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Methane adsorption on specially designed TiC and Mo_2C derived carbons with different pore size and surface morphology

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ABSTRACT

The effect of pore size and surface morphology of carbon materials on the adsorption of methane was studied selecting three microstructurally different carbide-derived carbons (CDC), synthesized from titanium carbide (TiC-CDC 950 °C and TiC-CDC 1100 °C HCl) and molybdenum carbide (Mo_2C-CDC 1000 °C). Nitrogen sorption and Raman spectroscopy methods were used to obtain the specific surface area, ratio of micro- and mesopores, the pore size distribution and disorder in structure, respectively. Studied CDCs had high surface area (>800 m^2 g^{-1}), but the pore size distribution was remarkably different. TiC-CDC 950 °C contains mainly micropores (from 0.5 to 1 nm), TiC-CDC 1100 °C HCl both micro- and mesopores (from 1.5 to 5 nm) and Mo_2C-CDC 1000 °C mainly mesopores (from 2.5 to 10 nm). Structural correlation lengths calculated from Raman spectra showed that CDC with the smallest pores (TiC-CDC 950 °C) was the most disordered of carbon materials studied. Excess isotherms (EI) of methane adsorption were measured at different temperatures (from −100 to 40 °C) and pressures (from 0.03 to 1.35 MPa) and modelled with modified Langmuir equation to obtain the absolute adsorption isotherms, enthalpies and entropies of methane adsorption. It was concluded that the change in entropy is the key factor determining the amount of gas adsorbed per unit of surface area of CDC and up to 55% more methane can be adsorbed if the structure of carbon material is optimized.

1. Introduction

Methane is a major component of natural gas and the emission of CO_2 generated from burning of methane is 25–30% lower per unit of produced energy than that generated from burning of gasoline or diesel fuel [1]. Methane has a low energy density at standard conditions, but it can be increased by compressing or adsorbing methane into microporous materials. Methane adsorption in microporous materials has the advantage of significantly lower storage pressure, thus, being safer and more economical than compressed methane [1,2]. Different work groups have researched the adsorption of methane into different microporous materials, e.g. metal-organic frameworks [3,4], zeolites [1] and various carbon materials [2,5–11], where the amount of adsorbed methane reaches as high as 25wt% at 6 MPa [11]. Amorphous carbon materials produced from various cheap and abundant precursor materials of natural or synthetic origin [12] have a clear advantage being lightweight and with high surface area.

Although, it has been demonstrated that methane adsorption depends strongly on the specific surface area of material [5–7,9,13–19], the effect of pore size and surface morphology (roughness, functional groups on carbon surface, pore shape) of carbon material has not been analysed in depth. For that purpose, an outstanding class of amorphous carbon material – carbide-derived carbons (CDCs) [5–9,19–24] – were selected for current studies. Compared to other amorphous carbon materials, CDCs have somewhat narrower and well-tunable pore size distribution and surface morphology depending on the precursor material, synthesis temperature and after-treatment conditions [5–9,19–24]. Thus, CDCs are suitable model materials to study the effect of pore size and surface morphology of carbon materials on the methane adsorption in detail.

Three different CDC-s with different pore size distribution were selected for this study: (a) TiC-CDC 950 °C prepared by etching TiC with Cl_2 at 950 °C (micropores from 0.5 to 1 nm), (b) TiC-CDC 1100 °C HCl prepared by etching TiC with HCl at 1100 °C (micro- and mesopores from 1.5 to 5 nm), and (c) Mo_2C-CDC 1000 °C prepared by etching Mo_2C with Cl_2 at 1000 °C (mainly mesopores from 2.5 to 10 nm). After synthesis, all carbon materials were treated

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with H_2 at 900 °C to remove the residues of Cl_2 or HCl. All studied CDCs were characterized by nitrogen sorption and Raman spectroscopy methods to establish the specific surface area, pore size distribution and the level of graphitization. Excess isotherms (EI) of methane adsorption were measured and modelled applying modified Langmuir equation to calculate the absolute adsorption, equilibrium coefficients, enthalpy and entropy of adsorption. Methane adsorption per sample mass and per available surface area of carbon materials were compared in detail with the properties of each carbon material to reveal the relation between pore size and structure of carbon material with adsorbed quantities of methane.

2. Experimental

2.1. Preparation of CDC materials

Based on our previous research data, three amorphous carbide-derived carbons with different pore size distributions and structural properties were selected to suit the purposes of this research [23,24]. Titanium carbide (TiC with purity 99.5%, -325 mesh powder, Sigma–Aldrich) or molybdenum carbide (Mo_2C with purity 99.5%, -325 mesh powder, Sigma–Aldrich) was etched with Cl_2 or HCl (AGA from The Linde Group, 99,99%) in a stationary quartz bed reactor at fixed reaction temperatures: 950 or 1100 °C for TiC-CDC 950 °C and TiC-CDC 1100 °C HCl, and at 1000 °C for Mo_2C-CDC 1000 °C, respectively (Table 1). In the case of TiC-CDC 1100 °C, hydrochloric acid was used instead of chlorine gas for etching to achieve desired pore size distribution [23]. After synthesis, all carbon materials were treated with H_2 at 900 °C to remove the residues of Cl_2 or HCl. Detailed description of synthesis is given elsewhere [23,24].

2.2. Surface area and pore size distribution analysis

Nitrogen adsorption isotherms (Fig. 1a) were measured on degassed (>24 h, 350 °C) carbon samples using an ASAP 2020 system (Micromeritics, USA) at −196 °C. The specific surface area (S_{BET}), micropore surface area (S_{micro}), total pore volume (V_{tot}) and micropore volume (V_{micro}) (Table 2) have been calculated from sorption data according to Brunauer–Emmett–Teller (BET) [25] and *t*-plot method [13–15,26]. V_{tot} has been obtained at the conditions near the saturation pressure, $p/p_0 = 0.95$. S_{micro} and V_{micro} values were calculated using the *t*-plot method. The pore size distributions (Fig. 1b) were calculated using non-local density functional theory (NLDFT) approximations [27–32] employing a regularization method combined with non-negativity constraints [33] with demo version of novel SAIEUS software (Micromeritics, USA) [34].

2.3. Raman spectroscopy

Raman spectra were recorded using an inVia micro-Raman spectrometer (Renishaw, UK) with excitation wavelength $\lambda_L = 514$ nm and normalized to the fitted height of a peak around 1580 cm^{-1} (Fig. 2). Raman spectra of investigated CDC materials demonstrated peaks in two different regions of wavelength: (1) from 1000 to 1650 cm^{-1}, i.e., in the so-called first-order Raman scattering region and (2) from 2300 to 2800 cm^{-1}, i.e., in the so-called second-order Raman scattering region.

To gain more information about the structure of CDC-s studied and to separate the partially overlapping peaks in Raman spectra from each other a combination of two Lorentzian and two Gaussian functions was used to model both, first- and second-order Raman scattering regions (Fig. 2 and Table 3). Also, various other

Table 1
Synthesis conditions for studied CDC materials.

Designation of CDC	Synthesis reaction	Temperature of chlorination
TiC-CDC 950 °C	$TiC(s) + 2Cl_2(g) \rightarrow TiCl_4(g) + C(s)$	950 °C
TiC-CDC 1100 °C HCl	$TiC(s) + 4HCl \rightarrow TiCl_4(g) + C(s) + 2H_2(g)$	1100 °C
Mo_2C-CDC 1000 °C	$Mo_2C(s) + 5Cl_2(g) \rightarrow 2MoCl_5(g) + C(s)$	1000 °C

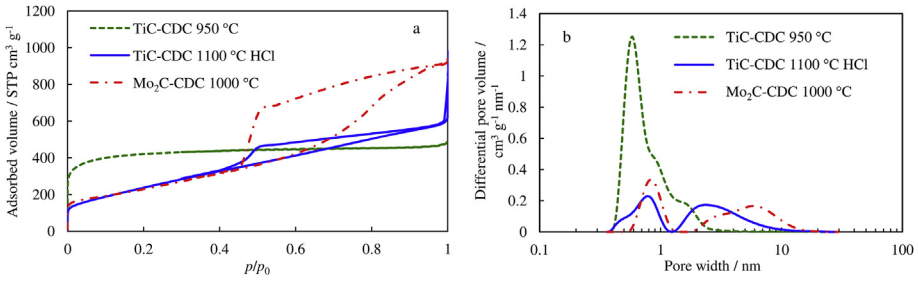

Fig. 1. (a) N_2 sorption isotherms for all carbon materials studied; (b) Pore size distribution calculated from N_2 adsorption isotherms using demo version of SAIEUS software and integrated regularizations.

Table 2
Characteristic properties of studied CDC-s obtained from the analysis of N_2 adsorption isotherms.

CDC	S_{BET} $m^2\ g^{-1}$	S_{micro} $m^2\ g^{-1}$	S_{micro}/S_{BET}	V_{tot} $cm^3\ g^{-1}$	V_{micro} $cm^3\ g^{-1}$	V_{micro}/V_{tot}
TiC-CDC 950 °C	1450	1420	0.98	0.75	0.67	0.89
TiC-CDC 1100 °C HCl	870	770	0.88	0.93	0.70	0.75
Mo_2C-CDC 1000 °C	820	250	0.30	1.47	0.09	0.06

S_{BET} – BET specific surface area, S_{micro} – micropore area, calculated using *t*-plot method, V_{tot} – total pore volume, V_{micro} – micropore volume.