Owing to their high surface areas, tunable pore dimensions, and adjustable surface functionality, metal-organic frameworks (MOFs) can offer advantages for a variety of gas separation applications. In an effort to help curb emissions from power plants, we are developing new MOFs for use in post- and pre-combustion CO₂ capture, and for the separation of O₂ from air, as required for oxy-fuel combustion. In particular, MOFs with open metal cation sites or alkylamine-functionalized surfaces are demonstrated to provide high selectivities and working capacities for the adsorption of CO₂ over N₂ under dry flue gas conditions. Breakthrough measurements further show compounds of the latter type to be effective in the presence of water, while calorimetry data reveal a low regeneration energy compared to aqueous amine solutions. MOFs with open metal sites, such as Mg₂(dobdc), are highly effective in the removal of CO₂ under conditions relevant to H₂ production, while redox-active Fe²⁺ sites in the isostructural compound Fe₂(dobdc) allow the selective adsorption of O₂ over N₂. Fe₂(dobdc) is further demonstrated to be effective for the fractionation of mixtures of C1 and C2 hydrocarbons, and for the separation of ethylene/ethane and propylene/propane mixtures. Finally, it will be shown that certain structural features possible within MOFs, but not in zeolites, can enable the fractionation of hexane isomers according to the degree of branching or octane number.