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# Coupling of Methane to Ethane, Ethylene and Aromatics over Nickel on Ceria-Zirconia at Low Temperatures

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**Abstract:** Methane is converted over nickel on ceria zirconia (Ni/CZ) to ethane, aromatics and hydrogen at steady state up to the thermodynamic limit at temperatures of 350 °C to 500 °C. At 450 °C and 500 °C, traces of ethylene are also produced. Ni/NiO particles activate methane and couple the resulting surface species to hydrocarbon products. Large Ni particles are responsible for the formation of carbonaceous deposits. In addition, aromatics are formed on these sites. Smaller Ni/NiO particles are responsible for the formation of ethane and ethylene and appear to provide sustained activity. On these sites, surface species couple into higher alkyl chains, which can be desorbed as ethane. It is suggested that these Ni sites are too small to assemble aromatic deposits and hence, they remain active throughout the reaction.

#### Introduction

The world is continuing its reliance on hydrocarbons as feedstocks for chemicals and fuels, especially with the discovery of increasingly abundant sources of natural gas in shale and offshore gas fields. Therefore, many efforts have been made to utilize methane, which is the main constituent of natural gas.<sup>[1-16]</sup>

Methane is a very stable molecule with four equivalent C-H bonds, which each have a bond energy of 438.8 kJ/mol.<sup>[17]</sup> The C-H bonds in methane are stronger than the ones in the possible products (hydrocarbons or oxygenates), which means that the products will be more reactive than methane.<sup>[17]</sup> Consequently, controlling the selectivity of methane conversion is a much bigger challenge than achieving high reactivity.

Several different approaches based on catalysis and reaction engineering have been proposed and reported, which can be grouped into two. The first one consists of indirect routes, in which methane is reformed into synthesis gas, which is further converted into useful chemicals and fuels like alkanes and oxygenates.<sup>[1-4]</sup> The second type of process involves a direct conversion of methane into C<sub>2+</sub> hydrocarbons and oxygenates without the production of syn-gas as an isolated intermediate.<sup>[5, 11, 12, 16, 17]</sup> Today, all large-scale commercial processes for

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natural gas conversion are performed through the indirect route.<sup>[1, 3, 4, 11, 14]</sup> Some of the large volume products from synthesis gas are methanol and longer chain hydrocarbons, which are produced through Fischer-Tropsch synthesis.<sup>[18-19]</sup> Over the past years, several commercial plants for Fischer-Tropsch synthesis (FTS) were built.<sup>[20]</sup> While this approach is in principle feasible for upgrading methane, the initial methane reforming step is extremely energy intensive, and FTS plants require large capital investment and a significant scale to be economically viable.<sup>[18]</sup> In particular, this limits the utilization of remote and inconveniently located natural gas fields, which accounts for a significant percentage of the world's reserves.<sup>[21]</sup>

A great motivation therefore still exists to develop processes for direct conversion of methane to value-added products without synthesis gas as an intermediate. For direct conversion of methane to higher hydrocarbons, two main reaction pathways have been considered in the literature, which are differentiated by the presence or absence of an oxidant. Oxidative coupling of methane (OCM) was intensely investigated in the mid-1980s to the mid-1990s.<sup>[22-23]</sup> This reaction, although thermodynamically favorable, suffers from selectivity issues due to over-oxidation to  $CO_2$ . No catalyst has been able to reach a  $C_{2+}$  yield higher than 30% and selectivity to  $C_{2\star}$  hydrocarbons higher than 80%.  $^{[17,\,23]}$ An alternative strategy is the production of higher hydrocarbons from methane in the absence of oxygen, so called non-oxidative coupling of methane (NOCM).<sup>[2, 24-27]</sup> Since there is no oxidizing agent in this reaction, over-oxidation is not an issue, and a high selectivity to C<sub>2+</sub> hydrocarbons could be attained. However, this reaction is thermodynamically limited because it is missing the coupled oxidation reaction as a driving force.

Various attempts to accomplish the NOCM reaction used classical and sometimes ill-defined heterogeneous catalysts in multistep processes: (i) methane dissociation on Ru or Pt particles by chemisorption (and stepwise surface carbon-carbon bond formation) and (ii) liberation of products by hydrogenation.<sup>[25, 27]</sup> Due to the thermodynamic constraints of NOCM, a number of researchers used very high temperatures (> 800 °C) to perform a direct conversion of methane to higher alkanes and aromatics.<sup>[2, 24]</sup> Isolated iron sites embedded in a silica matrix<sup>[2]</sup> and molybdenum oxide nanostructures in zeolites<sup>[24]</sup> were found to be the active sites for this reaction. However, the energy requirements for such processes are substantial, and it is challenging to avoid the formation of carbonaceous deposits and agglomeration of a highly dispersed active phase at such high temperatures. Another study demonstrated that a silica-supported tantalum hydride catalyst can directly couple methane into ethane at low temperatures up to the thermodynamic limit of the reaction.<sup>[26]</sup> The complex synthesis protocol to make the catalyst coupled with the unpredictable trend in tantalum price,<sup>[28]</sup> makes this material not very desirable for the preparation of industrial catalysts.

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Moreover, a steady decline in methane conversion was observed affording only a limited turnover number. Therefore, the development of a catalyst for non-oxidative coupling of methane with commercial viability still remains as a challenge.

Catalysts comprised of nickel particles on pure or doped ceria supports have been extensively used in the literature for the purpose of methane activation and reforming reactions.<sup>[29-32]</sup> This is because ceria and ceria-zirconia can stabilize small clusters of group 8, 9 and 10 metal nanoparticles with high thermal stability.<sup>[32]</sup> Typically, the supported metal nanoparticles act as the active sites for the activation of C-H bonds of hydrocarbons.<sup>[32]</sup> A study of the effect of the ceria to zirconia ratio on the performance of Ni/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> for steam reforming of methane revealed that higher thermal stability, higher redox properties, and smaller Ni crystallite size were some of the important descriptors for the performance of the catalysts.<sup>[33]</sup>

In this study, nickel supported on ceria-zirconia was used for methane activation and subsequent coupling to higher hydrocarbons and aromatics at temperatures not exceeding 500 °C. Continuous production of ethane up to the thermodynamic limit was observed over 2 wt.% Ni/CZ. Some ethylene and aromatics were also continuously produced.

#### **Results and Discussion**

**Structural and Textural Properties of the Catalysts.** The fractions of ceria and zirconia as determined by ICP-OES were 0.83 and 0.17, respectively. The actual content of nickel on ceria-zirconia (NiO/CZ) as determined by ICP-OES was 1.96 wt.% which is very close to the nominal value (Table 1).

Table 1. Physicochemical properties of ceria-zirconia based catalysts

whereas a concentration of 80 µmol.g<sup>-1</sup> was observed for NiO/CZ, indicating that the NiO clusters are Lewis acidic.<sup>[4]</sup> The characteristic band of pyridinium ions protonated on Brønsted acid sites was not observed for either sample.

The EDX maps of NiO/CZ revealed small and well-dispersed NiO particles on CZ (Figure 1). Specifically, NiO mainly existed as clusters below the detection limit of ~2-3 nm. The size of smaller particles cannot be determined reliably due to the limited stability of NiO clusters under high electron beam currents of modern EDX instruments. Nevertheless, the apparently uniform distribution of the Ni signal indicated well-dispersed NiO particles on the entire surface of the ceria-zirconia support, demonstrating that NiO clusters may be significantly smaller and that clusters containing only a few Ni atoms may be present. In addition to the small particles of NiO, some larger particles of up to 10 nm were observed. It is suggested that CZ stabilizes very small, well-dispersed nickel oxide clusters, which are capable of activating methane.<sup>[4]</sup> Previous studies showed that pure ceria can stabilize similar non-metallic Pt and Au species, which are very active for the water-gas shift reaction.[48]

**Reactivity for Coupling of Methane.** Previous studies showed that methane can be activated over NiO/CZ to form surface methyl groups, which can be further coupled to higher alkyl groups on the surface.<sup>[4]</sup> Based on this, it was hypothesized that higher hydrocarbons could be formed from methane over this catalyst. It was observed that these surface alkyl groups formed on NiO/CZ can be removed in high vacuum at 250 °C within 1 h as has been reported recently.<sup>[4]</sup> A similar desorption step should occur more readily at higher temperatures. However, the formation of higher alkanes (e.g., ethane) is thermodynamically limited (Table 2).

Table 1. Physicochemical properties of cena-zirconia based catalysis.										
Catalyst	Abbreviation	Metal loading (wt. %) <sup>a</sup>	Surface area (m <sup>2.</sup> g <sup>-1</sup> ) <sup>b</sup>	Average pore diameter (Å)°	Pore volume (cm <sup>3</sup> ·g <sup>-1</sup> ) <sup>d</sup>	LAS Conc. (µmol.g⁻¹)⁰	Dispersion <sup>f</sup>			
Ce <sub>0.83</sub> Zr <sub>0.17</sub> O <sub>2</sub>	CZ	N/A	85	66	0.097	3	N/A			
NiO/Ce <sub>0.83</sub> Zr <sub>0.17</sub> O <sub>2</sub>	NiO/CZ	1.96	78	69	0.098	80	0.26			

a Determined by ICP-OES analysis b Calculated from N<sub>2</sub> physisorption by BET method c calculated by BJH adsorption method d Determined by BJH cumulative pore volume e Determined by pyridine adsorption followed by FTIR spectroscopy f Dispersion of metal oxide determined from pyridine adsorption on Lewis acidic metal oxides

The X-ray diffraction patterns of CZ and NiO/CZ contained four prominent diffraction peaks associated with the (111), (200), (220), and (311) planes of CZ (Figure S1).<sup>[42-46]</sup> As in our previous work, all peaks in the diffractograms were attributed to the cubic fluorite phase of ceria-zirconia, indicating that no crystalline impurities were present.<sup>[35, 47]</sup> No peaks representative of the additional metal oxides were seen in the XRD patterns of NiO/CZ. This means that the NiO on CZ was well-dispersed. The crystallite size calculated by the Scherrer equation were approximately 8 nm for pure CZ as well as for NiO/CZ. The concentration of Lewis acid sites (LAS) on CZ as determined by pyridine adsorption followed by FTIR spectroscopy was very low (3 µmol.g<sup>-1</sup>),

During the conversion of methane at 450 and 500 °C, two distinct regimes were observed with a transition occurring after approximately 4 h. After activation in nitrogen, the conversion of methane at 350 – 500 °C initially increased with increasing time on stream. At 450 and 500 °C, it reached a maximum at 0.58  $\pm$  0.02% and 1.19  $\pm$  0.01%, respectively (Figure 2a). The conversion then declined and approached the thermodynamic limit for the conversion of methane to ethane. Specifically, the conversions of methane after 480 min at 500 °C, 450 °C and 350 °C were 0.39  $\pm$  0.01%, 0.26  $\pm$  0.04% and 0.11  $\pm$  0.02%, respectively, which is slightly lower than the equilibrium conversion for the reaction of methane to ethane (Table 2).

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The increase in methane conversion at the beginning is probably due to activation of the catalyst by progressive reduction of the NiO particles to metallic Ni (vide infra). The maximum of methane conversion in the earlier stages of the reactions at 450 and 500 °C is attributed to conversion of methane into aromatics and carbonaceous deposits, which were quantified based on the carbon balance and the oxidative formation of aromatics (Figure 2 b-d). The yield of hydrogen also went through a maximum in a similar fashion as the conversion of methane (Figure 2e) and the yield of carbon products (Figure S2), indicating that dehydrogenation of methane occurred as part of the formation of solid carbonaceous deposits (Table 2 Line 4), aromatics (Table 2, Line 5) and ethane (Table 2 Line 1). Multiple studies reported the formation of carbon nanotubes/nanofibers by methane dehydrogenation and C-C coupling over Ni based catalysts around 450 °C.[49-51] It is suggested that in the beginning of the reaction, the formation of the solid carbonaceous deposits can occur on Ni particles that are big enough for them to assemble, while smaller aromatic may also form on smaller NiO/Ni particles. An aromatic ring has a diameter of 0.45 nm,<sup>[52]</sup> but the minimum domain size for aromatization might be even larger than that. The formation of

aromatic products alongside the carbonaceous deposits probably results from the coupling of methane derivatives during dehydrogenation (Scheme 1). The thermodynamic data provided in Table 2 (Lines 5 and 6) shows that aromatization is much more favorable when some of the hydrogen atoms are oxidized to water. A certain amount of active oxygen from the redox active CZ support can be supplied for this purpose (vide infra). The formation of aromatics continued after oxygen from CZ was depleted but to a lower extent in the non-oxidative environment.



 $\mbox{Scheme 1.}$  Mechanism for the formation of aromatics and coke in methane aromatization.  $^{53}$ 

At 350 °C, the conversion of methane did not go through a maximum but continuously approached 0.118  $\pm$  0.002%, the thermodynamic limit for the conversion of methane to ethane in the absence of an oxidant (Table 2, Line 1). Previous studies showed that the reduction of surface ceria in CZ starts around 300 °C,<sup>[35]</sup> but at 350 °C, only a very small fraction of cerium at the surface is reduced. Hence, the amount of oxygen released at this temperature was significantly smaller than the amount released at 450 °C and 500 °C. As seen in Figure 2d, the selectivity to aromatics at 350 °C was very low compared to 450 °C (Figure 2c) and 500 °C (Figure 2b), which might be partially related to the limited oxygen supply from the reduction of ceria at this low temperature.



Figure 1. EDX maps of 2 wt.% NiO/CZ and plot showing the spectra at the marked points

The carbon containing products of the reactions at 500 °C, 450 °C and 350 °C were ethane, benzene, toluene and traces of ethylene (at 500 °C and 450 °C) and some heavier aromatics such as ethylbenzene, styrene, isopropyl benzene and n-propyl benzene. At the start of the reaction, aromatics were the main products. The selectivities to these aromatic products continuously declined, while the selectivity to ethane increased

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and reached  $80 \pm 1\%$  at 500 °C,  $81.4 \pm 1.6\%$  at 450 °C and  $96.3 \pm 0.7\%$  at 350 °C, all on a carbon atom basis. The selectivity to ethylene also increased during the reaction and reached  $4.2 \pm 0.2\%$  at 500 °C and  $1.3 \pm 0.2\%$  at 450 °C. No ethylene was observed at 350 °C. The yields of hydrogen at steady state was higher in the order of 500 °C > 450 °C > 350 °C, which is expected due to the endothermic nature of dehydrogenation reaction. The ratios of ethylene and hydrogen to ethane formed at 450 °C and 500 °C were slightly below the ratios expected under thermodynamic control. The decreasing selectivities of ethane coupled with an increase in the selectivity of ethylene at higher temperatures indicates that ethane is either undergoing a dehydrogenation reaction to form ethylene.

Ce L<sub>3</sub> and Ni K edges indicate that easily reducible ceria at or near the surface can supply oxygen to NiO clusters to keep them oxidized until the active oxygen species in CZ are depleted.<sup>[49]</sup> During the surface reduction with methane, oxygen atoms are removed and steam is formed. Hence, the reduction of ceria and eventually nickel oxide at the initial stage of the reaction supplies oxygen, which can promote methane aromatization for about the first 4 h on stream (Table 2, Line 6) (Scheme 1). After the reduction of NiO to Ni after 4 h, the formation of ethane becomes the dominant reaction path.

**Analysis of Carbonaceous Deposits**. To gain insight into the nature of the carbonaceous deposits, catalysts were analyzed by C1s XPS after reacting with methane for 4 h (Figure 4). The XP spectrum showed a C=C peak at 284.9 eV indicating that carbon was present in graphitic form.<sup>[54-55]</sup> Another peak at 283.9 eV suggested the presence of a hydrogen-poor sp-type of pre-

#### Table 2. Thermodynamics data for gas phase reactions of methane.

		∆G /kJ·mol <sup>-1</sup>			Хсн4 /%	
Reaction	350 °C	450 °C	500 °C	350	450	500
				°C	°C	۵°
$2CH_{4(g)} \leftrightarrow C_2H_{6(g)} + H_{2(g)}$	76	77	78	0.13	0.32	0.45
$2CH_{4(g)} \leftrightarrow C_2H_{4(g)} + 2H_{2(g)}$	137	126	121	0.019	0.11	0.23
$2CH_{4(g)} \leftrightarrow C_2H_{2(g)} + 3H_{2(g)}$	241	220	209	7.56.10 <sup>-06</sup>	9.31.10 <sup>-05</sup>	2.56.10-04
$CH_{4(g)} \leftrightarrow C_{(s)} + 2H_{2(g)}$	26	18	14	13	28	38
$6CH_{4(g)} \leftrightarrow C_6H_{6(g)} + 9H_{2(g)}$	335	303	288	0.13	0.53	0.94
$6CH_{4(g)}\textbf{+}4.5O_{2(g)}\leftrightarrow C_{6}H_{6(g)}\textbf{+}9H_{2}O_{(g)}$	-1592	-1583	-1579	100	100	100

 $X_{CH4}$  represents equilibrium conversion of methane.

Redox Activity of NiO/CZ during Reaction with CH4. In-situ XANES spectroscopy was used to probe the oxidation states of ceria and nickel during 5 h of exposure to methane at 450 °C in the absence of any oxidant (Figure 3). No shifts of the ceria or nickel edges were observed during activation in nitrogen. During the first 4 h of exposure to methane, a continuous shift of the position of the Ce L<sub>3</sub> edge to a lower energy indicated a reduction of some Ce<sup>4+</sup> species to Ce<sup>3+</sup> (Figure 3a). The position and white line intensity at the Ni K edge remained unchanged for the first 4 h of exposure to methane, indicating that oxidation state of nickel oxide remained approximately constant (Figure 4b). The reduction of big NiO particles that was proposed based on the conversion over time profile (Figure 2a, vide supra) was not observed in the XANES spectra. It is suggested that only a small fraction of Ni is present in such particles, so that their reduction has an insignificant effect on the spectrum. The white line then disappeared within 30 min, and the edge position shifted to lower energy, which shows that nickel oxide was reduced to metallic nickel. The combined observations from the

graphitic carbon.<sup>[56]</sup> No carbon species bound to oxygen were detected. Combustion analysis of the spent catalyst revealed that 3.3 wt.%, 4.6 wt.% and 7.6 wt.% of carbon and hydrogen were deposited during the reactions at 350 °C, 450 °C and 500 °C, respectively, which was in good agreement with TPO in a thermogravimetric analyzer (Figure 5a).

In-situ IR spectra during exposure of NiO/CZ to methane at 450 °C (Figure S5) contained several peaks corresponding to C=C bonds of aromatics and coke were also seen between 1653 cm<sup>-1</sup> and 1502 cm<sup>-1</sup>, but the accumulation of these species was relatively limited compared to their intensity after 1 h. It is suggested that some of these aromatic species desorb from the surface in the form of benzene, toluene and traces of heavier aromatics, such as styrene, ethylbenzene and propylbenzene, as seen on the reactivity results (Figure 2). A peak around 1580 cm<sup>-1</sup> was also observed and is assigned to graphitic coke.<sup>[63-64]</sup> The intensity of this peak increased slowly and approached an asymptotic limit. This indicates that most of the graphitic coke was formed within the first hour on stream.

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Figure 2. (a) Conversion of methane over NiO/CZ at different temperatures (b) Selectivity of carbon products over NiO/CZ at 500 °C (c) 450 °C (d) 350 °C (e) Yields of hydrogen at different temperatures.

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Figure 3. In-situ XANES of NiO/CZ during exposure to methane at 450 °C (a) Ce L<sub>3</sub>-edge (b) Ni K-edge.



Figure 4. X-ray photoelectron spectra in the C1s region of NiO/CZ after 4 h of methane exposure at 450 °C.



Figure 5. (a) Amount of carbon deposit on spent catalysts after reaction at different temperatures measured by combustion analysis and TPO using TG analysis (b) Raman spectra of spent catalysts after reactions at different

The Raman spectra of the spent catalysts showed signals at 1350 and 1590 cm<sup>-1</sup>, which represent "D" (disorder) and "G" (graphite) bands, respectively (Figure 5b).<sup>[57-58]</sup> However, these bands were deconvoluted to obtain detailed structural information (Figure S6). The two bands were fitted with four Lorentzian-shaped bands (D1, D2, D4 and G) at v = 1350, 1600, 1210 and 1575 cm<sup>-1</sup>, respectively and one Gaussian-shaped band (D3) at 1530 cm<sup>-</sup> <sup>1</sup>.<sup>[59-60]</sup> These components are assigned as graphene edges, graphene sheets, polyenes, graphitic carbon and amorphous carbon respectively. It has been suggested that the ratio  $I_{D1}/(I_G +$ I<sub>D1</sub> + I<sub>D2</sub>) is a measure of the degree of graphitization of carbonaceous materials in which I is the integral of the fitted peak.<sup>[60]</sup> The intensity ratio of the bands  $I_{D1}/(I_G + I_{D1} + I_{D2})$ 

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increased from 0.67 at 350 °C to 0.71 at 450 °C and 0.73 at 500 °C, which shows that the coke became more graphitic with increasing temperature. The amount of carbon deposit increased when the reaction was run at higher temperatures in agreement with the CH and TPO results.

**Strategy for Improved Performance.** The present contribution shows that Ni/CZ is capable of activating methane at low temperatures and coupling surface methyl groups to ethane. However, this endothermic reaction is thermodynamically limited to 0.45% conversion at 500 °C (Table 1). To improve the conversion to an acceptable level for industrial application without increasing the operating temperatures, these catalysts could be incorporated into membranes that can selectivity remove hydrogen to drive the reaction in the forward direction. Several studies in the literature have successfully demonstrated the use of such membranes on systems with either catalysts that are significantly more expensive than and not as active as the catalyst in this study or for non-oxidative methane aromatization at high temperatures (700 – 800 °C).<sup>[27, 65]</sup>

#### Conclusions

Nickel particles on ceria zirconia catalysts are active for the conversion of methane into ethane, ethylene and aromatics such as benzene, toluene, ethylbenzene, styrene and propylbenzene. The nickel sites are responsible for the activation of methane. Coupling of activated methane groups resulted in the formation of different products. Two types of Ni particles are present on CZ and play different roles in the conversion of methane based on their particle size. Bigger Ni particles, which are at least larger than 0.45 nm, are responsible for the formation of carbonaceous deposits because they have enough surface sites for aromatic species to assemble. Oxidation of surface hydrogen with active oxygen from CZ can promote the formation of aromatics. Ni particles that are smaller than a benzene ring (0.45 nm) are not involved in the formation of carbonaceous deposits. When the temperature is high enough, ethane can either be dehydrogenated to ethylene or the surface alkyl groups dehydrogenate before desorption. After 8 h on stream, the catalyst remains active for methane coupling to aromatics and higher hydrocarbons. Oxygen from CZ facilitates the initial formation of aromatics, while the formation of ethane dominates after this oxygen source is depleted. Thus, Ni/CZ is an efficient and cheap catalyst for converting methane into useful hydrocarbons in the absence of an oxidant within the thermodynamic limit at reasonably low temperatures. By selectively removing hydrogen from the product mixture in a membrane reactor the yields of higher hydrocarbons from methane could be improved in a non-oxidative environment.

#### **Experimental Section**

**Materials.** Cerium (III) nitrate hexahydrate (99% trace metals basis), zirconyl (IV) oxynitrate hydrate (99% trace metals basis), nickel (II) nitrate hexahydrate, and ammonium hydroxide (A.C.S. regent grade, 28–30% NH<sub>3</sub> content) were purchased from Sigma

Aldrich. Gases (methane and nitrogen) with ultra-high purity (UHP Grade 5) were purchased from Airgas. Dry air for calcination was generated in our labs using a Parker Balston Gas Generator 1000. Deionized water was obtained from a Barnstead NANOpure ultrapure water system which was purified to 18.2  $M\Omega$ /cm.

Catalyst Synthesis. The ceria zirconia support was prepared by coprecipitation of the precursors of ceria and zirconia.[34-35] Cerium nitrate hexahydrate and zirconyl nitrate hydrate were dissolved in deionized water to form a 0.1 M solution. The coprecipitation was modified by adding the 0.1 M precursor solution drop-wise to an aqueous ammonium hydroxide solution while stirring continuously. The precipitate was then filtered, rinsed with deionized water, and dried in an oven overnight at 373 K. The catalyst was then calcined for 4 h in 200 mL/min zero grade air at 450 °C with a ramp rate of 5 °C/min. Metal oxide clusters of Ni was deposited on the CZ support using conventional dry impregnation or pore volume impregnation.[36] For this purpose, the nickel precursor for 2 wt.% nickel loading was dissolved in deionized water equal to the pore volume of the ceria zirconia support, as determined by nitrogen physisorption. The resulting solution was added dropwise to the support and collected in a beaker at room temperature. It was mixed thoroughly for 30 minutes, dried at 100 °C for 5 h and then calcined for 4 h at 450 °C with a ramp rate of 10 °C/min.

**Characterization.** Nitrogen physisorption measurements of CZ and Ni/CZ were performed using a Micromeritics ASAP 2020 physisorption analyzer. The catalysts were degassed at 200 °C for 4 h prior to measurement. Surface areas and pore volumes were calculated based on the BET method<sup>[37]</sup> and BJH method,<sup>[38]</sup> respectively.

To determine the amount of ceria, zirconia, and nickel on the catalyst, ceria zirconia and NiO on ceria zirconia were sent to Galbraith Laboratories for inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis.

X-ray diffraction patterns were obtained using a Phillips X'Pert diffractometer equipped with an X'celerator module using Cu K $\alpha$  radiation. Diffractograms were collected at incident angles from  $2\theta = 5$  to  $90^{\circ}$  with a step size of 0.0167°.

Pyridine adsorption followed by FTIR spectroscopy was performed using a Nicolet 8700 FTIR spectrometer with an MCT/A detector. Each spectrum was recorded with 64 scans at a resolution of 4 cm<sup>-1</sup>. Each sample was pressed into a translucent self-supported wafer and loaded into a vacuum FTIR transmission cell. The sample was activated at 450 °C for 1 h under high vacuum and cooled to 150 °C. A background spectrum was taken. The chamber was dosed with 0.10 mbar of pyridine for 30 mins or until adsorption equilibrium of pyridine was reached. Subsequently, the cell was evacuated for 1 h to remove physisorbed pyridine and a spectrum was taken. After each experiment, the density of the wafer was determined by using a circular stamp of 6.35 mm to cut a disc of specific size from the wafer. The concentration of Lewis and Brønsted acid

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sites were determined by the Beer-Lambert law using the integral of the peaks at 1445 cm<sup>-1</sup> and 1540 cm<sup>-1</sup>, respectively. Extinction coefficients were used as reported by Tamura et al.<sup>[39]</sup>

In-situ XANES Ce L<sub>3</sub>-edge and Ni K-edge were collected at beamline 9-BM-C at the Advanced Photon Source of Argonne National Laboratories (Proposal GUP-43235). A Si(1 1 1) double monochromator was used to select the beam energy for all measurements. The beam size was 800 x 1000  $\mu$ m. Samples were pressed into wafers and placed in a cubic reactor. The beam was internally calibrated with a metallic cerium reference foil for Ce L<sub>3</sub>-edge and a metallic nickel reference foil for Ni K-edge. Spectra were then collected in fluorescence mode. A spectrum was first taken of each of the fresh samples. The samples were then activated in helium at 450 °C for 1 h in the cubic reactor while continuously taking spectra. The gas was then switched to 5% methane and balance helium and spectra were taken continuously. Separate experiments were performed under the same conditions for both Ce L<sub>3</sub>-edge and Ni K-edge.

XPS measurements were performed with a Physical Electronics Quantera Scanning X-ray Microprobe. This system uses a focused monochromatic AI Ka X-ray (1486.7 eV) source for excitation and a spherical section analyzer. The instrument has a 32 element multichannel detection system. The 83 W X-ray beam focused to 100 µm diameter was rastered over a 1.1 mm x 0.1 mm rectangle on the sample was used for the analysis. The X-ray beam is incident normal to the sample and the photoelectron detector is at 45° off-normal. High energy resolution spectra were collected using a pass-energy of 69.0 eV with a step size of 0.125 eV. For the Ag 3d5/2 line, these conditions produced a FWHM of 1.07 eV. The sample experienced variable degrees of charging. Low energy electrons at ~1 eV, 20µA and low energy Ar<sup>+</sup> ions were used to minimize this charging. The catalyst powder was pressed into 4 mm x 1 mm diameter holes machined into a custom 13 mm diameter SS sample stub designed for use with a custom modified ULVAC PHI XPS sample platen. The custom sample platen and sample stub including the fresh catalysts were placed into the XPS vacuum introduction system and pumped to <1x10-7 Torr using a turbomolecular vacuum pumping system prior to introduction into the XPS spectrometer ultrahigh vacuum system. The spectrometer vacuum system pressure was maintained at <1x10-9 Torr during analysis and pumped using a series of sputter ion and turbomolecular vacuum pumps. After XPS analysis of the fresh catalysts, the sample stub was transferred to an attached catalytic reaction side chamber also pumped by a series of sputter ion and turbomolecular vacuum pumps. The sample stub was then transferred from the catalytic side chamber into an attached high vacuum tube furnace. The pressure of the tube furnace was increased ~760 Torr using 5% methane/He at a flow rate of 100 SCCM. The catalyst was heated to 450 °C at a rate of 10 °C/minute and held for 4 hours. After the catalyst was cooled to room temperature, the gas was quickly removed using a turbomolecular vacuum pump attached to the tube furnace. The stub was then transferred into the UVH catalytic chamber and then into the XPS spectrometer vacuum for analysis. Quantification was performed using standard

sensitivity factors contained in the ULVAC-PHI, Inc. MultiPak V9.5.0.8 version date of 10-30-2013 software. Peak area intensities required for quantification were calculated after applying a Shirley background subtraction. These quantification results include the instrument transmission function, source angle, and asymmetry corrections. Typical XPS analysis depth for ceria based materials using inelastic mean free path calculation is up to 3 nm depending on the kinetic energy of the detected electron.<sup>[40]</sup> The majority of the electrons detected are coming from the first atomic layer.

EDX map was collected with a Scanning Transmission electron microscopy (STEM) (FEI Titan 80-300). The FEI Titan is equipped with CEOS GmbH double-hexapole aberration corrector for the probe-forming lens, which allows imaging with sub Angstrom resolution in STEM mode. EDX mapping was performed with FEI ChemiSTEM<sup>R</sup>, which comprise of four symmetrically arranged windowless silicon drift detectors (SDD) with solid angle of ~0.8 sr. Acquisition and evaluation of the spectra was performed with Bruker Espirit software package. In general, the STEM sample preparation involved mounting powder samples on copper grids covered with lacey carbon support films, and then immediately loading them into the STEM airlock to minimize an exposure to atmospheric O<sub>2</sub>.

The carbon content on the spent catalysts were determined using a TA instruments SDT Q600 TGA. An empty alumina crucible was used to tare the TGA before each analysis. Individual samples were then loaded on the crucible and put in the TGA for analysis. The samples were ramped to 800 °C at 20 °C/min in a 100 mL/min flow of dry air.

Spent catalysts were also sent to Atlantic Microlab for CHN analysis.

Raman spectroscopy was also performed on the spent catalysts. For this purpose, the samples were loaded on microscope slides. The microscope was then focused on the sample region of interest at 20x resolution. Using a WITEC spectrometer with a 532 nm laser, the structural fingerprint of the samples were measured to determine the molecules present. Three individual measurements were then taken with an integration time of 10 seconds each which were averaged. A smooth function was used to remove noise and/or interference.

In-Situ FTIR Spectroscopic Study during Reaction with Methane at 450 °C over NiO/CZ. 100 mg of the catalyst was pressed into a circular self-supported wafer with a diameter of 2 cm. The wafer was loaded into the sample holder, and it was assembled as part of the FTIR cell together with the cell body and heating block. The cell was built based on a design reported in the literature.<sup>[41]</sup> The assembled FTIR cell was placed into a Nicolet 8700 FTIR spectrometer. Each spectrum was recorded with 64 scans at a frequency of one per minute for 12 h during exposure to 5% methane and balance inert at 100 ccm total flow rate at 450 °C and atmospheric pressure.

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Reactivity Studies. Reactivity experiments for the coupling of methane were performed in a packed bed reactor. The studies were performed using 200 mg of catalyst sieved to 75 µm. Catalyst samples were activated in-situ at 450 °C in nitrogen for an hour prior to reactivity studies. A space velocity of 3000 h<sup>-1</sup> of reactant gas diluted in nitrogen (5% methane) was employed. The reaction was run at 350 °C, 450 °C and 500 °C for 8 h at each reaction temperature. A 100 ccm total flow rate of gas was used. The reactor was connected to an online Bruker 450-GC refinery gas analyzer (RGA) and a Hiden HPR20 mass spectrometer. The RGA is equipped with two TCD detectors and a FID. One TCD is used for analysis of hydrogen and the second for analysis of permanent gas mixtures (including methane). The FID channel allows for identification of methane and higher hydrocarbons. The TCD for hydrogen gas analysis uses a Molsieve 5A column while the TCD for permanent gas analysis uses a Molsieve 13x and Hayseep Q columns in series. The column to the FID is a BR-1. The GC was calibrated for all reactant and product gases by flowing 3-4 known amounts of the gas in question at the same temperature used in the reaction and monitoring the peak areas. Product gas was sampled at 10 minutes intervals using the RGA. The following definitions were used:

Conversion:  $X_R[\%] = \frac{F_{CH4,in} - F_{CH4,out}}{\pi} \times 100$ FCH4 in

C Product Selectivity:  $Y_p [\%] = \frac{v_p \cdot r_{p,out}}{F_{CH4,in} - F_{CH4,out}}$ - x 100

H<sub>2</sub> yield: [%] =  $\frac{F_{H2,out}}{2.F_{CH4,in}} \times 100$ 

Where  $v_p$  is the number of carbon atoms in the compound and  $F_x$  is the molar flow rate of the gas in question.

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Keywords: Lewis acid • carbon nanotubes • dispersion • coking nickel oxide

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**FULL PAPER** 

Ethane, Ethylene and Aromatics are produced continuously over nickel on ceria-zirconia in a non-oxidative environment at temperatures not exceeding 500 °C. NI NI CeO2-ZrO2 Chukwuemeka Okolie, Libor Kovarik, Eli Stavitski, Carsten Sievers\*

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Non-Oxidative Coupling of Methane to Ethane, Ethylene and Aromatics over Nickel on Ceria-Zirconia