# Partial oxidation of methane over a Ni/BaTiO<sub>3</sub> catalyst prepared by solid phase crystallization

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# Ni/BaTiO<sub>3</sub> catalyst has been prepared by solid phase crystallization (SPC) and used successfully for partial oxidation of CH<sub>4</sub> into synthesis gas at 800 °C. In the SPC method, Ni/BaTiO<sub>3</sub> catalyst is obtained *in situ* by the reaction of starting materials with nickel species homogeneously incorporated in the structure. For the starting reagents, materials of two compositional types were employed *i.e.*, perovskite structures $BaTi_{1-x}Ni_xO_{3-\delta}$ ( $0 \le x \le 0.4$ ) and stoichiometric structures, $BaTiO_3$ , $Ba_2TiO_4$ and $BaTi_5O_{11}$ , with 0.3NiO. The starting materials were tested for oxidation of CH<sub>4</sub> by increasing the reaction temperature from room temperature to 800 °C. The catalysts showed the highest activity for synthesis gas formation around 800 °C, and the highest value was obtained at a composition of x = 0.3 in the former catalysts. Among the latter catalysts, the highest activity was observed over $BaTiO_3 \cdot 0.3NiO$ , which was more active than $BaTi_{0.7}Ni_{0.3}O_{3-\delta}$ . On the both catalysts, nickel species originally incorporated in the structure were reduced to the metallic state during the reaction. The $BaTiO_3 \cdot 0.3NiO$ catalyst was further tested for 75 hours at 800 °C with no observable degradation and negligible coke formation on the catalyst. Thus, Ni/BaTiO<sub>3</sub> prepared *in situ* from the perovskite precursor, *i.e.*, by the SPC method, was the most active and resistant to coke formation and deactivation during the reaction. This may be due to well dispersed and stable Ni metal particles over the perovskite, where the nickel species thermally evolve from the catalons homogeneously distributed inside an inert perovskite matrix as the precursor.

### Introduction

Recently, intensive study has been carried out on the catalytic partial oxidation of CH4 to synthesis gas.<sup>1-13</sup> This process has advantages over the conventional steam reforming of CH4 to make synthesis gas, as the latter process is highly endothermic and produces synthesis gas having a  $H_2/CO$  ratio  $\ge 3$ . The partial oxidation of CH<sub>4</sub> is mildly exothermic on the whole process and affords synthesis gas having a H<sub>2</sub>/CO ratio of ca. 2, making methanol synthesis an ideal follow-up process. Ashcroft and co-workers<sup>1-3</sup> reported that the transition metals, Ni, Ru, Rh, Pd, Ir and Pt, supported on alumina were active in this reaction at temperatures of 775 °C. Schmidt and co-workers<sup>4-6</sup> reported that Pt and Rh surfaces in a metal-coated ceramic monolith afforded mostly H<sub>2</sub> and CO with almost complete conversion of CH<sub>4</sub> and O<sub>2</sub> with short residence times. Some transition metal oxides combined with alkaline earth or rare earth metal oxides, i.e. CoO-MgO, NiO-CaO, CoO-Yb<sub>2</sub>O<sub>3</sub> or Ni/Yb<sub>2</sub>O<sub>3</sub>, were interestingly found to be catalytically active at low temperatures below  $700\,^{\circ}\text{C}$ , <sup>7-10</sup> but hot spots have been observed in the catalyst bed.<sup>11-13</sup> Lunsford and co-workers<sup>14</sup> reported that the partial oxidation of  $CH_4$  over  $Ni/Al_2O_3$  involves first the oxidation of a part of CH<sub>4</sub> to H<sub>2</sub>O and CO<sub>2</sub>, followed by the reforming reactions of  $CH_4$  with  $H_2O$  and  $CO_2$ .

In the steam reforming of  $CH_4$  to synthesis gas, deactivation of supported metal catalysts by coke formation is a serious problem.<sup>15</sup> Actually in the industrial process, a large amount of steam was added in order to avoid coke formation. In the partial oxidation of  $CH_4$  to synthesis gas, coke formation over the catalyst frequently takes place, resulting in catalyst deactivation. Coke formation has been frequently ignored in the literature,<sup>1-14</sup> except in the case of Claridge *et al.*,<sup>16</sup> who observed that the relative rate of coke formation follows the order Ni > Pd  $\gg$  Rh, Ru, Pt, Ir. Nickel catalysts are highly effective for partial oxidation of CH<sub>4</sub> to synthesis gas, but they are unsatisfactory with respect to coke formation.<sup>17</sup> Slagtern and Olsbye<sup>18</sup> reported the *in situ* formation of and the high activity of metal species for synthesis gas production in LaRhO<sub>3</sub>, which kept high activity for 120 h on stream at 800 °C and showed highly dispersed Rh metal.

A high degree of dispersion of metal species over the catalyst may reduce coke formation.<sup>15</sup> Metal-supported catalysts are conventionally prepared by wet impregnation of different supports. This method is not fully reproducible and may give rise to some inhomogeneity in the distribution of the metal on the surface; therefore, the interest in preparation methods able to produce homogeneous distributions of metal inside in the structure of the precursors, which, on further calcination and reduction, give rise to well dispersed and stable metal particles. Here, we named this method 'solid phase crystallization' (SPC). A similar idea has been proposed by Basini and co-workers<sup>19</sup> in the preparation of new hydrotalcite-type anionic clays containing noble metals as the precursor for a catalyst for the partial oxidation of CH<sub>4</sub> to synthesis gas.

From the industrial viewpoint, Ni is preferable as the active species compared to an expensive precious metal such as Rh, Pd or Ru. We have reported sustainability and high activity of Ni/(Ca, Sr)TiO<sub>3</sub> in the oxidation of CH<sub>4</sub> to synthesis gas,<sup>20–23</sup> where the Ni catalyst supported on (Ca, Sr)TiO<sub>3</sub> perovskite was prepared by the SPC method. However, the precursor was not homogeneous and contained two types of nickel species; one was dissolved in the Ti site in (Ca, Sr)TiO<sub>3</sub> and the other was separated as NiO from the perovskite structure.

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Nickel dissolved in the perovskite structure was reduced to well dispersed, stable metal species, while the NiO was reduced to large Ni metal particles during the reaction. The well dispersed and stable nickel particles seem to be important for operation at low coke formation on the catalyst during the reaction.<sup>23</sup> BaTiO<sub>3</sub> can contain a higher amount of nickel in the Ti site compared to CaTiO<sub>3</sub> and give rise to more completely dispersed metal on the surface during the SPC preparation. Here, we report the preparation and thermal evolution of a catalyst containing well dispersed, stable nickel on the surface, resulting in sustainable catalytic activity for the partial oxidation of CH<sub>4</sub>.

### Experimental

### Synthesis of precursors

Samples of composition  $\text{BaTi}_{1-x}\text{Ni}_xO_{3-\delta}$ ,  $0 \le x \le 0.4$ , were prepared according to the Pechini patent<sup>24</sup> with some modifications of the procedure.<sup>25</sup> Ethylene glycol, citric acid, tetraisopropyl orthotitanate, barium carbonate and nickel nitrate were used as starting materials as described before.<sup>22,23</sup> Moreover, several model compounds with related stoichiometric Ba-Ti-O compositions and combined with nickel oxide, *i.e.*, Ba2TiO4 · 0.3NiO, BaTiO3 · 0.3NiO, BaTi5O11 · 0.3NiO and  $TiO_2 \cdot 0.3NiO$ , were also prepared in the same way. The solution obtained from the starting materials was evaporated at 80-90 °C to form a viscous liquid, followed by a two-step decomposition by heating at 200 °C for 5 h and 500 °C for 5 h and finally calcination at 850 °C in air for 10 h. Only  $TiO_2 \cdot 0.3NiO$  was finally calcined at 955 °C for 1 h to ensure the formation of the rutile crystal structure.<sup>26</sup> Cooling was slowly performed in air by turning off the furnace.  $Ni/\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by a conventional impregnation method using nickel nitrate and each form of Al<sub>2</sub>O<sub>3</sub>, and in situ reduction during the catalytic testing cited below.

### Catalytic testing

The powders produced by the above method were tested in a U-shaped fixed bed reactor in a mixture of  $CH_4$  (1.0 l h<sup>-1</sup>) and air (2.5 l h<sup>-1</sup>). The catalyst bed contained 300 mg of catalyst material in 2 ml of quartz wool to avoid sintering and clogging of the reactor.

The catalytic experiments were started by introducing CH<sub>4</sub> and air at room temperature, and carried out by increasing the reaction temperature from room temperature to 800 °C at a rate of 2.5 °C min<sup>-1</sup>. If not specifically mentioned in the text, gas samples for analysis of products were taken after 30 min equilibration at each temperature. Moreover, the reactions for testing the catalyst life were carried out at 800 °C for 75 h under the same conditions. Product gases from catalytic testing were analysed by a Shimadzu GC-8A gas chromatograph equipped with TCD detector. The selectivities to C<sub>2</sub> compounds, CO<sub>2</sub>, CO and H<sub>2</sub> were calculated based on the numbers of carbon and hydrogen atom in CH<sub>4</sub>.

After the tests, the catalytic experiments were stopped by exchanging the reaction mixture with nitrogen before opening the furnace and cooling the reactor.

### **Characterization of catalysts**

The powder X-ray diffraction (XRD) patterns of catalysts were recorded by using a MXP-18 diffractometer (MAC Science Co.) with Cu-K $\alpha$  radiation. Scanning electron microscopy (SEM) was carried out by using a Hitachi S 800 machine. Transmittance electron microscopy (TEM) was carried out on a JEM-2000FX (JEOL) electron microscope with an energy dispersion spectrometer (EDS: Northern). Surface areas of the catalysts were measured with a Micromeritics model 2200 instrument. Thermal analyses (TG/DTA) were carried out by using a Shimadzu DTA 50 and TGA 50 containing an electrobalance. Transmittance IR spectra were recorded by using a KBr disk and a JASCO FT/IR 7000 spectrometer. X-Ray photoelectron spectra (XPS) were obtained with a PHI-5000 spectrometer employing Mg-K $\alpha$  radiation (1253.6 eV) and an electron flood gun to provide charge neutralization of the non-conducting samples. All binding energy values were referenced to C 1 s (285.0 eV).

### Results

# $BaTi_{1-x}Ni_xO_{3-\delta}$ , synthesis, characterization and catalytic testing

The samples with the given formula (x = 0, 0.01, 0.05, 0.1, 0.2, 0.3 and 0.4) were synthesized by the modified Pechini method.<sup>24</sup> X-Ray diffraction patterns of powders after synthesis are illustrated in Fig. 1. The pattern of BaTiO<sub>3</sub> (perovskite) [JCPDS: 5-626] is observed for all the samples. The first sign of excess NiO [JCPDS: 4-835] is weakly seen for x = 0.3, and is clearly visible for higher nickel concentrations. The absence of NiO peaks at lower concentrations may be due to solubility of Ni in the perovskite, as well as crystallites too small to give a diffraction signal. Reflections from Ba<sub>2</sub>TiO<sub>4</sub> [JCPDS: 38-1481] can be seen increasing with the nickel concentration from x = 0.2. Ba<sub>2</sub>TiO<sub>4</sub> can be formed in the presence of excess Ba on A sites beyond the point of saturation of Ni on B sites.

After the catalytic testing, the XRD patterns still show BaTiO<sub>3</sub> to be the main constituent of the catalyst, as illustrated in Fig. 2. In these diffractograms we see neither NiO nor nickel metal [JCPDS: 4-850], except a small trace of NiO at the highest nickel concentration (x = 0.4). The second phase in the diffractograms is BaCO<sub>3</sub> [JCPDS: 5-378], which is seen to increase with the original nickel content of the

**Fig. 1** X-Ray diffractograms for several compositions of catalysts of the type  $\text{BaTi}_{1-x}\text{Ni}_xO_{3-\delta}$  after calcination in air at 850 °C. (a) x = 0, (b) 0.01, (c) 0.05, (d) 0.1, (e) 0.2, (f) 0.3, (g) 0.4. (O) BaTiO\_3, (**①**) Ba\_2TiO\_4, ( $\nabla$ ) NiO.





**Fig. 2** X-Ray diffractograms for several compositions of catalysts of the type  $\text{BaTi}_{1-x}\text{Ni}_xO_{3-\delta}$  after catalytic testing at 800 °C in a mixture of CH<sub>4</sub> and air (1 : 2.5). (a) x = 0.1, (b) 0.2, (c) 0.3, (d) 0.4. ( $\bigcirc$ ) BaTiO<sub>3</sub>, ( $\square$ ) BaCO<sub>3</sub>, ( $\bigtriangledown$ ) NiO, ( $\blacktriangledown$ ) Ni metal.

material.  $Ba_2 TiO_4$  disappeared after the catalytic testing. NiO which was visible in diffractograms after calcination was negligible after the catalytic testing. We believe a substantial part of nickel on the surface was reduced to its metallic form during the catalytic testing. The nickel metal particles are probably too small to give reasonable signals in XRD (vide infra).

Reaction with the reactor filled with quartz wool alone (*i.e.*, a blank test without catalyst) showed an oxygen conversion of less than 10% in the whole temperature range of this study. CH<sub>4</sub> conversion stayed below 1% and CO<sub>2</sub> was the only product. Samples of BaTi<sub>1-x</sub>Ni<sub>x</sub>O<sub>3- $\delta}$ </sub> (x = 0, 0.01, 0.05, 0.1, 0.2, 0.3 and 0.4) were tested for CH<sub>4</sub> oxidation. Representative data from the catalytic testing of these materials are given in Table 1. The oxygen conversion was high for all experiments at 750 and 800 °C. The CH<sub>4</sub> conversion increased with temperature and with nickel content. For low nickel content and low temperature, the catalysts showed a certain selectivity (*ca.* 

Table 1 CH<sub>4</sub> oxidation with air over a series of  $BaTi_{1-x}Ni_xO_{3-\delta}$  catalysts

catalyst x <sup>a</sup>	temperature /°C	conversion (%)		selectivity (%)			
		$CH_4$	O <sub>2</sub>	C <sub>2</sub>	$CO_2$	СО	$H_2$
0	750	39.5	94.5	33.0	63.2	3.8	6.2
	800	40.4	95.0	33.6	62.1	4.3	7.3
0.01	750	39.7	95.0	33.0	64.0	3.0	4.7
	800	39.8	94.9	31.8	65.0	3.2	5.3
0.05	750	37.1	95.0	28.7	69.7	1.6	3.2
	800	36.5	95.0	18.1	76.7	5.2	7.7
0.1	750	37.3	95.0	20.5	75.7	3.8	6.5
	800	75.5	95.0	n.d.	17.3	82.8	83.9
0.2	750	47.8	94.9	n.d.	20.3	79.7	79.1
	800	87.2	94.9	n.d.	10.2	89.8	87.9
0.3	750	88.8	95.0	n.d.	10.6	89.4	89.8
	800	92.2	94.5	n.d.	7.7	92.3	91.9
0.4	750	87.0	94.9	n.d.	12.4	87.6	89.3
	800	91.8	94.9	n.d.	9.0	91.0	89.9

<sup>*a*</sup> x is the nickel content of the catalyst. 300 mg of catalyst was used, and the feed consisted of  $1 \ l \ h^{-1}$  of CH<sub>4</sub> and 2.5 l  $h^{-1}$  of air at 1 atmosphere (CH<sub>4</sub>/O<sub>2</sub> = 1.9). n.d. = not determined.

30%) for C<sub>2</sub> products (ethane and ethene). However, the main product was CO<sub>2</sub>. At high nickel content and at 800 °C, the catalysts selectively produced synthesis gas. Visual observation, carbon mass balance of the gaseous products, as well as TG of used catalysts revealed no or very low (<0.1%) coke formation during the catalytic testing. Total carbon ( $\Sigma C =$ CO + CO<sub>2</sub> + unreacted CH<sub>4</sub>) in the effluent gas was 40.3 mmol h<sup>-1</sup> which agreed well with the value calculated from the CH<sub>4</sub> gas flow, 1.01 h<sup>-1</sup>, regulated at 30 °C by the mass flow controller.

## Related compounds, synthesis, characterization and catalytic testing

According to the phase diagram for  $BaO-TiO_2$ ,<sup>27,28</sup> several mixed oxides,  $Ba_2TiO_4$ ,  $BaTiO_3$ ,  $BaTi_3O_7$ ,  $Ba_4Ti_{13}O_{40}$ ,  $BaTi_4O_9$  and  $BaTi_5O_{11}$ , are expected to be formed in the present conditions. We have tried to synthesize these mixed oxides in the presence of Ni species by controlling the Ba : Ti ratio using the citrate method mentioned above. Among these mixed oxides,  $Ba_2TiO_4$ ,  $BaTiO_3$  and  $BaTi_5O_{11}$  were obtained as a single phase in the presence of NiO at a molar ratio of 1 : 0.3 by the citrate method.  $TiO_2 \cdot 0.3NiO$  was also prepared as a related compound.

Fig. 3 illustrates the XRD patterns of the related compounds before and after catalytic testing.  $BaTiO_3 \cdot 0.3NiO$  showed the XRD pattern of  $BaTiO_3$  and a trace of NiO



**Fig. 3** X-Ray diffractograms for several catalysts with a structure related to the present study before and after the catalytic testing at 800 °C in a mixture of CH<sub>4</sub> and air (1:2.5). (a) Ba<sub>2</sub>TiO<sub>4</sub> · 0.3NiO (before testing); (b) Ba<sub>2</sub>TiO<sub>4</sub> · 0.3NiO (after testing); (c) BaTi<sub>5</sub>O<sub>11</sub> · 0.3NiO (before testing); (d) BaTiO<sub>3</sub> · 0.3NiO (after testing); (e) BaTi<sub>5</sub>O<sub>11</sub> · 0.3NiO (before testing); (f) BaTi<sub>5</sub>O<sub>11</sub> · 0.3NiO (after testing); (g) TiO<sub>2</sub> · 0.3NiO (before testing); (h) TiO<sub>2</sub> · 0.3NiO (after testing); (f) BaTi<sub>5</sub>O<sub>11</sub> · 0.3NiO (after testing); (f) NiTiO<sub>2</sub> · 0.3NiO (f) NiO; (f) Ni metal.

**Table 2** Surface metal composition of  $BaTiO_3 \cdot 0.3NiO$  before and after the catalytic test determined by XPS

	content (%)		
catalyst	Ba	Ti	Ni
$\begin{array}{l} BaTiO_{3} \cdot 0.3NiO_{before} \\ BaTiO_{3} \cdot 0.3NiO_{after} \\ calculated \end{array}$	40.2 39.5 43.5	45.3 46.3 43.5	14.5 14.2 13.0

before the testing, while neither NiO nor Ni metal was observed after the testing. In the case of  $Ba_2TiO_4 \cdot 0.3NiO_4$ , NiO was weakly seen before testing and disappeared after testing. When the same catalyst was used for catalytic testing for 60 min at 800 °C, the XRD pattern was completely changed. Perovskite (BaTiO<sub>3</sub>) was the main compound, with BaCO<sub>3</sub>; no nickel was observed. together  $BaTi_5O_{11} \cdot 0.3NiO$  showed the peaks of  $BaTi_5O_{11}$  [JCPDS: 35-805]; neither nickel species nor substantial change were observed in the XRD patterns before or after the testing. The attempt to make TiO<sub>2</sub> · 0.3NiO as a related compound resulted in the formation of NiTiO<sub>3</sub> (illumenite) [JCPDS: 33-960] and TiO<sub>2</sub> (rutile) [JCPDS: 21-1276] after calcination for 1 h at 955 °C. After catalytic testing, XRD showed only rutile and metallic nickel. In this case, Ni metal was clearly observed, as in the cases of Ni/(Ca, Sr)TiO<sub>3</sub> and Ni/γ- $Al_2O_3$ .<sup>21–23</sup> The colour of the catalyst changed during the testing as follows: from grey to black for both  $Ba_2TiO_4 \cdot 0.3NiO$  and  $BaTiO_3 \cdot 0.3NiO$  and from yellow to black for  $TiO_2 \cdot 0.3NiO$ . The pale green colour of  $BaTi_5O_{11} \cdot 0.3NiO$  did not change during testing, suggesting that the nickel may be incorporated in the mixed oxide structure and cannot be reduced to the metallic state. The colour change to black strongly suggests the formation of metallic nickel species, nevertheless XRD measurement did not show the diffraction lines of Ni metal in the samples of  $Ba_2TiO_4 \cdot 0.3NiO$  and  $BaTiO_3 \cdot 0.3NiO$  after testing.

The presence of Ni on the catalyst surface is also evident from XPS of  $BaTiO_3 \cdot 0.3NiO$  before and after catalytic testing. The compositions of the metals were calculated from the spectra by using the method reported by Penn<sup>29</sup> and are shown in Table 2. The amount of Ni was obtained by summing Ni<sup>0</sup> and Ni<sup>2+</sup>, since the catalyst bed was composed of two zones, *i.e.*, the oxidized zone and the reduced zone (*vide infra*), and moreover the surface of the Ni metal on the catalyst was possibly oxidized by the exposure of the samples during testing in air. The binding energies of the main peaks of Ni  $3p_{3/2}$  used for the calculation were 854.8 and 853.4 eV and, 861.0 and 860.0 eV for the shake-up satellite peaks, for the sample before and after testing, respectively. The former values can be assigned to Ni<sup>2+</sup>, but the latter values are rather high for Ni<sup>0</sup>. BaTiO<sub>3</sub> · 0.3NiO after testing still shows the same amount of surface Ni as before testing. Thus, XPS shows strong evidence of Ni metal on the catalyst surface, and moreover no observation of Ni metal by XRD suggests the formation of fine Ni metal particles with a high degree of dispersion. The high values of the binding energy of Ni<sup>0</sup> observed for the sample after the testing also suggest the formation of finely dispersed Ni metal on the catalyst surface.

Catalytic data for the related compounds combined with NiO used in the CH<sub>4</sub> oxidation are summarized in Table 3.  $BaTiO_3 \cdot 0.3NiO$  showed higher activity for synthesis gas prothan  $BaTi_{0.7}Ni_{0.3}O_{3-\delta}$  (cf. Table duction 1).  $BaTi_5O_{11} \cdot 0.3NiO$  showed a high yield of  $CO_2$  as well as a small amount of C<sub>2</sub> products at all temperatures.  $Ba_2TiO_4 \cdot 0.3NiO$  gave  $CO_2$  as the main product, but showed a relatively high selectivity for C2 products (approximately the same as for pure BaTiO<sub>3</sub> perovskite). During testing at 800 °C, the selectivity gradually changed as the test was further extended to 60 min. During this period the catalyst increasingly promoted the production of synthesis gas, but was not as efficient a catalyst as BaTiO<sub>3</sub> · 0.3NiO. IR Spectra of  $Ba_2TiO_4 \cdot 0.3NiO$  after testing showed a strong broad band and a sharp band at ca. 1430 and at 859 cm<sup>-1</sup>, respectively, suggesting the formation of BaCO<sub>3</sub>. The same bands, much weaker, were observed on all catalysts containing Ba before and after testing, probably due to surface carbonate formation over the perovskite.

A comparison between the CH<sub>4</sub> conversion of the four catalysts,  $BaTiO_3 \cdot 0.3NiO$ ,  $BaTi_{0.7}Ni_{0.3}O_{3-\delta}$ ,  $Ba_2TiO_4 \cdot 0.3NiO$ and TiO<sub>2</sub>  $\cdot$  0.3NiO, at various temperatures is shown in Fig. 4. All the curves level out in two areas. The reaction dominating at lower temperatures mainly produces CO<sub>2</sub> and some C<sub>2</sub> products. The level at higher temperatures is dominated by synthesis gas production.  $TiO_2 \cdot 0.3NiO$  was active for complete oxidation at the lowest temperature, followed by BaTiO<sub>3</sub>  $\cdot$  0.3NiO and then BaTi<sub>0.7</sub>Ni<sub>0.3</sub>O<sub>3- $\delta$ </sub>. For synthesis gas production, both TiO<sub>2</sub> · 0.3NiO and BaTiO<sub>3</sub> · 0.3NiO showed slightly higher total conversions, but the difference in activation temperature mav not be significant.  $Ba_2TiO_4 \cdot 0.3NiO$  needed a higher temperature or a longer time to be activated, and the point of conversion after 60 min at 800 °C is included in Fig. 4.

 Table 3
 CH<sub>4</sub> oxidation with air over a series of Ba–Ti–Ni mixed metal oxide catalysts

		conversion (%)					
catalyst	temperature/°C	CH <sub>4</sub>	0 <sub>2</sub>	C <sub>2</sub>	CO <sub>2</sub>	СО	H <sub>2</sub>
Ba <sub>2</sub> TiO <sub>4</sub> · 0.3NiO	700	39.7	93.3	34.1	64.2	1.7	2.8
2 7	750	41.0	94.9	35.6	62.7	1.6	2.9
	800	38.0	94.9	22.2	70.0	7.8	10.4
	800 <sup>a</sup>	65.8	94.9	0.2	24.5	75.3	75.8
$BaTiO_3 \cdot 0.3NiO^b$	700	56.0	94.9	n.d.	44.1	55.9	99.9
5	750	94.8	94.9	n.d.	7.5	92.5	85.3
	800	98.0	94.9	n.d.	5.6	94.4	91.9
BaTi <sub>5</sub> O <sub>11</sub> · 0.3NiO	700	18.2	53.7	5.2	82.5	12.4	19.6
5 11	750	30.2	88.3	10.2	83.4	6.4	10.8
	800	32.7	93.8	11.3	82.7	6.0	8.2
TiO <sub>2</sub> · 0.3NiO	700	17.6	55.9	0.5	99.5	n.d.	0.1
2	750	94.7	94.9	n.d.	7.8	92.2	91.4
	800	98.1	95.0	n.d.	5.6	94.3	92.4
thermodynamics <sup>c</sup>	700	(89.2)	(100)		(9.4)	(90.5)	(93.7)
2	750	(93.5)	(100)		(5.2)	(94.9)	(95.9)
	800	(97.1)	(100)	—	(3.2)	(96.8)	(97.0)

300 mg of catalyst was used, and the feed consisted of  $1 \ln^{-1}$  of CH<sub>4</sub> and  $2.5 \ln^{-1}$  of air at 1 atmosphere (CH<sub>4</sub>/O<sub>2</sub> = 1.9). <sup>a</sup> Sampled after 60 min. <sup>b</sup> C<sub>2</sub> products were observed up to 650 °C. <sup>c</sup> Numbers in parentheses show the values calculated from thermodynamic equilibrium of reactions (1)–(3). n.d. = not determined.



**Fig. 4** CH<sub>4</sub> conversion as a function of temperature for the four catalysts in a mixture of CH<sub>4</sub> (1 1 h<sup>-1</sup>) and air (2.5 1 h<sup>-1</sup>) with 300 mg of catalyst. ( $\square$ ) BaTiO<sub>3</sub>·0.3NiO, ( $\blacksquare$ ) BaTiO<sub>1.7</sub>Ni<sub>0.3</sub>O<sub>3- $\delta$ </sub>, ( $\blacktriangle$ )TiO<sub>2</sub>·0.3NiO, ( $\bigcirc$ ) Ba<sub>2</sub>TiO<sub>4</sub>·0.3NiO. \* After reaction for 1 h at 800 °C.

TG was performed on catalysts before and after testing as illustrated in Fig. 5. All experiments were performed in flowing air (20 ml min<sup>-1</sup>). Around 400 °C a weight increase, probably due to the oxidation of Ni metal, is observed on used catalysts, while fresh catalysts show flat curves in the whole temperature range. The weight increases of the used samples of BaTiO<sub>3</sub> · 0.3NiO and Ba<sub>2</sub>TiO<sub>4</sub> · 0.3NiO amount to about 0.7% of the total mass of each sample. Assuming oxidation of Ni metal to NiO is the only reaction taking place, this corresponds to 10% of all the nickel being in the metallic form after testing. A substantial weight decease observed with  $Ba_{2}TiO_{4}\cdot 0.3NiO$  after testing above 800  $^{\circ}C$  may be due to the decomposition of bulk BaCO3. The sample of used  $TiO_2 \cdot 0.3NiO$  showed a weight increase of 4.8%, corresponding to 60% of the Ni in the reduced form.  $TiO_2 \cdot 0.3NiO$ showed lower activity for CH4 combustion at low temperatures compared with the other catalysts. This catalyst was also able to support synthesis gas production, but long-term



**Fig. 5** TG of ( $\bullet$ ) BaTiO<sub>3</sub> · 0.3NiO, ( $\blacksquare$ ) Ba<sub>2</sub>TiO<sub>4</sub> · 0.3NiO and ( $\blacktriangle$ ) TiO<sub>2</sub> · 0.3NiO ( $\longrightarrow$ ) before and (---) after catalytic testing. The heating rate was 10 °C min<sup>-1</sup>. Air was flowing constantly over the sample at a rate of 20 ml min<sup>-1</sup>. The curve for TiO<sub>2</sub> · 0.3NiO after the catalytic testing should be multiplied by a factor of 4 to be comparable with the other data.



**Fig. 6** Conversions and selectivities as a function of time for the long-term test on (a)  $BaTiO_3 \cdot 0.3NiO$  and (b)  $TiO_2 \cdot 0.3NiO$ . ( $\bigcirc$ )  $CH_4$  and ( $\bigcirc$ )  $O_2$  conversion; ( $\blacksquare$ ) CO and ( $\square$ )  $H_2$  selectivity. The temperature was 800 °C, and the feed was a mixture of  $CH_4$  (1 1 h<sup>-1</sup>) and air (2.5 1 h<sup>-1</sup>); the amount of catalyst was 300 mg.

testing showed the catalyst to be unstable, as will be shown below.

### Long-term testing of BaTiO<sub>3</sub> · 0.3NiO and TiO<sub>2</sub> · 0.3NiO

The best performing catalyst, BaTiO<sub>3</sub> · 0.3NiO, in this study was subjected to a continuous reaction test over 75 h at 800 °C [Fig. 6(a)]. There are no significant changes in the values of conversions of CH<sub>4</sub> and O<sub>2</sub> and selectivities for CO, H<sub>2</sub> and CO<sub>2</sub> over this catalyst for the period used in the test. The selectivity for CO<sub>2</sub> and  $\Sigma$ C showed almost constant



**Fig. 7** Temperature programmed oxidation of ( $\bullet$ ) BaTiO<sub>3</sub>·0.3NiO and ( $\blacksquare$ ) TiO<sub>2</sub>·0.3NiO after 75 h of the catalytic testing. The heating rate was 2.5 °C min<sup>-1</sup>. Air was flowing constantly over the sample at a rate of 20 ml min<sup>-1</sup>.

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values close to 5.0% and 40.3 mmol  $h^{-1}$ , respectively. After 75 h of testing, the reactor was filled with nitrogen and cooled according to normal procedures. Finally, a temperature programmed oxidation (TPO) experiment was performed by heating the reactor from room temperature to 950 °C at a rate of 2.5 °C min<sup>-1</sup>, with an air flow of 41 ml min<sup>-1</sup>. Off-gases were analysed as usual and the rate of CO<sub>2</sub> formation is plotted in Fig. 7. No significant amount of CO<sub>2</sub> was observed during this test with BaTiO<sub>3</sub> · 0.3NiO; CO<sub>2</sub> formation around 450 °C may be produced from coke formed on the catalyst which corresponded to 0.02 wt.% carbon on the catalyst. The peak observed above 750 °C may be due to the decomposition of surface BaCO<sub>3</sub> as already seen in the TG curve after the catalytic testing (Fig. 5). The observed amount of  $CO_2$  corresponded to the maximum of 3% BaCO<sub>3</sub> in the catalyst after 75 h of catalytic testing.

In the CH<sub>4</sub> oxidation over TiO<sub>2</sub> · 0.3NiO [Fig. 6(b)], the catalyst behaved initially like BaTiO<sub>3</sub> · 0.3NiO. At long times, however, the CH<sub>4</sub> conversion decreased, as did the selectivities to H<sub>2</sub> and CO; conversely, CO<sub>2</sub> selectivity increased from 5.0 to 7.0% with time.  $\Sigma C$  (40.3 mmol h<sup>-1</sup>) showed no significant change during the reaction. After 75 h of testing an amount of CO<sub>2</sub> corresponding to 0.41 wt.% of the catalyst being coked was measured (see Fig. 11, later). The CH<sub>4</sub> oxidation over the other conventional Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalysts under the same conditions as above has been tested. After 150 h of reaction, 29.3 and 16.8 wt.% of coke were observed over Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub><sup>2.2.3</sup> and Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst, respectively. Compared to the Ni/Al<sub>2</sub>O<sub>3</sub> catalysts, TiO<sub>2</sub> · 0.3NiO had a greater resistance to coking, and therefore the other deactivation mechanism, *i.e.*, sintering or oxidation of Ni metal, can be considered.

### Discussion

As previously mentioned for  $CH_4$  oxidation over Ni/Al<sub>2</sub>O<sub>3</sub> catalyst,<sup>14</sup> the present process is also thought to involve first the oxidation of part of  $CH_4$  to  $H_2O$  and  $CO_2$ , followed by the reforming reactions of  $CH_4$  with  $H_2O$  and  $CO_2$ .

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{1}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{2}$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \tag{3}$$

Therefore, the catalyst bed may be composed of two zones in the fixed bed reactor; the first zone is composed mainly of Ni in the perovskite under the oxygen-rich atmosphere and the second is of surface Ni metal under the reducing atmosphere. It is likely that the reaction is mainly controlled by the thermodynamic equilibrium of the reforming reactions [(2) and (3)] as seen in the values in parentheses in Table 3.

The BaTiO<sub>3</sub>  $\cdot$  0.3NiO catalyst showed the highest activity for synthesis gas production around 800 °C, which is probably related to the formation of metallic nickel on the surface of the catalyst. By XRD, trace NiO was observed before catalytic testing, but no Ni metal was observed after testing. Oxidation of the used catalysts by TG gave a strong indication of the presence of metallic nickel (Fig. 5). The presence of Ni on the surface of the catalyst is also evident from XPS measurements (Table 2). These facts strongly suggest the formation of finely dispersed Ni metal on the BaTiO<sub>3</sub>  $\cdot$  0.3NiO catalyst during the activation. TiO<sub>2</sub>  $\cdot$  0.3NiO also showed a high activity, but was gradually deactivated during long-term testing. Its TG behaviour (Fig. 5) is also reflected in the XRD results (Fig. 3), suggesting that nickel probably forms larger crystals on rutile than on the barium compounds.

TG of the used sample of  $Ba_2TiO_4 \cdot 0.3NiO$  shows an additional feature at temperatures above 800 °C, namely a weight loss of 8.0% (Fig. 5). XRD and IR analyses of this catalyst after testing revealed large amounts of  $BaCO_3$ , and we assume the weight loss corresponds to the thermal decomposition of  $BaCO_3$ , releasing  $CO_2$  to the atmosphere. A weight loss of 8% indicates that 35% of the catalyst after the testing is composed of  $BaCO_3$ . Thus, it is likely that  $Ba_2TiO_4$  is decomposed into  $BaTiO_3$  and  $BaCO_3$  in the atmosphere containing  $CO_2$ .

$$Ba_2TiO_4 + CO_2 \rightarrow BaTiO_3 + BaCO_3$$
 (4)

After the complete phase transfer from  $Ba_2TiO_4$  to  $BaTiO_3$ , the reduction of surface Ni species may start, resulting in the activation of the catalyst.

Scanning electron micrographs (SEM) of  $Ba_2TiO_4 \cdot 0.3NiO$ before and after catalytic testing are shown in Fig. 8. The plate-like crystals of the sample before testing [Fig. 8(a)] were completely changed into a porous structure having many crevices after testing [Fig. 8(b)]. This can be explained by the phase transfer from  $Ba_2TiO_4$  to  $BaTiO_3$  and  $BaCO_3$  [eqn. (4)], followed by a partial decomposition of  $BaCO_3$  at 800 °C.  $BaTiO_3 \cdot 0.3NiO$  showed no substantial change in the SEM morphologies during the reaction.  $TiO_2 \cdot 0.3NiO$  produced small particles (<0.1 µm) probably of Ni metal on the rutile  $TiO_2$  surface suggesting the decomposition of NiTiO\_3 to Ni



Fig. 8 Scanning electron micrographs of  $Ba_2TiO_4 \cdot 0.3NiO$  (a) before and (b) after catalytic testing

 Table 4
 Surface area and XRD data of Ba–Ti–Ni mixed metal oxide catalysts

	c a	observed phases			
catalyst	$/m^2 g^{-1}$	before testing	after testing		
Ba₂TiO₄ · 0.3NiO	2.3	$Ba_2TiO_4 + NiO$	$BaTiO_3 + BaCO_3$		
BaTiO <sub>3</sub> · 0.3NiO	8.9	$BaTiO_3 + NiO^b$	BaTiO <sub>3</sub>		
BaTi <sub>5</sub> O <sub>11</sub> · 0.3NiO	7.1	BaTi <sub>5</sub> O <sub>11</sub>	BaTi <sub>5</sub> O <sub>11</sub>		
TiO <sub>2</sub> ·0.3NiO	0.6	$NiTiO_3$ (illumenite) + $TiO_2$ (rutile)	$TiO_2(rutile) + Ni$		

<sup>a</sup> Fresh catalyst. <sup>b</sup> Traces of NiO peaks were observed.

metal and  $\text{TiO}_2$  as seen in the XRD measurements (Fig. 3). A summary of the observations of phase transfer is given in Table 4 together with measurements of the specific surface area before testing.

In the present study, XRD measurements simply indicate that the solubility of Ni is 10-20% on B-sites of BaTiO<sub>3</sub> (Fig. 1). The solubility will probably decrease upon lowering the temperature and the partial pressure of oxygen. In this respect, Ni may precipitate at the surface during the use of the catalyst under reducing atmospheres. The precipitation may produce well dispersed and stable Ni on the surface of the perovskite, and contribute to the formation of an active and sustainable catalyst. TEM observation of BaTiO<sub>3</sub> · 0.3NiO after the testing actually shows high dispersion of Ni species (Fig. 9). Ni is seen as dark spots (A and B in Fig. 9), where EDS shows the coexistence of Ba and Ti together with Ni. At site C, Ni is not observed, but Ba and Ti are detected by EDS. A TEM image of the dark spot at high magnifications (Fig. 10) suggests that the spot is composed of an agglomerate of fine Ni particles (diameter of the particle  $\leq 1$  nm). A TEM image of  $TiO_2 \cdot 0.3NiO$  after testing, for comparison, (Fig. 11) clearly shows the formation of larger Ni metal particles as black spots (A and B) which are mainly composed of Ni by



Fig. 9 Transmittance electron micrograph of  $BaTiO_3 \cdot 0.3NiO$  after testing



Fig. 10 Transmittance electron micrograph of  $BaTiO_3 \cdot 0.3NiO$  after testing

EDS. Thus, Ni metal is completely separated from  $TiO_2$  as the support in the case of  $TiO_2 \cdot 0.3NiO$  after testing, while BaTiO<sub>3</sub> perovskite can hold fine Ni metal particles on the surface. In the latter case, nickel is obviously distributed as



Fig. 11 Transmittance electron micrograph of TiO $_2 \cdot 0.3$ NiO after testing

fine particles, and we interpret this in terms of a more favorable interaction between nickel and the support. Several binary oxides of Ba and Ni are known, even in the temperature range of the present study.<sup>30–32</sup> Such phases indicate that there may be an increased 'affinity' between the nickel and the support during catalytic action. When nickel is precipitated at the surface, there will be a surplus of Ba on the A-sites of the perovskite material. Barium is one of the elements that are known to keep the level of coking on metals down. In the present set of experiments, coke was not formed to any obvious extent.

There are three advantages related to the present  $BaTiO_3 \cdot 0.3NiO$  catalyst prepared by the SPC method. (1) Precipitation from solid solution gives the optimum dispersion of Ni on the surface. The main fraction of Ni is dissolved in the lattice during calcination, and is precipitated during catalytic testing. (2) Ni has a greater 'affinity' for B-sites in the perovskite than for most traditional supports, like  $Al_2O_3$  and  $TiO_2$ . This results in a better dispersion and a low driving force for metal sintering. (3) Low coking is traditionally achieved by promoting catalysis with alkaline or alkaline earth metals. Abundant barium probably acts in this manner.

The main problem connected with the practical use of this kind of perovskite catalyst in an operating plant is probably the low surface area and the tendency to form fine particles during the catalytic action. This must be solved by using a binder or a certain support, like  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The latter study has just been undertaken in our laboratory.

### Conclusion

Several compositions of  $BaTi_{1-x}Ni_xO_{3-\delta}$ ,  $BaTiO_3 \cdot NiO$  and related compounds have been prepared and tested as catalysts for the partial oxidation of CH<sub>4</sub> to synthesis gas at 800 °C. Ni/BaTiO<sub>3</sub> catalyst prepared by solid phase crystallization (SPC) showed the highest activity as well as the highest sustainability against coke formation which may be due to well dispersed, stable metallic nickel particles on the BaTiO<sub>3</sub> surface. Testing this catalyst continuously over 75 h showed no significant coking or other changes in the reaction patterns.

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