

Towards highly active and stable Ni based dry reforming catalysts through decoupling of methane activation and carbon formation by introducing single Pt atoms to surfaces

Juntian Niu^{1,2}, Shirley E. Liland², Jia Yang², Kumar R. Rout³, De Chen^{2*}, Jingyu Ran^{1*}

1 Key Laboratory of Low-grade Energy Utilization Technologies and Systems, Ministry of Education of PRC, Chongqing University, Chongqing, 400044, China; 2 Department of Chemical Engineering, Norwegian University of Science and Technology, Trondheim, 7491, Norway; 3 SINTEF materials and chemistry, Trondheim, 7491, Norway

**Corresponding author: de.chen@nt.ntnu.no; ranjy@cqu.edu.cn*

Highlights

- Pt decreases the reduction temperature of Ni catalysts.
- Pt_{0.50}Ni_{(s)0.50} stands out of highest catalytic performance.
- Pt addition on the surface enhances the resistance to carbon formation.
- Pt presence lowers the H₂ formation barrier and increases the CO desorption possibility.

1. Introduction

Methane dry reforming (DRM) is a promising reaction that is of both scientific and industrial importance ^[1]. Ni was widely applied in this process because of low cost compared with noble metal catalysts, however, single component Ni catalysts are not able to meet the activity, selectivity and stability requirements ^[2]. There are several strategies to reduce the carbon formation. One is to reduce the activation of methane. It is often to reduce the activity to increase the stability. In this work, we introduce single Pt atoms into Ni surface, thus decreasing the CH₄ activation barrier and increasing the barrier of CH decomposition.

2. Methods

Monometallic 12 wt% Ni derived from hydrotalcite-like precursor has been prepared by co-precipitation using metal nitrites component. Then based on reduced Ni catalyst, we prepared the Ni-Pt surface alloy catalysts by redox reaction in inert gas with different surface Pt/Ni ratios, Pt_{0.25}Ni_{(s)0.75}, Pt_{0.50}Ni_{(s)0.50}, Pt_{0.75}Ni_{(s)0.25}, Pt_{1.00}Ni_{(s)0.00}, respectively. In activity test and selectivity test, the reaction temperature increased from 450 °C to 800 °C with an interval of 50 °C at GHSV = 1,200,000 mL h⁻¹ g_{cat}⁻¹, and stability test was performed at 700 °C for 30 h. Computational work: DFT calculations have been performed by using the Vienna Ab-initio Simulation Package (VASP) code ^[3]. The exchange and correlation energy was described using projector augmented wave (PAW) potentials with the generalized gradient approximation (GGA) using of BEEF functional ^[4]. A plane wave energy cutoff of 400 eV was used in this work.

3. Results and discussion

BET surface area for all catalysts is around 180 m²/g_{catal}. XRD patterns show the typical hydrotalcite-like structure after drying overnight. Total dispersion based on H₂ chemisorption presents a slight rise with the Pt loading increasing on the surface. In addition, H₂-TPR results show that with the increase of surface Pt loading, the start point for catalysts reduction shifts to low temperatures. Moreover, XPS indicates that the surface Pt/Ni ratio increases as we proposed. Furthermore, on Pt_{0.25}Ni_{(s)0.75}, activity and selectivity test shows that CO₂ and CH₄ conversions could reach 91.2% and 90.0% at 800 °C respectively, and Ni-Pt surface alloy catalysts have good performance for H₂ selectivity at high temperature and CO selectivity. Moreover, stability test reveals that both CO₂ and CH₄ conversions have a slight decrease on all samples after 30 hours experimental operation. Considering the activity and selectivity as well as stability, Pt_{0.50}Ni_{(s)0.50} stands out of highest catalytic performance. On the other hand, DFT calculations give some details on carbon deposition resistance as well as H₂ formation and CO adsorption on Ni@Pt(111) surface compared with pure Ni(111). Energy barrier for CH dehydrogenation on Ni@Pt(111) is remarkably increased by around 1.979 eV and the carbon adsorption energy is lower compared to that on Ni(111). In addition, the process H* + H* = H_{2(g)} + 2* is much easier to proceed with a low energy barrier of 0.36 eV and CO is more likely to desorb on the Ni@Pt(111) surface.

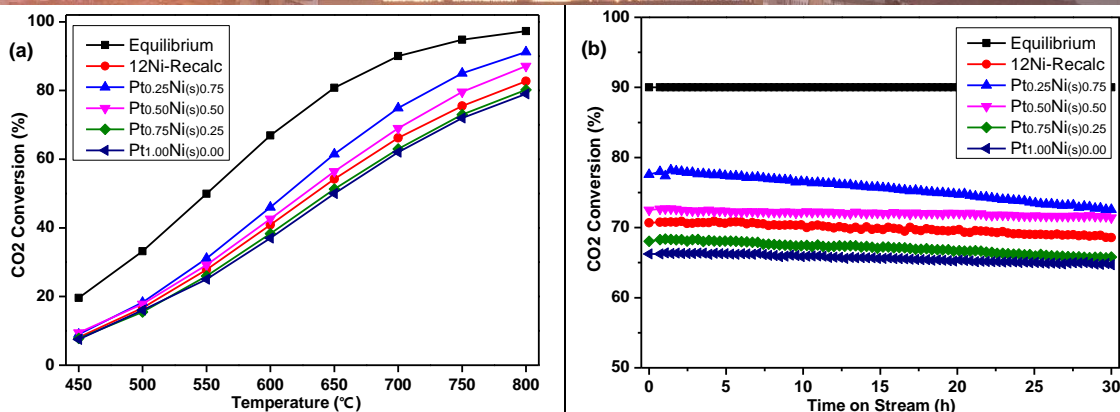


Fig. 1. Catalytic performance test for DRM: (a) Activity and selectivity test from 450 °C to 800 °C; (b) Stability test at 700 °C for 30 h. Reaction conditions: CO₂/CH₄/Ar = 30/30/140 mL/min, GHSV = 1,200,000 mL h⁻¹ g_{cat}⁻¹, 1 atm.

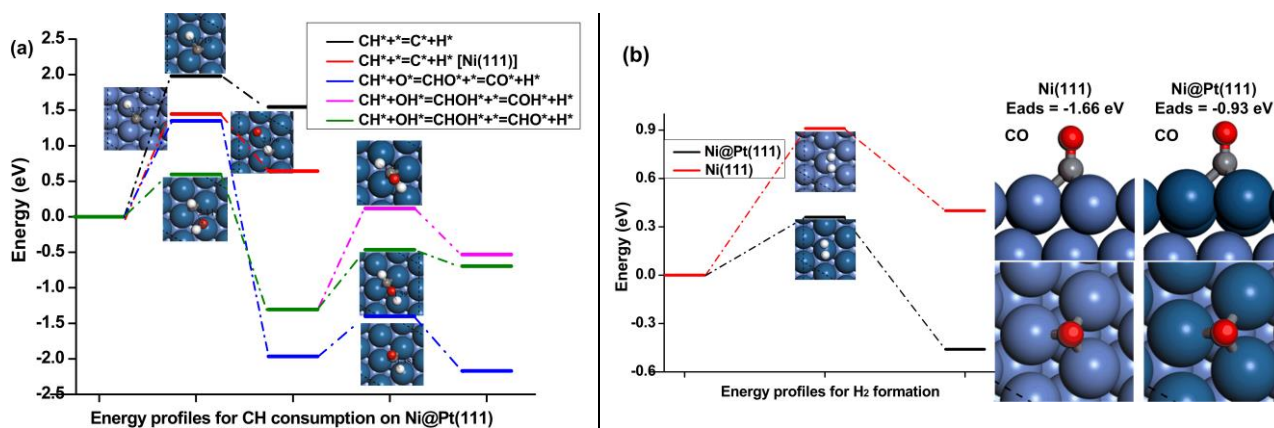


Fig. 2. DFT calculations: (a) CH consumption on Ni@Pt(111); (b) H₂ formation and CO adsorption on Ni@Pt(111) compared with Ni(111).

4. Conclusions

Combined experimental work with DFT calculations, we proposed that Pt addition on the Ni catalysts surface helps to increase the CO₂ and CH₄ conversions, decrease the reduction temperature of Ni catalysts and prolong the catalysts life. In addition, the presence of Pt on the surface enhances the resistance to carbon formation, and lowers the H₂ formation barrier and increases the CO desorption possibility. In addition, the effects of Pt-Ni surface alloy catalyst sites on TOF, activation energy and carbon formation in details will be studied in the following work. These results could provide new insights into Ni-Pt surface alloy catalysts in improving the activity and selectivity for DRM and ability to anti-carbon deposition of Ni catalysts from both industrial application and atomic scale.

References

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Keywords

Methane dry reforming; Catalytic performance, Surface Pt/Ni ratios; DFT