ID: 1004

Methane Conversion in Hydrogen on Copper-Based Catalysts

HENNI Hayat [1,2*], BENRABAA Rafik [3,4], ROSSEL Pascal[5], LOFBERG Axcel [5]

[1] Institut Algérien du Pétrole IAP/SONATRACH, Boumerdes, Algérie.
[2] Université 20 août 1955, Skikda, Algérie.
[3] Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique, Faculté de Chimie, USTHB, Bab Ezzouar, Alger, Algérie.
[4] Laboratoire de Physico-Chimie des Matériaux, Faculté des Sciences et de la Technologie, Université Chadli Bendjedid, El Tarf, Algérie.
[5] Université de Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 - UCCS – Unité de Catalyse et Chimie du Solide, F-59000 Lille, France.
*Corresponding author's email: hayat_h35@yahoo.fr, hayat.henni@sonatrach.dz

ABSTRACT

In recent years, there has been significant interest in the dry reforming of methane (DRM) process, aimed at converting methane and carbon dioxide—identified as the most abundant greenhouse gases—into synthesis gas, comprising hydrogen and carbon monoxide. This reaction offers the advantage of mitigating or even eliminating two molecules known to be harmful and environmentally polluting. However, the primary challenge associated with dry reforming is the gradual deactivation of catalysts over time. This is primarily due to the endothermic nature of the reaction, necessitating operation at high temperatures to achieve substantial conversion. This elevated temperature poses a significant risk of carbon deposition, leading to rapid catalyst deactivation. Within the same context, our study focuses on the dry reforming of methane using mixed oxide based on copper as a catalyst. A soft chemistry technique has been employed for the synthesis of our catalytic systems, followed by optional heat treatment at various temperatures. The preparation method significantly influences the textural and structural properties of the catalysts, as evaluated through thermogravimetric analysis (TGA) coupled with differential scanning calorimetry (DSC), X-ray diffraction (XRD), BET method, and high-temperature X-ray diffraction (XRD-HT), and, along with their reactivity in the dry reforming of methane. Strong correlations have been established between textural, structural and catalytic properties.

Keywords: Dry Reforming, Methane conversion, Selectivity, Hydrogen.

1. Introduction

In recent years, significant attention has been directed towards the DRM process, aiming to convert methane and carbon dioxide, identified as the most abundant greenhouse gases, into synthesis gas. This reaction offers the advantage of reducing or eliminating two environmentally harmful molecules [2]. However, a major drawback of DRM is the gradual deactivation of catalysts. The endothermic nature of the reaction requires high temperatures for substantial conversion, posing a significant risk of carbon deposition and rapid catalyst deactivation [3].

2. Experimental

Copper-based catalysts were synthesized by coprecipitation from nitrates. Various physicochemical methods were employed to characterize the synthesized materials. The prepared catalysts underwent DRM tests for hydrogen production. This reaction was carried out in a fixed-bed catalytic reactor consisting of a quartz tube.

3. Results and Discussion

3.1. Characterization

The thermal stability was assessed using TGA-DCS in the temperature range from ambient to 1000°C. Mass losses (Fig. 1) are attributed to the removal of adsorbed water on the surface of crystallites and intercalated water, as well as the decomposition of anions. This includes the decarboxylation of

DOI: 10.21467/abstracts.169 ISBN: 978-81-970666-4-1 (eBook)

compensating anions into CO_2, and nitrates into NO and NO_2, along with dehydroxylation, corresponding to the release of water.

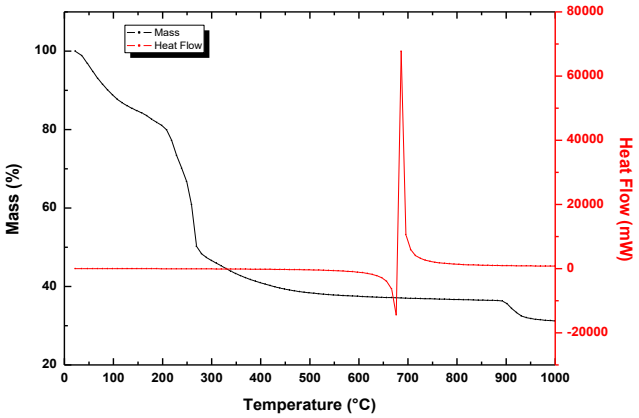

Figure 1: TGA-DSC curve

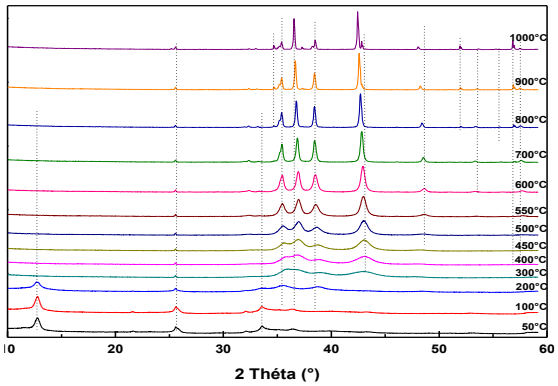

Figure 2: High-Temperature XRD

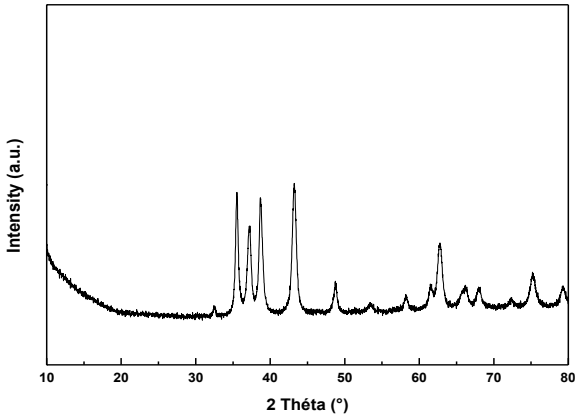

Figure 3: XRD of catalysts

The XRD-HT analysis (Figure 2) reveals amorphous solids up to 200°C. Beyond this temperature, crystallization is initiated with the appearance of oxide phases. The final structural composition is CuO and NiO. Based on the thermal analyses results, a calcination temperature of 600°C was chosen. The calcined catalysts were examined by XRD at room temperature. The XRD patterns in Figure 3 reveal the presence of NiO and CuO structures. Diffractograms show fine and generally intense lines, indicating good crystallization of the materials produced. X-ray diffraction analysis confirms the phases present in the catalysts (as observed by XRD-HT). The specific surface area was determined using the BET method, involving N_2 adsorption-desorption analysis. The surface area of the catalysts is good, measuring 23 m^2/g.

ISBN: 978-81-970666-4-1
Series: AIJR Abstracts
DOI: 10.21467/abstracts.169

3.2. Catalytic Performance in DRM

The catalysts obtained after calcination underwent DRM tests in the range of 400 and 650°C. Figures 4 and 5 illustrate the activity profiles which increase proportionally with the reaction temperature. Their optimal values are reached at a temperature of 650 °C. CH_4 conversion for the catalysts was 69%, while CO_2 conversion was 43%. The H_2/CO ratio was 1.8, and hydrogen selectivity was 58%. The H_2/CO ratio exceeds the theoretical value, suggesting the possibility of CO conversion through the Boudouard reaction or hydrogen overproduction due to methane cracking. The Boudouard reaction is thermodynamically favorable under our reaction conditions and could contribute to CO conversion.

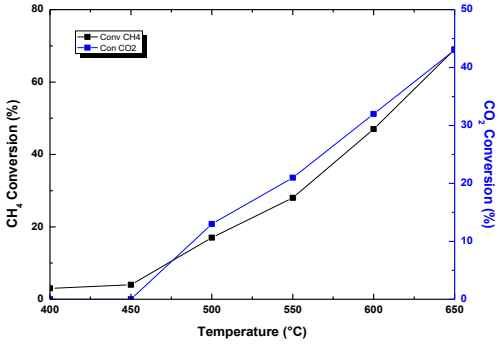

Figure 4: CH_4 and CO_2 conversion

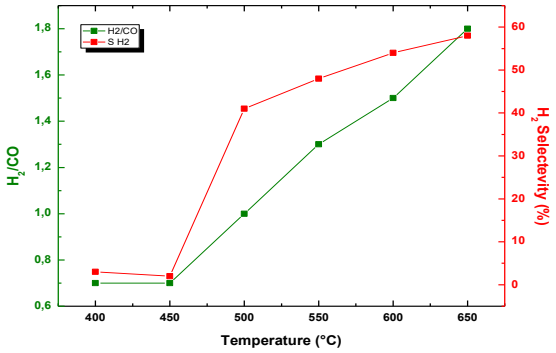

Figure 5: H_2/CO ratio and H_2 selectivity

4. Conclusions

The study focused on the thermal stability and structural characterization of catalyst precursor materials for application in the DRM process. Thermal analyses provided insights into the decomposition behavior and crystallization processes of the precursors. The selected calcination temperature of 600°C was determined based on the requirements of the DRM reaction. Upon calcination, the catalysts exhibited the presence of NiO and CuO structures, as confirmed by XRD analysis. Variations in the diffractograms indicated good crystallization of the produced materials. A detailed analysis of the catalysts' specific surface area using the BET method revealed a satisfactory surface area.The catalysts demonstrated good performance, and a temperature of 650°C appears to be a favorable operational point for the studied DRM process. These findings provide valuable insights for the selection of catalysts and operational conditions in methane reforming applications, with implications for the advancement of sustainable hydrogen production processes.

References

[1] Zhang , J.Liu, Y.Xu & Y.Sun. “A review of CH_4CO_2 reforming to synthesis gas over Ni-based catalysts in recent years (2010–2017)”. International Journal of Hydrogen Energy, 43(32), (2018), 15030-15054.

[2] N.A.K.Aramouni, J.G.Touma, B.A.Tarboush, J.Zeaiter & M.N.Ahmad. “Catalyst design for dry reforming of methane: Analysis review”. Renewable and Sustainable Energy Reviews, 82, (2018), 2570-2585.

[3] M.A.A.Aziz, H.D.Setiabudi, L.P.Teh, N.H.R.Annuar & A.A.Jalil. “A review of heterogeneous catalysts for syngas production via dry reforming”. Journal of the Taiwan Institute of Chemical Engineers, 101, (2019), 139-158.

ISBN: 978-81-970666-4-1

Series: AIJR Abstracts

DOI: 10.21467/abstracts.169