



# Understanding the role of Ni-Sn interaction to design highly effective CO<sub>2</sub> conversion catalysts for dry reforming of methane



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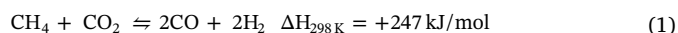
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## ABSTRACT

CO<sub>2</sub> reforming of methane is an effective route for carbon dioxide recycling to valuable syngas. However conventional catalysts based on Ni fail to overcome the stability requisites in terms of resistance to coking and sintering. In this scenario, the use of Sn as promoter of Ni leads to more powerful bimetallic catalysts with enhanced stability which could result in a viable implementation of the reforming technology at commercial scale. This paper uses a combined computational (DFT) and experimental approach, to address the fundamental aspects of mitigation of coke formation on the catalyst's surface during dry reforming of methane (DRM). The DFT calculation provides fundamental insights into the DRM mechanism over the mono and bimetallic periodic model surfaces. Such information is then used to guide the design of real powder catalysts. The behaviour of the real catalysts mirrors the trends predicted by DFT. Overall the bimetallic catalysts are superior to the mono-metallic one in terms of long-term stability and carbon tolerance. In particular, low Sn concentration on Ni surface effectively mitigate carbon formation without compromising the CO<sub>2</sub> conversion and the syngas production thus leading to excellent DRM catalysts. The bimetallic systems also presents higher selectivity towards syngas as reflected by both DFT and experimental data. However, Sn loading has to be carefully optimized since a relatively high amount of Sn can severely deter the catalytic performance.

## 1. Introduction

CO<sub>2</sub> dry reforming of methane (DRM) is an environmentally benefiting process due to its ability to utilize the two main greenhouse contributors (CH<sub>4</sub> and CO<sub>2</sub>) and transforms them into high value syngas (CO + H<sub>2</sub>), which can be further upgraded to long chain hydrocarbons via Fischer–Tropsch synthesis [1–3]. The overall reaction for DRM is shown in [Eq. (1)].



The industrial development of the (DRM) process faces several obstacles due to its endothermic reaction character which requires operating temperature between 800–1000 °C to attain high equilibrium conversion of CO<sub>2</sub> and CH<sub>4</sub> into syngas and to minimize the thermodynamic driving force for carbon deposition [1–4].

Nickel (Ni) based catalysts have received a general acceptance among scientific and industrial community as reference materials for DRM due to their high activity, selectivity, availability and low cost [4–7]. However, Ni undergoes severe coke deposition and sintering at high reaction temperatures during the DRM process which eventually leads to catalyst deactivation [5–8]. Most recently synthesis of new

yolk-shell based Ni catalysts have shown to reduce sintering and increase carbon resistance during DRM [9,10]. Price et al. used a ZnO/Ni@m-SiO<sub>2</sub> yolk-shell catalyst for DRM observing long term stability of the catalyst with high CO<sub>2</sub>/CH<sub>4</sub> conversion, but with some coking [9]. Zhao et al. using a NiCe@m-SiO<sub>2</sub> yolk-shell structure, with a combination of Ni nanoparticle and CeO<sub>2</sub> encapsulated inside silica shells restricted carbon formation during DRM [10]. Also, increase in surface oxygen species was observed on Ni nanoparticles confined in Cerium-modified silica aerogels, which play's a major role in suppressing coke formation [11]. Among the various strategies available for the development of Ni based catalysts, surface alloying is a promising alternative [12,13]. Here-in, a monometallic surface can be modified by the introduction of additional metals, thereby changing the surface ensemble of the metal and drastically reducing the potentiality of carbon deposition [12]. This enhanced carbon tolerance of the Ni catalyst has been reported, especially when alloying with noble metals such as Ru, Rh, Pd and Pt, both activity and stability of the Ni catalyst has increased considerably in comparison to mono-metallic Ni catalysts [13]. However, any capable Ni bimetallic catalysts comprising of noble metals, is less likely to be implemented in large scale industrial applications due to the trade-off between cost of the noble metals and the cost of

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development of the final process product. Therefore, it is important to develop noble metal free bimetallic Ni catalysts for DRM, with comparable carbon tolerance and catalytic properties to that of noble metals.

Tin (Sn) alloyed Ni catalyst is a promising economically viable alternative, which has been previously used in steam reforming reactions [14–17]. During steam reforming of methane (SRM) Sn alloying with Ni was observed to have a positive effect towards increased catalyst stability by inhibition of carbon nucleation on the active Ni sites [14–16]. In addition Sn/Ni alloyed catalyst surface exhibits a promoting effect towards carbon oxidation [16]. In case of DRM, experimental studies conducted by Hou et al., on Sn/Ni alloyed catalyst showcased an increased carbon tolerance and decreased sintering of the Ni catalyst [18]. This attribute of carbon tolerance due to Sn alloying may be due to the tetravalent similarity of electronic structure to that of carbon [19]. Further, small Sn doping on Ni, have shown to increase DRM products conversion [20]. However there remains some contradictions towards the performance of Sn/Ni catalyst in the DRM process. As, in a recent experimental study on silica supported Ni nano-particles, the doping of Sn at various concentrations, was not able to restrict coke formation and also had an adverse effect in decreasing activity of the Ni catalyst [21]. Similar loss in catalyst activity at higher Sn concentrations on Ni surface in DRM, was observed in other experimental investigations [20–22].

To have a clear picture of the effect of Sn alloying with Ni in DRM process, it has become imperative to develop a detailed mechanistic understanding leading to experimental investigation, which may provide vital insights to explain the aforementioned effects Sn/Ni alloy in improved carbon resistance and loss in catalyst activity due to higher tin concentration on the Ni Surface.

Density functional theory (DFT) is a reliable method to explore atomic understanding of gas phase molecules to surface interaction [23], and gain insights into the elementary catalytic reaction mechanisms. The literature on DFT studies, especially for DRM reaction on bimetallic catalyst surfaces, is however limited, with a major focus towards monometallic surfaces. For instance Wang et al. in their studies of DRM on Ni (111) surface found the C–H activation to be the rate determining step and CH–O oxidation route is more favourable than C–O route [24,25]. In comparison Zhu et al., in their DFT calculations on Ni (111) surface at 973 K, found the CH–O oxidation to be the rate determining step [26]. In addition the possible oxidation route during DRM is firstly through CH<sub>4</sub> dissociation to CH, thereafter oxidation of CH with O formed through direct dissociation of CO<sub>2</sub> [26,27]. This reaction step has been reported to be common on monometallic Ni, Pt and Pd catalysts [27]. Also, DFT studies of DRM on Pt (111) surface showed abundance of CH species during the dehydrogenation step, which resists coke deposition on the catalyst surface [28]. This increase in activation energy barrier of CH dissociation into C+H was also, evident over Pt–Ni bimetallic surface, where the CH dissociation barrier was found to be higher than that of pure Ni (111), and thereby increasing carbon tolerance of the Ni surface [29].

In this paper, we report a step forward approach for the catalysts design for the DRM reaction, by combining DFT studies with experimental work. In fact, this paper reveals through DFT studies: (i) the fundamental aspects of DRM in terms of mechanistic information, where catalyst models of a low and high Sn concentration is used to investigate the C–H bond activation and carbon resistance, (ii) the optimised Sn concentration model is used to ascertain key pathways for CO<sub>2</sub> activation, CH and C oxidation compared to mono-metallic Ni (111) surface. From the key insights developed in our DFT studies we have prepared real Sn/Ni bimetallic catalyst surfaces and have performed experimental tests of the long duration micro-activity, followed by catalyst surface evaluation in DRM. Using this catalyst development approach, we have established key insights towards Sn/Ni bimetallic catalysts development with potential applicability.

## 2. Methods

### 2.1. Computational method and model

In the present work all the DFT calculations are done using the Cambridge Sequential Total Energy Package (CASTEP) [30]. The calculations uses the generalized gradient approximation (GGA) and the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional [31]. The plane wave kinetic energy cutoff 400 eV is used in all the calculations. Spin polarization is considered for all the calculations. The electron occupancies were determined by Gaussian smearing method [32] with a smearing value of 0.2 eV. Brillouin zone sampling is performed using the Monkhorst–Pack method [33]  $3 \times 3 \times 1$  k-points grid is used to describe all the surfaces. The self-consistency field (SCF) is considered to be converged when the total energy of the system is below  $10^{-6}$  eV/atom. All geometries were optimized using the (BFGS) [34] algorithm, where, the geometries converged until the forces between atoms are 0.02 eV/Å. Additionally dipole correction to the energy is applied self-consistently in the z direction. Geometry of isolated species were optimized at  $\Gamma$  point in a cubic box of  $15 \text{ \AA} \times 15 \text{ \AA} \times 15 \text{ \AA}$ . Adsorption energy ( $E_{\text{ads}}$ ) of the surface adsorbed species is defined by  $E_{\text{ads}} = E_{\text{species} + \text{slab}} - E_{\text{slab}} - E_{\text{species}}$ , where  $E_{\text{species} + \text{slab}}$  represents the energy of the adsorbed species on the modelled surface,  $E_{\text{slab}}$  total energy of the clean surface slab and  $E_{\text{species}}$  corresponds to the energy of the gas phase molecules. The transition states (TS) searches are performed using the same level of theory for those applied to the reactants and products with the complete linear synchronous transit (LST)/quadratic synchronous transit (QST) method [35]. The convergence criterion for the transition state search is set to be 0.25 eV/Å root-mean-square forces on atoms. The uniqueness of the (TS) structures were confirmed using vibrational frequency analysis using the finite displacement method [36].

Based on the calculated bulk lattice constant of 3.525 Å in the present work which is in good agreement with experimental value of 3.52 Å [37], the Ni (111) and Sn–Ni (111) surfaces was developed. The surfaces were built by cleaving the Ni bulk lattice in [1 1 1] direction using a  $(3 \times 3)$  unit cell with 4 layers slab thickness and 12 Å vacuum towards z –direction to ensure negligible intermolecular interaction between the slabs. The bottom 2 layers of the surfaces were kept fixed to their bulk position during all geometry optimizations. The Sn–Ni bimetallic surfaces referred as NiSn<sub>1</sub> (Fig. 1a) and NiSn<sub>2</sub> (Fig. S6) were modelled by replacing one and two Ni atoms within the outermost surface with Sn atoms respectively. The two surface models with variable Sn coverage of 1/9 ML and 2/9 ML represents low and high Sn concentration on the Ni surface respectively.

### 2.2. Experimental study

#### 2.2.1. Catalyst preparation

All catalysts were prepared by sequential impregnation, where the support ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub> SCFa-230 Sasol) was first impregnated with Ni (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sigma-Aldrich) diluted in acetone, evaporated at reduced pressure in a rotavapor, dried overnight at 80 °C and calcined at 800 °C for 4 h. Afterwards, the solids were impregnated in a similar way with SnCl<sub>2</sub> (Sigma-Aldrich) and calcined at 800 °C for 4 h. In all cases the NiO content is calculated to be 10 wt.%. The Sn promoted catalysts were prepared to present Sn/Ni molar ratios of 0.02 and 0.04. These ratios were chosen based on previous works [18] and also to reflect the impact of low and relatively high Sn loading on the catalytic performance. For simplicity, all samples will be referred to by only the active components. Ni/Al refers to a catalyst composed of 10 wt.% NiO dispersed on Al<sub>2</sub>O<sub>3</sub>; NiSn0.02/Al and NiSn0.04/Al are 0.02 and 0.04 mol of Sn respectively for every mole of 10 wt.% NiO on an Al<sub>2</sub>O<sub>3</sub> base.

#### 2.2.2. Catalytic activity

The dry reforming of methane reaction was carried out in a tubular

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