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**Dry Reforming of Ethane and Butane with CO₂ over PtNi/CeO₂
Bimetallic Catalysts**

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ABSTRACT

Dry reforming is a potential process to convert CO₂ and light alkanes into syngas (H₂ and CO), which can be subsequently transformed to chemicals and fuels. In this work, PtNi bimetallic catalysts have been investigated for dry reforming of ethane and butane using both model surfaces and supported powder catalysts. The PtNi bimetallic catalyst shows an improvement in both activity and stability as compared to the corresponding monometallic catalysts. The formation of PtNi alloy and the partial reduction of Ce⁴⁺ to Ce³⁺ under reaction conditions are demonstrated by in-situ Ambient Pressure X-ray Photoemission Spectroscopy (AP-XPS), X-ray Diffraction (XRD) and X-ray Absorption Fine Structure (XAFS) measurements. A Pt-rich bimetallic surface is revealed by Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) following CO adsorption. Combined in-situ experimental results and Density Functional Theory (DFT) calculations suggest that the Pt-rich PtNi bimetallic surface structure would weaken the binding of surface oxygenates/carbon species and reduce the activation energy for C-C bond scission, leading to an enhanced dry reforming activity.

KEYWORDS: dry reforming; bimetallic catalyst; synthesis gas; ethane; butane; CO₂

1. INTRODUCTION

Catalytic conversion of CO₂ to chemicals has been widely investigated¹⁻⁴ as a promising approach to migrate potential problems caused by global CO₂ emission. Dry reforming of methane (DRM) is an attractive process as it converts two greenhouse gases (CO₂ and methane) into syngas (CO and H₂)⁵, which can be subsequently transformed into value-added chemicals and fuels by methanol or Fischer-Tropsch (FT) synthesis reactions. Supported precious metals (Pt, Ru, Rh, Pd) as well as inexpensive transition metals (Ni, Co, Fe) have been extensively explored as active DRM catalysts.⁶ However, DRM is a highly endothermic reaction and requires high operating temperatures to attain considerable conversion, leading to rapid catalyst deactivation due to carbon deposition.⁶ An alternative way to convert CO₂ to syngas is to use ethane and other light hydrocarbons (e.g., butane) in shale gas.^{7, 8} Dry reforming of ethane (DRE, Equation 1) and dry reforming of butane (DRB, Equation 2) produce syngas via

Under equilibrium conditions of stoichiometric ratio, the 50% conversion of CO₂ in DRE and DRB can be reached at 761 and 717 K, respectively (Figure S1), significantly lower than 863 K for DRM. The decrease of reaction temperatures provides more options in designing stable catalysts due to a lower extent of catalyst deactivation. These reactions also have important practical applications as ethane and butane are commonly found in shale gas, typically about 10 wt% and 0.2 wt%,

respectively^{7, 8}.

The modification of Ni-based catalysts is considered to be an effective way to increase the catalytic activity and stability.⁸⁻¹¹ Though catalysts with high loadings of precious metals (such as Pt) are generally uneconomical in large-scale processes, they typically show higher coking resistance and can be used to promote Ni-based catalysts in order to reduce carbon deposition and increase catalyst lifetime. Effective activation of CO₂ is also a critical step in improving the overall reaction activity. It is generally believed that the activation of CO₂ occurs at the support or the interfacial site between the active metal and the oxide support. Therefore, a key factor in activating CO₂ is the reducibility of the metal oxides.¹² CeO₂ is a highly reducible oxide, which can be readily reduced to Ce³⁺ thermally or chemically.^{13, 14} The reduced oxide has a strong tendency to react with CO₂, even causing direct C-O bond scission. The combination of bimetallic active sites over highly reducible oxides should increase the catalytic activity and coking resistance. However, little is known about the reaction and deactivation mechanisms when these catalysts are applied to DRE and DRB, which involve breaking both the C-H and C-C bonds, instead of only C-H scission in DRM.

In this study, dry reforming of ethane and butane on CeO₂ model thin films and supported powder catalysts has been explored using both experiments and Density Functional Theory (DFT) calculations. Multiple spectroscopic techniques including in-situ Ambient Pressure X-ray Photoemission Spectroscopy (AP-XPS), in-situ X-Ray Diffraction (XRD), in-situ X-ray Absorption Fine Structure (XAFS) and

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) are utilized to probe catalyst structures and surface species under reaction conditions. Kinetic studies using a flow reactor show that the PtNi/CeO₂ catalyst is more active and stable for both DRE and DRB. The formation of the PtNi alloy is observed by both the in-situ XRD and XAFS measurements. Ce³⁺ species under reaction conditions are identified by both in-situ XRD and AP-XPS. DFT calculations are performed to further understand the reaction mechanisms. The improved activity and stability of PtNi/CeO₂ over the corresponding monometallic catalysts can be attributed to the formation of the Pt-rich PtNi bimetallic surface, which decreases the activation energy of C-C bond scission and weakens the binding strength of adsorbed oxygenates.

2. EXPERIMENTAL AND THEORETICAL METHODS

2.1. AP-XPS on Model Surfaces

Thin films of PtNi/CeO₂, Pt/CeO₂ and Ni/CeO₂ were prepared by depositing small coverages of PtNi, Pt, or Ni (0.1 ML) onto a CeO₂ film (3 ML) over a TiO₂(110) substrate at 303 K. After sample preparation, survey scans in XPS were recorded at a photon energy of 700 eV. During the reaction, the C1s peaks in XPS were recorded at a photon energy of 538 eV. All reported binding energies were calibrated with the Au4f_{7/2} peak of a gold foil at 84.0 eV. Low pressure CO₂ (100 mTorr) and butane (200 mTorr) were leaked into the chamber and the subsequent surfaces with adsorbates were heated to 723 K. The surface carbon species generated by activation of CO₂ and butane were probed by XPS spectra, which were taken at 303 K (before

reaction) and 723 K (under reaction).

2.2. Preparation and Characterization of Supported Catalysts

The PtNi/CeO₂ bimetallic catalyst (1.7 wt% for Pt and 1.5 wt% for Ni, corresponding to an atomic ratio of 1:3 for Pt:Ni) and Pt/CeO₂ (1.7 wt% for Pt), Ni/CeO₂ (1.5 wt% for Ni) monometallic catalysts were synthesized by incipient wetness impregnation^{15, 16} over as-is commercial support (CeO₂, 35-45 m²/g, cubic, Sigma-Aldrich) with an aqueous solution of the respective metal precursors ((NH₃)₄Pt(NO₃)₂ and Ni(NO₃)₂·6H₂O from Alfa Aesar).

Pulse CO chemisorption was performed using an Altamira AMI-300 ip catalyst characterization system to measure the number of reduced metal sites (i.e., active sites) on each supported catalyst. Temperature Programmed Reduction (TPR) experiments using H₂ were carried out in the same Altamira AMI-300ip instrument to compare the reducibility of active metals in the supported catalysts.

In-situ XRD measurements of the PtNi/CeO₂ catalyst were performed using an amorphous silica capillary mounted to a flow cell setup, as described in detail in previous work^{17, 18}. During the measurement, a gaseous mixture of C₂H₆, CO₂, and He of volume ratio of 1:5:4 was passed through the capillary at a total flow rate of 10 ml/min. Temperature was increased from 300 K to 873 K at a rate of 10 K/min, then held at 873 K for 30 min before being ramped down to room temperature.

The in-situ Pt L3 edge (11564 eV) and Ni K edge (8333 eV) XAFS spectra were collected at beamline 2-2 of Stanford Synchrotron Radiation Lightsource (SSRL). 50

mg PtNi/CeO₂ powder catalyst (60-80 mesh) was loaded into a 3 mm OD glassy carbon tube, packed by quartz wools at both sides of the sample. The sample was first reduced in H₂/He flow (10 ml/min each) at 723 K for 30 min. To avoid the thermal disturbance at high temperature, the spectra (3 scans) were collected after the sample was cooled down to 373 K in the H₂/He flow. After measurement, the gas was switched to a mixture of reactants (10 ml/min CO₂, 5 ml/min C₂H₆ and 5 ml/min He), then the sample was heated to 873 K at a rate of 20 K/min. After 60 min reaction, the sample was cooled to 373 K in the CO₂/C₂H₆/He flow to take the XAFS spectra (3 scans). The data were treated using IFEFFIT package. Pt foil and Ni foil were employed as references of EXAFS fitting.

DRIFTS experiments were performed using an FTIR spectrometer (Thermo, Nicolet 6700). The background spectrum for each catalyst was recorded at room temperature after reduction in a 25% H₂/75% He mixture at 673 K. Following reduction, the sample was treated with a 25% CO/75% He mixture, then finally pure He. The sample spectrum was recorded after purge the reaction cell with He for 15 min.

Flow reactor studies of DRE and DRB over CeO₂ supported catalysts were performed in a quartz tube reactor with an inner diameter of 4 mm under atmospheric pressure. Catalysts were reduced under a H₂/Ar mixture at 873 K for 1 h prior to reaction. For steady-state measurements, the catalysts were held at 873 K for over 13 h. Then, the reaction temperature was changed from 873 K to 843 K with 5 K increments, in order to study the effect of temperature on the reaction rate of CO₂ and

ethane/butane as well as to obtain the apparent activation energies. More details about the experimental methods are provided in the Supporting Information (SI) Section S2.

2.3. DFT Calculations

Periodic self-consistent DFT^{19, 20} total energy calculations were carried out using the Vienna *Ab-initio* Simulation Package (VASP) code.^{21, 22} The Kohn-Sham one-electron wave functions were expanded by using a plane wave basis set with a kinetic energy cutoff of 400 eV. The Brillouin zone was sampled using a 3×3×1 Monkhorst-Pack k-point grid.²³ The exchange-correlation energy was described using projector augmented wave (PAW) potentials with the generalized gradient approximation (GGA)^{24, 25} using PW91 functionals²⁶. The spin polarized DFT calculations were performed to account for the magnetic nature of Ni atoms.

The Pt(111) and Ni(111) surfaces were modeled using a four layer 3×3 unit cell and the Pt-terminated-PtNi-Pt(111) surface was modeled by replacing subsurface (2nd layer) Pt atoms of the Pt(111) slab by Ni atoms. The mixed-PtNi-Pt(111) surface was modeled using a four layer 4 × 4 surface slab and it was modeled by replacing half of the Pt atoms in the top two layers of the Pt(111) surface with Ni atoms. A vacuum layer of ~14 Å thick was added in the unit cell along the direction perpendicular to the surface. During structure optimization calculations, the positions of the atoms in the bottom two surface layers were fixed while the positions of all the other atoms were fully relaxed until the Hellman-Feynman force on each ion was smaller than 0.02 eV/Å. The binding energy of an adsorbate is calculated as

$$BE_{adsorbate} = E_{slab+adsorbate} - E_{slab} - E_{adsorbate} \quad (3)$$

where $E_{slab+adsorbate}$, E_{slab} , and $E_{adsorbate}$ are the total energies of slab with adsorbate, clean slab, and adsorbate species in the gas phase, respectively.

3. RESULTS

3.1. AP-XPS on Model Surfaces

Figure 1 compares the XPS results of PtNi/CeO₂, Pt/CeO₂ and Ni/CeO₂ model surfaces after sample preparation and under reaction conditions. Due to the stronger interaction of butane over ethane with the model surfaces, the reaction of butane with CO₂ was investigated using AP-XPS. During the reaction, the chamber was filled with 100 mTorr CO₂ and 200 mTorr butane. CeO₂ was deposited on a TiO₂(110) substrate by physical vapor deposition of Ce under O₂ atmosphere. After the deposition of approximately 3 layers of CeO₂, Ti3p from the TiO₂ substrate is still visible in the spectra. After depositing CeO₂ multiple Ce 4d peaks, due to spin-orbit splitting in the 4d orbitals, and different 4f orbitals²⁷ are observed. The peaks at 125.5 and 122.2 eV are originated from the final state without any f electron (f^0), which is the typical XPS feature of CeO₂. Under reaction conditions, the features at 125.5 and 122.2 eV decrease in intensity, indicating that some of the Ce⁴⁺ are reduced to Ce³⁺. After sample preparation, the oxidation of the active metals (Pt and Ni) was found for all surfaces. Reduction of metals (shifting to lower binding energy in XPS) was observed after reaction for all catalysts except for the Ni of Ni/CeO₂. Interestingly, the Ni of PtNi/CeO₂ was reduced to Ni⁰, indicating that the presence of Pt promotes Ni

reduction.

Figure 2 shows the C1s region for carbon species in the gas phase and the surface adsorbates on PtNi/CeO₂, Pt/CeO₂ and Ni/CeO₂. After introducing 100 mTorr CO₂ and 200 mTorr butane at 303 K, three C1s peaks are observed and their intensities vary for each surface. The peak at 292.4–292.6 eV is due to gas phase CO₂. The peak at 285.2 eV is assigned to gas phase butane. The peak at 288.8–289.2 eV could be assigned as carbonate and carboxyl (CO₂^{δ-}), which have been identified by combined XPS and infrared reflection-absorption spectroscopy (IRRAS) measurements.²⁸ The observation of carbonates/carboxyl indicates that all three surfaces effectively activate CO₂.

Figure 1. AP-XPS of model thin film catalysts as prepared (303 K, blue line) and under reaction conditions (723 K, red line) after the exposure of 200 mTorr butane and 100 mTorr CO₂: (a) PtNi/CeO₂, (b) Pt/CeO₂, and (c) Ni/CeO₂

Figure 2. AP-XPS of C1s region for (a) PtNi/CeO₂, (b) Pt/CeO₂ and (c) Ni/CeO₂ before reaction (303 K, blue line) and under reaction conditions (723 K, red line) after the exposure of 200 mTorr butane and 100 mTorr CO₂

The C1s spectra in red are the surface species after the surfaces were heated to 723 K in the CO₂/butane mixture. Under reaction conditions there are mainly two peaks (289.8 and 284.5 eV) in the C1s spectra. The feature due to gas phase CO₂ is barely visible, indicating that the reaction consumed most the CO₂ near the surface. The peak at 289.8 eV could be assigned to the adsorbed formate,²⁹ which was formed through the hydrogenation of adsorbed carbonate and carboxylate species. The unsymmetric peak at 284.5 eV with its shoulder at 286.0 eV is assigned to the adsorbed O-C_xH_y species, generated from butane decomposition and surface oxidation at high temperatures. It is worth noting that the peak intensity of the adsorbed O-C_xH_y varies for different surfaces, following the trend of PtNi/CeO₂ > Ni/CeO₂ > Pt/CeO₂. This indicates that Ni is more active than Pt and the formation of the PtNi bimetallic surface further improves the activation of butane.

3.2. Supported Catalysts

3.2.1. TPR

TPR profiles of the three catalysts are shown in Figure 3. The profile of the Pt/CeO₂ catalyst shows two peaks at 370 and 390 K. The peak at 370 K is assigned to the reduction of surface PtO_x in contact with Pt⁰ species;³⁰ the peak at 390 K is attributed to the reduction of PtO_x species formed during the calcination step.³¹ A reduction peak at 561 K is observed for the Ni/CeO₂ catalyst, which can be assigned to the reduction of NiO particles.³² The PtNi/CeO₂ catalyst exhibits reduction peaks pertaining to PtO_x (387 K) and NiO (539 K). Compared to the monometallic Ni/CeO₂

catalyst, the reduction peak at 561 K is shifted to 539 K for the bimetallic catalyst. This indicates that the reduction of NiO species is promoted by the co-impregnated Pt. This suggests a synergistic interaction between the two metals, as indicated by the AP-XPS results in Figure 1. The formation of the bimetallic alloy on PtNi/CeO₂ after reduction in hydrogen was confirmed in our previous work¹⁵ by Extended X-ray absorption fine structure (EXAFS) characterizations.

Figure 3. TPR profiles ($m/e = 18$, corresponding to production of H₂O) for comparison of PtNi bimetallic catalyst (black line) with respective monometallic catalysts (Pt, blue line; Ni, red line)

3.2.2. In-situ XRD Characterization on PtNi/CeO₂ catalyst

The XRD pattern of the as-prepared PtNi/CeO₂ sample reveals that it contains crystalline CeO₂ with an average crystallite size of 19 nm. The size was calculated from the refined peak profile parameters using the GSAS software. Barely seen in the 2 θ range of 7° to 9° are two humps that can be assigned to the (111) and (200) reflections of NiO, as shown in the inset in Figure 4. XRD signatures of Pt or Pt oxides are not observed in the starting sample. Also plotted in Figure 4 is the XRD pattern after the reaction with CO₂ and ethane in the in-situ XRD cell. The main differences are the appearance of three weak peaks between 8°-9° of 2 θ . The one at 8.2° is assigned to the Pt(111) reflection and the calculated lattice constant using this diffraction peak is 3.924 Å, the same value as that of bulk Pt metal. The peak at 8.8° is assigned to the Ni(111) reflection, based on which the calculated lattice constant is 3.578 Å. This is slightly larger than the value of 3.527 Å for bulk Ni. The larger Ni cell parameter measured in this sample may indicate that the Ni particles are alloyed with Pt, or it is from the effect of being nano-particle sized. The peak in the middle of the three, at 8.5°, is not indexed to any known phases of Pt, Ni, Ce or their oxide forms. Considering that the position is between the Pt(111) and Ni(111) peaks, it is likely that the peak at 8.5° is associated with the formation of the PtNi alloy.

Figure 4. XRD profiles of PtNi/CeO₂ bimetallic catalyst before (blue line) and after reaction (red line)

Figure 5. Change of the CeO₂ lattice constant (a) and peak intensity of various phases (b) and evolution of XRD profiles between 7° and 9° (c) with the increase of temperature under the reaction atmosphere of CO₂ with ethane

The change of the CeO₂ lattice constant and the evolution of XRD profiles between 7° and 9° following the reaction of CO₂ with ethane are plotted as a function of reaction temperature in Figure 5. As shown in Figure 5(a), an abrupt lattice expansion occurred between 523 and 583 K, on top of an upward-sloping background line from the thermal effect. The abrupt expansion of the CeO₂ lattice corresponds to an increase of the average Ce-O bond length, indicating a partial reduction of Ce⁴⁺ to Ce³⁺.

As can be seen from the evolution of the hump centered at 8.2°, the reduction of amorphous Pt oxides starts at a temperature as low as 443 K. The reduction of the NiO phase can be tracked by following its (111) peak at 7.5° or Ni (111) peak at 8.8°, which does not show a clear decrease in intensity until above 533 K. The formation of the PtNi alloy (a broad hump centered at 8.5°) can be observed once the Pt oxides are reduced. This indicates that metallic Pt facilitates the reduction of NiO to Ni by decreasing the reduction temperature, where bulk NiO is usually reduced at around 673 K.³³ This observation is consistent with the TPR results (Figure 3) which illustrate that the presence of Pt decreases the reduction temperature of NiO. Moreover, the fact that the reduction temperature of surface CeO₂ (523-583 K) is much lower compared to 723 K, the reduction of pure ceria,³⁴ may also be attributed to the presence of Pt.

3.2.3. In-situ XAFS measurement on PtNi/CeO₂ catalyst

As shown in Figure 6, the Pt L3 edge and Ni K edge XANES spectra of

PtNi/CeO₂ catalyst indicated that the active metals were reduced after 723 K H₂ treatment. The XANES spectra also suggest that the valence state and local structure of both Pt and Ni remain relatively stable under reaction conditions at 873 K, although a slight increase at the “white-line” was observed. Detailed EXAFS fittings of the Pt L3 edge and Ni K edge spectra were carried out to investigate the specific structure of Pt and Ni in the PtNi/CeO₂ catalyst (Table 1). After H₂ reduction at 723 K, the Pt L3 edge EXAFS fitting results suggest that Pt atoms form chemical bonds with both Pt (2.70 Å) and Ni (2.58 Å). The corresponding coordination number (CN) of Pt-Pt and Pt-Ni shells are determined to be 2.6 and 6.4, respectively. The relatively large CN of Pt-Ni compared to that of Pt-Pt demonstrates that Pt forms alloy with Ni in which the Pt-Ni intermetallic coordination is the main component of Pt local environment. This conclusion is also confirmed by the Ni K edge fitting results (Ni-Pt with bond length of 2.58 Å and CN of 3.2). Under the reaction conditions, the Pt-Ni shell is still observed with bond length of 2.57 Å and CN of 8.8. Meanwhile, Ni-Pt is also one of the main components at the Ni K edge spectrum, suggesting that the bimetallic particle is still in the form of Pt-Ni alloy.

Table 1. EXAFS fitting results of the PtNi/CeO₂ catalyst under reduction and reaction conditions

Sample	Edge	Shell	Bond length (Å)	Coordination Number	σ^2 (Å ²)	E ₀ shift (eV)
PtNi/CeO ₂	Pt L3 edge	Pt-Pt	2.70±0.02	2.6±0.8	0.003	-0.1

after reduction	Ni K edge	Pt-Ni	2.58±0.01	6.4±1.0	0.007	0.3
		Ni-Pt	2.58±0.01	3.2±1.4	0.007	
		Ni-Ni	2.47±0.01	7.2±1.9	0.006	
PtNi/CeO ₂ under reaction	Pt L3 edge	Pt-Pt	-	-	-	9.4
		Pt-Ni	2.57±0.01	8.8±1.4	0.008	
		Ni-Pt	2.57±0.01	5.8±1.7	0.008	-9.4
	Ni K edge	Ni-Ni	2.51±0.01	6.2±1.7	0.007

Figure 6. XAFS characterization of PtNi/CeO₂ catalyst after reduction and under reaction conditions: (a) Pt L3 edge and (b) Ni K edge XANES spectra of fresh,

reduced and under reaction catalysts with Pt/Ni foil reference; (c) Pt L3 edge and (d) Ni K edge EXAFS fitting results in R space

3.2.4. DRIFTS

The DRIFT spectra following the adsorption of CO at room temperature are compared for the reduced Pt/CeO₂, Ni/CeO₂, and PtNi/CeO₂ catalysts in the region of 2150–1750 cm⁻¹. As shown in Figure 7, adsorption of CO on Pt/CeO₂ produces two main bands at 2066 and 1965 cm⁻¹. The strong, broad band at 2066 cm⁻¹ is assigned to the linear (on top) CO species adsorbed on the terrace or step site of Pt⁰ atoms.³⁵ The band at 1965 cm⁻¹ and a weak band at 1882 cm⁻¹ are assigned to bridge-bonded CO species.³⁶⁻³⁸ However, the main CO absorption bands on Ni/CeO₂ are observed at 1967 and 1880 cm⁻¹, which can be assigned to bridge-bonded CO species. While the weak band at 2050 cm⁻¹ is attributed to linear-adsorbed CO on Ni.³⁹

A strong band at 2062 cm⁻¹ is observed on the bimetallic PtNi/CeO₂ catalyst, which is similar to the vibrational frequency of the Pt/CeO₂ catalyst. The absorption band corresponding to CO adsorption on Ni is largely suppressed and the band due to bridge-bonded CO species is weakened in the bimetallic sample. The comparison of the three spectra indicates that the PtNi bimetallic surface is much richer with Pt atoms, resulting from the formation of the Pt-dominant PtNi bimetallic surface on CeO₂. This is consistent with previous DFT studies of stable surface structures of Ni/Pt(111), predicting that a Pt-terminated bimetallic surface is thermodynamically stable after reducing the surface with H₂.⁴⁰

Figure 7. DRIFT spectra of CO adsorption on reduced PtNi bimetallic catalyst (black line) with respective monometallic catalysts (Pt, blue line; Ni, red line) at room temperature

3.2.5. Flow reactor evaluation

The conversions of CO₂ and ethane as a function of time on stream are shown in Figure 8 for bimetallic and monometallic catalysts at 873 K. The steady-state conversion, turnover frequency (TOF) and space-time yield (STY) are listed in Table 2. Two definitions of TOF, one is calculated by normalizing conversion with the CO uptake value of the freshly reduced catalyst (Table S1), and the other one is obtained by normalizing conversion with the loading amount of active metals for each catalyst, are adopted in this work. The activities of PtNi/CeO₂, Pt/CeO₂, and Ni/CeO₂ for DRB

are summarized in the same fashion, as shown in Figure 9 and Table 3.

Table 2. Summary of CO uptake and flow reactor results for CO₂ + ethane reaction (2:1 ratio, 20 ml/min CO₂ + 10 ml/min C₂H₆ + 50 ml/min Ar) at 873 K. Values of conversion, TOF and STY calculated by averaging data points between 11-13 h on stream

Catalyst		PtNi/CeO ₂	Pt/CeO ₂	Ni/CeO ₂
CO uptake value, $\mu\text{mol}\cdot\text{g}^{-1}$		25.4	14.3	15.2
Conversion, %	CO ₂	35.8	6.4	15.1
	C ₂ H ₆	28.1	3.1	9.4
TOF ₁ , $\text{time}\cdot\text{site}^{-1}\cdot\text{min}^{-1}$	CO ₂	561.9	180.2	395.6
	C ₂ H ₆	220.1	51.6	123.5
TOF ₂ , $\text{mol}\cdot\text{mol}_{\text{metal}}^{-1}\cdot\text{min}^{-1}$	CO ₂	41.7	30.1	23.5
	C ₂ H ₆	16.4	8.6	7.3
STY, $\text{mol}\cdot\text{mol}_{\text{metal}}^{-1}\cdot\text{min}^{-1}$	H ₂	33.3	4.8	9.8
	CO	73.8	45.2	37.4
	C ₂ H ₄	0.06	0.67	0.08

Table 3. Summary of flow reactor results for CO₂ + butane reaction (4:1 ratio, 20 ml/min CO₂ + 5 ml/min C₄H₁₀ + 55 ml/min Ar) at 873 K. Values of conversion, TOF and STY calculated by averaging data points between 11-13 h on stream

Catalyst		PtNi/CeO ₂	Pt/CeO ₂	Ni/CeO ₂
Conversion, %	CO ₂	18.5	0.6	12.1
	C ₄ H ₁₀	12.4	0.9	8.6
TOF ₁ , time·site ⁻¹ ·min ⁻¹	CO ₂	551.7	31.3	628.0
	C ₄ H ₁₀	91.9	12.0	111.9
TOF ₂ , mol·(mol metal) ⁻¹ ·min ⁻¹	CO ₂	41.0	5.2	37.3
	C ₄ H ₁₀	6.8	2.0	6.6
STY, mol·(mol metal) ⁻¹ ·min ⁻¹	H ₂	18.1	0.0	18.0
	CO	69.0	7.5	63.4
	C ₄ H ₈	0.12	0.51	0.11

Tables 2 and 3 show that the steady-state conversions of CO₂ and ethane/butane on the bimetallic catalyst are higher than the sum of those on the corresponding monometallic catalysts. Furthermore, the TOF values and STYs of products in Table 2 clearly suggest that the PtNi/CeO₂ catalyst has much higher activity for the DRE reaction, compared to the monometallic catalysts. As shown in Table 3, the PtNi/CeO₂ catalyst also presents the highest activity for DRB reaction on the basis of active metal loading amount, though its activity is only slightly higher than that of Ni/CeO₂.

As shown in Figure 8, the steady-state ethane conversion on the Pt/CeO₂ and Ni/CeO₂ monometallic catalysts decreases by about 46% and 38%, respectively, compared to their initial value. The corresponding value for the bimetallic catalyst declines by a lower extent, 28%. The same trend is observed in Figure 9 which shows that the decrease in catalytic activity for butane conversion on PtNi/CeO₂ (17%) is

less than that on Pt/CeO₂ (38%) and Ni/CeO₂ (35%), illustrating that the PtNi/CeO₂ bimetallic catalyst is more stable.

Figure 8. Conversions of CO₂ (a) and ethane (b) on PtNi/CeO₂, Pt/CeO₂ and Ni/CeO₂ plotted versus time on stream for reaction of CO₂ and ethane (2:1 ratio, 10 ml/min CO₂ + 5 ml/min C₂H₆ + 25 ml/min Ar) at 873 K

Figure 9. Conversions of CO₂ (a) and butane (b) on PtNi/CeO₂, Pt/CeO₂ and Ni/CeO₂ plotted versus time on stream for reaction of CO₂ and butane (4:1 ratio, 12 ml/min CO₂ + 3 ml/min C₄H₁₀ + 25 ml/min Ar) at 873 K

The reaction rates of CO₂ and ethane, as well as that of CO₂ and butane on PtNi/CeO₂, Pt/CeO₂, and Ni/CeO₂ at different temperatures after 13 h operation are plotted as a function of 1/T in Figure 10 and Figure 11, respectively. It is apparent that the PtNi/CeO₂ bimetallic catalyst is more active for both DRE and DRB reactions over a wide range of temperatures. The apparent activation energies on these three supported catalysts for both CO₂ and ethane/butane can be estimated from the Arrhenius plot. For the DRE reaction, the apparent activation energy on the bimetallic

catalyst is much lower than the two on the monometallic catalysts, indicating that the ethane reforming activity is greatly improved over the bimetallic catalyst. For the DRB reaction, the apparent activation energy on the PtNi/CeO₂ and Ni/CeO₂ catalysts are almost the same, while the Pt/CeO₂ catalyst shows a very low butane reforming activity. In most cases, the activation energy of CO₂ is smaller than the corresponding value of ethane/butane. This is due to the fact that the reforming reaction is always accompanied with the reverse water gas shift (RWGS) reaction, and its activation barrier is much lower than that of the dry reforming reactions (Figures S2 and S3). Previous studies have shown that CO₂ activation by H₂ occurs readily at 573 K over PtNi/CeO₂.^{8, 15} In comparison, the dry reforming reactions (activation of CO₂ by ethane and butane) require significantly higher temperatures, suggesting that the activation of alkane should be a key step for dry reforming over the PtNi/CeO₂ catalyst.

Figure 10. Arrhenius plot for reaction rate of CO₂ (a) and ethane (b) on PtNi/CeO₂, Pt/CeO₂ and Ni/CeO₂ at different temperatures with 5 K temperature increment

Figure 11. Arrhenius plot for reaction rate of CO₂ (a) and butane (b) on PtNi/CeO₂, Pt/CeO₂ and Ni/CeO₂ at different temperatures with 5 K temperature increment

3.3. DFT Calculations

In order to further understand the bimetallic effects, the binding energies of potential reaction intermediates for the C-C bond cleavage in ethane (listed in Table 4) are calculated on Pt(111), Ni(111), Pt-terminated-PtNi-Pt(111) and mixed-PtNi-Pt(111) surfaces. Herein, the surface models without the support (CeO₂) are used to study the oxidative C-C bond cleavage of ethane as our previous study showed that such models are adequate to identify the trend in energy profiles for the C-C bond cleavage in ethane.⁸ The DFT calculated binding energies in Table 4 show

that O-bound surface species, O, CH₃CH₂O, CH₃CHO and CH₃CO (Figure 12), bind more strongly on Ni(111) than on Pt(111). In contrast, C-bound surface species, CH₃ (Figure 12), bind more strongly on Pt(111) than on Ni(111). In comparison, on the Pt-terminated-PtNi-Pt(111) surface, the binding strength of all intermediates is generally weaker than on both Pt(111) and Ni(111) surfaces. It is also noted that the binding energies of the intermediates on the mixed-PtNi-Pt(111) surface are very close to those on the Ni(111) surface due to the presence of Ni on the surface. Thus the mixed-PtNi-Pt(111) surface is predicted to show similar activity/selectivity in ethane reforming reaction with the Ni(111) surface.

Table 4. DFT calculated binding energies (in eV) of potential ethane reforming intermediates and atomic O on Pt(111), Ni(111), Pt-terminated-PtNi-Pt(111) and mixed-PtNi-Pt(111) surfaces

Species	Pt(111)	Ni(111)	Pt-terminated-PtNi-Pt(111)	mixed-PtNi-Pt(111)
CH ₃ CH ₂ O	-1.62	-2.70	-1.33	-2.78
CH ₃ CHO	-0.31	-0.50	-0.23	-0.86
CH ₃ CO	-2.36	-2.10	-1.97	-2.67
CH ₃	-2.11	-2.04	-1.78	-2.08
CO	-1.76	-1.94	-1.27	-1.87
O	-4.11	-5.33	-3.61	-5.14

The change in binding energies along with a potential reforming pathway for ethane, via the C-C bond cleavage leading to products *CH₃, *CO and H₂(g), is

calculated on Pt(111), Ni(111), Pt-terminated-PtNi-Pt(111) and mixed-PtNi-Pt(111) surfaces in the presence of pre-adsorbed O atoms. The DFT-calculated energy diagrams show that the C-C bond cleavage (via the pathway in Figure 13) is energetically least favorable on Ni(111) and most favorable on Pt-terminated-PtNi-Pt(111), while Pt(111) lies in between Ni(111) and Pt-terminated-PtNi-Pt(111). In contrast, mixed-PtNi-Pt(111) lies very close to Ni(111) in Figure 13. Therefore the DFT calculations predict that Pt-terminated-PtNi-Pt(111) would show better activity for ethane reforming than Pt(111) and Ni(111). It is noted that the catalytic activity predicted on the basis of DFT-calculated thermodynamics decreases with O binding energy. Surfaces that bind O strongly are less active than the surfaces that bind O weakly for O-assisted ethane reforming (via the pathway shown in Figure 13). Ni(111) binds O most strongly and is predicted to be least active for ethane reforming while Pt-terminated-PtNi-Pt(111) binds O most weakly and is predicted to be most active among Pt, Ni, Pt-terminated-PtNi-Pt(111) and mixed-PtNi-Pt(111) surfaces.

Figure 12. DFT optimized structures. Side and top views of (a) Pt-terminated-PtNi-Pt(111) and (b) mixed-PtNi-Pt(111) slabs. Side and top views of (c) O, (d) CO, (e) $\text{CH}_3\text{CH}_2\text{O}$, (f) CH_3CHO , (g) CH_3CO and (h) CH_3 on Pt-terminated-PtNi-Pt(111) surface. Binding geometries of all intermediates on Pt(111), Ni(111) and mixed-PtNi-Pt(111) surfaces are similar to those shown here on Pt-terminated-PtNi-Pt(111) surface. Light grey: Pt, green: Ni, dark grey: C, red: O and blue: H, respectively

Figure 13. DFT calculated energy profiles of reforming of ethane on Pt(111), Ni(111), Pt-terminated-PtNi-Pt(111) and mixed-PtNi-Pt(111) surfaces

4. DISCUSSION

Results from both model surfaces and supported catalysts reveal that the PtNi/CeO₂ bimetallic catalyst shows higher activity than the corresponding monometallic catalysts. The AP-XPS measurements for butane reforming on the PtNi/CeO₂ model surface show that the presence of Pt promotes Ni reduction, suggesting a synergistic interaction between the two metals during the high temperature reaction. This PtNi/CeO₂ model surface then exhibits the highest extent of butane activation and results in the most intense C1s peak of the adsorbed O-C_xH_y, indicating that the formation of the PtNi bimetallic surface enhances the activity in activating butane. The model surface results are well supported by DFT calculations of the O binding energy on different surfaces for the reaction of ethane. For O-assisted

ethane reforming, the weaker surface O binding strength makes adsorbed O more reactive to form the C-O bond (i.e., O-C_xH_y species). Therefore, the Pt-terminated-PtNi-Pt(111) surface that binds O most weakly is predicted to be the most active for alkane reforming compared to Pt and Ni surfaces.

The presence of Pt can facilitate the reduction of NiO and surface CeO₂ species (from Ce⁴⁺ to Ce³⁺) by decreasing the reduction temperature on the supported PtNi/CeO₂ bimetallic catalyst, observed in the TPR experiments and in-situ XRD characterization. The reduced state of CeO₂ shows a strong tendency to react with CO₂ and promotes its dissociation,^{12,14} leading to a higher CO₂ activation. The formation of the PtNi alloy under reaction condition was evidenced with the detection of the reflection peak at 8.5° in the in-situ XRD measurements, as shown Figure 4. The formation of the PtNi alloy after H₂ reduction at 723 K and under reaction conditions at 873 K was further confirmed by in-situ XAFS characterizations. The XANES spectra suggested that the valence state and local structure of both Pt and Ni under both conditions were basically the same. Detailed EXAFS fittings of Pt L3 edge and Ni K edge spectra revealed the formation of the PtNi alloy, indicating that Pt-Ni intermetallic coordination was the main component of the Pt local environment while Ni-Pt was also one of the main components of the Ni local environment. The supported PtNi bimetallic catalyst shows a Pt-like CO binding behavior (DRIFT spectra in Figure 7), suggesting that the PtNi bimetallic alloy has a Pt-rich surface. Pt-terminated-PtNi-Pt(111) and mixed-PtNi-Pt(111) surfaces were therefore employed as different simplified parts of the Pt-rich bimetallic surface. The calculated

energy required for C-C bond breakage for the DRE reaction via the pathway shown in Figure 13 follows the trend of $\text{PtNi/CeO}_2 < \text{Pt/CeO}_2 < \text{Ni/CeO}_2$, which is consistent with the trend of ethane reforming activities in terms of the steady-state formation rate of CO in the flow reactor tests (73.8, 45.2, and 37.4 $\text{mol} \cdot \text{mol}_{\text{metal}}^{-1} \cdot \text{min}^{-1}$ for PtNi/CeO_2 , Pt/CeO_2 and Ni/CeO_2 , respectively). Furthermore, DFT calculations show that the bimetallic surface binds C most weakly, which potentially reduces the stability of deposited carbon atom on the surface. This could enhance the resistance to coke formation and is consistent with the experimental observation of a higher steady-state stability of the bimetallic PtNi/CeO_2 catalyst (Figures 8 and 9).

As listed in Table S1, the CO uptake values of the spent PtNi/CeO_2 catalysts after oxygen treatment (to completely remove carbon deposits on the surface) for DRE and DRB are almost the same as those of the freshly reduced catalysts, suggesting that the deactivation of the bimetallic catalyst is mainly caused by coking on the surface rather than sintering of the active metals. The conclusion is further confirmed by both EDX-STEM mappings (Figure S4) and TEM images (Figure S5) of the reduced and spent PtNi/CeO_2 catalysts for both DRE and DRB reactions. The EDX element mappings show that the active metals, Pt and Ni, are still well dispersed on the spent sample even though a very small agglomeration of Ni is observed. The average metal particle sizes estimated from the TEM images are 2.3, 2.3 and 2.5 nm for reduced, spent PtNi/CeO_2 catalysts for DRE and for DRB, respectively, indicating that the metal particle sintering was almost negligible during the reaction. The CO uptake value of the spent PtNi/CeO_2 catalysts for the DRE reaction before oxygen treatment

is 13.7 $\mu\text{mol CO/g catalyst}$, suggesting that about 40% of the active sites on the spent catalyst was covered by carbon deposits. The CO uptake value of the spent PtNi/CeO₂ catalysts after oxygen treatment is 22.6 $\mu\text{mol CO/g catalyst}$, which is very close to that of the fresh sample, suggesting that the sintering of the active metals is not significant. According to the TPO-TGA results (Figure S6), three types of carbon deposits on the spent PtNi/CeO₂ catalyst for the DRE reaction are identified by its distinct peaks (peak 1 at 664, peak 2 at 767 and peak 3 at 846 K). All these carbon deposits could be removed in the air flow below the reaction temperature (i.e., 873 K), indicating that the in-situ regeneration of the spent PtNi/CeO₂ catalyst can be easily achieved.

Although DRB is thermodynamically more favorable than DRE, the catalytic activity evaluation on the PtNi/CeO₂ bimetallic catalyst shows an opposite trend. The steady-state formation rate of CO, which represents the activity of the dry reforming reaction, are 73.8 and 69.0 $\text{mol}\cdot\text{mol}_{\text{metal}}^{-1}\cdot\text{min}^{-1}$ over PtNi/CeO₂ in DRE and DRB, respectively. The apparent activation energy on the bimetallic catalyst at steady-state also follows the reverse trend of DRE (71.6 kJ/mol) < DRB (101.8 kJ/mol), which indicates that DRE is kinetically more favorable than DRB.

5. CONCLUSIONS

Dry reforming of ethane and butane are studied on the PtNi/CeO₂ bimetallic catalyst and the corresponding monometallic catalysts using model surfaces and supported catalysts. The results show that the bimetallic catalyst presents an enhanced

reforming activity over the monometallic catalysts. Results from DFT calculations and in-situ experimental measurements indicate that the enhanced activity of bimetallic catalyst is attributed to the formation of the Pt-Ni bimetallic bonds. DFT calculations show that the Pt-dominant bimetallic surface would not only weaken the surface O binding strength to improve the activity, but also reduce the stability of deposited carbon atom to potentially improve the stability. Results from the current study also demonstrate the importance of combining DFT calculations, in-situ characterization, and reactor evaluation for understanding catalytic properties of bimetallic catalysts.

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Supporting Information. Thermodynamic analysis for DRM, DRE and DRB; Model surfaces preparation; Supported catalyst preparation and characterizations: pulse CO chemisorption, TPR, in-situ XRD, DRIFTS, flow reactor evaluation, EDX-STEM mappings, TEM images, and TGA. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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