Structural studies on NiO-CeO₂-ZrO₂ catalysts
for steam reforming of ethanol

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Received 8 August 2002; received in revised form 6 January 2003

Abstract

The influence of Ce/Zr ratio on the redox behavior of Ni in a series of NiO-CeO₂-ZrO₂ catalysts was investigated using in situ electron paramagnetic resonance (EPR), diffuse reflectance UV-visible (DRUV-visible) and X-ray photoelectron spectroscopy (XPS). At all concentrations, a small amount of Ni (species I) substitutes in the fluorite lattice. Superparamagnetic, nanosize Ni crystallites (species II) were found in samples with 1–5 wt.% NiO and ferromagnetic, larger Ni crystallites (species III) were detected in samples with 20 wt.% or more NiO when contacted with hydrogen. Ce promoted the reduction of Ni. The reducibility of Ni decreased in the order: I > III > II. At steam reforming conditions (in the presence of H₂ + H₂O + hydrocarbon/alcohol at 773 K), the extent of Ni reduction varies in the order: H₂ + alkane > H₂ + alcohol > H₂ alone. Catalytic activity and especially stability in the steam reforming of bio-ethanol (containing 5 ppm S) correlates with the type III Ni species and is influenced by both the Ni-content and the Ce/Zr ratio in the support. A catalyst of composition NiO (40 wt.%)-CeO₂ (30 wt.%)-ZrO₂ (30 wt.%) maintained its activity for more than 500 h without deactivation.

Keywords: Solid oxide fuel cell catalysts; Nickel-ceria-zirconia; NiO-CeO₂-ZrO₂; Hydrogen generation; Redox behavior of Ni; EPR and diffuse reflectance UV-visible spectroscopies of Ni; Steam reforming of ethanol; Benzene hydrogenation

1. Introduction

There has been renewed interest in the area of steam reforming and autothermal reforming in recent years for generation of hydrogen in polymer electrolyte membrane-based fuel cells and solid oxide fuel cells [1–5]. Conventional catalysts (e.g. nickel supported on oxides like SiO₂, Al₂O₃, MgO, MgAl₂O₄ or their mixtures) are not suitable. Their operating temperatures are too high, they require too high steam-to-carbon ratios and they undergo catalytic deactivation due to sintering of nickel crystallites and carbon deposition. They also require deep desulphurisation (to less than 0.5 ppm S). Their relatively low catalytic activities require large volumes of catalysts difficult for adoption in “on-board” hydrogen generation for PEM fuel cells in automobiles. Hence, worldwide efforts are in progress to discover novel, more active and more stable catalysts. One of the promising catalyst systems is metal-CeO₂-ZrO₂, where the metal is nickel, platinum or palladium [6–14]. We had earlier reported the preparation and steam reforming of n-decane by crystalline, mesoporous NiO-CeO₂-ZrO₂, NiO-Y₂O₃-ZrO₂ and NiO-Al₂O₃-Y₂O₃-ZrO₂ [15,16]. When nickel was
supported on partially reducible oxides like CeO₂, its catalytic behavior was found to be superior to that observed with the conventional insulator supports like SiO₂, Al₂O₃ or MgO [15,16]. CeO₂ and CeO₂-ZrO₂ are, of course, used as supports (for Pt, Pd, Rh) in 3-way catalysts for automobile exhaust pollution control. Ceria promotes the stability of the catalysts and platinum-dispersion. Ceria’s ability to store and release oxygen is a crucial feature in its superior performance [17–22].

We now report the structural investigations of our NiO-CeO₂-ZrO₂ catalysts using especially the electron paramagnetic resonance (EPR) technique to probe the paramagnetic nickel and oxygen ions formed on their surface. We also report, for the first time, in situ EPR investigations under steam reforming conditions. EPR spectroscopy is ideally suited to characterize the reactive oxo intermediates formed from H₂O•₉O₂• in 3-way catalysts for automobile exhausts. Prior to the EPR experiments, the samples were treated with dry hydrogen at elevated temperatures (Tf = 573–798 K). The spectra were recorded at 298 or 88 K using a Bruker VT 3000 variable temperature controller. The redox behavior of the catalysts was investigated also at artificial steam reforming conditions. In those experiments, the catalysts were treated

2. Experimental

2.1. Materials and sample preparation

The NiO-CeO₂-ZrO₂ catalysts of different compositions (Table 1) were prepared hydrothermally, using a rotating hydrothermal synthetic reactor (Hiro Co., 6) Ni(NO₃)₂ and Zr, respectively.

With a scan speed of 0.02°/min. The average crystallite size of the samples was determined from the line widths of the XRD peaks at ca. 2θ = 29 and 48.5° corresponding to (1 1 1) and (2 2 0), respectively, using the Scherrer equation [17].

The chemical composition of the calcined samples was determined by EDX. The specific surface area (BET) was estimated from the N₂ adsorption/desorption isotherms at the liquid nitrogen temperature using a Coulter 100 instrument. The crystalline phase and purity were identified by a Rigaku Geigerflex X-ray diffractometer with nickel-filtered Cu Kα radiation (λ = 1.5406 Å, 40 kV, 30 mA) in the range, 2θ = 20–90° and with a scan speed of 0.06°/min. The average crystallite size of the samples was determined from the line widths of the XRD peaks at ca. 2θ = 29 and 48.5° corresponding to (1 1 1) and (2 2 0), respectively, using the Scherrer equation [17].

The EPR spectra were recorded on a Bruker EMX spectrometer operating at X-band frequency (ν = 9.4 GHz) and a 100 kHz field modulation. For in situ measurements, the calcined samples (in the form of powders) were taken in a specially designed quartz cell (o.d. = 4 mm) fitted with greaseless stopcocks and provisions for adsorption/desorption of gases. Prior to the EPR experiments, the samples were evacuated at 773 K for 6 h (10⁻³ mm) and then

(1, 24.2 mg; 2, 5 mg; 6, 7 and 8, 2 mg each) were treated with dry hydrogen at elevated temperatures (Tf = 573–798 K). The spectra were recorded at 298 or 88 K using a Bruker VT 3000 variable temperature controller. The redox behavior of the catalysts was investigated also at artificial steam reforming conditions. In those experiments, the catalysts were treated
Table 1
Composition, structural parameters and BET surface area of NiO-CeO₂-ZrO₂ catalysts

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Catalyst system (input composition in wt.%)</th>
<th>Unit cell parameter of CeO₂-ZrO₂ (nm)</th>
<th>CeO₂-ZrO₂ crystallite size (nm)</th>
<th>NiO crystallite size (nm)</th>
<th>S\textsubscript{BET} (m²/g)</th>
<th>Chemical analysis\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NiO (1)-CeO₂ (49.5)-ZrO₂ (49.5)</td>
<td>0.526</td>
<td>5.9</td>
<td>84</td>
<td>2.8, 2.1 (1.9)</td>
<td>43.4, 42.6 (40.9)</td>
</tr>
<tr>
<td>2</td>
<td>NiO (5)-CeO₂ (47.5)-ZrO₂ (47.5)</td>
<td>0.526</td>
<td>5.6</td>
<td>95</td>
<td>10.0, 10.3 (9.2)</td>
<td>40.0, 40.4 (37.9)</td>
</tr>
<tr>
<td>3</td>
<td>NiO (10)-CeO₂ (45)-ZrO₂ (45)</td>
<td>0.526</td>
<td>5.1</td>
<td>95</td>
<td>19.9, 20.2 (17.6)</td>
<td>36.3, 35.9 (34.6)</td>
</tr>
<tr>
<td>4</td>
<td>NiO (20)-CeO₂ (40)-ZrO₂ (40)</td>
<td>0.527</td>
<td>4.7</td>
<td>107</td>
<td>36.6, 37.5 (32.5)</td>
<td>28.7, 29.3 (28.2)</td>
</tr>
<tr>
<td>5</td>
<td>NiO (30)-CeO₂ (35)-ZrO₂ (35)</td>
<td>0.527</td>
<td>4.7</td>
<td>89</td>
<td>49.6, 49.3 (45.2)</td>
<td>23.9, 23.4 (22.9)</td>
</tr>
<tr>
<td>6</td>
<td>NiO (40)-CeO₂ (30)-ZrO₂ (30)</td>
<td>0.526</td>
<td>4.6</td>
<td>92</td>
<td>59.5, 59.4 (56.2)</td>
<td>18.3, 18.3 (18.3)</td>
</tr>
<tr>
<td>7</td>
<td>NiO (40)-CeO₂ (5.4)-ZrO₂ (54.6)</td>
<td>0.510</td>
<td>7.9</td>
<td>86</td>
<td>56.6, 56.8 (53.3)</td>
<td>3.3, 2.9 (11)</td>
</tr>
<tr>
<td>8</td>
<td>NiO (40)-CeO₂ (60)</td>
<td>0.542</td>
<td>6.4</td>
<td>71</td>
<td>60.7, 60.6 (60.6)</td>
<td>39.3, 39.1 (39.6)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} EDX analysis in two different regions. Theoretical (or input) values are in the parentheses.
In DRUV-visible measurements, a known amount of the catalyst (150 mg) was mixed with 2 g of spectral grade BaSO₄ and used to fill a powder sample holder. The spectra of the calcined and the hydrogen treated samples were then recorded on a Shimadzu UV-2550 spectrophotometer equipped with an integrating sphere attachment unit (ISR-2200). Spectral grade BaSO₄ was used as the reference material. XPS measurements were made on a VG Microtech Multilab ESCA 3000 spectrometer with Mg Kα radiation (hν = 1253.6 eV). Temperature programmed reduction (TPR) was performed in a quartz tube reactor using a Micromeritics AutoChem 2910 instrument. Hydrogen consumption was measured by a TCD. A weighed amount (4 mg) of the sample was placed in the reactor and reacted with a 22% O₂–78% He (v/v) gas mixture at 773 K for 2 h; then 25 ml/min of the 5% H₂–95% Ar gas mixture was allowed to flow through the reactor. The temperature was increased to 773 K at a heating rate of 10 K/min. To calibrate the amount of H₂ consumption, a standard NiO powder was used.

2.3. Catalytic activity studies

2.3.1. Benzene hydrogenation

The reaction was carried out in a fixed-bed down-flow glass reactor (i.d. = 15 mm), using a 1.0 g charge of the catalyst. The catalyst sample was made into a pellet (with no binder), crushed and sized (12–16 mesh). Then, it was activated at 773 K for about 14 h in flowing air and then for 2 h in flowing dry hydrogen. In a typical hydrogenation reaction, benzene free from sulfur (9 ml/h) and dry hydrogen (120 ml/min) (1:4 mole ratio) were fed to the reactor. The products were cooled using a water condenser and collected periodically for analysis by a gas chromatograph (Shimadzu GC-15). Benzene, free from sulfur, was prepared by shaking the commercial benzene (S.D. Fine Chem. Ltd., India) with concentrated H₂SO₄, in a separating funnel, till the concentrated H₂SO₄ layer was colorless. The sulfur-free benzene thus obtained was further washed with water and distilled. Sulfur-resistance of the catalysts was investigated by carrying out the reactions with benzene-containing thiophene (20 ppm).

2.3.2. Steam reforming of ethanol

Catalytic reactions were carried out in a fixed-bed down-flow glass reactor (i.d. = 15 mm) connected online to a gas chromatograph fitted with a thermal conductivity detector. Prior to reactions, the catalyst, in the form of crushed pellets (0.653 g; 12–16 mesh), was activated by heating at 773 K for 6–7 h and then reducing overnight with H₂ (30 ml/h). The reaction was carried out at 823 K, using ethanol and water feed (1:8 mol; LHSV = 6; 3 ml/h).

3. Results

3.1. Chemical composition, structural and textural properties

3.1.1. Chemical composition

The chemical composition of the catalysts is given in Table 1. The present method of preparation using a rotating hydrothermal synthetic reactor yielded smaller NiO-CeO₂-ZrO₂ crystallites having a larger...
surface area. The specific surface area ($S_{BET}$) of samples 1–7 containing Ni, Ce and Zr is in the range 84–107 m$^2$/g (Table 1). Sample 8 containing no Zr has $S_{BET}$ of 71 m$^2$/g. The surface area increased with increasing Ni content up to 20 wt.% and then decreased.

### 3.1.2. X-ray diffraction

The calcined samples showed XRD patterns with peaks in the $2\theta$ range of 28–90$^\circ$ consistent with the formation of CeO$_2$-ZrO$_2$ solid solutions, with a cubic fluorite structure (Fig. 1) [17]. No separate phase due to CeO$_2$ or ZrO$_2$ was detected. The peak position of CeO$_2$-ZrO$_2$ was invariant with the Ni-content, and the peak width changed only marginally. In the samples with 5 wt.% Ni or more, additional peaks due to NiO phase (unit cell parameter = 0.591 nm) were observed. The intensity of these peaks increased with the Ni-content. A small amount of Ni substitution in the CeO$_2$-ZrO$_2$ lattice, however, could not be excluded (EPR studies (vide infra)). The average crystallite sizes of CeO$_2$-ZrO$_2$ and NiO were estimated from the X-ray linewidths of the peaks corresponding to (1 1 1) or (2 2 0) using the Scherrer equation [17]. The dimensions of CeO$_2$-ZrO$_2$ crystallites were in the range of 4.6–7.9 nm (Table 1). The crystallite size of the CeO$_2$-ZrO$_2$ composites decreased with increasing Ni-content (up to 20 wt.%). Above this value, the change was negligible (Fig. 2). Simultaneously,
the size of NiO crystallites decreased from 10.4 to 7.3 nm with increasing Ni-content in samples 4–7 (Table 1). Sample 8 containing no Zr has the largest NiO crystallites (17.2 nm). The peaks corresponding to the CeO₂-ZrO₂ solid solution (SS) shifted with a change in the Ce/Zr ratio (as indicated by arrows in Fig. 1). The unit cell parameter changes (from 0.510 to 0.542 nm) with the Ce/Zr ratio (Table 1). NiO peaks (Ni) were narrower in sample 8 (containing no Zr) than in 6 and 7 (containing Ce and Zr in 1:1 and 1:10 ratio, respectively) (Fig. 1; compare trace (a) with traces (b) and (c)). The crystallite size of NiO also varied (from 7.3 to 17.2 nm) with the Ce/Zr ratio.

3.1.3. EPR spectroscopy

The EPR spectrum of the calcined samples of I (Fig. 3) reveals oxygen radicals (O²⁻ and O⁻) and Ni⁺ ions. The assignment of the set of signals at 1.965 and 1.943 (Fig. 3) is controversial. These signals had been attributed to the Ce³⁺ ions associated to an anion vacancy (and in an asymmetric environment that could quench to some extent the spin lattice relaxation) as well as the “quasi-free” or trapped electrons at anion vacancies perhaps interacting with Ce⁴⁺/Zr⁴⁺ orbitals [17–19]. The weak signal at 2.008 corresponds to O⁻ ions and the set of signals at 2.083, 2.033 and 2.001 are due to superoxide anions (O₂⁻⁻) attached to the Ni⁴⁺ ions and the CeO₂-ZrO₂ solid support (Fig. 3) [23]. With increasing Ni-content, the intensity of the superoxide ion signals decreased, perhaps broadened due to spin-spin interactions with NiO. In addition to these oxide ion signals, samples 1–6 showed a broad feature at g = 2.21 due to Ni⁴⁺ ions [23,24]. In 8, this signal occurred at g = 2.36. Interestingly, sample 7 containing less amount of Ce did not show this signal, indicating that Ce promotes Ni reduction. Fig. 4 reveals the effect of Ce/Zr ratio on the EPR spectrum.

Sample 1, reduced in dry hydrogen (for 1 h at elevated temperatures) showed two types of Ni signals. Species I is characterized by sharp signals at g∥ = 2.08 and g⊥ = 2.009; the intensity of these signals did not change with the reduction temperature (T_r). Species II is characterized by a broad signal (ΔH(pp) = 340 G) at g = 2.20; the intensity of this signal increased with the reduction temperature (Fig. 5(a)). Sample 2 reduced with hydrogen (containing 5 wt.% NiO) showed three types of species (species III in addition to the species I and II observed in sample 1). The spectra of 2 at
Fig. 5. EPR (at 298 K) of (a) NiO (1)-CeO₂ (49.5)-ZrO₂ (49.5) and (b) NiO (5)-CeO₂ (47.5)-ZrO₂ (47.5) reacted with hydrogen at different reduction temperatures. Signals due to species I, II and III are marked.

Different reduction temperatures are shown in Fig. 5(b). Species III is characterized by a very broad signal on which the signals due to species I and II are superimposed. Species I was observed throughout the reduction temperature (573–798 K), species II (with significant intensity) was seen above 748 K and species III from 673 K onwards. The signal intensity of III did not change significantly beyond 773 K, but that of II increased continuously with the reduction temperature.

The spectra of samples 6–8 (containing 40 wt.% NiO) reacted with hydrogen are mainly due to species III. Species II was present, but the signals were weak and masked by the intense, broad signal of species III. The signal of species III shifted to the high field side with increasing reduction temperature (the g-value changes from 3.4 to 3.05; Fig. 6), but there was no change in the linewidth. Samples 7 and 8 showed similar spectra to that of 6. The Ce–Zr composition has an effect both on signal position and linewidth (g-value, linewidth, G) at Tᵣ = 798 K: sample 6 = 3.1 (1660), sample 7 = 3.1 (2130) and sample 8 = 2.4 (1850). The shift in the EPR signal with Tᵣ was smaller (100 G) in sample 7 (containing more Zr than Ce) than in 6 (320 G; Ce/Zr = 1:1) and 8 (600 G; containing only Ce) (Fig. 6). It may be noted (Fig. 6) that species III could be reduced even at 573 K in samples containing only Ce. Such a reduction was not significant in 7 containing a smaller amount of Ce. In other words, Ce facilitates the reduction of Ni.

3.1.4. Diffuse reflectance UV-visible spectroscopy

Samples 1–6 activated at 473 K showed an intense, asymmetric UV band with a maximum at 240 nm and a shoulder around 310 nm. The former dominated in samples with higher Ni-content, indicating its origin from O → Ni charge transitions [25]. The shoulder is due to O → Ce/Zr transitions [26,27]. Additionally, weak d–d bands of octahedrally coordinated Ni²⁺ were also observed at 724, 649 and 400 nm [25,28]. The intensity of these bands increased with increasing Ni-content. The Ce/Zr ratio considerably affected the DRUV-visible spectra (Fig. 7). Sample 8 (activated at 473 K) showed an additional, asymmetric broad band in the region 400–650 nm attributable to the d–d transitions of Ni²⁺ ions [28]. Such diffuse reflectance spectroscopic results thus lend additional support to the conclusions drawn earlier from the EPR spectroscopy, namely, that Ce promotes the Ni reduction.

On treating with dry H₂, the intensity of the charge transfer band reduced considerably and the d–d bands disappeared. The samples became blackish and the reflectance was considerably lower. A broad absorption beyond 350 nm appeared. All these features suggest that Ni²⁺ ions in the original samples were reduced to metallic nickel [29,30].

3.1.5. X-ray photoelectron spectroscopy and temperature programmed reduction

XPS reveals that Ni is essentially in +2 and Zr and Ce are in +4 “formal” oxidation states in the calcined
Fig. 6. EPR of NiO-CeO$_2$-ZrO$_2$ reacted with hydrogen showing the effect of reduction temperature and Ce/Zr ratio.

Fig. 7. DRUV-visible spectra of NiO-CeO$_2$-ZrO$_2$ revealing the effect of Ce/Zr ratio; d-d bands due to Ni$^{2+}$ and Ni$^+$ are marked.

samples (Fig. 8). Zr 3d$_{5/2}$ and 3d$_{3/2}$ lines appear at 182 and 184.6 eV, respectively. The lines corresponding to Ce appeared in the range 882–918 eV. The main lines of Ni 2p$_{3/2}$ and 2p$_{1/2}$ were observed at 855.2
and 872.3 eV, respectively (Fig. 8). Lines due to Ni\(^{2+}\) could not be separated. Upon reaction with hydrogen at 723 K for 1 h, an additional low binding energy feature at 853 eV due to metallic Ni was observed. TPR studies indicated that Ni\(^{2+}\) in NiO phase of the NiO-CeO\(_2\)-ZrO\(_2\) samples is reduced to metallic Ni at around 648 K.

3.1.6. In situ spectroscopic studies at steam reforming conditions (773 K)

The redox behavior of Ni was investigated by in situ EPR, DRUV-visible and XPS techniques in streams containing H\(_2\), H\(_2\)O and hydrocarbons/alcohols. Sample 2 (5 wt.% Ni) was selected for the EPR studies as it contained all the three types of Ni species: I, II and III. In the presence of water, only a small amount of species II was noticed (Fig. 9). Over methanol it was almost absent. The signal intensity of species II increased with an increase in the chain length of alcohol in the order: methanol < ethanol < \(n\)-butanol < \(n\)-nonanol. The line shape and position of species III signal changed with alcohol. Reductions were also carried out in the presence of alkanes (Fig. 9). The extent of Ni reduction was higher in the presence of alkanes than in alcohols and varied in the order: hexane > heptane > nonane \(\approx\) cyclohexane > no solvent. DRUV-visible and XPS of sample 6 provided complementary evidence. Ni reduction was more in the presence of hydrocarbons than with hydrogen alone (XPS curves—Fig. 8; H\(_2\) + \(n\)-octane > H\(_2\) + nonanol > H\(_2\)).

3.2. Catalytic activity

3.2.1. Benzene hydrogenation

Benzene hydrogenation is a “facile” reaction and is indicative of the number of surface Ni\(^0\) atoms available for catalysis. The activity of the catalysts in benzene hydrogenation reaction was investigated at 453 K. Cyclohexane was the only product of the reaction. The activity of the catalysts (turnover number) (Table 2) increased with increasing Ni content (samples 2–4) up to 20 wt.%. When the Ni-content was doubled (to 40%, sample 6) benzene conversion was also doubled, while the turnover number remained constant. When the Ce:Zr ratio in the support was changed (samples 7 and 8), catalytic activity declined (Table 2). The catalysts with Ce:Zr = 1:1 were not

![Fig. 9. EPR (298 K) of Ni (5)-Ce (47.5)-Zr (47.5) reacted with hydrogen and hydrocarbons.](image)

Table 2

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Catalyst</th>
<th>Benzene conversion (wt.%)</th>
<th>TOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>NiO (40)-CeO(_2) (30)-ZrO(_2) (30)</td>
<td>18.1</td>
<td>3.5</td>
</tr>
<tr>
<td>6</td>
<td>NiO (40)-CeO(_2) (30)-ZrO(_2) (30)</td>
<td>1.5</td>
<td>0.3</td>
</tr>
<tr>
<td>7</td>
<td>NiO (40)-CeO(_2) (54.6)-ZrO(_2) (45.4)</td>
<td>11.4</td>
<td>2.2</td>
</tr>
<tr>
<td>8</td>
<td>NiO (40)-CeO(_2) (60)</td>
<td>8.1</td>
<td>1.6</td>
</tr>
<tr>
<td>4</td>
<td>NiO (20)-CeO(_2) (80)-ZrO(_2) (20)</td>
<td>9.2</td>
<td>3.5</td>
</tr>
<tr>
<td>3</td>
<td>NiO (10)-CeO(_2) (45)-ZrO(_2) (55)</td>
<td>0.9</td>
<td>0.7</td>
</tr>
<tr>
<td>2</td>
<td>NiO (5)-CeO(_2) (47.5)-ZrO(_2) (47.5)</td>
<td>0.6</td>
<td>0.9</td>
</tr>
</tbody>
</table>

\(a\) Reaction conditions: catalyst = 1 g, benzene:H\(_2\) = 1:4, temperature = 453 K, time = 1 h.

\(b\) TOF: turnover frequency (number of moles of benzene converted per mole of Ni per hour).

\(c\) Reaction with toluene (20 ppm)-containing benzene feed.
only more active but were also stable during the reaction. In the reactions with thiophene-containing benzene, the catalysts deactivated in about 30 min. The XRD of the used catalysts indicated a loss of crystallinity when thiophene was present in the feed (see Fig. 10, curve c). The crystallinity was not affected significantly (curves a and b of Fig. 10) when thiophene was absent in the feed. Sulfur compounds, not surprisingly, will poison NiO-CeO₂-ZrO₂ catalysts severely.

3.2.2. Steam reforming of ethanol

Even though all the samples containing 20 wt.% or above of Ni exhibited similar activity and selectivity (Table 3), their stabilities over a 500 h duration run varied; sample 6, with 40% Ni and a CeO₂-ZrO₂ ratio of 1 was the most stable.

Table 3

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Catalyst</th>
<th>H₂ in dry gas (vol.%)</th>
<th>CH₄ (vol.%)</th>
<th>CO (vol.%)</th>
<th>CO₂ (vol.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>NiO (40)-CeO₂ (60)</td>
<td>67.9</td>
<td>7.4</td>
<td>3.0</td>
<td>21.7</td>
</tr>
<tr>
<td>7</td>
<td>NiO (40)-CeO₂ (54)-ZrO₂ (56)</td>
<td>68.0</td>
<td>6.7</td>
<td>3.2</td>
<td>22.1</td>
</tr>
<tr>
<td>6</td>
<td>NiO (40)-CeO₂ (30)-ZrO₂ (30)</td>
<td>68.0</td>
<td>6.5</td>
<td>2.9</td>
<td>22.6</td>
</tr>
<tr>
<td>5</td>
<td>NiO (30)-CeO₂ (35)-ZrO₂ (35)</td>
<td>69.0</td>
<td>6.0</td>
<td>3.7</td>
<td>21.3</td>
</tr>
<tr>
<td>4</td>
<td>NiO (20)-CeO₂ (40)-ZrO₂ (40)</td>
<td>67.5</td>
<td>6.5</td>
<td>3.7</td>
<td>22.3</td>
</tr>
</tbody>
</table>

* Reaction conditions: catalyst = 0.677 g, feed—ethanol:water = 1:8 (mol), LHSV = 6, temperature = 823 K, time-on-stream = 5 h. Conversion of ethanol was above 95% in all cases.

4. Discussion

The NiO-CeO₂-ZrO₂ samples crystallized in a cubic fluorite structure [17]. The unit cell parameter (a) of samples 7 and 8 agree well with that of pure cubic ZrO₂ (0.510 nm) and CeO₂ (0.541 nm), respectively. An intermediate value of a = 0.526 nm for samples 1-6 (with Ce/Zr = 1) confirms the formation of CeO₂-ZrO₂ solid solutions. The hydrothermal synthesis by the rotation method has yielded materials with smaller crystallite size and larger specific surface area (71–107 m²/g). The Ce/Zr ratio and Ni-content both influenced the crystallite sizes. The crystallite size of NiO increased with an increase in the Ce content. At the same time, with increasing Ni content the crystallite size of CeO₂-ZrO₂ solid solution decreased. Most of the Ni in 2-8 (5% Ni and more) is present as a separate NiO phase supported on the CeO₂-ZrO₂ composite oxides. However, a small amount of Ni incorporation (<1%) in the CeO₂-ZrO₂ lattice cannot be excluded.

Ni²⁺ (electronic configuration—t₆²g²e², S = 1) is a Kramers’ ion. The EPR signals due to isolated Ni²⁺ ions are usually observed at liquid helium temperatures provided the zero-fielding splitting is of the order of hν (ℏ is Planck’s constant and ν is the spectrometer frequency). However, NiO is antiferromagnetic and EPR silent at low temperatures. Thus, the EPR signals due to Ni²⁺ in the present system could not be seen at our experimental conditions (80–298 K). The ceria-zirconia mixed oxides are an improvement over ceria in the formulation of three way catalysts due to their improved redox properties, higher oxygen storage capacity and oxygen buffering action. These mixed oxides are thermally stable and the oxygen storage capacity is retained even after many
consecutive redox cycles of reduction at high temperature followed by re-oxidation. Martinez-Arias et al. [17–19] and Mamontov et al. [20] reported that the role of zirconia when incorporated in ceria is to retard the sintering of ceria crystallites, to facilitate the reduction of Ce\(^{4+}\) to Ce\(^{3+}\) and to preserve the oxygen vacancies which are the source of oxygen storage capacity in ceria-based catalyst supports. Mamontov et al. [20] also demonstrated, using the pulsed neutron diffraction technique, that the oxygen storage capacity in ceria-zirconia compared to pure ceria as a consequence of an increase in the Frankel-type anion defects (oxygen vacancies and interstitial ions) in the former oxide. When Ce\(^{4+}\) (coordination number = 8 in the CeO\(_2\) lattice) is substituted for a six-coordinated Zr\(^{4+}\) ion in the ZrO\(_2\) lattice, defect centers are created. Also, doping ceria with zirconia promotes formation of Ce\(^{3+}\) ions due to the smaller size of Zr\(^{4+}\) cations that take part in removing the strain associated with the increase of ionic size accompanying the Ce\(^{4+}\) to Ce\(^{3+}\) transition. These defects in solid CeO\(_2\)-ZrO\(_2\) superlattice and the redox properties of Ce and Zr ions at temperatures above 873 K are responsible for the superior oxygen storage capacity and the ion transport properties.

EPR spectroscopy has identified three types of paramagnetic defects in CeO\(_2\)-ZrO\(_2\) oxides, viz. electrons, “quasi-free” or trapped in anion vacancies (signals at \(g = 1.965\) and 1.943), O\(^{2-}\) ions (signal at \(g = 2.008\)) and O\(^{2-}\) ions (signals at \(g = 2.083, 2.033\) and 2.001) [17–19,23]. These species arise by the following interactions:

\[
\begin{align*}
\text{Ce}^{3+} + \text{O}_2 & \rightarrow \text{Ce}^{4+}(\text{O}_2^-) \\
\text{Ni}^{2+} + \text{O}_2 & \rightarrow \text{Ni}^{3+}(\text{O}_2^-) \\
\text{Ce}^{3+} + \text{O}_2 & \rightarrow \text{Ce}^{3+}(\text{O}_2^-)
\end{align*}
\]

The oxygen storage capacity of CeO\(_2\)-ZrO\(_2\) catalysts was correlated in the past to the concentration of these oxide ion species [17–22]. The \(g\) value of the superoxide ion is sensitive to the cation with which it is associated. For the cations with +4 oxidation state, the \(g\) value lies in the range of 2.02 to 2.03 and for the ions with +2 state, it is in the range of 2.05 to 2.17. The signal at 2.083, therefore, probably arises from Ni\(^{2+}(\text{O}_2^-)\) and that at 2.033 from Ce\(^{3+}/\text{Zr}^{4+}(\text{O}_2^-)\) species (Fig. 3).

Sample 8 showed a signal at \(g = 2.36\) and sample 6 at \(g = 2.21\) (Fig. 4). The origin of this is due to a small amount of Ni substituted in the CeO\(_2\)-ZrO\(_2\) solid lattice, which is reduced to Ni\(^{+}\) species as described:

\[
\begin{align*}
\text{Ce}^{4+} + \text{O}_2 & \rightarrow \text{Ce}^{3+}(\text{O}_2^-) \\
\text{Ni}^{2+} + \text{O}_2 & \rightarrow \text{Ni}^{3+}(\text{O}_2^-) \\
\text{Ni}^{2+} + \text{O}_2 & \rightarrow \text{Ni}^{3+}(\text{O}_2^-)
\end{align*}
\]

Although it had been postulated that CeO\(_2\) promotes NiO reduction, no experimental evidence had been reported in the literature so far. The present work offers such a support (Fig. 4). Part of the Ni\(^{+}\) ions subsequently react with aerial oxygen and form Ni\(^{2+}(\text{O}_2^-)\) species.

The reduction experiments have revealed at least three types of Ni-species in different NiO-CeO\(_2\)-ZrO\(_2\) samples: (I) Ni substituted in the lattice forming Ni(O\(^{2+}\)) ions (signals at \(g_1 = 2.028\) and \(g_2 = 2.009\) [23], (II) nanosize crystallites of NiO forming superparamagnetic metallic Ni \((g = 2.195; \text{linewidth} = 340\text{G})\) [31] and (III) larger particles of NiO forming ferromagnetic Ni [32]. Sample 1 (1 wt.% Ni) contained species I and II, sample 2 (5 wt.% Ni) contained all the three species, while samples 6–8 (40 wt.% Ni) contained species I and III. The reducibility of these species decreased in the order: \(1 > \text{III} > \text{II}\). The experiments at steam reforming conditions (i.e. in the presence of both H\(_2\) and hydrocarbons) have shown an increased reducibility in the presence of hydrocarbons and long chain alcohols.

All the samples containing 20% or more of Ni exhibited good activity in the steam reforming of ethanol. Sample 6 (NiO (40 wt.%)-CeO\(_2\) (30 wt.%)-ZrO\(_2\) (30 wt.%)) with Ce/Zr = 1:1 exhibited the highest catalytic stability over a period of more than 500 h. The Ce/Zr ratio has a marked effect on the catalytic stability of these materials.

5. Conclusions

NiO-CeO\(_2\)-ZrO\(_2\) catalysts, with varying NiO (1–40 wt.%) and CeO\(_2\)/ZrO\(_2\) ratios of 1:10, 1:1 and 100:0 were prepared hydrothermally using a rotating autoclave. This method of preparation yielded small crystallites (CeO\(_2\)-ZrO\(_2\) = 4.6–7.9 nm,
NiO = 7.3–17.2 nm) with larger specific surface area (71–107 m²/g). XRD confirmed the formation of CeO₂-ZrO₂ solid solutions with a cubic fluorite structure. The catalysts exhibited good catalytic activity and stability in the steam reforming of ethanol. Their redox behavior at the steam reforming conditions was investigated by in situ EPR, DRUV-visible and XPS spectroscopies. EPR spectroscopy identified defect centers (“free” electrons trapped in anion vacancies, O⁻ and O₂⁻) and different types of Ni (Ni-incorporated in the lattice, smaller and larger particles of Ni). While the defect centers are responsible for the oxygen storage capacity, larger crystallites of Ni exhibiting ferromagnetism are involved in the steam reforming. The Ni content, Ce/Zr ratio and specific surface area influence the catalytic activity. Catalysts with Ce/Zr ratio of 1 are superior to the other compositions. A catalyst with a composition of NiO (40 wt.%)-CeO₂ (30 wt.%)-ZrO₂ (30 wt.%) was stable for more than 500 h in the steam reforming of bio-ethanol containing 5 ppm S.

Acknowledgements
The authors thank Dr. C.S. Gopinath, Dr. S.P. Mirajkar, Dr. P. Manikandan, Ms. M.S. Agashe and Ms. Violet for the help in experiments.

References