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Experimental Determination of P-V-T-X Properties and Adsorption Kinetics in the CO_2-CH_4 System under Shale Gas Reservoir Conditions

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Introduction

Shale gas production via hydrofracturing has profoundly changed the energy portfolio in the USA and other parts of the world. Under shale gas reservior conditions, CO_2 and H_2O, either in residence or injected during hydrofracturing or both, co-exist with CH_4. One important feature characteristic of shale is the presence of nanometer-scale (1-100 nm) pores in shale or mudstone. The interactions among CH_4, CO_2 and H_2O in those nano-sized pores directly impact shale gas storage and gas release from the shale matrix. Therefore, a fundamental understanding of interactions among CH_4, CO_2 and H_2O in nanopore confinement would provide guidance in addressing a number of issues encountered during the recovery process, such as rapid decline in production after a few years and low recovery rates. We are systematically investigating the P-V-T-X properties and adsorption kinetics in the CH_4-CO_2-H_2O system under reservior conditions.

We have designed and constructed a unique high temperature and pressure experimental system that can measure both P-V-T-X properties and adsorption kinetics sequentially. We are measuring the P-V-T-X properties of CH_4-CO_2 mixtures with CH_4 up to 95 vol. %, and adsorption kinetics of various materials, under conditions relevant to shale gas reservoirs. We used three types of materials: (I) model materials, (II) single solid phases separated from shale samples, and (III) crushed shale samples from known shale gas producing formations and from shale gas barren formations. The model materials are well characterized in terms of pore sizes. Therefore, the results associated with the model material serve as benchmarks for our model development.

The P-V-T-X properties obtained in this study will be used ro establish a high precision equation of state (EOS) applicable to shale gas recovery in confined nano-pore environments. An equation of state (EOS) that can accurately describe interactions in the CH_4–CO_2–H_2O system for a wide range of ionic strengths in a confined environment is an important and essential tool that enables efficient resource recovery from fewer, and less environmentally impactful wells. However, such an EOS does not exist at present. For the bulk properties, Duan et al. (1992) proposed an EOS for the CH_4–CO_2–H_2O system. Their EOS was based almost solely on experimental data for the following binary systems, i.e., CH_4–H_2O, CO_2–H_2O, and CH_4–CO_2. As they pointed out, "ternary data are almost nonexistent." In their parameterization, there were two experimental investigations addressing the ternary system as described in the following. Price (1981) measured solubility of CH_4 and CO_2 in brine containing 5 wt% NaCl at 150°C and 345 bars. Ramboz et al. (1985) investigated the CH_4–CO_2–H_2O system at temperatures above 370°C, which is not applicable to the conditions for shale gas recovery. After the publication of Duan et al. (1992), number of studies on the CH_4–CO_2–H_2O system at temperatures below room temperature were initiated. The aim of these studies was to determine the hydrate equilibrium (e.g., Bruusgaard et al., 2010), but again these studies are not relevant to the conditions applicable for shale gas recovery.

Sorption capacities, sorption and desorption kinetics are highly relevant to shale gas recovery. We systematically measure sorption capacities, sorption and desorption kinetics for the afore-mentioned three types of materials under reservoir relevant conditions. These results will be used for molecular dynamics (MD) modeling of the interactions in a multiple component system.

Experimental Methods

In this study, we employed the gravimetric method using a Netzsch STA 409 thermal gravimetric analyzer (TGA) with differential scanning calorimeter (DSC) and Differential temperature analyzer (DTA) that is adapted for measurement of adsorption capacities and kinetics of the three types of materials at reservoir relevant temperatures up to 125°C and constant pressures up to 1 bar. We studied the adsorption kinetics by monitoring the evolution of the weight change as a function of time from the instant a dose of CO_2 and CH_4 gas mixture is adsorbed onto the sample, until the moment saturation equilibrium is reached.

At high pressures and high temperatures, sorption isotherms and desorption kinetics will be determined via a volumetric method (Krooss et al., 2002). In each experiment, two reaction vessels will be used, one serving as a reference cell, and the other as a sample cell. The volumes of the reference and sample cells will first be calibrated by helium expansion by introducing known amounts of helium at certain pressures. The volumes can be calculated based on ideal gas law. Alternatively, the volume of reference and sample cells can be directly measured by adding a known volume of a liquid to the reaction vessel.

In the experimental set-up, there is a valve between the reference cell and sample cell. After the sample is loaded into the sample cell, the valve is closed. Then, a known amount of gas is introduced into the reference cell. After that, the valve is opened. The amount of gas absorbed can be calculated based on the void volume. The amount of absorbed gas (n_{absorbed}) is defined as the difference between the total amount of gas (n_{total}) present in the system and the amount occupying the void volume (V_{void}), i.e., the volume not occupied by the solid sample. The void volume is calculated from the molar concentrations (c_{gas}) in the gas phase, which is obtained from an equation of state (EOS) of the gas for the corresponding pressure and temperature:

$$\begin{aligned} n_{\mathrm{absorbed}} &= n_{\mathrm{total}} - \mathrm{c}_{\mathrm{gas}}\, V_{\mathrm{void}} \\ &= n_{\mathrm{total}} - \mathrm{c}_{\mathrm{gas}}\, (V_{\mathrm{sample\ cell}} - V_{\mathrm{sample}}) \end{aligned}$$

where V_{sample} is measured by helium expansion before experiments. The total amounts of gas introduced into the system are computed from the amounts of gas transferred successively through the reference volume V_{ref} into the sample cell.

Results

In this presentation, preliminary results regarding sorption capacities and sorption kinetics for the model materials obtained using the TGA are reported. To demonstrate that the method is working, we first study adsorption capacities and kinetics of tested materials with the noble gas krypton (Kr). In Figure 1, it is shown that the adsorption capacity of the tested material for Kr is obtained based on attainment of adsorption saturation equilibrium in adsorption curves. In the linear portion of an adsorption/sorption curve before reaching the adsorption/sorption saturation, the adsorption/sorption kinetics can be obtained. As a demonstration, shown in Figure 2 is the adsorption kinetics of the tested material with Kr with an adsorption rate constant of 6.62×10^{-1} mg/g min^{-1}.

In Figure 3, the sorption capacity and sorption kinetics of montmorillonite (< 75 µm) for the mixture of 85% CH_4 and 15% CO_2 at room temperature and the total pressure of 1 bar are presented. The sorption capacity is ~1.9 mg/g. The sorption rate constant for the mixture is 4.67×10^{-2} mg/g min^{-1}.

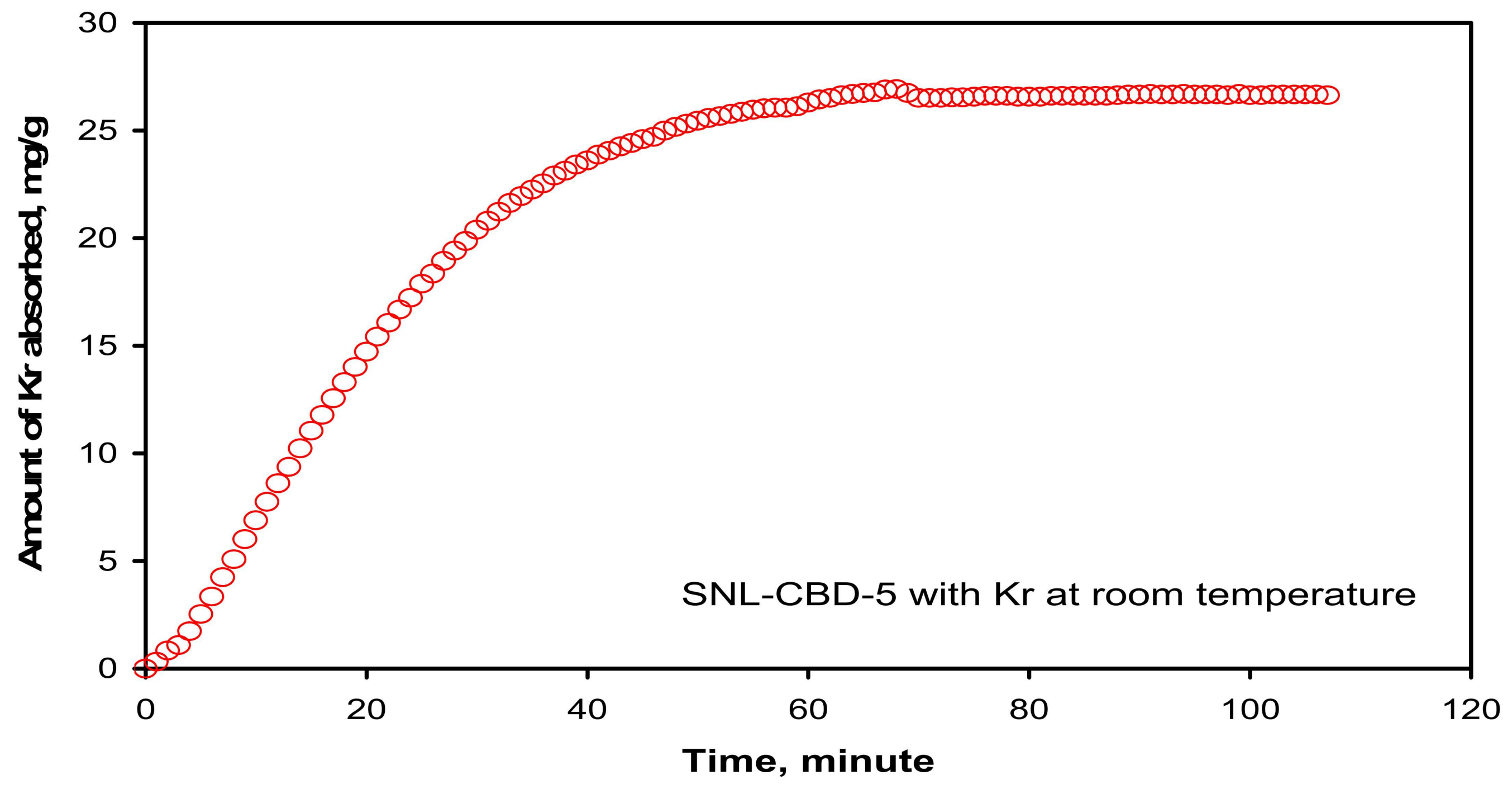

Figure 1. Adsorption Capacities with Kr for the model material at room temperature and 1 bar.

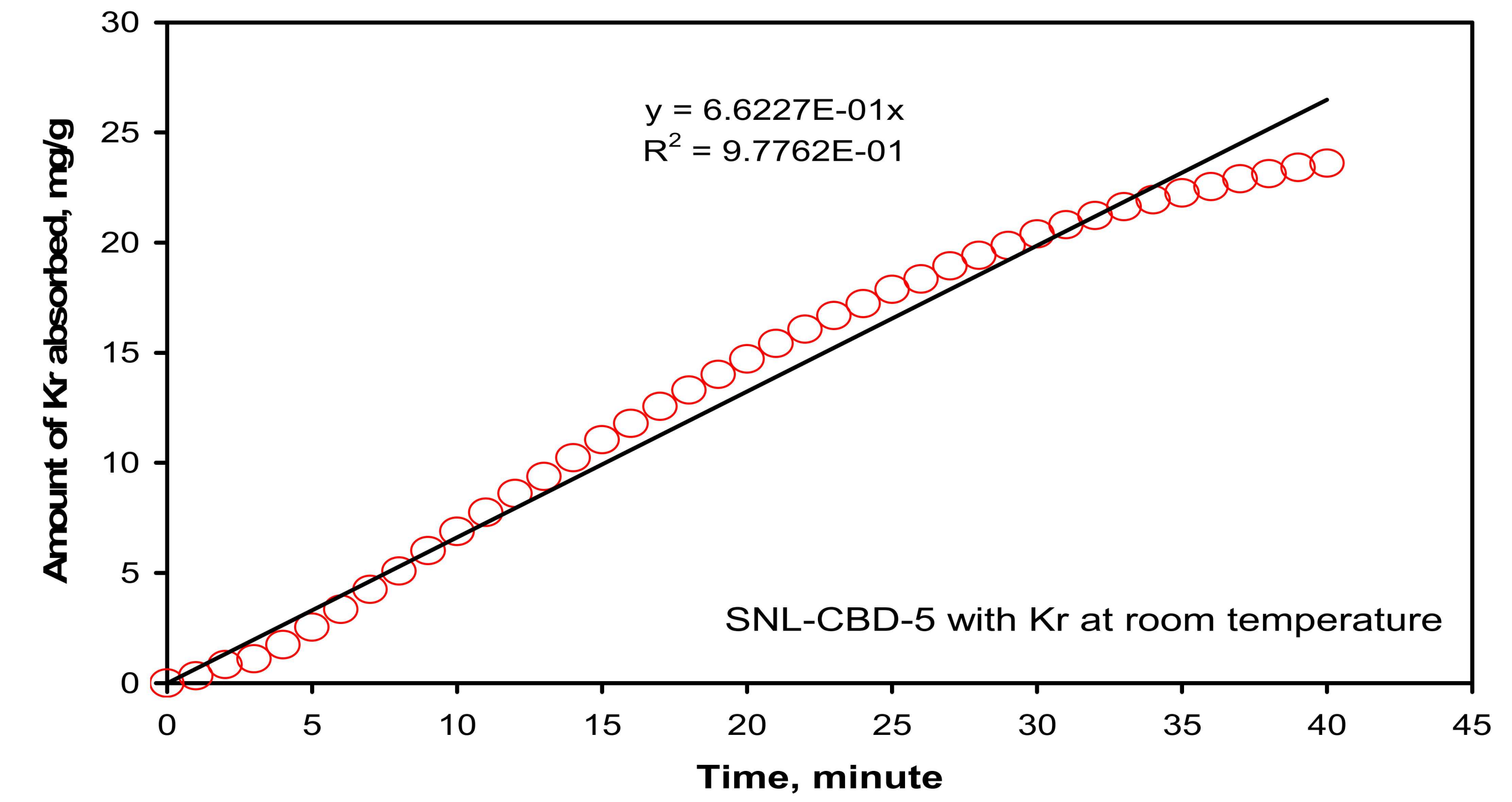

Figure 2. Adsorption kinetics with Kr for the model material at room temperature and 1 bar.

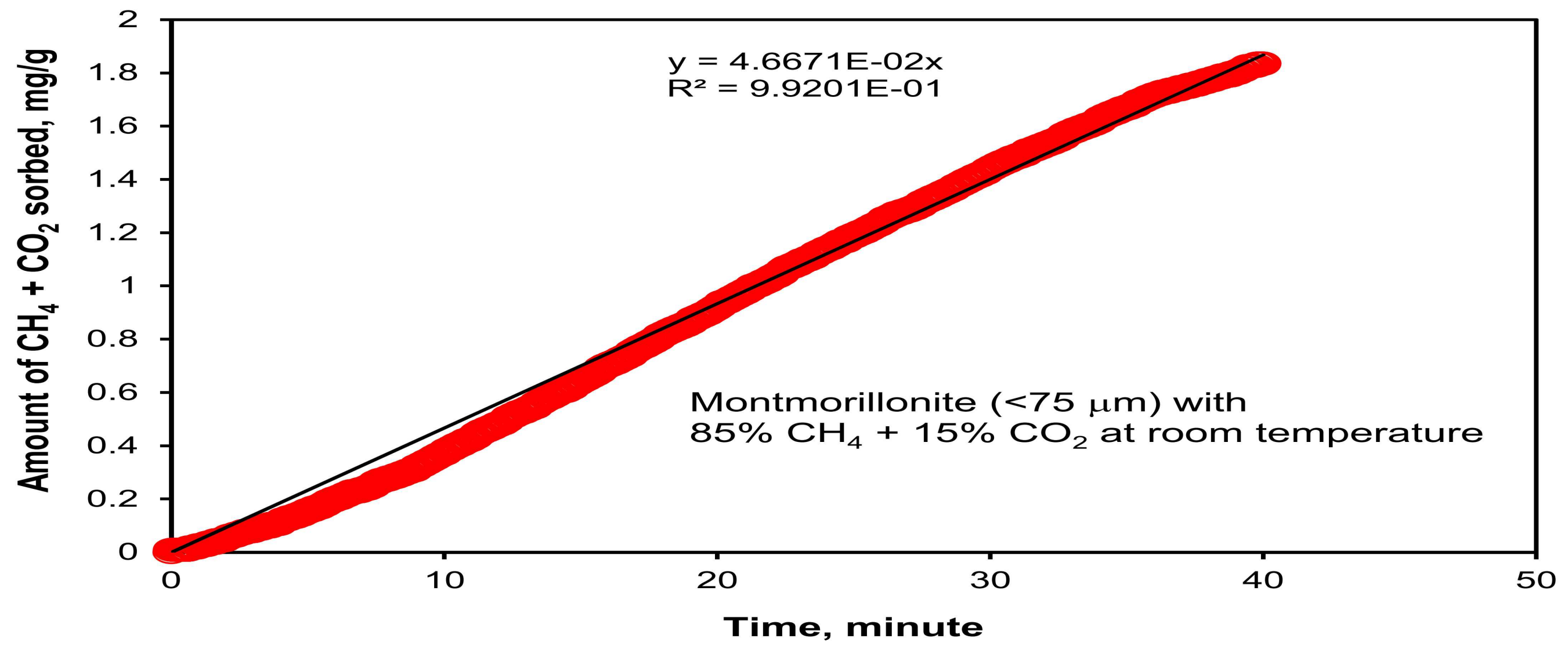

Figure 3. Sorption Capacity and kinetics with CH_4 + CO_2 for montmorillonite at room temperature and 1 bar.

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