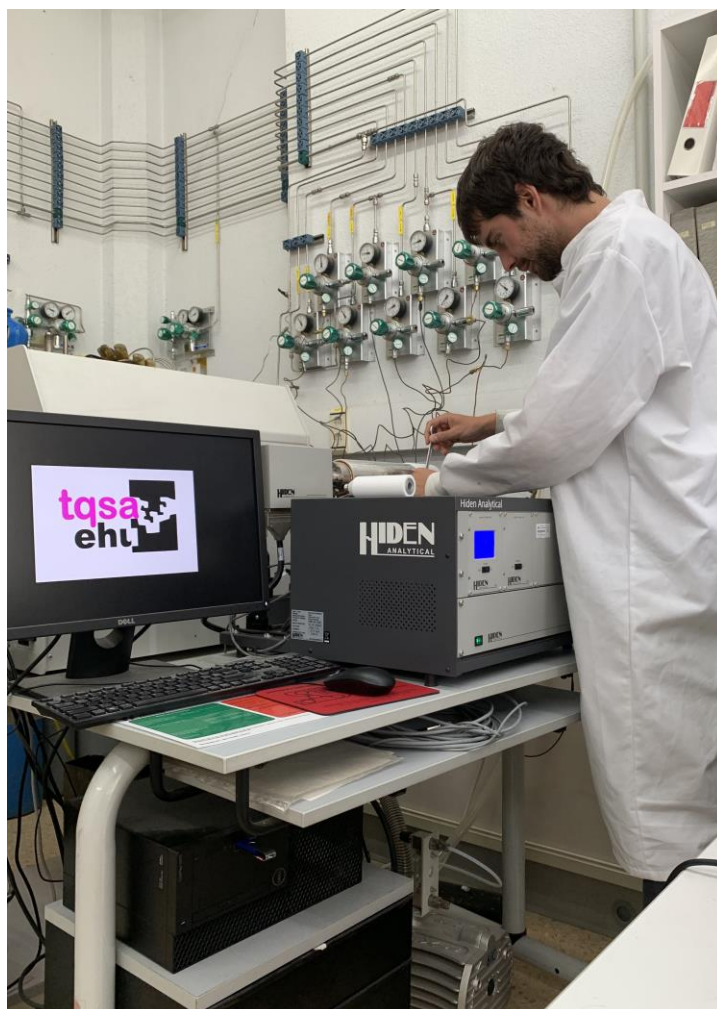


Tuning basicity of dual function materials widens operation temperature window for efficient CO₂ adsorption and hydrogenation to CH₄

The cyclic process of CO₂ adsorption and CH₄ hydrogenation on dual function materials (DFMs) has shown increasing interest in recent years. This form of operation eliminates the costly CO₂ purification step required for methanation with continuous CO₂ and H₂ feed. The DFMs present a CO₂ adsorbent compound and a metal that assists its methanation. The objective of the work is to modulate the basicity of a DFM through the joint presence of Ca and Na to extend the temperature window with high CH₄ production.

Five DFMs identified as Ru-xNa/yCa (x%/y%=0/16, 4/12, 8/8, 12/4, 16/0) were prepared on γ -Al₂O₃ as support. The synthesis was performed by sequential wet impregnation, first the adsorbent material. The physico-chemical properties of the DFMs were determined by N₂ adsorption-desorption, H₂ chemisorption, XRD, H₂-TPR, CO₂ TPD and TEM. All temperature programmed experiments were monitored with a **Hidden Analytical HPR-20 EGA mass spectrometer**. The catalytic activity was evaluated in a vertical tubular reactor, with downward flow. Prior to analysis, the sample was reduced in a stream composed of 10% H₂/Ar at 400 °C for 60 min. CO₂, CH₄, CO and H₂O concentrations were continuously monitored by on-line FTIR, during the CO₂ storage/capture period (10% CO₂/Ar, 1 min) followed by its hydrogenation/methanation (10% H₂/Ar, 2 min), with an intermediate Ar purge. The experiments were carried out with a flow rate of 1200 ml min⁻¹ (45000 h⁻¹), in the temperature range 280-400 °C.

The incorporation of Ca, Na and Ru reduces the specific surface of the DFMs compared to γ -Al₂O₃ due to the decrease in the amount of mesoporous solid (γ -Al₂O₃) and, to a lesser extent, by the partial blocking of the pores of smaller size. Values between 104-111 m² g⁻¹ were obtained. In the XRD spectra of the calcined DFMs, a seen with peaks corresponding to RuO₂ and nitrogenous compounds remaining from the precursor salts. However, for the already reduced DFMs, only peaks belonging to metallic Ru were observed. This confirms that the reduction treatment at 400 °C, prior to the activity tests, is sufficient to obtain the DFMs with the desired phases, as can also be deduced from the H₂-TPR results.



The Hidden Analytical HPR-20 EGA in the Laboratory

The joint presence of Na and Ca in the DFM favours the Ru dispersion. The distribution of basic sites was studied by CO₂-TPD. Weak basicity predominates in the DFM containing only Na and strong basicity in the DFM with only Ca. In the DFMs with both adsorbents, medium basicity predominates, presenting the highest DFM Ru-8Na/8Ca. Therefore, by adding a given Na/Ca distribution, the basicity strength of DFMs can be modulated.

The catalytic activity in cycles of CO₂ adsorption and hydrogenation to CH₄ presents different trends with the operating temperature according to the Na/Ca ratio. The Na presence favours the CH₄ production at intermediate temperatures (310 °C), while the Ca presence favours production at high temperatures (400 °C), which correlates with the basicity results. Importantly, the presence of both adsorbents, in general, boosts the CH₄ production in the entire temperature range studied (280-400 °C). The DFM Ru-8Na/8Ca, achieved higher activity and selectivity. The improved ruthenium dispersion and the presence of a greater number of basic sites with medium strength boost the CO₂ adsorption and hydrogenation to CH₄, and enhances the contact between the carbonates and the metal sites, which favours a fast kinetics of CH₄ production.

Project summary by:

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Hiden Product:

[HPR-20 EGA](#)