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# Adsorption of dimethyl ether (DME) on zeolite molecular sieves

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## HIGHLIGHTS

- Dimethyl ether adsorption on molecular sieves Mol4A and Mol5A is experimentally investigated.
- Adsorption capacity of Mol5A is over eight times greater than Mol4A.
- Different adsorption mechanisms dictated by difference in pore size and surface area.
- Freundlich model fitted the adsorption isotherms for both adsorbent.
- Maximum heat of adsorption for both adsorbents is around 25.0 kJ mol$^{-1}$.

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## ABSTRACT

In recent years there has been growing interest in the use of dimethyl ether (DME) as an alternative fuel. In this study, the adsorption of DME on molecular sieves 4 Å (Mol4A) and 5 Å (Mol5A) has been experimentally investigated using the volumetric adsorption method. Data on the adsorption isotherms, heats of adsorption, and adsorption kinetic have been obtained and used to draw conclusions and compare the performance of the two adsorbents. Within the conditions considered, the adsorption capacity of Mol5A was found to be around eight times higher than the capacity of Mol4A. Low temperature adsorption and thermal pre-treatment of the adsorbents in vacuum were observed to be favourable for increased adsorption capacity. The adsorption isotherms for both adsorbents were fitted to the Freundlich model and the corresponding model parameters are proposed. The adsorption kinetic analysis suggest that the DME adsorption on Mol5A is controlled by intracrystalline diffusion resistance, while on Mol4A it is mainly controlled by surface layering resistance with the diffusion only taking place at the start of adsorption and for a very limited short time. The heats of adsorption were calculated by a calorimetric method based on direct temperature measurements inside the adsorption cell. Isosteric heats, calculated by the thermodynamic approach (Clasius–Clapeyron equation), have consistently shown lower values. The maximum heat of adsorption was found to be 25.9 kJ mol$^{-1}$ and 20.1 kJ mol$^{-1}$ on Mol4A and Mol5A, respectively; thus indicating a physisorption type of interactions.

## 1. Introduction

Gas separation and purification by adsorption has been widely studied in the past for broad range of applications involving various types of adsorbate/adsorbent. Methane, ethane, butane, propane, aromatics and air pollutants are examples of gases that have received much attention for adsorption due to their relevance to industrial applications [1,2]. This study is focused on the adsorption of dimethyl ether (DME), also known as methoxymethane ($CH_3OCH_3$), on zeolite molecular sieves. DME is a relatively unexplored gas in adsorption applications. It has numerous advantages including, but not limited to, high hydrogen to carbon ratio, high energy density, non-corrosive, non-carcinogenic, non-toxic nature and no carbon—carbon bonds. Consequently, it can be easily handled, stored, transported and burned with limited negative environmental impacts. These factors make DME an attractive option for use as an alternative fuel for internal combustion engines. Currently, the most common method for the commercial production of DME is by catalytic dehydration of methanol [3,4]. DME is also produced as a by-product of methanol synthesis [5] and from biomass driven syngas [6]. On the one hand, DME has a large potential for future applications but since it is environmentally benign [7] and only synthesised in small quantities developments of methods that allow for purification or selective separation of DME are required.

Synthesized zeolites, collectively referred to as molecular sieves are of crystalline lattice structure and highly porous giving rise to

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## Nomenclature

| | |
|---|---|
| Å | angstroms |
| $A$ | heat transfer area (m$^2$) |
| $C_P$ | specific heat capacity (kJ kg$^{-1}$ K$^{-1}$) |
| $E_a$ | activation energy (kJ mol$^{-1}$) |
| $F$ | flow meter |
| $g$ | gravitational acceleration (m s$^{-2}$) |
| $Gr$ | Grashof's number (–) |
| $h$ | heat transfer coefficient (W m$^{-2}$ K$^{-1}$) |
| $\Delta H_s$ | heat of adsorption (kJ mol$^{-1}$) |
| $K$ | parameter in Eq. (10) (Freundlich model) |
| $k_1$, $k_2$ | parameters in Eqs. (11) and (12) (Freundlich model) |
| $k$ | thermal conductivity (W m$^{-1}$ K$^{-1}$) |
| $L$ | height of adsorption cell (m) |
| $m$ | parameter in Eq. (12) (Freundlich model) |
| $m_{g_{ads}}$ | mass of adsorbed gas (kg) |
| $m_{g_{free}}$ | mass of free gas (kg) |
| $m_s$ | mass of adsorbent (kg) |
| $m_{th}$ | mass of thermocouple (kg) |
| MV | manual valve |
| $n_{ads}$ | amount of gas adsorbed (mol kg$^{-1}$) |
| $n^{ex}$ | excess gas adsorbed (mol kg$^{-1}$) |
| $\Delta n$ | adsorption uptake (mol kg$^{-1}$) |
| Nu | Nusselt's number (–) |
| $P$ | pressure (atm) |
| $P_o$ | vapour pressure (atm) |
| $Pr$ | Prandtl's number (–) |
| $Q_{g\ ads}$ | heat gained by adsorbed gas (kJ) |
| $Q_{g\ free}$ | heat gained by free gas (kJ) |

| | |
|---|---|
| $Q_{ads}$ | total heat released during adsorption (kJ) |
| $Q_{loss}$ | heat loss (kJ) |
| $Q_S$ | heat gained by adsorbent (kJ) |
| $Q_{th}$ | Heat gained by thermocouple (kJ) |
| Ra | Rayleigh's number (–) |
| $t_o$ | initial time for adsorption (seconds) |
| $t_{ads}$ | time for adsorption (s) |
| $T_{AC}$ | temperature in adsorption cell (°C) |
| $T_{amb}$ | ambient room temperature (°C) |
| $T_b$ | temperature in the adsorption cell (°C) |
| $T_M$ | temperature in the manifold (°C) |
| $t_{max}$ | time for maximum temperature in adsorption cell (s) |
| $T_W$ | wall temperature in adsorption cell (°C) |
| $V_0$ | void volume (cm$^3$) |
| $V_{AC}$ | volume of adsorption cell (cm$^3$) |
| $V_{gb}$ | volume of glass beads (cm$^3$) |
| $V_M$ | volume of manifold (cm$^3$) |
| $z$ | compressibility factor (–) |

Greek symbols

| | |
|---|---|
| $\beta$ | coefficient of thermal expansion (–) |
| $\mu$ | dynamic viscosity (m$^2$ s$^{-1}$) |
| $\rho$ | density (kg m$^{-3}$) |
| $\alpha$ | parameter in Eq. (10) (Freundlich model) |
| $\theta$ | adsorbent coverage (=$n/n_{max}$) |
| $\delta$,$\gamma$ | parameters in Eq. (8) (–) |

high adsorptive qualities at a high chemical and thermal stability. Zeolites can separate mixtures via adsorption, diffusion differences and molecular sieving effects. The kinetic selectivity and molecular sieve properties are determined by the nominal diameter of the windows in the channel structure. Borgmann et al. [8] reported that small molecular sieves in the range of 4.3–5.0 Å are more favourable for the adsorption of DME.

A review of the literature reveals that there is only handful of studies on DME adsorption. The most five relevant studies [9–13] are summarised in Table 1. Robinson and Ross [9] and Anderson and Rochester [10] both reported experimental investigations of DME adsorption on silica gel. In and both studies it was noted that DME adsorbs on silica gel as a result of hydrogen bonding. Robinson and Ross [9] study was carried out at the boiling point of DME (much lower temperature compared to this study) by measurements of the adsorption/desorption isotherms and isothermal calorimetric heats of adsorption. The heat of adsorption was found to be in the range of 20–16 kcal mol$^{-1}$. It was also shown that the thermal pre-treatment of the gels at lower temperatures resulted in increased sorption, but when impregnated with aluminium the adsorption favoured gels treated at higher temperatures. Anderson and Rochester [10] reported that for weakly adsorbed DME only one methoxy group in each molecule was bonded to a silanol group. The stronger mode of adsorption involved both methoxy groups in each DME molecule bonded to the adsorbent and therefore formed a dominant mode of adsorption at low coverage. However, it was also cited that due to the strong hydrogen bonds, subsequent desorption showed evidence of resistance even after prolonged vacuum. Reyes et al. [14] investigated pressure swing adsorption (PSA) and temperature swing adsorption (TSA) separation of DME from a hydrocarbon gas mixture using eight membered ring zeolites. It was reported that these zeolites have window sizes comparable to the molecular dimensions of DME. The upper adsorption temperature limit for PSA was recommended to be in the range 323–523 K for the pressure range of 5–200 kPa. In the TSA, the recommended operating temperature was in the range of 323–423 K for the pressure range of 20–200 kPa. The upper temperature limit was specified to avoid unwanted side reactions and polymerisation during desorption stage.

The literature review suggests that the adsorption of DME is achievable on both silica gel and molecular sieves, with the latter appearing more attractive due to its high selectivity. Nevertheless, there is still a gap of knowledge due to limited published data and lack of details in terms of adsorption isotherms, kinetics and heat of adsorption, particularly with molecular sieves. Therefore, the main goal of this study was to investigate the DME adsorption and the underlying bonding mechanisms on two different types of zeolites adsorbents and provide quantitative data that may help in developing processes for its selective separation. For this purpose, volumetric adsorption experiments were carried out within the pressure range of 0–4.0 atm on Type-*A* zeolites 4 Å (Mol4A) and 5 Å (Mol5A). Both selected adsorbents have a pore size distribution close to the molecular size of DME. Details on the adsorbents surface area, morphology, chemical composition, thermal stability and moisture contents were determined using various analytical tools. In order to understand the gas binding behaviour the heat of adsorption was calculated using a new calorimetric method and the results were compared with the widely used isosteric heat of adsorption obtained from the Clasius–Clapeyron equation [15,16].

## 2. Experimental

### 2.1. Apparatus

The adsorption analysis was carried out using the volumetric adsorption method. Fig. 1 shows the experimental set-up which