

Development of a catalyst-sorbent system for Sorption Enhanced Steam Reforming of Ethanol (O-18H)

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1. Introduction

The growing concern about global warming and climate change has driven many countries to take action and generate new policies for environmental protection. Among human activities which generate greenhouse gases (GHG), energy production accounts for around 75% of the total shares [1]. As 90% of the energy-related emissions derived from the oxidation of carbon, CO₂ is considered the largest source of GHG in this category. Strategies like low carbon-energy production have been raised. Between these technologies, hydrogen production through reforming of bioethanol is an interesting alternative due to the low cost and high disponibility of bioethanol, their easy handling and storage, etc. In this context, Ni and Co based-catalysts have been proposed as cost-effective catalysts. The ethanol reforming process can be intensified by *in situ* CO₂ sequestration in the Sorption Enhanced Steam Reforming of Ethanol (SESRE), which could yield higher concentrations of H₂ [2]. For this purpose, combinations of catalysts+CO₂ sorbents as well as bifunctional catalysts have been proposed. Therefore, this contribution presents a preliminary study of the SESRE reaction using a combination of a Ni-ZrO₂ catalyst and a Li₂ZrO₃-based sorbent. The solids were prepared by wet impregnation and characterized by XRD and Raman Spectroscopy. CO₂ capture tests were performed for the sorbent, while for the evaluation of the SESRE reaction, a mixture of catalyst+sorbent was employed.

2. Experimental

2.1 Material synthesis

The catalyst and sorbent were synthesized by coimpregnation of nickel acetate and alkaline carbonates, respectively, in a colloidal suspension of ZrO₂ nanoparticles stabilized in acetic acid (Nyacol-AC), and calcined at 650 °C for 6 hours in a stream composed of 45%O₂-55% N₂. A zirconia excess was used to improve the capture properties [3]. More details are given in Table 1.

Raman spectra were acquired in a LabRam (Horiba-Jobin-Yvon) spectrometer coupled to an Olympus (50X) microscope equipped with a CCD detector cooled at -70 °C using the Peltier effect. XRD patterns were obtained in a PANalitan Empyrean with Cu K α radiation at 45 kV-45 mA.

Capture properties evaluated through Temperature Programmed Desorption (TPD), with isothermal capture steps at 500 °C and different gas feedings; and regeneration steps in N₂, heating up to 700 °C (10 °C.min⁻¹) and maintaining the

temperature during 20 minutes. In the later, the stream was fed to a methanation reactor and then analyzed on-line in a FID chromatograph (Shimadzu GC-8a). Moreover, TGA capture experiments were performed in a Mettler Toledo Star, TGA/SDTA 851, using the same capture/regeneration conditions.

Table 1. Synthesis details of the catalyst and sorbent

Sample	Composition	Reagents
KLiZr-AC	K:Li:Zr=0.01:1.2:1	Li ₂ CO ₃ , K ₂ CO ₃ , Nyacol-AC
KNiZr-AC	K:Ni:Zr=0.01:0.09:1	C ₄ H ₆ O ₄ Ni, K ₂ CO ₃ , Nyacol-AC

For the SESRE reaction, 120 mg of well mixed catalyst:sorbent=1:1 along with 60 mg of quartz (Mesh 70) were loaded. The solids were pretreated by heating up to 700 °C and cooling to 500 °C (reaction temperature) in Ar. Then, the gas stream was switched to pure H₂ for 2 hours. The reaction feeding was water/ethanol with a molar ratio (R)=5, diluted in Ar, with a W/F = 1.7 × 10⁻² g h L⁻¹. The liquid mix was fed using a pump (Apema PC11U) and an evaporator operating at 220 °C. The feed and effluent pipes were heated to avoid any condensation. Effluent gases were analyzed in a Shimadzu GC-214 chromatograph, equipped with Hayesep D[®] column (10 m) and a TCD.

3. Results

3.1 Structural characterization

XRD patterns of KLiZr-AC and NiKZr-AC are shown in Figure 1. The catalyst presented signals corresponding to c-NiO along with m-ZrO₂ and t-ZrO₂, while t-Li₂ZrO₃, m-ZrO₂ and t-ZrO₂ were observed in KLiZr-AC. Zirconate and zirconia phases were also confirmed by Raman spectroscopy, though c-NiO was not detected in NiKZr-AC (Figure 2).

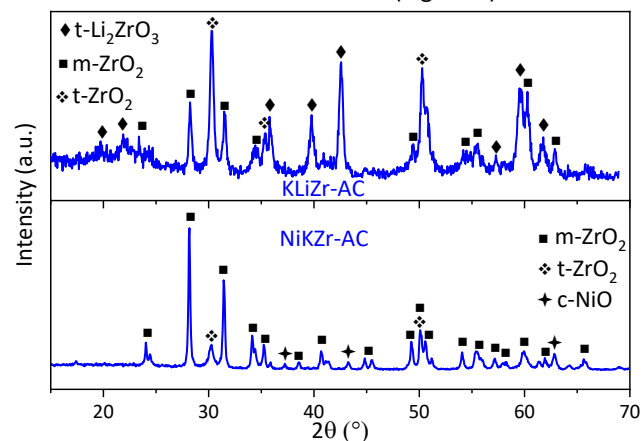


Fig. 1. XRD patterns of KLiZr-AC and NiKZr-AC samples.

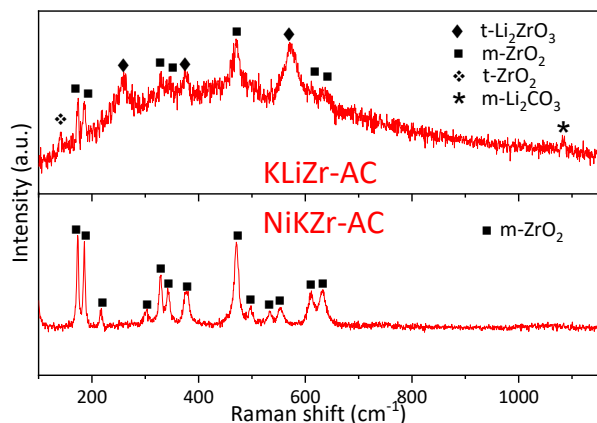


Fig. 2. Raman spectra of KLiZr-AC and NiKZr-AC samples.

3.2 Capture/regeneration properties

TGA and TPD sorption tests were performed with 50% CO₂ at 500 °C (not shown). In these conditions, KLiZr-AC reached 0.16 g CO₂.g mat⁻¹, (89% respect the maximum theoretical capture capacity) in only 20 minutes. Moreover, the sorbent was tested using similar SESRE conditions (500 °C, 15% CO₂-20% H₂O), reaching 0.15 g CO₂.g mat⁻¹ after 60 minutes of reaction. Finally, a stability test of 10 consecutive cycles in these conditions was carried out, where the capture properties remained almost constant, showing excellent stability.

3.3 Catalytic activity

The NiKZr-AC+KLiZr-AC system evaluated in SESRE resulted active for the reaction (Figure 3), presenting a high EtOH conversion (around 80%) and a H₂ yielding around 2.5. The system presented good stability, maintaining similar values of conversion and H₂ yield during at least 7 hours.

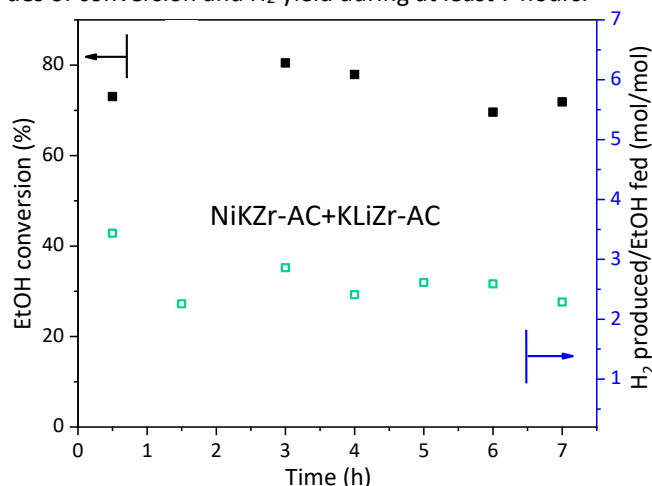


Fig. 3. EtOH conversión and H₂ yielding. T=500 °C. P=1 atm. R=5. W/F=1.7 × 10⁻² g h L⁻¹.

The product distribution (Figure 4), remained almost constant during 7 hours of reaction, being H₂ the main product (above 70%), with around 20% CO₂, and CH₄ and CO <5%. Additionally, negligible amounts of CH₃COH and C₂H₄ were present in the reaction products.

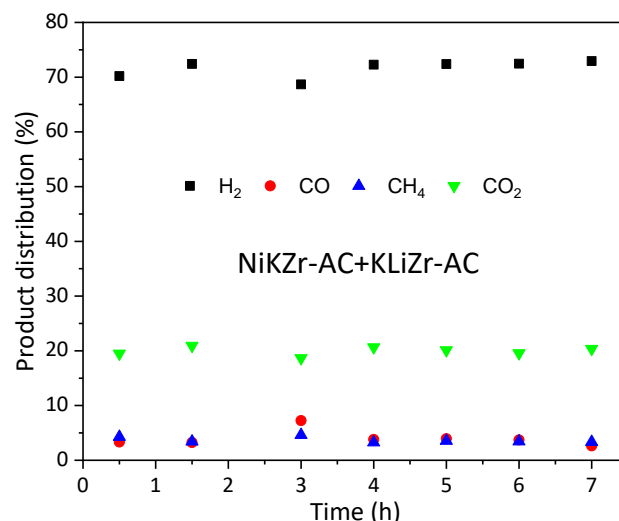


Fig. 4. Product distribution. T= 500 °C. R= 5. W/F=1.7 × 10⁻² g h L⁻¹.

4. Discussion

The presence of the c-NiO and t-Li₂ZrO₃ phases were confirmed through XRD analysis. However, only zirconia and zirconate phases were detected by Raman spectroscopy, which could be related with the differential sensivity of this technique.

The incorporation of 5 wt% NiO in ZrO₂ resulted in a catalyst active for the SESRE reaction, stable and selective to H₂. For this system, the size and morphology of the support (ZrO₂) could affect the particle size of the active phase (Ni), as well as their interaction with the support, producing species with different reducibilities which, in turn, influence the catalytic activity. The low % of CO could be associated with the occurrence WGS reaction, whose products are H₂ and CO₂. In this sense, the presence of a sorbent could remove *in situ* part of the CO₂, shifting the equilibrium of the WGS reaction to more H₂ [2].

5. Conclusions

A Ni-ZrO₂ catalyst and a Li₂ZrO₃-based sorbent were synthesized through wet impregnation. The NiO, zirconate and zirconia phases were confirmed through Raman spectroscopy and XRD. The catalyst+sorbent system was active for the SESRE, with a EtOH conversion of around 70% after 7 hours of reaction. Moreover, the system presented a good and stable H₂ yield with low % of by-products. Finally, the results presented in this contribution constituted a starting point for the investigation of new and more efficient catalytic systems for the SESRE process.

References

- [1] IEA, World Energy Outlook 2020, IEA, Paris, 2020.
- [2] R. Avendaño, M. Dieuzeide, P. Bonelli, N. Amadeo, Sorption-Enhanced steam reforming of ethanol for hydrogen production, *Latin American Applied Research*, 50 (2020) 121-126.
- [3] D. Peltzer, J. Múnera, L. Cornaglia, Study of the sorption properties of alkali zirconate-based sorbents at high temperature in the presence of water and low CO₂ concentration, *Journal of Alloys and Compounds*, 895 (2021) 162419.