Low-carbon hydrogen production via reactive intensification technologies: Rational design of materials

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Highlights
- Bimetallic hydrotalcites exhibit competitive performance for low-carbon hydrogen.
- Graphene structures enhance the activity and multicycle stability of hydrotalcites.
- A pore diffusion model with Freundlich and multicomponent isotherms gives good data description.
- The data obtained can be used to design reactive units operating under realistic conditions.

1. Introduction

The use of hydrogen as a clean energy vector is expected to provide deep decarbonisation in several sectors including transportation, heat and power for industry, and chemical and refinery feedstock applications. Low-carbon hydrogen produced by steam methane reforming coupled with carbon capture and storage (CCS) is a key cost competitive solution to meet stringent environmental targets in these sectors. In this regard the so-called sorption-enhanced (SE) and chemical looping (CL) processes are promising intensification technologies to boost the industrial production of hydrogen and simultaneously reduce the emissions associated with them.[1] However, the selection of suitable materials is currently one of the main challenges to deploy these processes commercially.

In this work, we investigate comprehensively the use of a wide range of mixed oxide materials as catalysts and adsorbents to be used in these low-carbon H_2 technologies. It is found that bimetallic hydrotalcites (HTs) with metal combinations such as Mg-Al, Cu-Al and Ni-Al are highly effective for the reactions involved. The addition of graphene supports and alkali promoters to these nanoparticles significantly enhances their activity and stability.[2,3] The use of MgO and FeO based structures are also investigated systematically.[4] The experimental studies presented are carried out under realistic conditions and are complemented with equilibria and kinetic mathematical analyses. Overall, the work provides new data regarding the fundamentals of the adsorptive-reactive performance of these materials, which is useful in the design of the novel H_2-CCS processes.

2. Methods

Unsupported and graphene supported HTs are synthesised via a co-precipitation method. MgO and FeO based structures are also prepared by coprecipitation. Commercial solids are also studied. The materials are fully characterised using a wide range of physicochemical techniques including BET, TGA, XRD, TEM, XPS, FTIR, ICP and crushing strength. State-of-the-art equipment including an Intelligent Gravimetric Analyser, and a fluidised bed reactor are used to gain fundamental insights into reaction-adsorption performance. Full details are given elsewhere.[2-4] Dynamic models are developed and validated for the simulation of temperature-pressure swing operated reactors, using primarily gPROMS. Complementary equilibria and kinetic analyses are carried out using Matlab, Excel and Aspen Plus.

3. Results and discussion

The results of this work show that the bimetallic HTs exhibit competitive adsorption capacities at 573 K and pressures up to 10 bar compared to other relevant solid CO_2 sorbents (e.g., zeolites). However, the HTs show a decrease in capacity upon pressure and temperature swing cycling. Different functional groups to those of the fresh HTs are present in the samples exposed to the CO_2 containing stream. In addition, the multicycle isotherms of HTs are not reversible showing the presence of a

hysteresis loop. This can be correlated with the decrease in capacity observed. The fresh and cycled adsorption isotherms can be fitted by the Freundlich model.[2] Graphene oxide (GO) appears to enhance the multicycle-stability of HTs whereas alkali promotion increases their capacity under the operating conditions investigated. For instance, the initial capacity of the pure HT drops by 20-30% upon cycling while the uptake of the GO hybrids is reduced only by 1-5%. The substantial benefits obtained by the presence of GO in HTs are attributed to electrostatic compatibility, excellent electrical conductivity, and enhanced mesoporosity and particle dispersion.[3]

The kinetics of mass transfer, along with the effect of particle porosity on the adsorption of CO_2 on HTs in SE and CL are studied. A 1-D fixed bed reactor model based on a linear driving force description of the intraparticle mass transfer is developed. The model considers particle porosity and the non-linearity of the isotherms. Simulations show that a pore diffusivity model coupled with the Freundlich isotherm gives a good description of the CO_2 adsorption on HTs. Competitive multicomponent (CO_2-H_2O) isotherms are suitable to simulate larger scale and high-pressure systems. The use of fluidised bed reactors is also discussed in this work.
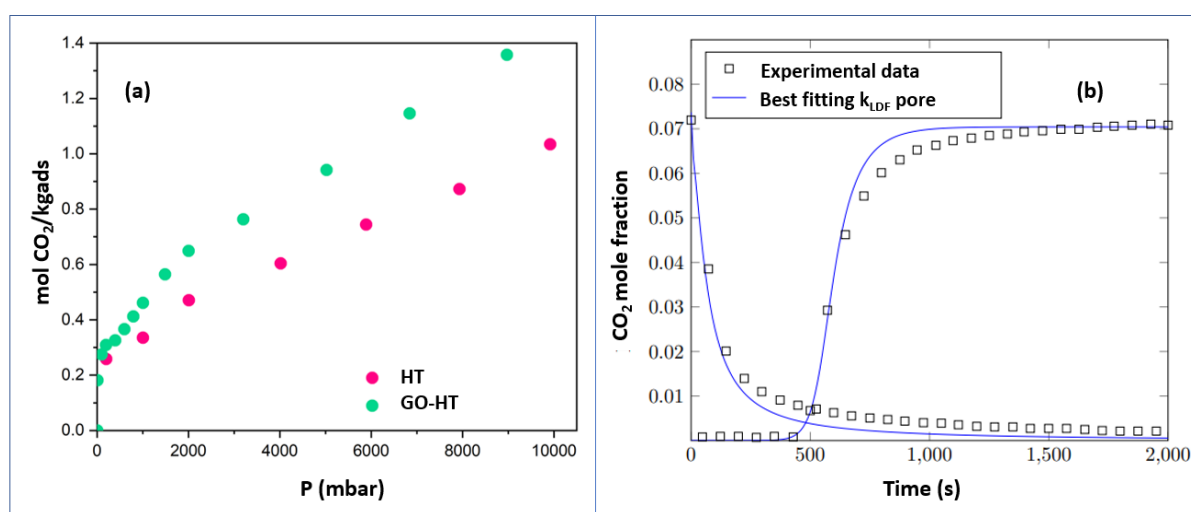

Figure 1. a) High pressure CO_2 adsorption isotherms of HT and GO-HT. b) Pore diffusivity adsorption-desorption model compared to experimental data.

4. Conclusions

This study shows that bimetallic HTs are promising sorbent-catalysts to be used in low-carbon H_2 intensification technologies. The use of graphene structures as support for HTs enhances their capacity and effectively prevents sintering of the HT nanoparticles upon multicycles. This work provides the first data of carbon supported HTs at both elevated temperature and partial pressures of CO_2. The low loadings of GO needed in the hybrids benefit the design of compact and efficient reactors. Pore diffusivity models coupled with Freundlich, and multicomponent isotherms predict the performance of the reactors. The use of other promising mixed oxides for SE and CL is also investigated.[4] The findings of this work constitute an important step towards the fundamental understanding and design of commercial reactors for low-carbon H_2 production.

References

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Keywords

Low-carbon hydrogen, mixed-oxides, sorption-enhancement, chemical-looping