Oxidative Reform of biogas over NiO/Nb₂O₅/MgO catalysts.

Yvan J. O. Asencios¹, Elisabete M. Assaf²

¹Instituto do Mar, Universidade Federal de São Paulo, Santos SP, 11030-400, Brazil.
²Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos-SP, 13560-970 Brazil
*corresponding author: easaf@iqsc.usp.br

Introduction

Biogas is considered a first generation biofuel. The anaerobic fermentation of organic waste breaks down the organic matter producing biogas, a mixture which contains methane and carbon dioxide as main components (average composition of 55-65% CH₄, 30-45% CO₂, 0.5-2% H₂S and traces of H₂ and NH₃)[1]. CO₂ and CH₄ are the two main greenhouse effect gases, so the conversion of both gases into synthesis gas (syngas: H₂/CO= 1, 2, 3, etc.) is very beneficial from an environmental point of view.

Most part of Syngas for industrial uses is produced through steam reforming of methane (SRM). The biogas can be used as a substitute of natural gas in reforming processes, which is advantageous since biogas can be considered a renewable energy source. Considering the principal components of biogas, with a molar composition: 1.5CH₄:CO₂, syngas can be produced through two coupled processes with the addition of oxygen: Dry Reforming of methane (DRM, reaction 1), and the excess methane can be transformed by Partial oxidation of methane (POM, reaction 2)[2]

DRM: 1.5 CH₄ + 1 CO₂ → 2CO + 2H₂ + 0.5 CH₄ ΔH⁰=260.5 kJ.mol⁻¹ (1)
POM: 0.5 CH₄ + 0.25O₂ → 0.5 CO + H₂ ΔH⁰=−22.6 kJ.mol⁻¹ (2)

Syngas is a very valuable raw material for the petrochemical industry. The produced syngas from reactions 1-2, as a H₂/CO ratio near 1:2, allows its direct use in the syngas to dimethyl-ether process, (dimethyl-ether is a promissory clean fuel, which can substitute the commercial diesel).

Materials and Methods

The catalysts were prepared by impregnation method using the three salt precursors. The catalytic supports Nb₂O₅/MgO were prepared firstly. In this step, niobium oxide (Nb₂O₅) and magnesium oxide (MgO) were mixed by impregnation method (MgO in the Nb₂O₅). The mass relation (Nb₂O₅: MgO) used were 0:100, 10:90, 40:60, 60:40, and 100:0, further these supports were calcined at 750 °C in the presence of air. Once obtained the supports, these were impregnated with nickel using Ni(NO₃)₂/6H₂O; 99.99%,); the nickel percent was kept constant (20 wt%) for each catalyst. The calcination of the catalysts was carried out at 750 °C for 3 hours in air. The catalysts were characterized by Energy Dispersive X-Ray Spectroscopy (EDX), X-ray powder diffraction (XRD), Specific Surface Area (BET) and Temperature Programmed Reduction (H₂-TPR). The catalysts were performed in a continuous flow reactor, under the following reaction conditions: 1 atm, 750 °C, and stoichiometric gaseous feed 1.5CH₄:1CO₂:0.25O₂. The total gases flow-rate was 107.5mL.min⁻¹ over 100mg of the catalyst.

Results and Discussion

Figure 1 shows the continuous displacement of the principal peak of NiO (NiO or MgO) to higher Bragg angles indicates the contraction lattice parameter. This contraction indicates that the Ni²⁺ cation replaced some Mg²⁺ cations in the crystal lattice of the MgO, leading to the formation of NiO-MgO solid solution. This fact is reasonable since the ionic radius of Ni²⁺ (0.55 Å) is smaller than that of Mg²⁺ (0.77 Å) [2]. This solid solution is present in each sample containing the three oxides: NiO/MgO/Nb₂O₅.

The mixture of NiO/Nb₂O₅ (NiNb catalysts) lead to the formation of a single phase of nickel niobate (orthorhombic NiO-Nb₂O₅, JCPDS 15-159 and JCPDS 76-2354). The TPR and XRD analyses showed that the NiO-MgO solid solution and the nickel niobate (NiNb₂O₅) are both present in the catalysts containing Ni, Mg, and Nb. These two solid solutions together present in the corresponding catalysts increased the catalytic performance progressively: NiNb₂O₅ (40% conversion of CH₄)< Ni10NbMg (52%)< Ni40NbMg (63%)< Ni60NbMg=NiMg (74%). Despite NiMg and Ni60NbMg catalysts reached the highest conversion values, the carbon deposition rates of NiMg (0.45 mmolC.h⁻¹) was higher than Ni60NbMg catalysts (0.35 mmolC.h⁻¹). Figure 1 shows the SEM image of our best catalyst before reaction, sample Ni60NbMg: according to the EDX/MEV analyses, that particles correspond to nickel niobate covering NiO-MgO agglomerates. The type of carbon formed over Ni60NbMg (see Figure 1) is of filamentous type, the morphology of this carbon varied for each catalyst according to the load of NbOₓ on the mixture.

Significance

The oxidative reform of biogas is an alternative way to transform a renewable source (biogas, CH₄ and CO₂ being the main greenhouse effect gases) into a valuable raw material (syngas). This study shows a set of catalysts with original compositions which can be used in the oxidative reforming of biogas.

References