

Silica supported DFM catalysts for CO_2 Capture, Storage and Re-use Technology. Comparative study with Al_2O_3 -based model catalyst.

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Introduction and Motivations

The growing concern about global warming and climate change has driven many countries to take action and generate new policies for environmental protection. CO₂ is considered the largest source of greenhouse gas (GHG) emissions. Although decarbonization technologies and strategies show a rapid and steadily developing, they are still incipient and require high investments. CO₂ Capture and Storage and Utilization (CCSU) catalytic strategies have emerged to prevent the CO₂ releasing and reduce its atmospheric concentration. In this context, dual-function materials (DFM) are potentially proposed for cyclic CO₂ capture and methanation technology, acting as both as solid adsorbents catalytic materials for carbon capture for capture CO₂ (the material is exposed to a CO₂-containing gas stream until saturation, enabled by the functionalization with alkaline and/or alkaline-earth) and as catalysts for fuel production upon H_2 exposure (where the CO_2^{stored} is converted to CH_4 through catalytic hydrogenation, $CO_2+4H_2 \rightarrow CH_4+2H_2O$, typically improved by the incorporation of metals such as Ru or Ni)¹. In literature, successful DFMs consist of redox metals-supported mostly over alumina and doped with alkaline or alkaline-earth ions². However, the growing interest in the use of more economical materials within the idea of circular economy has positioned silica as a possible effective alternative as a catalytic support for DFMs due to its interesting morphological, physical and chemical properties and its use as a fundamental material in numerous industrial applications. Moreover, the recovered silica from industrial wastes could be employed and reused as silica-based support³.

This contribution presents a comparative study of the catalytic performance with the analysis of the surface-species involved in the cyclic alternating catalytic process of CO_2 capture and reuse of DFMs supported on a commercial silica compared to model DFMs supported on alumina.

Materials and Methods

Silica-supported ternary catalysts were prepared by sequential impregnation as previously reported, incorporating Ru (0.5% wt), and different Alkaline(-earth) oxides such as Ba and K (16% wt)². These catalysts, together with the binary formulations (Me/SiO₂) and the support (commercial silica) were characterized by N₂ physisorption, XRD, SEM-EDX, CO₂ TPD, H₂-TPR, among others. Microreactor experiments were carried out in a quartz tubular reactor, with a space velocity of 100 L(STP)/h/g. The gases leaving the reactor were analyzed by means of a mass spectrometer, a FT-IR spectrometer, and a micro gas chromatograph. CO₂ capture/reduction cycles were performed at constant temperature in the range 250-400°C. Every cycle is composed by an adsorption phase (1% CO₂/He) and a reduction phase (4% H₂/He), separated by an inert purge. Advanced spectroscopy characterization methodology was carried out for silica and alumina-based-DFMs to investigate acidity and basicity and surface OH groups distribution. CO₂ adsorption and desorption was also tested using *in situ* FT-IR techniques. A

Results and discussion

The catalytic performance data for CO₂ reduction with H₂ are presented in Table 1. CO₂ conversion achieved by Ru-Ba catalysts appears to be independent of the support material (Al₂O₃ or SiO₂). However, Ru-Ba/SiO₂ shows a higher methane selectivity compared to Ru-Ba/Al₂O₃ with same composition at lower temperature range, achieving comparable values beyond 400°C. The CO₂ storage capacity of Ru-Ba/SiO₂ was approximately 230 μ mol/g_{cat} (43% lower than that of the Al₂O₃-supported



catalyst), producing 63 μ mol/g_{cat} of CH₄ in the subsequent reduction with H₂. This observation implies that not regenerable carbonate species may remain on the surface after the reduction step which do not take part in the methanation reaction.

Temperature (ºC)	Ru/SiO ₂		Ru-Ba/SiO ₂		Ru-Ba/Al ₂ O ₃	
	$X_{CO_2}(\%)$	$S_{CH_4}(\%)$	$X_{CO_2}(\%)$	$S_{CH_4}(\%)$	$X_{CO_2}(\%)$	$S_{CH_4}(\%)$
300	20.0	95.1	11.7	86.1	4.4	41.1
400	29.5	58.2	33.1	39.2	32.0	16.1
500	52.8	20.3	53.6	12.9	53.2	6.8

Table 1. TPR experiment results: temperature ramp (from RT to 500°C @10°C/min) in CO₂ (1% v/v) + H_2 (4% v/v) He-balanced.

Experiments conducted with FTIR analysis of the species arising from CO_2 adsorption (Fig. 1), revealed the formation of a complex population of carbonate-type species over the catalyst surface, also depending on the support material employed. Both samples exhibited an initial population of bulky carbonates related to the presence of Ba (1400–1500 cm⁻¹ region) stable up to 500°C. Adsorbed surface and carbonates (likely bidentate species) are detected on both samples, remaining stable following degassing. Hydrogen carbonate species observed in the Al₂O₃-supported catalyst (1227 cm⁻¹) are likely due to the interaction of CO_2 with the support itself, while the same species could be formed over the silica supported catalysts following interaction of CO_2 with the basic oxide phase. However, in the Ru-Ba/Al₂O₃ sample (Fig. 1b), signals around 1560 and 1355 cm⁻¹—linked to the presence of bidentate carbonates on the Ba phase—shifted in the silica-supported material (Fig. 1a), indicating a different nature of these species, which remained present only in Ru-Ba/Al₂O₃-supported materials.



Figure 1. FT IR spectra of surface species arising from CO₂ adsorption and desorption at R.T. for (a) Ru-Ba/SiO₂ and (b) Ru-Ba/Al₂O₃. Activated spectrum was subtracted.

The use of silica as a catalytic support for synthesizing DFMs emerges as a sustainable alternative to Al_2O_3 , enabling the development of catalysts with high CO_2 capture capacity, with the capacity of generation of more labile carbonate species, and with a significant catalytic performance in CO_2 Capture and Re-Use process for stationary sources.

References

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