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Methanol steam reforming over Ni-CeO_2 model and powder catalysts: Pathways to high stability and selectivity for H_2/CO_2 production

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ABSTRACT

Nickel-ceria has been reported as a very good catalysts for the reforming of methane. Here, the methanol steam reforming reaction on both powder (Ni-CeO_2) and model (Ni-CeO_{2-x}(111)) catalysts was investigated. The active phase evolution and surface species transformation on powder catalysts were studied via *in situ* X-ray diffraction (XRD) and diffuse reflectance infrared transform spectroscopy (DRIFTS). Phase transitions of NiO → NiC → Ni and CeO_2 → CeO_{2-x} were observed during the reaction. The simultaneous production of H_2/CO_2 demonstrates that the active phase of the catalysts contains metallic Ni supported over partially reduced ceria. The DRIFTS experiments indicate that a methoxy to formate transition is associated with the reduction of ceria whereas the formation of carbonate species results from the presence of metallic Ni. A study of the reaction of methanol with Ni-CeO_{2-x}(111) by X-ray photoelectron spectroscopy (XPS) points to the essential role of metal-support interactions in an oxygen transfer from ceria to Ni that contributes to the high selectivity of the catalysts.

1. Introduction

Although fuel cells are very attractive as an environmentally friendly technology, the application of a direct hydrogen fuel cell can be problematic due to the difficulties of transportation and storage of hydrogen. An alternative route is to make use of the so-called onboard fuel cell technology, where hydrogen is produced "onboard" to feed the cell through the steam reforming of alcohol [1,2]. Owing to the absence of a C—C bond, steam reforming of methanol (MSR: $CH_3OH + H_2O \rightarrow CO_2 + 3H_2$) naturally has a lower activation temperature and better selectivity (less CO or coke formation) than other heavier alcohols [3]. This makes methanol as a promising candidate for onboard fuel cell applications.

Cu-based metal-oxides are the most common studied catalysts for methanol steam reforming because of copper's well-known capability of catalyzing methanol synthesis in the industry, which is a reverse way of the reforming reaction [4–8]. The main drawbacks of Cu-based catalysts used for MSR are their pyrophoricity and catalytic deactivation due to metal sintering. To overcome these issues, noble metals such as Pd [9–11], Pt [12,13], and Au [14,15] have been proposed for this reaction, and some of them exhibited catalytic activity comparable to that of Cu-based catalysts but with much better stability. Recently, Ni has been reported as a non-expensive alternative metal that shows promising catalytic activity and selectivity for the MSR reaction [16–18]. Although Ni on its own is vulnerable to the coke formation, in our earlier studies for methane and ethanol reforming, we have shown that a combination of Ni with ceria significantly inhibited the formation of surface carbon to steer the catalytic reaction to the desired pathways [19–22]. Furthermore, the superior ability of Ni-ceria to activate the C—H and/or O—H bonds in methane and ethanol indicates that this system could be a good catalyst for the MSR reaction as well.

Even though methanol is a simple C-1 molecule, the reaction mechanism for the MSR process remains split between two pathways including (1) a direct decomposition route and (2) a dehydrogenation route that involves a formate intermediate. Understanding better the reaction mechanism may point to a rational way of further improving the activity/selectivity of methanol steam reforming in fuel cell applications. Thus, numerous studies have been focused on revealing the catalytic active phase and identifying reaction intermediates, and some of these have provided interesting perspectives of the reaction pathways via *in situ* characterization techniques [12,23–26]. In addition, adsorption and reaction of methanol on well-defined model surfaces have also been investigated extensively in the literature. Thus, articles have been reported studying the surface chemistry of this molecule on Cu(111) [27], Au(111) [28], Ni(111) [29,30], Pt(111) [31,32], CeO_2(111) [33,34], TiO2(110) [35], Cu-TiO2(110) [36], and Pt-

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CeO_2(111) [37]. Nevertheless, none of the studies correlate the information from a perspective of both powder and model systems, and thus a molecular level understanding of the structure-reactivity relationship for methanol steam reforming is rather limited.

In this study, we deal with a Ni-CeO_2 catalyst that is active and selective for the methanol reforming reaction, and for the first time, powder and model system studies are combined to provide insights regarding structure-reactivity correlations, especially for the role of metal-oxide interactions in the catalytic selectivity. In this work, we first examined the performance of Ni-ceria catalyst for MSR by using *in situ* XRD and DRIFTS, aiming at elucidating the structure related surface mechanism under reaction conditions. Then, we correlated this knowledge with a study of the surface chemistry of methanol on a well-defined Ni-CeO_{2-x}(111) model system to further reveal the synergy between the metal and oxide support, and its effect on the catalytic selectivity to minimize CO production.

2. Experimental

Ni/CeO_2 was prepared by an incipient wetness impregnation method. 20% Nickel nitrate was mixed with cerium oxide in molar ratio. The sample was dried and calcined at 500 °C in air. Characterization by powder XRD showed that the as-prepared sample contained 8.5 wt% NiO and 91.5 wt% CeO_2, from which the calculated mole ratio of Ni to Ce is 0.21–1. The average crystal size estimated with XRD was 8 nm for CeO_2 and 12 nm for NiO. Following previous studies the content of nickel was kept small (< 10 wt%) to optimize catalyst performance [21,22].

Temperature-programmed reduction (TPR) and steam reforming experiments in conjunction with XRD and a residual gas analyzer (RGA) were performed at beamline X7 B (λ = 0.3196 Å) of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). Under room temperature, the saturation vapor pressure of methanol is 0.18 bar. The generation of the steam vapor (MeOH/H_2O = 1:3) was achieved by passing He through a bubbler filled with a mixture of methanol and water. The gas flow rate used in this study, 10 cc/min, was sufficiently low to guarantee that the gases passing through the bubbler reached a vapor saturated state. The reaction cell and other parts of the gas flow system have been described in detail elsewhere [38]. Powder samples of 2–3 mg were loaded into a silica capillary (0.9 mm ID, 1.0 mm OD) mounted in the flow cell system. A Perkin Elmer Amorphous Silicon Detector was used to collect two-dimensional transmission diffraction data, which were subsequently processed with the program Fit2D [39] to obtain XRD profiles (Intensity versus 2θ). Lattice parameters and phase quantities were analyzed by Rietveld Refinement using the program GSAS [40,41].

DRIFTS data were collected on Ni/CeO_2 sample under steam reforming conditions using a Bruker Equinox 55 FTIR spectrometer equipped with a modified Harrick Praying Mantis DRIFTS cell connected to a gas flow system similar to the one used in XRD experiments. Details of the instrument can be found in ref [42]. The MeOH/H_2O ratio was kept at 1/3.

Transmission electron microscopy (TEM) images were obtained using a JEOL JEM 2100 instrument operating with an acceleration voltage of 200 kV. Sample powders were dispersed as a suspension in deionized water and sonicated for 60s. After being well dispersed, a droplet of suspension was deposited on Holey-Carbon coated Cu grids and allowed to dry before imaging.

Soft X-ray photoelectron spectroscopy (XPS) was conducted using synchrotron radiation at beamline U12a at the National Synchrotron Light Source (NSLS). O 1s and C 1s sXPS were recorded using 700 and 395 eV photon energies for excitation, respectively. The instrumental resolution was ca. 0.2 eV. The Ce 4d photoemission lines were used for binding energy calibration using the 122.8 eV satellite features [43]. The methanol source (Pharmco-aaper, ACS/USP grade) was freeze-pumped-thawed in liquid nitrogen to remove gaseous contaminants. The adsorbate was introduced to the UHV chamber using a “backfilling” method via a high precision leak valve.

For Ni-CeO_{2-x}(111) film preparation, Ce metal was first evaporated onto the Ru crystal held at 427 °C (700 K) in the presence of 5×10^{-7} Torr O_2, and then annealed at 527 °C (800 K) for 10 mins with the same O_2 pressure. For sub-stoichiometric film CeO_{2-x}(111), 2×10^{-8} Torr O_2 pressure was used during the Ce deposition at 427 °C (700 K) [44], and a reduced surface containing ~40% Ce^{3+} was obtained, as determined by XPS. After deposition, the surface was subsequently annealed at 527 °C (800 K) in UHV for 10 mins. The ceria films were estimated to be ca. 2–4 nm thick (7–10 layers of O—Ce—O) based on the attenuation of the Ru 3d XPS signal, which can eliminate the interference of Ru $3d_{3/2}$ (284 eV) with the C 1 s signal. Ni was vapor deposited on the as-prepared ceria film at 27 °C (300 K) under vacuum and then annealed at 427 °C (700 K) for 1 min. Ni coverage was estimated by thermal desorption of CO/Ni-CeO_{2-x} [20], whereas desorption peak area was calibrated by the 0.58 monolayer (ML) saturation coverage of CO on clean Ru(0001) [45]. The deposition rate of Ni was estimated to be 0.20 ML/min.

3. Results and discussion

3.1. MSR over powder Ni-CeO_2 catalysts: structure, chemical state and mechanism

Fig. 1a shows a series of *in situ* XRD profiles of a NiO/CeO_2 precursor under temperature programmed reduction of methanol. The as-prepared catalyst contains NiO particles impregnated on the ceria support, as indicated by the NiO diffraction peaks in Fig. 1a. As the temperature is increased, a NiO → Ni phase transition and a slight shift of the ceria peak position are clearly seen. Rietveld refinement was used to quantitatively analyze these phenomena as a function of temperature as shown in Fig. 1b. The NiO phase starts to be reduced from 250 °C and a hexagonal intermediate phase emerged and then further transforms into metallic fcc-Ni from 400 °C, as marked in the upper panel of Fig. 1b. This intermediate phase is assigned to a Ni carbide phase, which will be ascertained later from the XPS study. Additionally, through Rietveld refinement, we can also extract the CeO_x lattice parameter (Fig. 1b). This can be monitored as a function of heating, depicting a nonlinear lattice expansion of ceria, and the expansion rate involved a sharp rate of increase from 225 to 260 °C. The non-thermal increase of the lattice constant suggests the reduction of Ce(IV) to Ce (III) occurs since Ce(III) ion has larger atomic radii [19]. As a result, in the TPR process, the catalyst transforms from NiO/CeO_2 to Ni/CeO_{2-x} which means that a significant amount of metallic Ni centers and O vacancies/Ce(III) sites are generated.

The catalytic activity of the Ni-CeO_2 catalyst for methanol steam reforming was tested using a methanol/water ratio of 1/3. The sample was stepwise heated from 25 to 400 °C, meanwhile the phase evolution was recorded by the *in situ* XRD and the gas products were monitored by a mass spectrometer, as shown in Fig. 2. Similar to the TPR reduction of methanol, Rietveld refinement of the phase transition plotted in the upper panel of Fig. 2 indicates NiO was reduced to metallic Ni with the same nickel carbide intermediate phase appearing at temperatures around 250 °C. However, the amount of the Ni carbide phase formed in the methanol/water gas stream is much smaller than that under pure methanol vapor, suggesting that the presence of water inhibits the formation of Ni carbide. Moreover, as the temperature increased to 350 °C, the fast disappearance of Ni carbide associated with the sharp increase of metallic Ni indicates that water started precipitating into the reaction by taking C from Ni carbide, as evident by the CO/CO_2 production in the mass-spectrometer.

The catalytic activity associated with this chemical and structural transformations is shown in the lower panel of Fig. 2. Before the reduction of NiO at 250 °C, the production of CO_2/H_2 was negligible. Once the NiO starts to be reduced after 250 °C, simultaneous production