ABSTRACT

This work focuses on to study the effect of functionality on gas adsorption properties of various categories of MOFs *viz.* [{Cu_2(abtc)$_3$] (functional groups N=N and NH–NH), Cu–BTC (–H, –Br, and –I), and UiO–66 (–H, –NH_2, –NO_2, –COOH, and –(COOH)$_2$). The equilibrium adsorption measurements of gases varying polarity were measured over a wide range of temperature and pressure to understand the role of functionality, pore volume, and presence of accessible metal sites on physical properties of gases.

In the first part of the work, the adsorption characteristics of CO_2, CO, N_2, CH_4, C_2H_6, C_3H_8 and O_2 on Cu–abtc and Cu–hbtc MOFs were evaluated at three different temperatures *viz*. 294, 317, and 356 K and pressures ranging from 0–80 bar. Due to the presence of accessible open metal sites in both frameworks, electrostatic interactions are likely to be present. Thus, CO with significant dipole moment has higher adsorption capacity at lower pressures compared to that of CH_4. However, at higher pressures these metal sites are occupied and adsorption occurs mainly due to dispersion interactions. As a result, the adsorption uptake for CH_4 (which has higher polarizability) is more than that of CO in the high pressure region. This "cross-over" in selectivity between CO and CH_4 occurs at about 4 bar pressure. The adsorption enthalpy for CO_2 is slightly higher on Cu–hbtc compared to that Cu–abtc, indicating grater affinity of the NH–NH bond for the adsorbates. However, in the case of N_2, adsorption enthalpy on Cu–hbtc is only slightly lower compared to that on Cu–abtc. As a result of this behavior, the selectivity of for CO_2 over N_2 will be significantly higher for Cu–hbtc compared to that on Cu–abtc.

In the second part, the role of functionality on adsorption characteristics of well-known Cu–BTC MOF and its derivatives were analyzed. The presence of halo-functional groups *viz.* Cu–(bromo)BTC and Cu–(iodo)BTC and their effect on industrially important gases such as CO_2, CO, CH_4, and N_2 at three different temperatures (294, 317, 356 K) and up to high pressures

was studied. Cu–BTC exhibits increased gravimetric uptake capacity (at saturation) for CO_2 (15.4 mol kg^{-1}) followed by Cu–(iodo)BTC (13.2 mol kg^{-1}) and Cu–(bromo)BTC (10.4 mol kg^{-1}). On the other hand, compared on a unit cell basis the uptake capacities increase due to functionalization. This can be readily explained by increased molar mass of the MOFs after addition of functional groups. Similar trends also followed for other gases such as CH_4 and CO as well. Minor variations in the enthalpy of adsorption for various gases were also observed.

In the final part of this work, the effect of functionalization on pure gas adsorption of CO_2, CH_4, CO, and N_2 on a series of functionalized UiO–66 *viz.* UiO–66–NH_2, UiO–66–NO_2, UiO–66–COOH, and UiO–66–$(COOH)_2$ was studied. Among the studied gases, the highest up take capacity observed for CO_2 followed by CH_4, CO, and N_2. For CO_2 adsorption, we observed two distinct effects with respect to organic linker functionalization. At low pressure region, the CO_2 uptake increases by the introduction of polar functional groups and such improvement are more pronounced for functional groups with larger polarity. This kind of consistent behavior observed in previously reported IRMOFs. The main reason is that at pressures up to ~2 bar (low pressure region) larger functional groups in framework provides optimized pore diameter, then CO_2 molecules in the pores were tightly attached, attributing to the interactions between CO_2 molecules and complex functionalized framework play the dominant role. So, at low pressure region the highest adsorption for UiO–66–$(COOH)_2$ followed by UiO–66–COOH, UiO–66–NO_2, UiO–66–NH_2 and UiO–66. At upon substantial increment of increasing pressure up to saturation (~30 bars) levels, the advantage of the polar functional groups becomes less evident and highest uptake capacity was followed with respect to pore volume of the MOF. At 294 K, up to saturation pressure, the highest up take was observed for UiO–66 followed by UiO–66–NH_2, UiO–66–COOH, UiO–66–NO_2, and UiO–66–$(COOH)_2$. The selectivity of CO_2 over N_2 following order UiO–66–$(COOH)_2$>UiO–66–COOH>UiO–66–NH_2>UiO–66>UiO–66–NO_2 at saturation. In CO_2 selectivity over CO, UiO–66–$(COOH)_2$

shows ~2.2 times more selective over unfunctionalized UiO–66. In case of UiO–66–COOH and UiO–66–NH$_2$ is ~2 fold more selective over UiO–66. Initially, for UiO–66–COOH and UiO–66–NO$_2$ having more selective over UiO–66, as gradually pressure increases the selectivity is decreased, for UiO–66–(COOH)$_2$ is small increment in selectivity and whereas in UiO–66 and UiO–66–NH$_2$ does not change appreciably.