New Mesoporous Silica Supported Nickel Catalysts for Biomass Conversion

David T. Lundie[1], *Steven Fiddy*[1], *Simon Hodgson*[2], *Maria Olea*[2] *and Wei Wang*[2]

[1]**Hiden Analytical Ltd, 420 Europa Boulevard, Warrington, WA5 7UN, UK. dlundie@hiden.co.uk**

[2]**School of Science and Technology, University of Teesside, Middlesbrough TS1 3BA, UK.**

INTRODUCTION

Organic waste through biomass conversion can be used for energy production and the synthesis of a variety of chemicals. One of the synthesis routes is via biogas to syngas catalytic conversion, by CO_2 reforming of CH_4. For the methane reforming reaction, all metals of the VIIIA group on a large variety of supports have been studied. Nickel shows good catalytic activity, especially when well dispersed on the support.

EXPERIMENTAL

Catalyst Preparation.

1.0g silica support (SBA-15) was impregnated with 12 ml water solution containing 0.153g Nickel acetate tetrahydrate. After sonication for several minutes, the mixture was stirred for 1h at room temperature. Impregnated silica was collected and dried at 100˚C in vacuum and calcined at 550˚C for 2h with heating rate of 10˚C min^{-1}. This process was repeated several times to increase the Ni content. After 2 cycles the Ni content was about 5%. After 5 cycles the Ni content was about 10-11%.

Characterisation.

Temperature programmed reduction (CH_4-TPR), oxidation (O_2-TPO), and reaction (TPRx CH_4:CO_2 = 1.5:1) experiments were performed using a CATLAB microreactor – MS system (Hiden Analytical, UK) on fresh and in situ reduced Ni catalysts. Heating rates were 10˚C min^{-1}. In situ reduction was performed under a H_2 flow by heating to 550˚C at 10˚C min^{-1} and holding at this temperature for 1 hour. XRD data were obtained on a Bruker D8 diffractometer.

RESULTS AND DISCUSSION

Figures 1 and 3 show The TPR results of the 5 and 11 % Ni samples respectively to have high activity with CH4 reduction occurring at around 580˚C in both samples.

The 11% Ni sample shows considerably more consumption of CH_4 as would be expected due to the higher Ni content.

Figures 2 and 4 show the TPRx results of pre-reduced 5 and 11% Ni samples.

In the 5% Ni sample, conversion of $CH_4 + CO_2 \longrightarrow 2H_2 + 2CO$ occurs at around 450˚C with complete conversion of the CO_2 occurring at around 700˚C.

In the 11 % Ni sample, conversion of $CH_4 + CO_2 \longrightarrow 2H_2 + 2CO$ occurs at around 400˚C with complete conversion of the CO_2 occurring at a similar temperature of the 5% sample at around 700˚C

The results show that an increase in Ni content decreases the temperature at which reaction starts although complete conversion of the CO_2 occurs at a similar temperature.

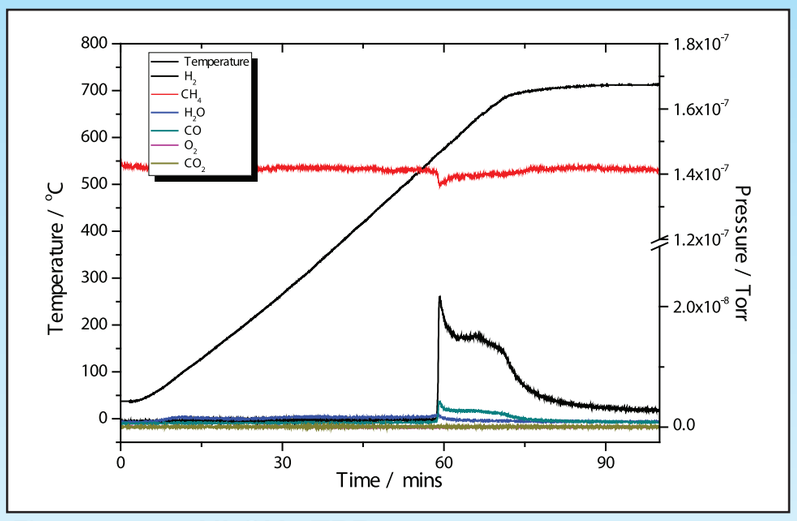

Figure 1: **5% Ni CH_4 TPR**

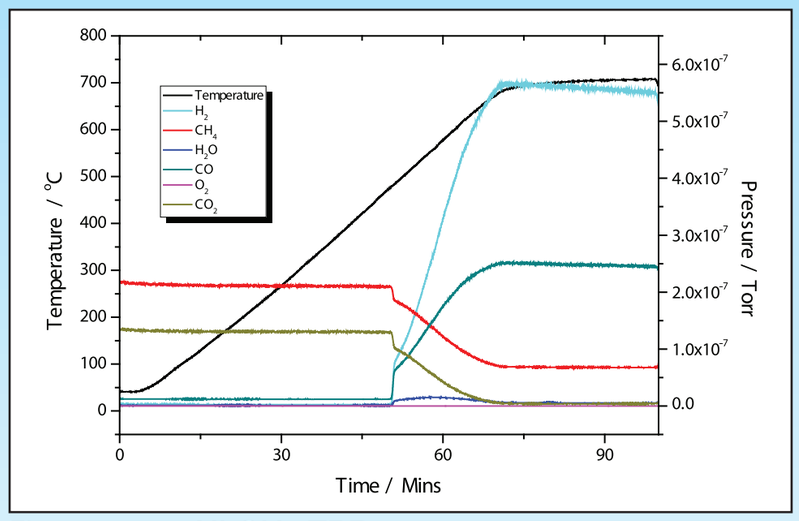

Figure 2: **5% Ni CH_4 TPRx**

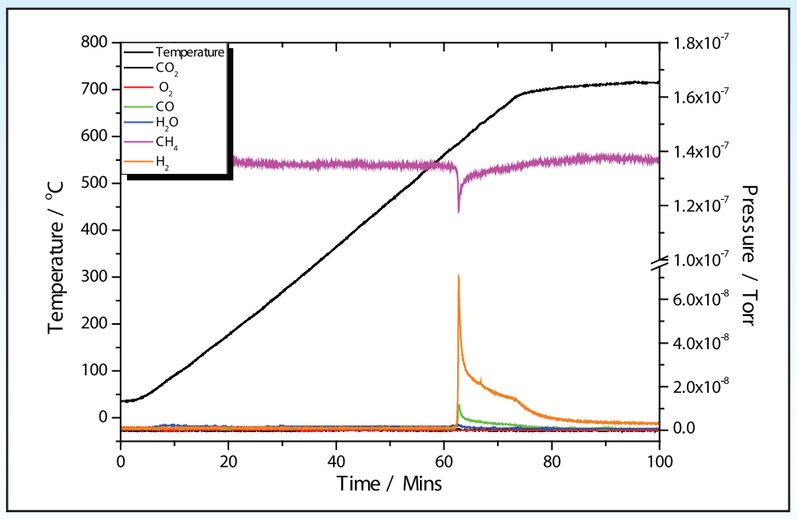

Figure 3: **11% Ni CH_4 TPR**

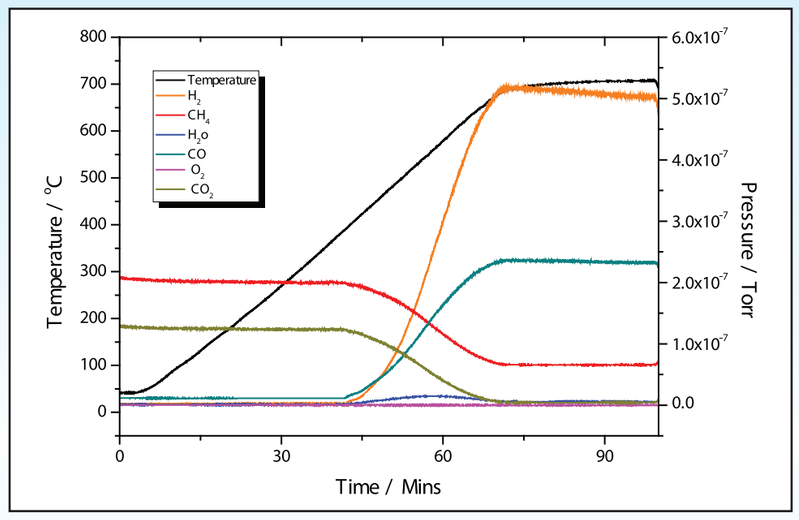

Figure 4: **11% Ni CH_4 TPRx**

The low-angle XRD results shown in Figure 5, demonstrate the existence of well-ordered mesopores with long range order and retention of the mesostructure after introduction of nickel species. Before and after impregnation, the mesoporous silica and mesoporous nickel-containing silica all possess similar structure as reported [1-2]. For the post-synthetic method, the main disadvantage is that the loadings of Ni can often lead to the deterioration of the mesostructure or the blockage of mesochannels by large guest Ni (NiO) particles. In this work, upon loading of nickel species, the mesostructures underwent only slight shrinkages, as indicated in Figure 5, which might be caused by the thermal treatment after each loading of nickel. The retention of the higher angle peaks clearly indicates that the mesostructure did not deteriorate significantly. This can be attributed to the thicker more robust framework walls of SBA-15, which offers good hydrothermal and thermal stability during the preparation.

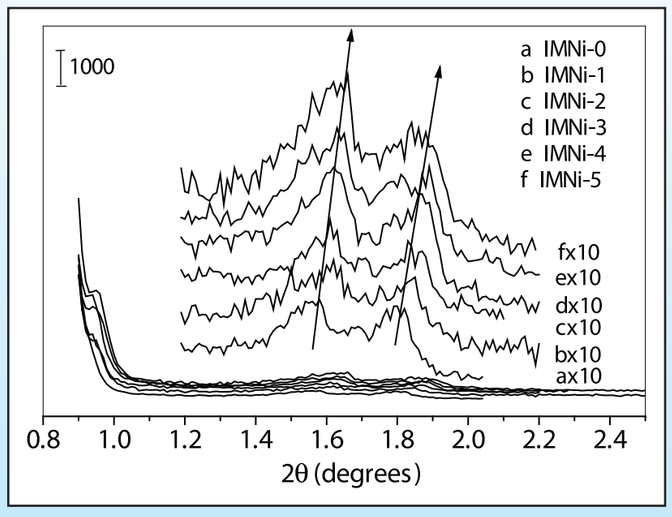

Figure 5:
Low-angle XRD patterns of nickel-containing mesoporous silicas after each impregnation cycle
(a) 0 cycles,
(b) 1 cycle,
(c) 2 cycles,
(d) 3 cycles,
(e) 4 cycles,
(f) 5 cycles.

Conclusions:

- **Methane activation occurred at relatively low temperatures.**
- **TPReaction demonstrate the high activity and selectivity of these catalysts.**
- **Structural and textural properties of the mesoporous support are retained independent of the Ni loading.**
- **Ni is well dispersed inside the mesopores.**

References:

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(c) W. Wang, M. Song, Mater. Res. Bull., 41(2), 2006, 436.

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Tel: +44 (0)1925 445 225 Fax:+44 (0)1925 416 518 E-Mail: info@hiden.co.uk www.HidenAnalytical.com

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