# Influences of doping Cr/Fe/Ta on the performance of Ni/CeO$_2$ catalyst under microwave irradiation in dry reforming of CH$_4$

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## ARTICLE INFO

## ABSTRACT

The structure of Ni/CeO$_2$ catalyst with doping of Cr, Fe and Ta was investigated with XRD, N$_2$ physisorption, XPS and HRTEM and the catalytic activity of the catalysts under microwave irradiation in dry reforming of methane was tested in a microwave reactor. The results show that the introduction of Cr and Ta to Ni/CeO$_2$ can enhance the interaction between Ni and the support/promoter and inhibit the enlargement of NiO particles during the synthesis. The CH$_4$ conversions in dry reforming on the catalysts follow the order: Ni/CeO$_2$ < 2Fe–Ni < 2Ta–Ni < 2Cr–Ni. The superior performance of 2Ta–Ni and 2Cr–Ni may be attributed to the locally-heated Ni particles caused by the strong microwave absorption of the in-situ grown graphene attached on them under microwave irradiation.

## 1. Introduction

Utilization of fossil fuel resources, such as coal, crude oil and natural gas, results in the greenhouse effect due to methane and carbon dioxide. One of the most effective ways to address this problem is recycling of the two important greenhouse gases via catalytic CO$_2$ reforming of CH$_4$ (i.e., dry reforming of CH$_4$) to produce syngas − a fuel gas mixture consisting of H$_2$ and CO [1,2]. Syngas is widely used as an intermediary building block for production of various fuels such as synthetic natural gas, ammonia, methanol and hydrocarbon fuels [3]. But there lacks a method for commercially feasible syngas production via dry reforming because of (i) the undesired rapid deactivation of catalysts due to the deposition of carbon on active sites and (ii) sintering of active metallic particles under high reaction temperatures [4–6].

Although noble metals (Pt, Pd, Rh and Ru) work well with minimum carbon formation [7,8], the scarcity and high cost exclude them in industrial scale use. Nickel (Ni) has been proved suitable to replace noble metals due to its comparative catalytic performance and low cost. However, it is severely limited by clusters forming with unreactive carbons deposited on the catalyst surface [9,10]. To date, much efforts are focussed on suppressing, reducing and even removing the deposited carbons from catalyst surface. Promising strategies to address these challenges include

(i) doping a small amount of promoters such as Ag, Au, Sn, Cu, Co into Ni catalysts to modify Ni particles [11–14] and the surface properties of the carriers [15], (ii) generating nanosized Ni particles by strengthening the interaction between Ni particles and the carrier and [1,2], and (iii) improving the particles dispersion on the carrier [16].

Microwave energy is cost-effective in comparison with the conventional heating systems [17–19]. It has been increasingly used for the growth of carbon materials [19,20], but few studies have adopted it for syngas production [21,22]. Research is rarely done on syngas production using metal catalysts under microwave irradiation as well [23]. Ni/CeO$_2$ will be employed as catalyst and the research will focus on (i) the performance of Ni metal catalysts in syngas production under microwave irradiation, and (ii) the presence of a doped promoter for preventing the aggregation of Ni nanoparticles or modifying the catalysts' microwave absorption towards superior syngas yields. By considering the speciality of the microwave irradiation, Cr, Fe and Ta were selected to be doped into Ni/CeO$_2$, respectively, because (i) Cr metal has a low solubility of carbon and Cr$_2$O$_3$ has a low microwave absorption ability [24]; (ii) Fe can easily form alloy with Ni to modify energetic state of Ni and has a good microwave absorption ability; and (iii) Ta metal has a low solubility of carbon and Ta$_2$O$_5$ has a low microwave absorption ability, and additionally Ta has a high melting point (3017 °C) and may prevent the agglomeration of Ni particles as a physical barrier [25]. To the best of our knowledge, these researches in dry reforming of methane have not been reported yet.

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**Table 1**
List of catalysts and names of the hybrid materials.

|  | System 1 | System 2 | System 3 | System 4 |
|---|---|---|---|---|
| Catalyst composition | 2% Cr–40% Ni/CeO$_2$ | 2% Fe–40% Ni/CeO$_2$ | 2% Ta–40%Ni/CeO$_2$ | 40% Ni/CeO$_2$ |
| Catalyst names | 2Cr–Ni | 2Fe–Ni | 2Ta–Ni | Ni/CeO$_2$ |
| Composition of carbon on catalysts | MWCNT/layered graphene composite | MWCNT/cup-stacked CNT composite | MWCNT/graphitic nanofiber/layered graphene composite | MWCNT/graphitic nanofiber composite |
| Product acronyms | M/GR[a] | M/CSCNT[a] | 3-phase composite[a] | M/GNF[a] |

[a] M/GR – in situ grown MWCNT/layered graphene composite+2Cr–Ni, M/CSCNT – in situ grown MWCNT/cup-stacked CNT composite+2Fe–Ni, 3-phase composite – in situ grown MWCNT/graphitic nanofiber/layered graphene composite+2Ta–Ni and M/GNF – in situ grown MWCNT/graphitic nanofiber composite+Ni/CeO$_2$.

## 2. Experimental

### 2.1. Chemicals and materials

Metal precursors were all purchased from Sigma-Aldrich, including nickel nitrate (Ni(NO$_3$)$_2$·6H$_2$O), iron nitrate (Fe(NO$_3$)$_3$·9H$_2$O), cerium nitrate (Ce(NO$_3$)$_3$·6H$_2$O), chromium nitrate (Cr(NO$_3$)$_3$·9H$_2$O), tantalum oxide (Ta$_2$O$_5$), and sodium hydroxide (NaOH).

### 2.2. Catalyst preparation

A CeO$_2$ support was synthesized through a hydrothermal process. Specifically, 60 mL of NaOH solution (9.17 mol/L) was dropped to Ce(NO$_3$)$_3$·6H$_2$O solution (0.46 mol/L) under continuous stirring for 60 min. The slurry was transferred into a 100 mL autoclave and heated in an electric oven for 72 h at 100 °C. The precipitates were filtered, washed with deionized water, and dried in an oven overnight at 100 °C. The material was then calcined at 500 °C in air for 5 h to obtain the ceria support.

Mono- and bi-metal incorporated ceria samples were prepared by co-impregnation with solutions of the appropriate metal precursors dissolved in deionized water. The co-impregnation of the aqueous solution of the respective metal precursors containing 40 wt% of Ni and 2 wt% of promoters (Cr, Fe and Ta) was conducted under magnetic stirring at about 60 °C. This was followed by drying in an oven at 100 °C overnight and calcination at 400 °C for 2 h in air. The mono-metal incorporated ceria is denoted as Ni/CeO$_2$, while the bimetallic catalysts are designated as 2Cr–Ni, 2Fe–Ni and 2Ta–Ni, for 2Cr–Ni/CeO$_2$, 2Fe–Ni/CeO$_2$ and 2Ta–Ni/CeO$_2$ (Table 1).

### 2.3. Characterization of catalysts

Phase purity of the catalysts was determined by x-ray diffraction (XRD) in a Bruker Advanced x-ray diffractometer using nickel-filtered Cu Kα x-ray source radiation. High resolution transmission electron microscopy (HRTEM) was recorded on a JEOL 2100 microscope. X-ray photoelectron spectroscopy (XPS) was acquired on a Kratos Axis ULTRA x-ray photoelectron spectrometer. Raman spectra were collected with a Renishaw inVia Raman spectrometer using a 514 nm Ar$^+$ ion laser as an excitation source. N$_2$ adsorption measurements were performed using a Tristar II 3020. The reducibility of catalysts was studied by H$_2$ temperature-programmed reduction (H$_2$-TPR) on a BELCAT apparatus. The H$_2$-TPR of the samples was investigated by heating the samples (50 mg) in H$_2$ (5 vol%)/Ar flow (50 mL/min) at a heating rate of 10 °C/min from 50 to 800 °C. A Perkin Elmer Instruments STA 6000 Thermo Gravimetric Analyzer (TGA) was used to measure the mass loss of the catalyst samples with the formed carbon after reaction of dry reforming as a function of temperature. Samples were heated at a rate of 5 °C/min to a maximum temperature of 850 °C in a flowing atmosphere of 5% O$_2$/He.

### 2.4. Catalytic activity measurements

The catalytic activity of Ni-based catalysts in dry reforming of methane was carried out under atmospheric pressure using a microwave reactor consisting of a reaction chamber and microwave transparent walls. The output power of the microwave generator could be changed continuously from 0 to 2000 W at a fixed frequency of 2.45 GHz. The catalyst surface temperature during the reaction was measured by an infrared temperature transducer attached to the microwave reactor. After 500 mg of catalyst was loaded into the chamber, the reactor was vacuum pumped for about 1 h. The reactor is connected to a vacuum system with a typical base pressure of ~10$^{-2}$ Torr. Once the pressure was stable, H$_2$ gas (15 mL/min) was introduced into the reactor, and then the microwave power was increased to 120 W and maintained for 30 min for catalyst surface reduction. After the reactor was purged with argon gas for ~45 min, the reactant gases were introduced into the system. A feed with a constant CH$_4$/CO$_2$ molar ratio of 1:1 was used throughout the experiments. The activity screening tests of the catalysts were investigated in the range of 350–600 W using steps of 50 W with a gas flow rate of 85 mL/min. The stability test of the catalysts was carried out at a constant microwave power of 500 W for 14 h time-on-stream (TOS). The product composition was analyzed using an on-line gas chromatograph equipped with a Porapak Q column and a thermal conductivity detector (TCD). The conversions of CH$_4$ and CO$_2$ were calculated by the following equations [21]:

$$CH_4 \text{ conversion, } \% = \left[ F_{CH_4 \text{ inlet}} - F_{CH_4 \text{ outlet}} \right] / F_{CH_4 \text{ inlet}} \times 100$$

$$CO_2 \text{ conversion, } \% = \left[ F_{CO_2 \text{ inlet}} - F_{CO_2 \text{ outlet}} \right] / F_{CO_2 \text{ inlet}} \times 100$$

where $F_{\text{inlet/oulet}}$ is the flow rate of each component in the feed or effluent.

## 3. Results and discussion

### 3.1. XRD analysis and textural properties of the Ni-based catalysts

Fig. 1a presents x-ray diffraction patterns for the freshly calcined Ni/CeO$_2$, 2Cr–Ni, 2Fe–Ni and 2Ta–Ni. All samples showed diffraction peaks at 28.5°, 33.1°, 47.5°, 56.3°, 59.1°, 69.4°, 76.7° and 79.1° corresponding to (111), (200), (220), (311), (222), (400), (331), (420) and (422), respectively, of the cubic fluorite structured CeO$_2$ (JCPDS 34-0394). Peaks observed at 63°, 43.5° and 37.5° over all samples can be assigned to (220), (200) and (111) crystal planes, respectively, of face-centered cubic NiO (JCPDS 04-0835). No diffraction peaks corresponding to Cr, Ta and Fe metals or oxides were observed in the XRD patterns, indicating the good dispersion of the metal ions on the ceria support.

The nitrogen adsorption and desorption isotherms of the samples displayed type IV isotherm with type H1 hysteresis loops