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Tuning the catalytic performance of Ni-catalysed dry reforming of methane and carbon deposition via Ni-CeO_{2-x} interaction

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ABSTRACT

The role of tuning metal-support interaction in determining the catalytic activity and carbon formation in dry reforming of methane to syngas was examined over CeO_2 supported Ni nanoparticles. The catalysts pre- and post- reaction were subjected to characterisation in terms of N_2 physisorption, TPR, XRD, TEM, XPS and TGA-DTG. Reduction of Ni/CeO_2 in H_2 in the temperature range (773–973 K) generated a strong bonding between Ni and CeO_2 that inhibited Ni particle sintering (8.7–9.4 nm). High-temperature (≥873 K) reduction induced decoration/encapsulation of Ni nanoparticles by a thin layer of reduced ceria support with partial coverage of Ni surface. The decoration/encapsulation effect strongly influences the catalytic properties of Ni, which enables to tune the catalytic activity of Ni/CeO_2 and carbon deposition in dry reforming of methane.

1. Introduction

In supported metal catalysis, strong support (generally oxides) and metal interaction (SMSI) including electron transfer, support decoration of metal nanoparticles and cluster stabilisation can often determine catalytic reactivity and/or selectivity [1,2]. Ceria is a typical case of oxide support that is facile to generate interaction with the supported metal (e.g., Pd, Ru and Rh) phase following thermal activation in H_2 [3]. A number of studies have reported metal-ceria interaction serves to increase rates or control product selectivity for reactions involving redox steps (e.g., CO oxidation over Pt/CeO_2 [4], water gas shift (over Pt/CeO_2 [5], Au/CeO_2 [6]) and CO_2 hydrogenation over Cu/CeO_2 [7]).

Dry reforming of methane to syngas, an intermediate for synthesis of methanol and Fischer-Tropsch products, is a promising route for conversion of methane to value-added chemicals/fuels and reduction of greenhouse gas (e.g., CO_2 and CH_4) emission. This reaction has been experimentally and theoretically studied over noble (Pt [8], Ru [9], Rh [10–12] and Pd [13]), non-noble metal (Ni [14–17] and Co [18]) and bimetallic (NiCo [19], FeNi [20], PdNi [21] and NiPt [22]) catalysts. Inexpensive Ni-based catalysts exhibited comparable activity to noble metals due to the outstanding capacity for activation/dissociation of the C—H bond of methane [23]. There is a consensus that methane activation is the rate-determining step in the dry reforming of methane [24]. Metal-support interaction is critical in determining adsorption/dissociation of methane. A search through literature found that Liu et al. [25] studying dry reforming of methane over Ni-CeO_2 (111) surfaces using in situ XPS and DFT calculation, demonstrated strong metal-support interaction can activate Ni for methane dissociation at 300 K. Higher catalytic stability of Ni/CeO_2 in dry reforming of methane (1023 K) relative to steam reforming was linked to strong metal-support interaction on the basis of in situ XAS and XANES analysis [26]. The degree of metal-support interaction can modify the characteristics of the supported metal phase and reactant adsorption. SMSI can alter the metal electronic properties via charge transfer between metal and support, stabilise small metal clusters in support surface vacancies and induce support decoration of metal surface via migration of support oxide to the metal particles [1,2]. Moreover, solid solutions can be generated via dissolution of metal in support oxide lattice. It is known that SMSI-induced decoration/encapsulation of metal nanoparticles contributes to suppression of H_2 and CO chemisorption over reducible oxides (e.g., TiO_2, CeO_2 and $CeTbO_x$) supported noble metals (e.g., Ru, Rh and Pt) [27–30]. In the reported studies up to date the influence of Ni-CeO_2 interaction on the morphology of Ni particles and activation of CH_4 and CO_2 in dry reforming have not been studied to any significant extent. In this study, we examine the impact of SMSI-induced decoration/encapsulation of Ni particles on the catalytic response in dry reforming of methane over CeO_2 supported Ni. Carbon deposition was studied as one critical consideration for the decoration/encapsulation effect on the catalyst stability.

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2. Experimental

2.1. Materials and catalyst preparation

Commercial CeO_2 (Sigma-Aldrich) was used as received. (5% w/w) Ni on CeO_2 was prepared by wet-impregnation. CeO_2 (5 g) was added to aqueous solution of $Ni(NO_3)_2$ (Alfa Aesar, 98%, 9×10^{-2} M, 50 cm^3) and stirred (500 rpm) at room temperature overnight. The solid was obtained by evaporation and dried in air at 393 K overnight. The resultant sample was sieved (ATM fine test sieves) to mean particle diameter = 75 μm, activated at 773–973 K in H_2 (10 cm^3 min^{-1}) for 1 h, cooled to ambient temperature and passivated in 1% v/v O_2/N_2 for 1 h for *ex situ* characterisation (including N_2 physisorption, XRD and HRTEM).

2.2. Catalyst characterisation

Nitrogen physisorption was performed on the Micromeritics ASAP 2020 system. Specific surface area (SSA) and pore volume were calculated using the standard BET method and BJH desorption, respectively. Prior to analysis, samples were vacuumed and outgassed at 573 K for 1 h. Temperature programmed reduction (TPR) was conducted in a quartz tube cell. The sample (Ni precursor on CeO_2) was heated in 84 cm^3 min^{-1} 5% v/v H_2/Ar at 10 K min^{-1} to 1073 K. Hydrogen consumption was monitored by a thermal conductivity detector (TCD). X-ray diffractograms (XRD) were recorded on a Bruker D5000 X-ray diffractometer using Cu Kα radiation. Samples were scanned at 0.01° $step^{-1}$ over the range 20° ≤ 2θ ≤ 80° at ambient temperature and the diffractograms identified against the JCPDS-ICDD reference standards. Metal particle morphology (size and shape) was examined by high resolution transmission electron microscopy (HRTEM, JEOL 2100 LaB6), employing Gatan Digital Micrograph for data acquisition/manipulation. Samples for analysis were prepared by dispersion in ethanol and deposited on a holey carbon/Cu grid. Mean Ni size (*d*) was obtained from a count of at least 200 particles. XPS measurement of the reduced sample was performed on a Kratos Axis Ultra DLD spectrometer using a monochromated Al kα X-ray source. The Ni $2p_{3/2}$ and Ce 3d spectra were collected. Characteristic Ni $2p_{3/2}$ binding energy (BE) for metallic Ni is 852.5 ev and 856.3 ev; for NiO is 853.7 ev, 855.4 ev and 861.0 ev [31]. The BE scale was calibrated by adventitious carbon (BE = 285.0 ev). The data were analysed in CasaXPS, using Shirley backgrounds, mixed Gaussian-Lorentzian (Voigt) line shapes and asymmetry parameters where appropriate. The fixed positions of the components were similar to those reported elsewhere [31]. The peak asymmetry was defined in the form of LA (α, β, *m*), where α and β refer to the spread of the tail on each side of the Lorentzian component; *m* is the width of the Gaussian for convolution of the Lorentzian line. The surface element composition was calculated from the peak area. Thermogravimetric-derivative thermogravimetric analysis (TGA-DTG) of the spent Ni/CeO_2 catalysts for evaluation of carbon deposition was carried out on a thermal analyser (NETZSCH STA449). The samples (ca. 10–20 mg) were heated in 50 cm^3 min^{-1} air to 973 K (at 10 K min^{-1}).

2.3. Catalyst testing

Dry reforming of methane was carried out at atmospheric pressure after in situ activation in a continuous flow fixed bed tubular reactor (10 mm i.d.). Reactions were conducted under operating conditions that ensured negligible mass/heat transport limitations. Isothermal conditions (± 1 K) were ensured by diluting the catalyst bed with ground glass (75 μm); the ground glass was mixed thoroughly with catalyst before loading into the reactor. Reaction temperature was continuously monitored by a thermocouple inserted in the catalyst bed. A co-current flow of CO_2 (BOC, 99.99%), CH_4 (BOC, 99.99%), N_2 (BOC, 99.99%) and Ar (BOC, 99.99%) was introduced to reactor by Brooks mass flow controller (SLA5800 series) at gas hourly space velocity (GHSV) = 4.8×10^4 h^{-1}. 10–40% (vol.%) CH_4 was diluted in N_2 and Ar. Inlet CH_4 to CO_2 feeding rate was fixed at 1:1. 0.03 g catalyst was used in the reforming reaction. The molar Ni to inlet CH_4 feeding rate n/F_{CH_4} was 4.8×10^{-3} h. The reactor effluent was analysed using online gas chromatography (Shimadzu 2014) equipped with a 0.5 cm^3 sampling loop, thermal conductive detector (TCD) and flame ionization detector (FID), employing serial Hayesep Q (3.0 m × 2.1 mm i.d.) and Molecular Sieve 5 A packed columns (2.0 m × 2.1 mm i.d.). Data acquisition and manipulation were performed using GCsolution Lite (Version 2.4) chromatography data system. Reactant i (i = CH_4 or CO_2) fractional conversion (X_i) is calculated by

$$Xi = \frac{F_{[reactant]i,in} - F_{[reactant]i,out}}{F_{[reactant]i,in}} \quad (1)$$

Reactant (i) consumption rate (R_i, h^{-1}) was obtained from:

$$Ri = \frac{F_{[reactant]i,in} \times X_{i,s}}{n} \quad (2)$$

where subscripts "in" and "out" refer to inlet and outlet gas streams; "n" refers to mole number of Ni; "$X_{i,s}$" refers to steady-state conversion. The inlet fractional concentration was defined by the molar flow rate of reactant to the total flow rate. In blank tests, passage of CH_4 and CO_2 through the empty reactor or over support alone did not result in any detectable conversion. Repeated reactions delivered data reproducibility and carbon balance within 7%.

3. Results and discussion

3.1. Catalyst characterisation

Ni/CeO_2 post-reduction at 773 K exhibited a SSA (11 m^2 g^{-1}, Table 1), close to that (9 m^2 g^{-1}) reported in the literature [32]. Reduction at higher temperature (773 → 973 K) resulted in a loss of SSA and pore volume (Table 1), which can be linked to grain sintering and agglomeration [33]. TPR profiles of CeO_2 support and Ni precursor on CeO_2 are presented in Fig. 1. Thermal treatment of ceria **(I)** generated two broad peaks at 742 K and 1148 K that can be linked to surface (720–790 K) and bulk (> 1059 K) reduction [34,35]. TPR analysis of Ni precursor on CeO_2 **(II)** generated multiple signals. The sharp TPR peaks with associated temperature maxima (T_{max}) of 582 K and 587 K can be attributed to the decomposition of nickel precursor to NiO. Moraes et al. [36] studying the reducibility behaviour of Ni/CeO_2, ascribed a TPR peak (T_{max} = 588 K) to the decomposition of nickel nitrate. A subsequent reduction of NiO to metallic Ni was responsible for the higher T_{max} peak (616 K) recorded in this study. Mahammadunnisa [37] and Moraes [36] have attributed reduction peaks with T_{max} in the temperature range of 588–653 K to reduction of NiO in the TPR analysis of 5–10% Ni/CeO_2 (w/w). Hydrogen consumption signals at T_{max} = 706 K and at the extended isothermal hold (1073 K) can be linked to surface and bulk reduction of ceria, where addition of Ni to CeO_2 lowered the requisite temperature. Structure analysis by XRD generated diffraction patterns are shown in Fig. 2. Diffraction signals at $2\theta = 44.5°$ can be attributed to Ni (111). The peak intensity increased with increasing reduction temperature. In addition to Ni signals, diffraction peaks at 2θ = 28.6°, 33.2°, 47.6°, 56.4°, 59.2°, 69.6°, 76.8° and 79.2° can be

Table 1
Effect of reduction temperature on SSA and pore volume of Ni/CeO_2 pre- and post-reaction.

Sample		773 K	873 K	973 K
Pre-reaction	SSA (m^2 g^{-1})	11	8	8
	Pore volume (cm^3 g^{-1})	0.032	0.024	0.024
Post-reaction	SSA (m^2 g^{-1})	21	10	8
	Pore volume (cm^3 g^{-1})	0.036	0.021	0.025

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