Oxidative Reform of biogas over $NiO/Nb_2O_5/MgO$ catalysts.

Yvan J. O. Asencios[1], Elisabete M. Assaf[2*]
[1]*Instituto do Mar, Universidade Federal de São Paulo, Santos SP, 11030-400, Brazil.*
[2]*Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos-SP, 13560-970 Brazil*
**corresponding author: eassaf@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% CH_4, 30-45% CO_2, 0.5-2% H_2S and traces of H_2 and NH_3) [1]. CO_2 and CH_4 are the two main greenhouse effect gases, so the conversion of both gases into synthesis gas (syngas: H_2/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: $1.5CH_4{:}CO_2$, 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: $1.5\ CH_4 + 1\ CO_2 \rightarrow 2CO + 2H_2 + 0.5\ CH_4$ ΔH^o=260.5 kJ.mol^{-1} (1)

POM: $0.5\ CH_4 + 0.25O_2 \rightarrow 0.5\ CO + 1H_2$ ΔH^o=-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 H_2/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 Nb_2O_5/MgO were prepared firstly. In this step, niobium oxide (Nb_2O_5) and magnesium oxide (MgO) were mixed by impregnation method (MgO in the Nb_2O_5). The massic relation (Nb_2O_5: 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 $Ni(NO_3)_2.6H_2O$; 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 (H_2-TPR). The catalysts were performed in a continuous flow reactor, under the following reaction conditions: 1 atm, 750 ºC, and stoichiometric gaseous feed $1.5CH_4{:}1CO_2{:}0.25O_2$. 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 Ni^{2+} cation replaced some Mg^{2+} 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 Ni^{2+} (0.55 Å) is smaller than that of Mg^{2+} (0.57 Å) [2]. This solid solution is present in each sample containing the three oxides: $NiO/MgO/Nb_2O_5$.

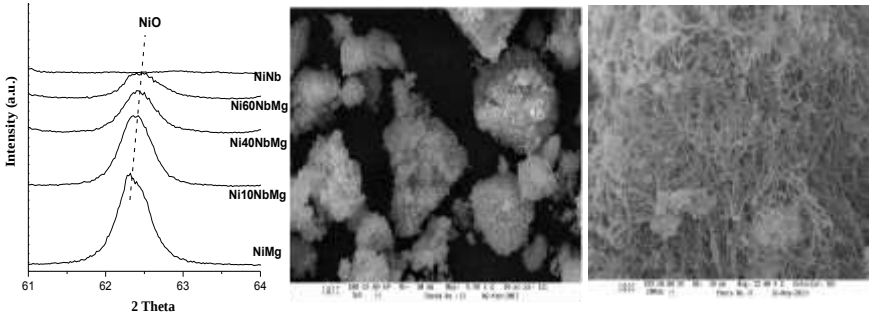

Figure 1. XRD patterns of catalysts before reaction, SEM image of Ni60NbMg (x5000) before reaction and SEM image of Ni60NbMg (x25 000) after reaction.

The mixture of NiO/Nb_2O_5 (NiNb catalysts) lead to the formation of a single phase of nickel niobate (orthorhombic $NiNb_2O_6$, JCPDS 15-159 and JCPDS 76-2354). The TPR and XRD analyses showed that the NiO-MgO solid solution and the nickel niobate ($NiNb_2O_6$) 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: NiNb (40% conversion of CH_4)< 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 aglomerates. 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 Nb_2O_5 on the mixture.

Significance

The oxidative reform of biogas is an alternative way to transform a renewable source (biogas, CH_4 and CO_2 being the two 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

1. Xu, J., Zhou, W., Li, Z., Wang, J., Ma, J., *Int. J. Hydrogen Energ.* ***2009****, 34, 6646.*
2. Asencios, Y.J.O., Rodella, C.B., Assaf E.M., *Appl. Catal. B,* ***2013****,132-133, 1.*