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Ni/SBA-15 catalysts for methane dry reforming

[R. Ahmed[1]*, S. Tanasoi[3], M. Olea[2], A. Urda[3], I. Sandulescu[3]]

***Abstract*— Methane and carbon dioxide are the major components of biogas produced by anaerobic digestion of biomass and conversion of biogas to syngas is of great interesting for making use of the sustainable biomass resource. The present paper deals with catalyst development and testing for the dry reforming of methane (DRM). Three different SBA-15 supported nickel catalysts were prepared, with nickel loadings from 5 to 20 wt. %, using a mixture of nickel precursors (acetate and nitrate). A cobalt modified Ni catalyst was also prepared using sequential impregnation. The catalysts were characterized by SEM/EDS, XRD, TEM and BET measurement. The mesoporous structure of the SBA-15 support was maintained and good dispersion and reasonably high loadings of nickel nano-particles on the support were obtained for all prepared catalysts. These samples were tested against the DRM, at different temperatures and CH_4:CO_2 molar ratios, in order to assess their activity and selectivity. High methane conversion was achieved (90 %) at optimal condition.**

***Keywords*— Ni-on-silica catalysts, Ni-precursor, DRM catalytic activity.**

I. Introduction

The development of sustainable technologies with low environmental impact is of increasing significance in regard to science and engineering researches. As it is known, the landfill gas emissions contribute to 40% of UK methane emission, in total 3% of UK greenhouse emissions, GHGs cause global warming with methane about 23 times more potential than carbon dioxide. To reduce this negative environmental impact of landfill, the landfill gas currently is considered to be one of the most important sources of renewable energy in UK and over the world [1].

Therefore, using renewable feedstock such as biomass is the major part of this project, in order to addresses the conversion of biomass through anaerobic digestion to biogas, and then through Fischer-Tropsch routes to fuel and gasoline. As an intermediate step, the project deals with the catalytic conversion of the biogas, the outcome of the anaerobic digestion, to syngas, which is the suitable feedstock for the Fischer-Tropsch routes [1, 2, and 3].

Methane reforming with CO_2 (DRM) is a promising process for the production of synthesis gas with a suitable CO/H_2 ratio for methanol or Fisher–Tropsch syntheses [2, 3]. However, catalyst deactivation by coking is currently a serious problem [2-4], and research is focused on improving activity and stability by using different supports or preparation methods [5, 6].

This work presents the preparation of newly-developed nickel catalysts supported on mesoporous SBA-15 silica and the use of them for DRM reaction. A modified sol-gel method was chosen for the support preparation and impregnation method was used to incorporate the active phase, namely nickel, onto the support. The efficiency of prepared Ni/SBA-15 catalysts for DRM reaction was studied with regard to catalyst composition and reaction conditions and optimal catalyst and operating conditions were obtained.

II. Experimental

A. *Materials*

Tri-block copolymer Poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) ($EO_{20}PO_{70}EO_{20}$, P_{123}, typical M_n = 5800), tetraethyleorthosilicae (TEOS), and DL-lactic acid 90% in water were purchased from Sigma-Aldrich and hydrochloric acid 37%, nickel nitrate hexahydrate 99%, nickel acetate and ammonium hydroxide 35% were from Fisher Scientific, UK. All chemicals were used as received. Deinoised water was used throughout the experiments.

B. *Catalyst synthesis and catalysis of DRM*

Three Ni/SBA-15 catalysts were synthesized by a sol-gel method, with different Ni loading, together with a Ni-Co/SBA-15 sample, and were tested in the CO_2 reforming of methane. The processing condition and the final composition of the resulting supported catalysts are also listed in Table 1.

R. Ahmed [1]

1-Kurdistan Institution for Strategic Studies and Scientific Research (KISSR) / Qirga, Slemani, Al Sulaymaniyah, Iraq
*Corresponding author; e-mail address:
Mobile No.: 00964 7510405929
R. Ahmed[1] and M. Olea[2]
2 –School of Science & Engineering, Teesside University , Middlesbrough, Tees Valley, TS1 3BA, United Kingdom
S. Tanasoi[3], A. Urda[3], I. Sandulescu[3]
3–Dept. of Chemical Technology and Catalysis, Faculty of Chemistry, University of Bucharest, Bd. Regina Elisabeta 4-12, 030018, Bucharest, Romania.

Table 1. The preparation conditions of catalysts.

Ni-acetate	Ni-nitrate	Co-acetate	Catalysts	NiO/SBA-15	Ni/Co % loading
0.33	0.33	/	5IMPNiA/N-A	0.667/2	5/0
0.667	0.667	/	8IMPNiA/N-B	1.33/2	8/0
1	1	/	16IMPNiA/N-C	2/2	16/0
2	-	1	19IMPNi21CoA-D	2/ 0.96	19/21

IMP = impregnation; A = acetate, N = nitrate.

Methane (99.95%, Messer) and CO_2 (99.5%, SIAD) were used as reactants. The experiments were performed in a quartz fixed bed catalytic reactor (0.5 g of catalyst) with a GHSV of 3600 mL(g_{cat} h)$^{-1}$, temperatures of 600-800°C (heating/cooling rate 2°C min^{-1}), atmospheric pressure and CO_2:CH_4 molar ratios of 1:1, 1.5:1 and 1:1.5. Before the catalytic reaction, in some experiments, the catalyst was reduced in hydrogen flow (20 mL min^{-1}, at 550°C for 2 hours). Reaction products were analysed by gas chromatography (CE Instruments Trace GC, TCD detector, CTR 1 packed column) every 50°C.

C. *Characterisation*

BET specific surface area and pore size distribution were determined by N_2 adsorption using a Belsorp-mini of BEL JAPAN Inc at 77 K after degassing the samples at 200^{o}C for 3 hours. The BJH (Barret-Joyner-Halenda) method was used to calculated pore size distribution and pore volume. XRD data were obtained on a Bruker D8 diffractometer (Cu Kα, λ=0.1543 nm, 20° < 2ϴ < 80°) [6]. SEM micrographs were obtained on a Hitachi S-3400N, Scanning Electron Microscope equipped with energy dispersive spectroscopy (EDS). TEM observations were done with a JEM2010F TEM, with a resolution of 0.23 nm, and accelerating voltage 80 to 200kV.

III. Results and discussion

Fig. 1 shows the low angle XRD pattern of the silica support for accommodating the nickel nanoparticles. Peaks denoted as (d_{100}), (d_{110}) and (d_{200}) [7] reflections are associated with a hexagonal symmetry (p6mm), revealing that the mesoporous are arranged over long range order.

Fig. 2A presents the TEM images of the SBA-15 sample, aged for 24 hr. The mesopores are arranged in a hexagonal honeycomb-like structure, separated by thin amorphous silica pore walls (black). The pores are reasonably straight with the pore size of approximately 7.6 nm in diameter and the pore wall thickness about 3 nm. The most striking fact about the

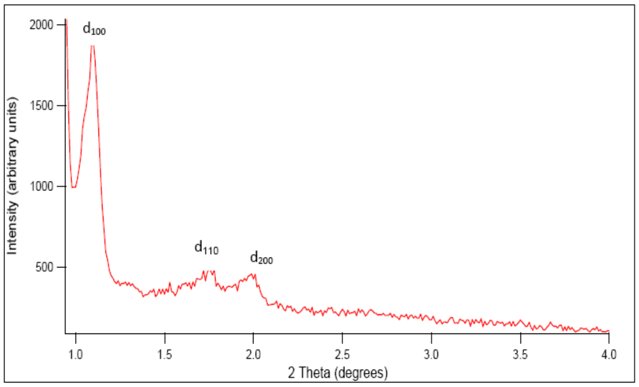

Figure 1. Typical low angle XRD pattern of SBA-15 synthesized in this study.

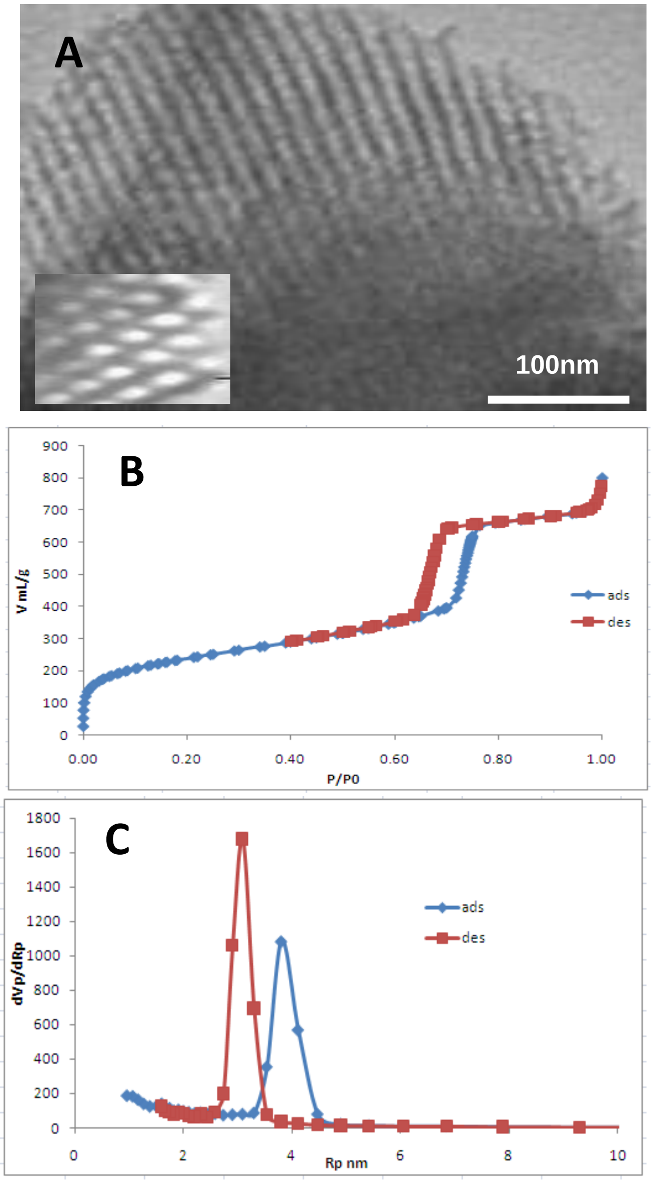

Figure 2. A) TEM micrograph, B) N_2 adsorption/desorption & C) pore size distribution of SBA-15 support.

SBA-15 material is that, although composed of amorphous silica, it displays a highly ordered structure with uniform mesopores which are big enough to accommodate catalytic components and are accessible for a range of molecules. This makes it very suitable to be a catalyst support.

Fig. 2B and C demonstrate the typical N_2 adsorption-desorption curves and the pore size distribution of the SBA-15 sample used in this research. It follows the type IV isotherm and H1 hysteresis loop, according to IUPAC classification. Clear adsorption step of capillary condensation at intermediate relative pressure was observed, indicating quite large mesoporous diameter and uniformity of the framework mesoporosity. This confirms that the SBA-15 has monomodal narrow pore size distribution, centred at around 3 (desorption) and 3.8 nm (adsorption), and the pore diameter is 7.6 nm, as it was expected using BJH method [8,9]. The calculated BET-specific surface area is 834 m^2/g for this sample.

In order to check for conversion contributed by side reactions, catalytic tests were performed with CH_4:N_2 and CO_2:N_2 mixtures (1:1 molar ratios) on the oxidized form of the catalyst 16IMPNiA/N-C, at constant temperature (700°C) for 270 min. For CO_2 the conversion was very low (below 0.1 %), while for CH_4 the values were less than 5 % (with H_2 and carbon as products). When a CH_4:CO_2 mixture (1:1) was reacted on the same catalyst, the conversion values remained very low, suggesting that the oxidized catalyst does not lead to significant transformation for the reactants (results not show here).

The same experiments were performed on the pre-reduced catalyst C. While the CH_4 conversion slightly increases compared to the oxidized form (~7%), CO_2 conversion in the reaction mixture CO_2:N_2 reaches ~8%, indicating an interaction with the reduced catalyst.

The reaction between CH_4 and CO_2 was studied as a function of temperature on all four pre-reduced catalysts, which behaved in a similar manner. Fig. 3 shows CH_4 and CO_2 conversion on catalyst A, determined in increasing and decreasing temperature processes. Several interesting aspects are noticed. First, CH_4 conversion values are much lower than those for CO_2 on the whole temperature range. It is also true for all the tested catalysts. This observation can be explained only by admitting a partial CO_2 decomposition, which is confirmed by the presence of oxygen in the reaction products. Secondly, only small differences were obtained between conversion values when temperature was increased and decreased, suggesting that the carbon deposit does not inhibit the catalytic process.

Fig. 4 displays the results obtained on the four pre-reduced catalysts for methane conversion. Catalysts A-C (containing only Ni) shows that conversions in the low temperatures range (up to 700°C) depend largely on the Ni loading: values increase with Ni content. As temperature rises, the differences diminish at 800°C and about 60% CH_4 conversion is obtained. For all catalysts the CO_2 conversion is almost double compared to the CH_4 conversion. The Ni-Co catalyst has a low activity at 600°C, but becomes the most active at high temperature (~ 70 %), probably due to the intrinsic activity of the two active metals.

Different molar ratios between the reactants were investigated with catalytic tests on pre-reduced catalyst B. With CO_2 excess (CH_4:CO_2 = 1:1.5), ~ 90% CH_4 conversion was obtained, while with CH_4 excess values were lower than those with equimolar mixture. So, the presence of a CO_2 excess favors the dry methane reforming process, considering also the fact that CO_2 excess is easier to remove from the products than methane, by absorption and desorption, and then reused.

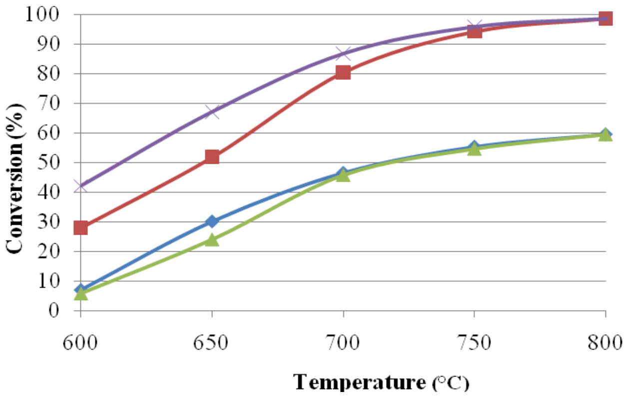

Figure 3. Conversion values for CH_4 (♦-increasing and ▲-decreasing temperature) and CO_2 (■-increasing and x-decreasing temperature) in the dry reforming reaction on pre-reduced catalyst A ; GHSV = 3600 mL /(g_{cat} h), CO_2:CH_4 = 1:1 (molar ratio).

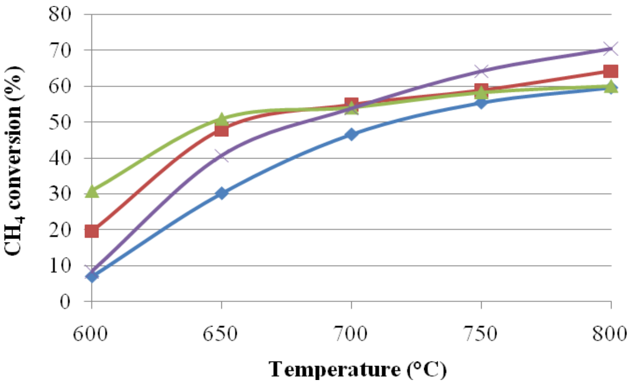

Figure 4. CH_4 conversion in the dry reforming reaction on pre-reduced A-C (♦-A; ■-B; ▲-C) si Ni-Co/SBA-15 (X) catalysts; GHSV = 3600 mL /(g_{cat} h), CO_2:CH_4 = 1:1 (molar ratio).

IV. Conclusion

Three Ni/SBA-15 catalysts were synthesized by a sol-gel method, with different Ni loading, together with a Ni-Co/SBA-15 bi-metal catalyst, and were tested in the CO_2 reforming of methane. The catalysts with the metals in oxide form were not active, whilst the pre-reduced samples showed good activity in the DRM process. The best result was obtained on the Ni-Co bi-metal catalyst at 800°C. CO_2 excess in the feedstock leads to higher CH_4 conversions than equimolar mixtures.

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About Author (s):

Dr. Rawaz. Ahmed

She worked at Teesside University, with valuable experience in heterogeneous catalysis and sustainable technology having won the top poster prize in catalysis by Royal Chemical Society at Johnson Matthey Conference, Biillingham in March, 2011, and The optimised preparation method and results obtained over the catalyst with optimal formulation are the subject of a patent application (P136962GB; New UK Patent Application; Supported Metal Catalyst; Teesside University). She worked as Research Associate: biomass carbonisation at Teesside University after her Phd study. The major subject is focus on the biomass hydrothermal carbonization. Dr. Ahmed's is currently working on a number of research projects on heterogeneous catalysis at KISSR.

Professor Maria Olea is working on a number of research projects on heterogeneous catalysis in her quest to save the planet for future generations including converting biomass and municipal solid waste into fuel. But teaching is also an extremely important part of her duty.

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