

Transformation of greenhouse gases to synthesis gas: understanding the catalytic reforming of methane with carbon dioxide using bimetallic nanoparticles

The ultimate goal of the research was the development of a carbon tolerant catalyst for the carbon dioxide reforming of methane (dry reforming). This reaction might have great importance in the near future when global warming becomes the most important problem of humankind. With dry reforming, two greenhouse gases can be converted to a useful product (synthesis gas), which can be further transformed to various chemicals and fuel by Fischer-Tropsch synthesis. Furthermore, if renewable energy sources are used for these reactions, energy can be stored in the form of chemicals and can be released on demand.

The idea behind this research project was to modify the economically feasible supported nickel catalyst by addition of indium and/or tin to the nickel phase to modify its active surface and enhance its carbon tolerance. This idea was based on the fact that these metals (In, Sn) decrease the carbon formation tendency on supported platinum catalysts used for dehydrogenation of light alkanes.

The initial plan was to control the interaction of the two metals during the preparation of bimetallic nanoparticles using Schlenk-technique. The catalysts prepared by deposition of bimetallic Ni-In nanoparticles onto silica support were not active at all in dry reforming of methane. Unfortunately, it turned out that the stabilizing agent (trioctyl phosphine) applied during the particle synthesis reacted with the nanoparticle surface thereby poisoning the active sites. We haven't been able to find other appropriate capping agents for the synthesis of bimetallic nanoparticles that provides the desired particle size and distribution.

Therefore we used a conventional catalyst preparation method, by which the interaction of the two metals is likely, but not well-controlled. Silica supported bimetallic catalysts were prepared by deposition-precipitation with urea using nickel nitrate and indium chloride aqueous solutions. By this way, we not only were able to prepare working catalysts, but also we have found that there was no carbon formation on the bimetallic catalysts during dry reforming of methane (Figure 1).

Temperature-programmed reduction studies showed that both of the metals in metallic state after high temperature reduction at 700 °C. Without nickel on the surface, the indium irreversibly aggregated, which was not observed on bimetallic catalyst. This suggested the

bimetallic interaction of the metals. X-ray photoelectron spectroscopy studies together with the results of CO adsorption measurements by DRIFT spectroscopy further supported the intimate contact between nickel and indium on the silica surface. It was found that after reduction, there are indeed bimetallic particles on the catalysts surface and the In is enriched on the surface regions of the nanoparticles. Catalytic tests showed that the presence of indium on the catalyst has no influence on the conversion of methane and carbon dioxide, that is, the monometallic and bimetallic catalysts had the same catalytic activity.

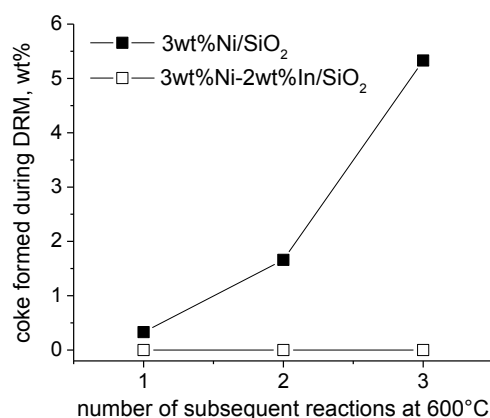


Figure 1. Carbon formation on Ni/SiO₂ and Ni-In/SiO₂ catalysts during repeated catalytic runs.

To complete our understanding and to find convincing direct evidences for the bimetallic interaction Near Ambient Pressure XPS (NAP-XPS) and HAADF-STEM-EDX measurements were carried out. The NAP-XPS investigation was done at Charles University in Prague supported by CERIC-ERIC. The results were quite controversial due to the intense charging of the samples (silica support). It was found however, that irreversible changes of the Ni surface occurred upon addition of CH₄ and (CH₄+CO₂) mixture at 750 K on both catalysts, probably due to carbide formation on the particles. It was also found that indium could react with CO₂ to form indium suboxide in the presence of the reaction mixture. The Ni-In/SiO₂ catalysts were investigated by HAADF-STEM-EDX measurements in collaboration with Claudio Evangelisti from CNR, Milano. These results unambiguously showed the homogeneous distribution of the metals on the catalyst surface and the existence of the bimetallic interaction in the form of Ni₂In and NiIn nanoparticles.

The results obtained on Ni-In/SiO₂ catalysts used in dry reforming of methane was published in an article titled “Carbon dioxide reforming of methane over Ni-In/SiO₂ catalyst without coke formation” in the *Journal of Industrial and Engineering Chemistry*.

According to the research plan, in the second year, the work continued with the preparation of Ni-Sn/SiO₂ catalyst. The same composition was chosen as in the case of Ni-In/SiO₂, that is the Ni:Sn molar ratio was 3:1. XRD results of the catalyst after reduction at 700 °C showed the Ni-Sn alloy formation, and the presence of small particles (average crystalline size was 3.4 nm). TPR experiments showed that the reduction profile of the tin containing catalyst profoundly differed from that of the monometallic catalyst: the main reduction peak maxima shifted from 550 °C to 330 °C. XPS measurements showed that both metals were in metallic state after reduction at 700 °C and based on the surface metal ratios, significant increase of tin on the surface was observed. The catalytic activity and stability of the Ni-Sn/SiO₂ catalyst could not be paralleled to the stability of Ni-In/SiO₂ catalysts. Severe deactivation was observed during 2 hour time on stream.

As the tin containing catalysts showed very limited activity in dry reforming, attempts were made to describe the role of indium in the carbon formation reactions (methane decomposition and CO disproportionation) occur during dry reforming of methane.

Therefore, decomposition of methane has been investigated by MS assisted methane pulse chemisorption experiments at 600 °C using freshly reduced, partially carburized and extensively carburized Ni/SiO₂ and Ni-In/SiO₂ catalysts. It was found that hydrogen production during CH₄ pulses decreased on both catalysts as the extent of carburization of the surface increased. Under our experimental conditions, formation of various carbonaceous structures separated from the metal particles was not observed by TPO and HRTEM measurements, however it was pointed out that carbon atoms diffused into the metal nanoparticles. It was shown that the presence of surface carbon on Ni/SiO₂ significantly changed the hydrogen content of chemisorbed species obtained upon CH₄ impulses. Methane chemisorption was only slightly affected by the surface carbon content on Ni-In/SiO₂, the H/C ratio of the surface species was equal to or higher than 4 during the experiments (Figure 2).

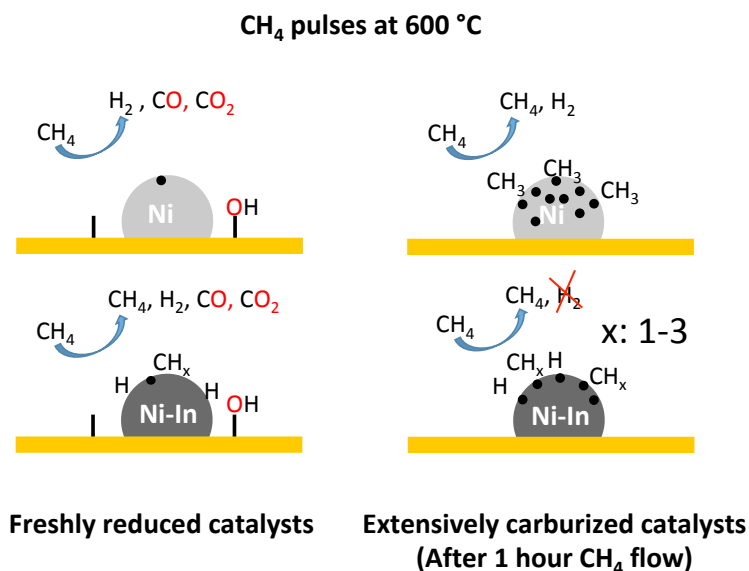


Figure 2. Schematic illustration of methane decomposition at 600 °C on freshly reduced and extensively carburized Ni/SiO₂ and Ni-In/SiO₂ catalysts.

Based on the high H/C ratio of surface species and the low hydrogen production and limited carbon formation of the bimetallic catalyst, the role of indium in methane decomposition is twofold: First, it changes the surface structure of adsorption sites so that the complete dissociation of methane is hindered. Secondly, it has an electronic effect on nickel which leads to stronger hydrogen chemisorption compared to the monometallic catalyst. This difference in methane activation might be one of the responsible factors for the coke-free operation of the bimetallic catalyst during dry reforming of methane. Based on these findings, an article titled “Hindered methane decomposition on a coke-resistant Ni-In/SiO₂ dry reforming catalyst” was published in *Catalysis Communications*.

The research continued with the study of CO disproportionation ($2 \text{ CO} \leftrightarrow \text{CO}_2 + \text{C}$). Similar to the above experiments, mass spectroscopy assisted CO pulse chemisorption at 600 °C was done. Unlike to the methane decomposition, the reaction of CO was very similar on both of the monometallic and bimetallic catalysts. The results showed no or little carbon deposition, in fact, the mass balance of the inlet and outlet flow showed complete oxidation of CO instead of disproportionation on both catalysts. This was explained by the contribution of surface OH-groups in the close vicinity of the metal nanoparticles, the presence of indium did not have influence on the reaction of carbon monoxide on the bimetallic catalyst. It was also observed that CO disproportionation, that is carbon deposition, was very intense on Ni/SiO₂ catalyst with large

average particle size (~15 nm). These results suggest that the amount of carbon deposited during CO disproportionation is more dependent on the average particle size than the composition of the catalytically active sites. The research continues with in situ DRIFTS measurements with CO and CO₂/CH₄ mixture on Ni/SiO₂ and Ni-In/SiO₂ catalysts after different heat treatments. The results will be published in a third article.