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Partial oxidation and dry reforming of methane over Ca/Ni/K(Na) catalysts

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Partial oxidation and dry reforming of methane to synthesis gas over Ca/Ni/K(Na) catalysts have been studied. Effects of temperature, pressure, and oxygen/methane ratios on catalytic activity, selectivity, and carbon formation have been determined. Also reforming of $^{13}CH_4$ in the presence of CO_2 and Temperature-Programmed Oxidation (TPO) of deposited carbon after the reaction indicated that both methane and CO_2 contribute to carbon formation. The TPO of deposited carbon on Ca/Ni/K catalyst showed that the catalyst consumed a significant amount of oxygen, only a fraction of which was consumed by carbon species on the surface, indicating that the surface oxygen plays a significant role in oxidizing and removing carbon species from the catalyst surfaces

KEY WORDS: synthesis gas; dry reforming; catalysis; carbon formation.

1. Introduction

Catalyst containing Ca/Ni/K has been studied extensively for the direct conversion of methane to ethane and ethylene for producing liquid fuels [1–4]. Despite intensive efforts in this area, little progress has been achieved because ethane and ethylene are more reactive than methane, reacting with oxygen and forming CO and CO_2, as we reported earlier [4]. It appears that the alternative method, making synthesis gas from methane and converting it into liquid fuels, is a more attractive one. Nickel catalysts used in this process also catalyze carbon formation, which greatly contributes to catalyst deactivation [5–8]. Carbon accumulates in the catalyst bed, causing catalyst deactivation and plant shutdown. This problem is solved by addition of excess steam or oxygen, which increases the cost of syngas production.

The key issue in improving catalyst performance is to avoid the formation of carbon on the catalyst. Temperature, pressure, promoter, catalyst support, and catalyst particle size have been shown to be very important in controlling carbon formation on nickel catalysts [9–11]. Reducing carbon formation requires a multi-facetted approach: (1) a better understanding of the reforming reactions; (2) using more expensive noble metal catalysts such as ruthenium and rhodium; (3) increasing the oxygen content of the support; (4) using supports such as CaO and MgO or a combination of both; and (5) decreasing the rate of carbon formation by addition of alkali metals such as Li, Na, K, and Cs.

Alkali-metal salts have been extensively used to catalyze carbon gasification as reviewed by Wood and Sancier [12] and also by Wigmans [13]. Alkali metals have also been used to reduce the rate of carbon formation on the catalyst: Bengaard and his co-workers [14] reported that methane-sticking probability was reduced when potassium was present on Ni(100) and Ni(111) surfaces [11]. They also explained the results by conducting large-scale density functional theory calculations that showed the barrier for dissociation of methane increased by 0.2 eV with the adsorption of potassium. Ito and his co-workers [15] studied the effects of Li, K, and Cs on carbon formation on Ni/alumina catalyst and reported that addition of Li stabilized the catalyst and also produced less carbon. Therefore, this study was initiated to study the effects of alkali metals (Na and K), temperature, pressure, and oxygen/methane ratios on catalytic activity, selectivity, and on carbon formation.

2. Experimental

Two catalysts, one containing calcium, nickel, potassium (Ca/Ni/K = 2:1:0.1) and the other containing sodium instead of potassium (Ca/Ni/Na = 2:1:0; 0.1), were prepared as reported by Pereira *et al.* [3]. Prior to reaction the catalysts were reduced at 600 °C for one hour in 30 cm^3/min flow of pure H_2. A 0.3-m long ceramic tube (6.35-mm o.d., 4.0-mm i.d.), sealed inside a stainless steel tube at higher pressures,

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containing a quartz thermocouple well was used as a fixed-bed reactor. The reactor was loaded with 0.012–0.5 grams of catalyst (−28/+48 mesh) mixed with silica and held in place by quartz wool.

Temperature-Programmed Oxidation (TPO) of deposited carbon after the reaction was performed by heating the sample from 30 to 950 °C at a rate of 20 °C/min in flow of 2% oxygen in helium (40 cm^3/min). The exit gases were analyzed using a thermal conductivity detector and a quadrupole mass spectrometer.

3. Results and discussion

3.1. Dry reforming

The effect of temperature on the reforming of methane in the presence of CO_2 (CO_2/CH_4 = 1.1) over Ca/Ni/K was studied at atmospheric pressure and the results are shown in table 1. As the temperature increased to 900 °C the methane and CO_2 conversions and the H_2/CO ratios were increased. However, raising the temperature from 800 to 900 °C didn't significantly change the catalyst activity because most of reactants were consumed at about 800 °C. The main objective was to study carbon formation and catalyst deactivation at high conversions. Therefore, the catalyst was optimized and tested at high conversion to accelerate carbon formation and possibly catalyst deactivation. No significant amount of carbon or no loss of activity were observed when the catalyst was tested at 760 °C and 1 atm for about 360 hours as shown in figure 1. More than 95% of methane and CO_2 were converted producing a CO yield of more than 95% with H_2/CO ratio of one.

With a few exceptions most of the results reported in the literature for reforming methane with CO_2 are collected at atmospheric pressure. Since most of the industrial processes that use hydrogen or synthesis gas operate at higher pressure (>10 atm) therefore, we tested this catalyst at 1, 8, and 14 atm to study catalyst deactivation and also carbon formation in the catalyst bed.As shown in figure 2, methane and CO_2 conversions with H_2 /CO ratios decreased with increasing pressure. Furthermore, the amount of carbon formed in the catalyst bed was also increased as the pressure increased from 1 to 14 atm. The catalyst was also tested for more than 10 h at 14 atm with no significant changes in activity or selectivity as shown in figure 3, CH_4/CO_2 = 2 was used to accelerate carbon formation. The initial activity of as prepared Ca/Ni/K catalyst with atomic ratio of 2:1:0.1 was significantly lower than the catalyst treated with synthesis gas at 900 °C for three hours. The initial activity increased with time on stream as shown in figure 4. The as prepared catalyst contained

Table 1
Effect of temperature on reforming of methane with CO_2 over Ca/Ni/K catalyst, GHSV = 5040 mL g^{-1} h^{-1}, CO_2/CH_4 = 1.1, 1 atm

Temperature (°C)	H_2/CO ratio	%CO yield	$\%CH_4$ conversion	$\%CO_2$ conversion
650	0.4	21.0	10.9	18.5
750	0.7	60.0	46.0	60.0
850	1.0	98.0	95.9	96.3
900	1.0	100.0	98.8	96.9
800[a]	1.0	98.9	98.7	96.0
850[a]	1.0	99.6	99.5	96.3

[a]After 180 h on stream.

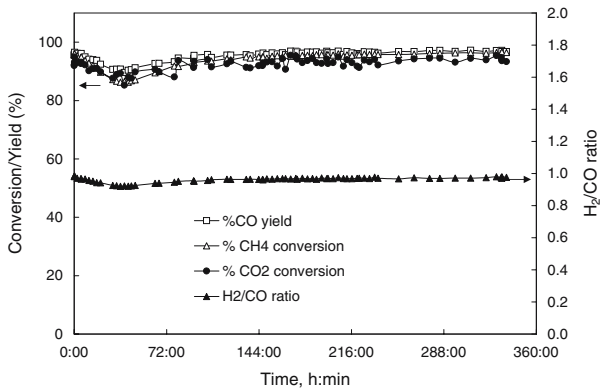

Figure 1. Reforming of methane with CO_2 over Ca/Ni/K catalyst, CO_2/CH_2 = 1.1, 860 °C, GHSV = 5040 mL g^{-1} h^{-1}, 1 atm.

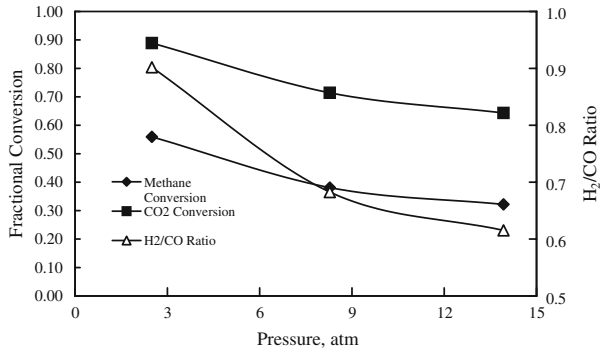

Figure 2. Effect of pressure on methane/CO_2 conversions and H_2/CO ratio, over Ca/Ni/K catalyst at 800 °C, CH_4/CO_2 = 2, GHSV = 72000 mL g^{-1} h^{-1}.

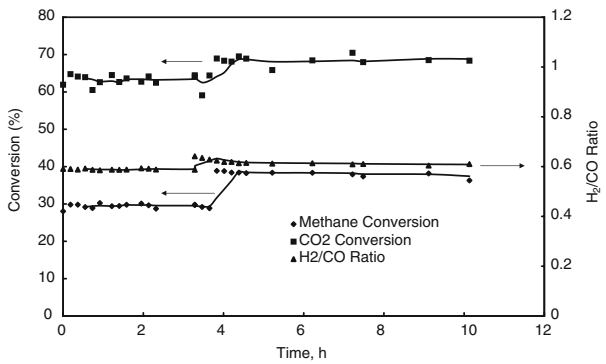

Figure 3. Reforming of methane with CO_2 over Ca/Ni/K catalyst, CH_4/CO_2 = 2, GHSV = 72000 mL g^{-1} h^{-1} at 800 °C, 14 atm.

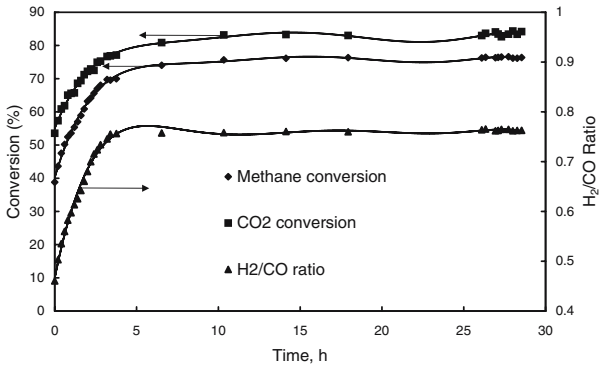

Figure 4. Reforming of methane with CO_2 over Ca/Ni/K catalyst at 900 °C, CO_2/CH_4 = 1.1, GHSV = 6×10^5 mL g^{-1} h^{-1}, 14 atm.

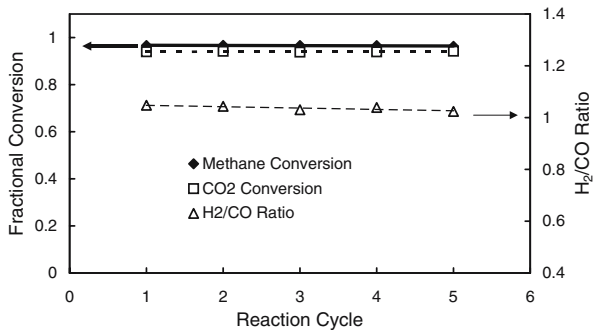

Figure 6. Catalytic activity of Ca/Ni/K catalyst at 800 °C, 1 atm, after removal of deposited carbon.

$Ca(OH)_2$, NiO, and CaO and the pretreated (reduced with hydrogen or synthesis gas) catalyst contained Ni, CaO, and $CaCO_3$ as indicated by X-ray diffraction. The increase in activity with time is mainly resulted from the removal of excess potassium. Elemental analysis of pretreated or used catalyst with higher activity showed significantly less potassium than the fresh catalyst.

Carbon formation on Ca/Ni/K catalyst was conducted at 1 atm, 800°C and GHSV = 120 00 mL g^{-1} h^{-1} and carbon was removed by temperature-programmed oxidation (TPO) with 2–15 vol% O_2 in He as shown in figure 5. There are at least two peaks for CO_2, small one around 590 °C and a larger one around 758 °C. There are also two major peaks for oxygen consumption one at 510 °C and the other at 760 °C. The amount of oxygen consumed by the catalyst was significantly larger than that consumed by carbon, indicating that oxygen reacts with catalyst first oxidizing the catalyst and then the surface oxygen reacts with carbon at higher temperature producing CO or CO_2 depending on O_2/C ratio. The Ca/Ni/K catalyst was tested five times at 800 °C and 1 atm and after1-h test the deposited carbon was removed by TPO forming CO and CO_2. As shown in figure 6, no significant catalyst deactivation was observed and average methane and CO_2 conversions of 93 and 94% with H_2/CO = 1.0 were measured.

Reforming of $^{13}CH_4$ over Ca/Ni/K catalyst at 800 °C and 1 atm, in the presence of CO_2 (CO_2/CH_4 = 1.1) was studied to identify the sources of carbon. Carbon containing species such ^{12}CO, ^{13}CO, $^{12}CO_2$, and $^{13}CO_2$, were monitored using a quadrupole mass spectrometer as shown in figure 7. Equal concentrations of $^{12}CO_2$ and $^{13}CO_2$ were observed; indicating the oxygen exchange reaction between CO and CO_2 is very fast. The carbon deposited on the catalyst was removed by TPO and the reaction products are mainly CO and CO_2 as shown in figure 8. The ratio of CO/CO_2 is largely dependent on oxygen to carbon ratio and with higher oxygen concentration more CO_2 produced. Almost equal concentrations of ^{12}C- and ^{13}C-products were measured, indicating that both methane and CO_2 contribute to carbon formation, possibly due to disproportionation of CO.

3.2. Partial oxidation

The Ca/Ni/K catalyst was tested for partial oxidation of methane. The effect of temperature on conversion and selectivity is shown in table 2. As the temperature increased methane conversion and the CO yield were also increased. Higher concentration of CO_2 was

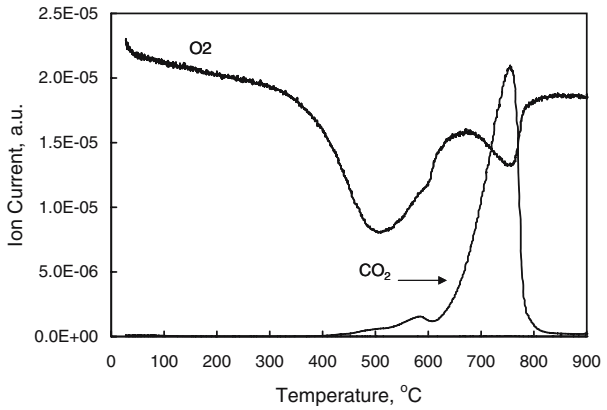

Figure 5. TPO of deposited carbon on Ca/Ni/K catalyst after reaction of $^{12}CH_4$ with CO_2 for1 h at 800 °C and 1 atm.

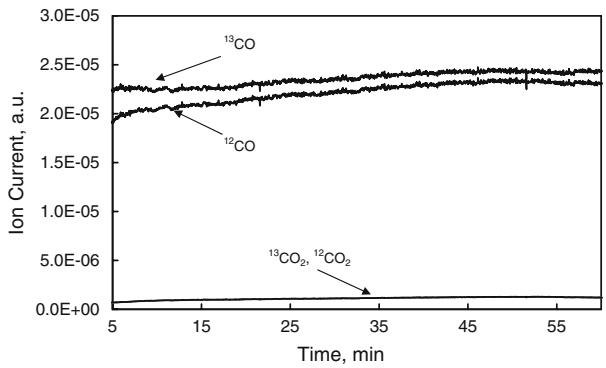

Figure 7. Reaction of $^{13}CH_4$ with CO_2 over Ca/Ni/K catalyst at 800 °C, 1 atm, 20 cc/min, CO_2/CH_4 = 1.1.

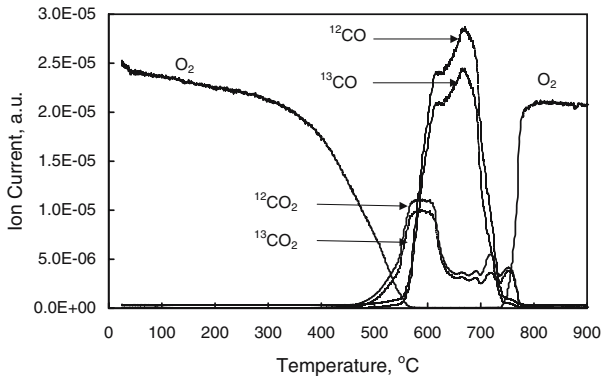

Figure 8. TPO of deposited carbon on Ca/Ni/K catalyst after reaction of $^{13}CH_4$ with CO_2 for 1 h at 800 °C and 1 atm.

Table 2
Effect of temperature on partial oxidation of methane over Ca/Ni/K catalyst, GHSV = 3600 mL g^{-1} h^{-1}, CH_4/O_2 = 2, 1 atm

Temperature (°C)	H_2/CO ratio	$\%CO_2$ vol%	%CO yield	$\%CH_4$ conversion	$\%O_2$ conversion
650	2.6	7.5	48.8	56.8	100.0
750	2.2	1.5	81.0	85.6	100.0
850	2.2	0.2	91.2	95.2	100.0

observed at lower temperatures. The oxygen was completely converted at 650 °C and further increase in methane conversion is possibly due to reactions of methane with reaction products, H_2O and CO_2. Effect of space velocity on catalyst activity and selectivity is show in table 3. As expected, lower methane conversion and lower CO yield was observed when the space velocity increased from 3600 to 13500 mL g^{-1} h^{-1}. Furthermore, more carbon was deposited on the catalysts at higher space velocities.

The O_2/CH_4 ratios were varied and the results are shown in table 4. As this ratio increase from 0.49 to 0.77 the concentration of CO_2, methane conversion, and the CO yield increased while the H_2/CO ratio remains almost constant. The reaction continued at 850 °C, CH_4/O_2 = 2:1, and GHSV = 3600 mL g^{-1} h^{-1} (1 atm) for two hours without any significant changes in catalyst activity or selectivity as shown in figure 9.

Table 3
Effect of space velocity on partial oxidation of methane over Ca/Ni/K catalyst, CH_4/O_2 = 2, 1 atm

GHSV (mL/g^{-1} h^{-1})	H_2/CO ratio	$\%CO_2$ vol%	%CO yield	$\%CH_4$ conversion	$\%O_2$ conversion
3600	2.1	0.4	93.6	96.8	100.0
5400	2.2	0.4	87.7	93.3	100.0
10800	2.1	0.4	91.6	93.8	100.0
13500	2.1	0.4	90.6	92.7	100.0

Table 4
Effect of oxygen to methane ratio on partial oxidation of methane over Ca/Ni/K catalyst at 750 °C, 1 atm, GHSV = 3900 mL g^{-1} h^{-1}

O_2/CH_4 Ratio	H_2/CO Ratio	$\%CO_2$ vol%	%CO Yield	$\%CH_4$ Conversion	$\%O_2$ Conversion
0.49	2.2	1.7	80.9	85.5	100.0
0.54	2.2	2.1	85.3	87.8	100.0
0.77	2.3	6.4	97.3	95.1	100.0

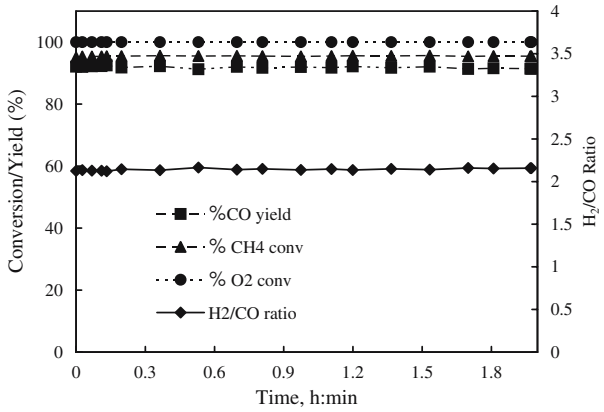

Figure 9. Partial oxidation of methane over Ca/Ni/K catalyst at 850 °C, CH_4/O_2 = 2:1, GHSV = 3600 mL g^{-1} h^{-1} and 1 atm.

3.3. Ca/Ni/Na catalyst

The Ca/Ni/Na catalyst with atomic ratio of 2:1:0.1 was also prepared and tested at 800 °C and 1 atm. This catalyst produced more carbon than the catalyst with potassium. However, when carbon was removed and the catalyst was tested five times, at 800 °C and 1 atm, no significant changes were observed in catalyst activity or selectivity as observed for catalyst with potassium (figure 6). Average methane and CO_2 conversions of 97 and 94% with H_2/CO = 1.0 were measured. The TPO of deposited carbon is shown in figure 10. Since more

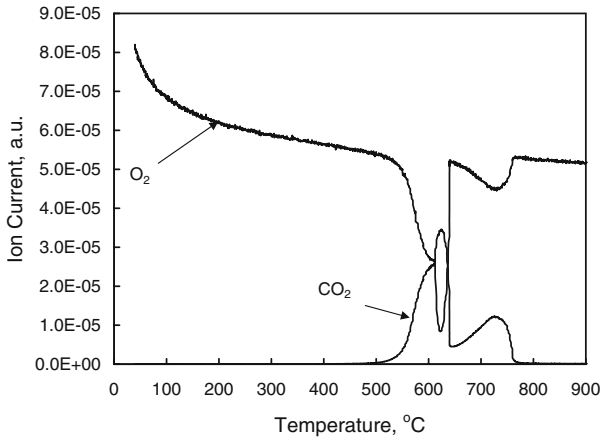

Figure 10. TPO of deposited carbon on Ca/Ni/Na catalyst after reaction of $^{12}CH_4$ with CO_2 for 1 h at 800 °C and 1 atm.

carbon (0.12–5 wt%) was deposited on this catalyst, higher concentration (10 vol%O_2 in He) of oxygen was used to remove carbon. Several broad peaks were observed for both CO_2 formation and O_2 consumption. Contrary to the results obtained for the catalyst containing potassium, the oxygen and the CO_2 peaks are mirror images of each other and no sharp peak was observed for oxygen consumption by the catalyst, indicating that most of the oxygen is consumed by the carbon deposited on the catalyst.

4. Conclusion

Partial oxidation and dry reforming of methane to synthesis gas over Ca/Ni/K(Na) catalysts have been studied. Effects of temperature, pressure, and oxygen/methane ratios on catalytic activity, selectivity, and carbon formation have been determined. Lower methane and CO_2 conversions, lower H_2 /CO ratio, and higher carbon deposition was observed at higher pressures. Lower catalyst activity observed at higher concentrations of K or Na, however, as the concentrations were reduced by high-temperature treatment under reaction conditions (reducing) the catalytic activity was increased, producing significantly less carbon. Also reforming of $^{13}CH_4$ in the presence of CO_2 over K- or Na-promoted catalysts indicated that carbon formed on the catalyst originated from both methane and CO_2. It appears that during oxidation of carbon deposited on Ca/Ni/K catalyst oxygen reacts with catalyst first before reacting with surface carbon, providing surface oxygen for both oxygen-assisted activation of methane and also for oxidation of surface carbon. However, in case of Ca/Ni/Na catalyst, the oxygen peak and the CO_2 peak are mirror images of each other, indicating that most of the oxygen consumed by the carbon deposited on the catalyst.

Acknowledgments

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References

[1] H.-F. Liu, K.Y. Liu, R.E. Johnson and J.H. Lunsford, J. Am. Soc. 106 (1984) 117.
[2] A. Shamsi and K. Zahir, Energy & Fuel 3 (1989) 727.
[3] P. Pereira, S. Lee, G. Somorjai and H. Heinemann, Catal. Lett. 9 (1991) 395.
[4] A. Shamsi, Catal. Lett. 25 (1994) 97.
[5] K. Tomishige, Y.-G Chen and K. Fujimoto, J. Catal. 181 (1999) 91.
[6] L. Xiancai, W. Min, L. Zhihua and H. Fei, Appl. Catal. A: General 290 (2005) 81.
[7] T. Sperle, D. Chen, R. Lødeng and A. Holmen, Appl. Catal. A: General 282 (2005) 195.
[8] W.-Z. Sun, G.-Q. Jin and X.-Y. Guo, Catal. Commun. 6 (2005) 135.
[9] S.M. Stagg and D.E. Resasco, Stud. Surf. Sci. Catal. 119 (1998) 813.
[10] S.M. Stagg, E. Romeo, C. Padro and D.E. Resasco, J. Catal. 178 (1998) 137.
[11] L. Wenying, F. Jie and X. Kechang, React. Kinet. Lett. 64(2) (1998) 381–388.
[12] B.J. Wood and K.M. Sancier, Catal. Rev. Sci. Eng. 26(2) (1984) 233.
[13] T. Wigmans, Ph.D. Thesis, University of Amsterdam (1982).
[14] H.S. Bengaard, I. Alstrup, I. Chorkendorff, S. Ullmann, J.R. Rostrup-Nielsen and J.K. Norskov, J. Catal. 187 (1999) 238.
[15] M. Ito, T. Tagawa and S. Goto, Appl. Catal. 184 (1999) 73.