

Raman study of the sulfur poisoning of multimetallic catalysts for the self-reforming of biogas

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Introduction

Biogas reforming is an eco-friendly alternative for syngas or hydrogen production, as it generates low, or even negative, carbon emissions. If a proper amount of steam is added to the untreated biogas, a steam compensated self-reforming ($\text{CO}_2 + \text{H}_2\text{O}$) may be implemented¹. However, the presence of sulphur species in raw biogas could promote the catalyst poisoning. In this sense, commercial Ni-based catalysts may be deactivated with sulphur concentrations as low as ppb. One alternative is the employment of sulphur tolerant catalysts. Therefore, the main goal of this contribution is to study the effect of sulphur poisoning on the structure of a multimetallic non-supported catalyst for the self-reforming of biogas. The studied catalysts are based on Ni and Ce, adding Rh and Sn as promoters for the reforming activity, coke resistance, and sulphur tolerance.

Materials and Methods

The non-supported multimetallic catalyst was synthesized by incorporation of Rh and Sn on a Ni-Ce, previously obtained by coprecipitation (identified as RhSnNiCe reference catalyst). The sample was dry overnight at 90 °C calcined at 700 °C for 2 hours ("As calcined" sample). The nominal ratios were the same that of a previous Al_2O_3 -supported multimetallic catalyst synthesized in our laboratory, which is included in this work for comparison purposes (Ni:Ce ratio=1.8, Rh:Ni=1:10,000, Sn:Ni=1:1,000)¹. This supported catalyst presented very good activity and H_2/CO yielding, though it was deactivated in the presence of 50 ppm of DMS¹. For the sulphur poisoning test, the analyzed samples were: "As calcined", "reduced", and "sulphur-poisoned". The catalysts reduction was performed at 700 °C during 30 minutes in 10% H_2 -90%He atmosphere ("reduced" sample). A portion of 20 mg of the reduced material were poisoned by adding 0.3 mL of DMS solution (125 ppm) and heated in air up to 700 °C ("sulphur-poisoned"). All the samples were analyzed by Raman spectroscopy.

Results and Discussion

Raman spectra of the samples are shown in Fig. 1. The "as calcined" samples show a main band located at 463 cm^{-1} , attributed to the F_{2g} vibrational mode of the cubic fluorite-type structure of cerianite². Two other Raman modes at near 552 and 635 cm^{-1} originate from defect structures in the lattice³, while a third band at 595 cm^{-1} is related to Ni-O-Ce bonds. The non-supported reduced catalyst present bands related to Ni-O species in the medium and high frequencies region, while the Ce- F_{2g} signal was still observed in the reduced supported

catalyst. The Raman modes related to the cerianite and oxygen vacancies reappear in the "sulphur-poisoned" samples, though with different intensities. However, no sulphur related species are detected.

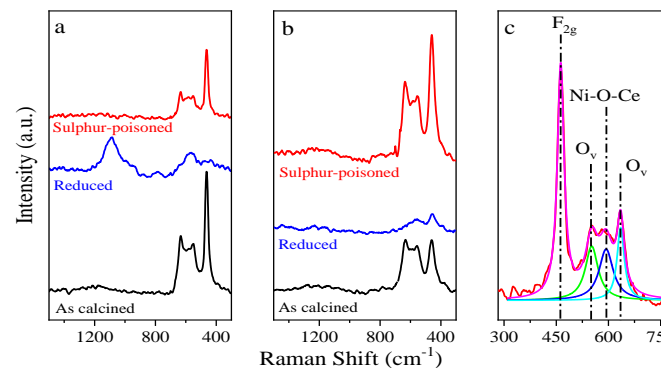


Figure 1. Raman spectra of the non-supported (a) and supported (b) in three conditions. (c) Sulphur-poisoned non-supported catalyst as an example of signal deconvolution.

From the deconvolution of the signals in the medium region (400-700 cm^{-1}), clear differences were observed between the "As calcined" and "sulphur-poisoned" catalysts. The "oxygen vacancies"/ F_{2g} ratio reduces 39% in the supported catalyst, while in the non-supported the reduction is only 28%. Moreover, the ratio between the Ni-O-Ce and F_{2g} bands reduced 24% in the supported catalyst, while it remains constant in the non-supported catalyst. These observations indicate a greater effect of sulfur species on the supported catalyst structure. The presence of S causes a reduction in oxygen vacancies and a decrease in Ni-O-Ce signals due to the interaction of S species through S-O-Ce or S-Ni bonds formation.

These preliminary results encourage continuing the study of the effect of sulfur on these catalytic structures, to better understand the deactivation caused by S poisoning and the reduction of H_2/CO yield in the biogas self-reforming process.

Significance

This contribution studies the effect of sulfur poisoning on supported and unsupported multimetallic catalysts for the self-reforming of biogas, which is of great interest to improve the performance and tolerance to sulfur in this type of systems.

References

1. E. Poggio-Fraccari, C. Herrera, M.A. Larrubia, L. Alemany, M. Laborde, F. Marino, *Int. J. Hydrog. Energy*, **2023**, *7*, 325
2. D. Harshini, D.H. Lee, J. Jeong, Y. Kim, S.W. Nam, H.C. Ham, J.H. Han, T.-H. Lim, C.W. Yoon, *Appl. Catal. B*, **2014**, *148*, 415
3. D. Chen, D. He, J. Lu, L. Zhong, F. Liu, J. Liu, J. Yu, G. Wan, S. He, Y. Luo *Appl. Catal. B*, **2017**, *218*, 249