

Characterisation of hydrocarbon deposits present on methane reforming catalysts

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Introduction

With oil reserves dwindling and becoming increasingly difficult to access, methane from natural gas offers an attractive alternative both as a fuel and a chemical feedstock as it is relatively cheap and abundant. However, methane is unreactive so to utilise it as a feedstock its conversion to synthesis gas (syngas, CO + H₂) is an important industrial process.

The process is carried out over an alumina supported nickel catalyst and either steam (1) or carbon dioxide (2) is used as the oxidant:



Reaction (2), dry reforming, has the advantage that the CO:H₂ ratio is better suited to Fischer-Tropsch chemistry, although it is typically carried out at ~800°C rather than the 650°C of steam reforming. Reaction (3) is reverse water gas shift and is a detrimental side reaction. For both processes, catalyst deactivation is a major problem, with carbon laydown leading to a progressive decrease in activity as a function of time. Recent work by Ormerod *et al* [1] has shown that gold doped nickel catalysts have similar activity as the conventional catalysts but are much less susceptible to deactivation. The long term aim of the work is to understand the reasons for the carbon tolerance. As a first step, we have set out to characterise the nature of the carbon overlay on the catalysts.

Materials and Methods

Ni/Al₂O₃ (10 and 20 wt% Ni) and Au/Ni/Al₂O₃ (5 wt% Au, 20 wt% Ni) were prepared as described previously [1]. Reaction testing and temperature programmed oxidation (TPO) was carried out in a conventional microreactor on 20 mg samples. Vibrational spectra of the samples were recorded by infrared spectroscopy (self-supporting wafers, Bruker Vertex 70), Raman spectroscopy (powder, in-house built spectrometer with 532 nm excitation, Renishaw InVia with 785 nm excitation) and inelastic neutron scattering (INS) spectroscopy (powder, TOSCA and MAPS spectrometers at ISIS [2]). The INS experiments required much larger samples, ~20 g, and these were prepared on a catalyst test rig at ISIS.

Results and Discussion

Comparisons of catalytic performance between conventional microreactor studies and the INS reaction studies show excellent correspondence despite a thousand fold scale-up. Figures 1 shows the infrared (left) and INS (right) spectra of the catalysts after reaction. The spectra of the conventional and the gold-doped catalyst are similar in both cases, indicating that

the surface layers are similar and, presumably, also the surface chemistry. The infrared spectra show strong features at 3400 and 2900 cm⁻¹, which are assigned to support hydroxyl groups and C-H stretching modes for hydrocarbon fragments bound to the metal surface, respectively. The latter indicates the presence of aliphatic and aromatic entities. The INS spectra for the catalysts show similar features to the infrared spectrum, however, whilst exhibiting inferior resolution to the optical spectroscopic measurement, the INS spectra are readily quantified. Thus, the surface hydroxyl group concentrations are estimated to be 600 and 200 ppm, whilst the unresolved C-H stretch corresponds to a hydrocarbonaceous overlayer of 200 and 90 ppm, for the conventional and the gold-doped catalysts respectively.

Significance

This work has shown that very little hydrogen is retained by the overlayer. INS spectra of the low energy region (not shown), supported by TPO measurements, indicate that the carbon is not graphitic but is similar to amorphous carbon and is the same on both the doped and conventional catalysts. These studies seem to indicate that the two catalysts behave comparably. However, in dry reforming, the gold doped system actually lays down more carbon, but, crucially, it seems that it favours hydrogen formation by suppressing reverse water gas shift activity. These observations will be rationalised within a postulated reaction scheme.

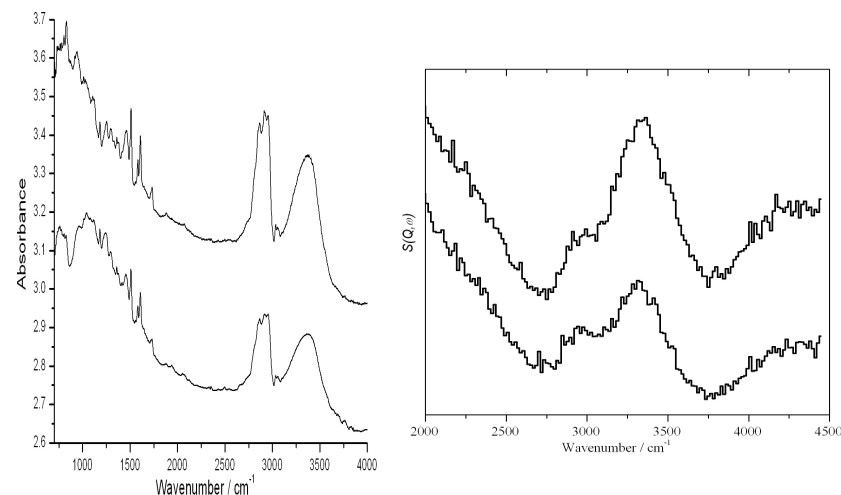


Figure 1. Post-reaction spectra of the Ni(20%)/Al₂O₃ (lower) and Au(5%)/Ni(20%)/Al₂O₃ (upper) catalysts. Left: infrared spectra, right: INS spectra.

References

1. Diskin AM, Cunningham RH, Ormerod RM, *Studies Surf. Sci. Catal.* 122, 393 (1999).
2. <http://www.isis.rl.ac.uk/instruments/index.htm>