has been satisfied only for some activated carbon [1, 2] and metal-organic frameworks (MOFs) [3–5]. For some MOF compositions, the highest methane storage capacity, ≈ 230 V(STP)/V, 28 % above the DOE target, was reported [3]. Such behavior has been ascribed to the presence of a specific methane interaction with available open metal sites at the material cavities surface [4, 5]. The methane molecule can be adsorbed through both dispersive and electrostatic interactions. The electron cloud of this molecule has certain ability to be polarized by a charge center. Its polarizability constant (α) is 2.60 Å$^3$, above three times the value for $H_2$ (0.8023 Å$^3$), for instance [6].

Porous Prussian blue (PB) analogues and related zeolite-like zinc hexacyanometallates represent unique families of porous solids, where information on the relative contribution of both dispersive and electrostatic interactions to the adsorption forces for the methane molecule can be obtained. In this study two series of these families of porous materials where considered: $T_3[Co(CN)_6]_2$ with $T$ = Mn, Co, Ni, Cu, Zn, Cd; and $Zn_3A_2[Fe(CN)_6]_2$ with $A$ = Na, K, Rb, Cs. In the following these series will be labeled as $T_3Co_2$ and $Zn_3A_2Fe_2$, respectively. From the recorded methane adsorption data information on the nature of the prevailing adsorption forces was obtained. These two series of porous solids have been evaluated for hydrogen storage [7–14] but, to the best of our knowledge, this is the first study on the methane adsorption in their porous frameworks.

## Results and Discussion

### *Characterization of the Samples to be Studied*

Information on the crystal and electronic structures and thermal stability for the materials under consideration is available from previous studies [14, 15] and here only a summary of their features is provided. The PB analogues series crystallizes with a cubic unit cell, where the cell edge corresponds to the

* Prof. Dr. E. Reguera
E-Mail: ereguera@yahoo.com
[a] Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada del IPN
Unidad Legaria
CICATA-Legaria
Legaria 694 Col. Irrigacion Del. M. Hidalgo
México City 11500, México
[b] Laboratorio de Polímeros
Instituto de Investigaciones en Materiales, UNAM
México City 11500, México
[c] Instituto de Ciencia y Tecnología de Materiales
Universidad de La Habana
La Habana, Cuba
Supporting information for this article is available on the WWW under **http://dx.doi.org/10.1002/zaac.201000227** or from the author.