

Alkali Metal Salt-Promoted MgO-Based CO₂ Sorbent for Sorption-Enhanced Water Gas Shift Reaction

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Highlights

- A novel MgO-based CO₂ sorbent promoted by mixed alkali metal salts was prepared.
- The MgO-based sorbent had high CO₂ uptake, fast kinetics and good stability.
- The water gas shift reaction was enhanced by in situ CO₂ removal with the sorbent.

1. Introduction

The water gas shift (WGS) reaction is commonly used for H₂ production from syngas that is generated from steam reforming of methane or coal gasification. However, the reversible and exothermic nature of WGS results in two or more reactors required in industry in order to achieve high H₂ yield. In addition, another stage is needed to separate CO₂ from the gas stream. If CO₂ can be removed in situ from the reaction place, the chemical equilibrium will shift to the right based on Le Chatelier's principle. As a result, high conversion of CO and high purity of H₂ are anticipated. Moreover, the WGS process will be simplified to some extent. This technology is called sorption-enhanced water gas shift (SEWGS). The industrial feasibility of SEWGS depends mainly on the CO₂ sorbents, which should have fast kinetics, high CO₂ capture capacity and good sorption-regeneration cyclic stability at 250-400 °C. Unfortunately, most sorbents available show low CO₂ uptake (< 0.1 g_{CO2}/g_{sorbent}) under the above temperature range^[1]. Here, we present a MgO-based sorbent promoted by mixed alkali metal nitrate and carbonate, which shows high CO₂ uptake, rapid sorption rate and long-term durability in CO₂ capture. This sorbent is also successfully applied to the SEWGS process.

2. Methods

2.1. Preparation of MgO-based sorbent

The alkali metal salt-promoted MgO-based CO₂ sorbents were prepared by a two-step method^[2]. The former step was to prepare MgO by precipitating MgCl₂ with NH₃·H₂O to form Mg(OH)₂ followed by calcination, and the latter was deposition of alkali metal nitrates and carbonates onto MgO by methanol evaporation-induced surface precipitation. By varying the ratio of nitrate to carbonate (X) and the ratio of total salts to MgO (Y), a series of MgO-based sorbents were prepared, which were denoted by MgO-X-Y.

2.2. Preparation of CuO-CeO₂-ZrO₂ catalyst

A CuO-CeO₂-ZrO₂ catalyst was prepared by coprecipitation using an aqueous solution of metal nitrates by adding a NaOH solution. The atomic ratio of Cu:Ce:Zr was 1.6:1.4:1.

2.3. CO₂ capture and SEWGS

The CO₂ capture performance of MgO-X-Y was tested in a thermogravimetric analyzer (TGA), with sorption at 350 °C for 60 min in pure CO₂ or CO₂/N₂, and regeneration at 400 °C for 20 min in pure N₂. The SEWGS was conducted in a fixed bed reactor at 350 °C and 8 atm with a mass ratio of sorbent to catalyst of 2. The molar ratio of CO to H₂O in the inlet stream was 1 and the gas hourly space velocity was 800 mL(STP)/(g·h). After 90 min of operation, a regeneration step was carried out at 400 °C in pure N₂ for 1 h.

3. Results and discussion

Both MgO and alkali metal salt-promoted MgO-based sorbent exhibit a sheet-like geometry (Fig. 1(a)). MgO shows an interconnected pore network, while the MgO-based sorbent has few pores, implying successful

deposition of alkali metal salts on MgO. The BET surface area and pore volume of MgO are $139.4 \text{ m}^2/\text{g}$ and $0.29 \text{ cm}^3/\text{g}$, respectively, which are greatly reduced to $15.0 \text{ m}^2/\text{g}$ and $0.12 \text{ cm}^3/\text{g}$, respectively.

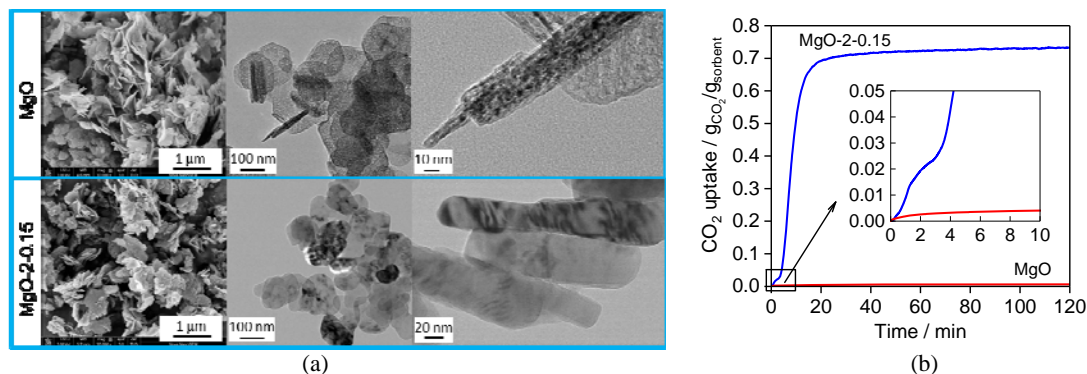


Figure 1. Micromorphology (a) and CO₂ uptake (b) of MgO and alkali metal salt-promoted MgO-based sorbent.

In contrast to the very low CO₂ uptake of MgO ($< 0.01 \text{ gCO}_2/\text{g}_{\text{sorbent}}$), MgO-2-0.15 has an uptake as high as $0.73 \text{ gCO}_2/\text{g}_{\text{sorbent}}$ (Fig. 1(b)); moreover, the sorption rate of MgO-2-0.15 is much higher than that of MgO. The reason mainly lies in that the alkali metal nitrate coated on MgO is in the molten state, which can dissolve a certain amount of MgO, whereby the high lattice energy of MgO is reduced and thus benefits the CO₂ sorption^[2]. MgO-2-0.15 has good stability over 20 consecutive cycles, whose CO₂ uptake is maintained at $0.56 \text{ gCO}_2/\text{g}_{\text{sorbent}}$ in the case of pure CO₂ used or $0.52 \text{ gCO}_2/\text{g}_{\text{sorbent}}$ when only 40% of CO₂ is employed. To the best of our knowledge, it is the best CO₂ capture performance reported to date for MgO-based sorbents.

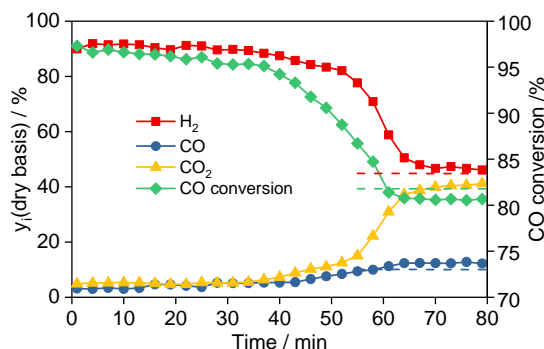


Figure 2. Molar fraction (dry basis) profiles of H₂, CO and CO₂ as well as CO conversion during the SEWGS process.

When MgO-2-0.15 and CuO-CeO₂-ZrO₂ are applied to the SEWGS process, there are three stages in the concentration profiles (Fig. 2): prebreakthrough ($< 35 \text{ min}$), breakthrough ($35\text{-}60 \text{ min}$) and postbreakthrough ($> 60 \text{ min}$), which correspond, respectively, to three states of sorbent in terms of saturation degree, i.e., far from, gradual and complete saturation. At the prebreakthrough stage, the H₂ concentration (ca. 91%) and CO conversion (ca. 96%) are much higher than their counterparts at the postbreakthrough that are close to the equilibrium values in WGS (shown by the dashed lines), demonstrating the enhanced H₂ production by in situ removal of CO₂ with the alkali metal salt-promoted MgO-based sorbent.

4. Conclusions

A novel MgO-based sorbent promoted by mixed alkali metal nitrate and carbonate exhibits high CO₂ capture performance at intermediate temperature, making it a potential material for SEWGS.

References

- [1] J. Wang, L. Huang, R. Yang, et al., Energy Environ. Sci. 7 (2014) 3478-3518.
- [2] L. Wang, Z. Zhou, Y. Hu, et al., Ind. Eng. Chem. Res. 56 (2017) 5802-5812.

Keywords

Water gas shift reaction; Sorption-enhanced; MgO-based sorbent; CO₂ capture