The reactivity of carbon-containing species on nickel. Effects of crystallite size and related phenomena

F. van Looij * and J.W. Geus

Debije Institute, Department of Inorganic Chemistry, Utrecht University, Sorbonnelaan 16, 3584 CA Utrecht, The Netherlands
E-mail: Looij1@sic.shell.nl

Received 9 December 1996; accepted 26 March 1997

A pronounced variation of the reactivity of sub-monolayers of carbon-containing species deposited from synthesis gas with the nickel crystallite size is observed. Nickel crystallites of about 4 nm display the presence of a carbon-containing ad-layer of maximum reactivity. The rate of methanation is discussed in terms of the reactivity of the carbonaceous fragments, and the catalyst preparation procedure.

Keywords: carbon deposition, nickel, methanation, crystallite size, syngas reaction

1. Introduction

Carbonaceous surface species are important intermediates in the Fischer–Tropsch reaction [1], steam reforming [2], and isomerization [3,4]. A cocktail of carbidic CH_x (where $0 \leqslant x \leqslant 3$), amorphous, and graphitic carbon can be present on the surface of the working catalyst [5–8]. The reactive carbidic CH_x fragments are generally accepted as the reaction intermediates in the conversion of synthesis gas to both methane [9–11] and higher hydrocarbons [12–14]. The metal–carbon bond strength of these CH_x species is likely to be one of the important parameters determining the rate of their hydrogenation to methane [15–17].

The nature of the metal controls the metal–carbon bond strength [13,15–18]. Less is known about the influence of the metal crystallite size on the reactivity of the carbon fragments. With fcc metals such as nickel, particles below about 4 nm expose crystal faces different from larger crystallites. In addition, the amount of coordinatively less saturated sites varies with the metal crystallite size [19]. The surface structure affects both the activation of carbon-containing molecules such as CO and CH_4, and the metal–carbon bond strength of CH_x fragments. Nickel surface science studies show that both CO [20] and CH_4 [21] are readily activated on open crystal planes, while surface defects enhance the activation of CO, too [22,23]. Ion bombardment of Ni(111) can increase the methanation rate by up to 400%, suggesting a sensitivity to structure on the scale of surface defects [24]. Small nickel particles, viz. 2 to 3 nm, are more efficient in the dissociative adsorption of CH_4 than larger crystallites [25]. CH_x fragments are strongly bonded to the hollow sites on Ni(111) and Ni(100) [26,27]. The atop adsorption sites are energetically less favorable [27]. In addition, calculations suggest significant differences in the binding energies of single carbon atoms to Ni(100), Ni(111), and Ni(110) [28]. The question is whether these differences will be reflected in the reactivity of the carbon species deposited on supported metal particles.

2. Experimental

The catalysts were prepared by homogeneous deposition precipitation of nickel hydroxide from an aqueous solution of nickel nitrate (Merck, p.a.) onto a suspended silica support (Aerosil 200V, DEGUSSA, surface area 200 $m^2\ g^{-1}$) by means of urea decomposition at 363 K as described by Hermans et al. [29]. The catalysts were filtrated, washed, and dried at room temperature for 40 h. The catalysts were subsequently calcined in air at 673 K for 3 h. One catalyst was prepared by incipient wetness impregnation of the silica support using an aqueous solution of nickel nitrate. The catalyst was dried at room temperature for 40 h, and subsequently calcined in air at 673 K for 3 h.

The mean nickel crystallite sizes in Å as calculated from the extent of hydrogen chemisorption at 303 K of the various reduced samples are summarized in table 1. The catalysts prepared by means of homogeneous deposition precipitation are referred to as P*x* in which *x* denotes the mean nickel crystallite size. Besides catalyst P22, all catalysts were reduced by first heating the calcined samples in a stream of argon (Hoek Loos, 99.999%) to about 760 K in 60 min, and subsequently reducing the thus dried catalysts in a stream of 10 vol% hydrogen (Hoek Loos, 99.999%) in argon at 763 K for

---

[*] To whom correspondence should be addressed. Present address: Shell Research and Technology Center Amsterdam, PO Box 38000, 1030 BN Amsterdam, The Netherlands.

Table 1
Characteristics of the employed silica-supported nickel catalysts

Sample	Method of preparation	Nickel loading (wt%)	Crystallite size (Å)
P22	precipitation	5	22
P38	precipitation	10	38
P46	precipitation	25	46
P71	precipitation	50	71
I267	impregnation	25	267

5 h. Catalyst P22 was obtained by reduction at 743 K for 5 h.

The flow experiments were performed at atmospheric pressure in a fully automated continuous microflow apparatus. 300 mg catalyst of a sieve fraction between 150 and 425 micron was placed into a quartz reactor of an internal diameter of 8 mm. The total flow rate was 100 ml(STP)/min, and was directed down-stream. The temperature was measured with a chromel–alumel thermocouple situated at the bottom of the catalyst bed. Subsequent to reduction, the temperature of the catalyst bed was adjusted at a temperature of 523 K. The freshly reduced catalyst was purged in a stream of argon at 523 K for 1 min. Subsequently, carburization was performed by feeding a gas mixture containing 2 vol% hydrogen (Hoek Loos, 99.999%) and 1 vol% carbon monoxide (Hoek Loos, 99.5%) in argon to the reactor. The product gases were analyzed with a Balzers mass spectrometer (Balzers QM420) every 5 to 240 s. The turn-over number (TON) is expressed as the number of methane molecules produced per second per initial unit of nickel surface area at 9.5 h on-stream, assuming a nickel density of 1.5×10^{19} atoms per square meter. After 9.5 h, the reactor was purged in argon for 1 min, and quenched to room temperature. The temperature of the catalyst bed was well below 373 K within 90 s.

The reactivity of the thus deposited carbon species was investigated by means of temperature-programmed surface reaction (TPSR) experiments in a flow of 2.8 vol% water in argon. The sample was heated from room temperature to 900 K at a heating rate of 10 K/min, and kept at 900 K for 10 min. In a few experiments temperature-programmed surface reaction experiments were conducted in a mixture 10 vol% hydrogen in argon.

Transmission electron microscopy (TEM) investigations were carried out in a Philips EM 420 apparatus.

3. Results and discussion

We investigated the reactivity of the carbonaceous fragments deposited under methanation conditions by means of temperature-programmed surface reaction (TPSR) experiments in 2.8% water vapor in argon. The product gas predominantly consisted of hydrogen and carbon dioxide, and traces of methane. The reactor was operated differentially during both the carburizing and gasification experiments. Figure 1 shows that all samples prepared by means of homogeneous deposition precipitation, containing small nickel crystallites, viz. mean crystallite sizes in the range from 22 to 71 Å, display the

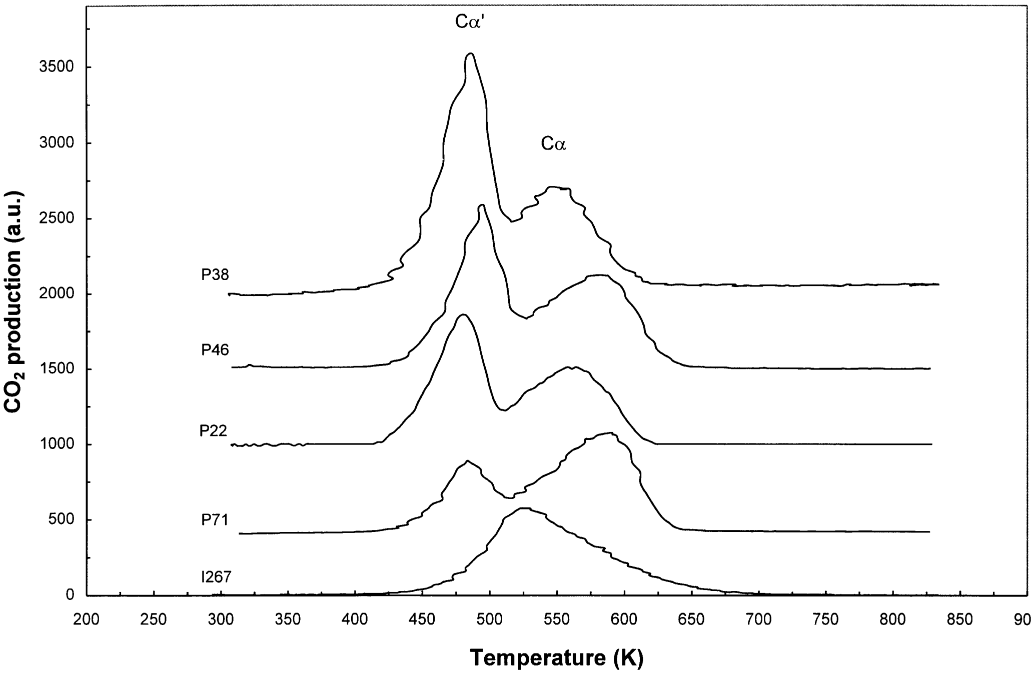

Figure 1. Temperature-programmed surface reaction (TPSR) patterns obtained for several nickel catalysts subsequent to methanation for 9.5 h. The nickel catalysts had been prepared by means of either homogeneous deposition precipitation (samples P22, P38, P46, and P71) or impregnation (I267). The TPSR patterns are normalized with respect to the nickel loading.

presence of two classes of carbon-containing species of clearly distinct reactivity subsequent to methanation. The onset-temperatures of gasification by water vapor are about 415 and 450 K, respectively. The sample prepared by means of impregnation, containing large crystallites, viz. particles of 267 Å, is characterized by one broad peak which is not easily deconvoluted. Besides a small fraction of highly reactive species, the onset-temperature of the bulk of the peak seems to be close to 450 K.

Qualitatively the same results were obtained when employing hydrogen instead of water vapor. The corresponding onset-temperatures of the formation of methane were considerably lower, viz. (below) room temperature and 335 K, respectively. Please note that the thus obtained carbon species react at lower temperatures than adsorbed carbon monoxide [12,30–32]. Because of the high reactivity of the carbon species with respect to hydrogen we employed water vapor for the present TPSR experiments. In line with the notation employed by McCarty and Wise [30], we denote the presently observed carbidic carbon species as $C\alpha'$ and $C\alpha$, respectively.

Methanation on nickel catalysts reportedly involves the deposition of surface carbon from carbon monoxide, followed by the hydrogenation of the thus deposited carbon via carbidic CH_x (where $1 \leqslant x \leqslant 3$) species to methane [9–11,33–38]. Along with the deposition and the hydrogenation of these highly reactive carbon fragments, less reactive "spectator" carbon species may be formed by the direct deposition from the carbon-containing compounds, and/or by the (ir)reversible transformation of the high activity intermediates. Accordingly, the steady-state carbon ad-layer can be inhomogeneous as to its reactivity. Several studies in the field of methanation confirm the presence of carbon species of different reactivity on the surface of the working catalyst [36,39,40]. These investigations, however, usually employ catalysts prepared by means of impregnation, containing predominantly large nickel crystallites. Subsequent to reaction, moreover, these nickel particles commonly contain several monolayers of carbon. Accordingly [11], both carbidic carbon $C\alpha$ and the relatively inactive amorphous carbon $C\beta$ are commonly present. In contrast, in the present investigations we deposited small amounts of carbon on highly dispersed nickel catalysts with the objective to produce exclusively carbidic carbon species. Amorphous carbon $C\beta$ was indeed not detected under the presently employed conditions.

The metal–carbon bond strength is generally believed to be one of the important parameters determining the rate of the hydrogenation of the carbon intermediates to methane [15–17]. The influence of the metal on the bond strength of the carbon fragments onto the catalyst is likely to be more pronounced at low carbon coverage than in the presence of several carbon monolayers. Since the carbon surface coverage was well below one monolayer for all precipitated samples, while for sample I267 a surface coverage of almost three monolayers was calculated, the present discussion primarily focuses on the samples prepared by means of homogeneous deposition

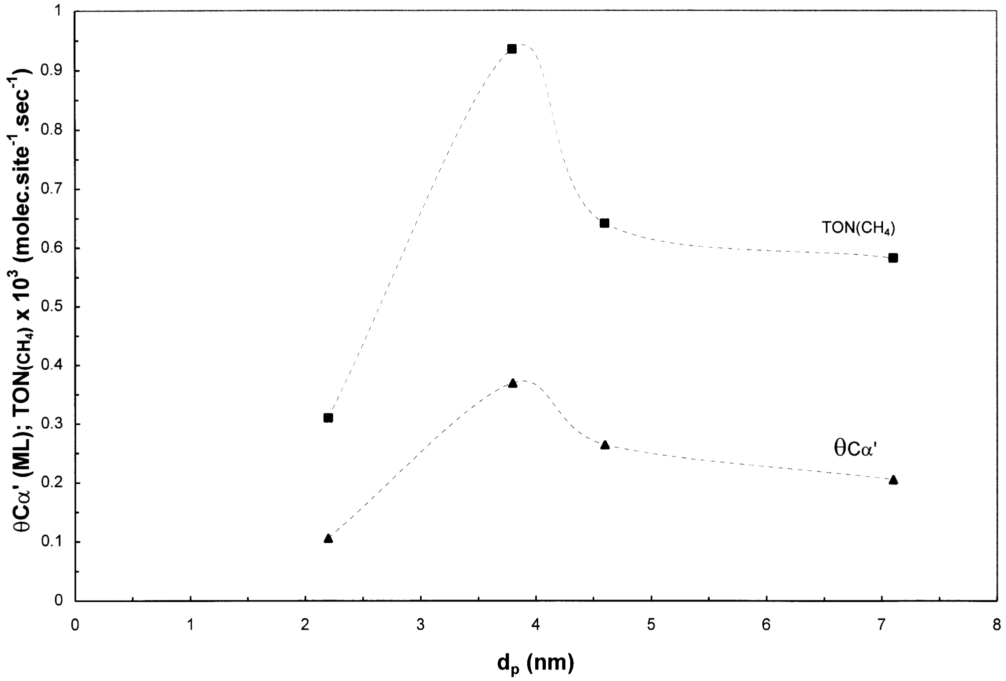

Figure 2. The $C\alpha'$ surface coverage and TON (turn- over number) for the production of CH_4 from CO and H_2 as a function of the mean nickel crystallite size. The dotted line is meant to guide the eye.

precipitation. Figure 2 compares the methanation activities with the surface coverages of Cα' on the corresponding catalysts. Nickel crystallites of about 4 nm display an optimum methanation activity, employing catalysts prepared by means of homogeneous deposition precipitation. This result is in excellent agreement with those reported by Coenen and coworkers, who used the same catalyst preparation method [33,41,42]. Analogously to the variation of the methanation activity, the variation of the surface coverage of Cα' with the nickel crystallite size displays a maximum at about 4 nm. In calculating the carbon surface coverages $\Theta_{C\alpha'}$, we assumed that all carbon atoms were located at the surface. Since the presence of carbon in subsurface sites can not be excluded the thus calculated surface coverages represent a maximum value.

The good agreement between the response to the nickel crystallite size of the methanation activity and the surface coverage of the simultaneously deposited highly reactive carbon species Cα' is evident. Differences in the reactivity of the carbon ad-layer seem to control the observed variation of the methanation activity with crystallite size.

Since the surface coverage of a carbon species reportedly is a function of the total surface coverage [15,18], we verified that the observed trend cannot be attributed to the total carbon surface coverage Θ_C. The importance of employing catalysts of a narrow crystallite size distribution is evident. Transmission electron microscopy (TEM) revealed that the crystallite size distribution of silica-supported nickel catalysts prepared by means of homogeneous-deposition precipitation was relatively narrow, while the impregnated catalyst displayed a broad particle size distribution. This observation agrees nicely with the results of previously conducted low-field magnetic measurements in our laboratory [43].

The question arises whether the variation of Cα' and Cα with the nickel particle size is a direct crystallite size effect, i.e. related to the exposition of specific sites or crystal planes. With fcc metals such as nickel, large particles predominantly expose (111) and (100) faces, while with small particles, viz. below about 4 nm, the contribution of the (110) and (113) faces is more pronounced [19]. The sharp decrease in the coverage of Cα' with nickel crystallites in the range from about 4 to 7 nm seems difficult to rationalize in terms of the exposition of specific crystal planes. The relative amount of corners and edges increases at decreasing crystallite size [19,44,45], while the degree of reduction of these nickel catalysts decreases at increasing nickel dispersion [29,46]. CO reportedly is rapidly activated at ordered defects [22,23]. In addition, the presence of oxidic patches on the metal surface can facilitate the activation and reaction of CO, too [47–50]. Hence, we speculate that Cα' is associated with the presence of either corners and edges (crystallite size effect) or oxidic patches (promoter effect) or a combination of these two factors.

The postulate of Cα' being the methanation intermediate associated with either surface defects or surface ions seems to be in line with the hypothesis that the surface contains active sites, where CO dissociates readily, and less active sites, where adsorbed CO (CO_{ads}) is stored [12,37,38]. The latter postulate was based both on the kinetic equivalence of adsorbed carbon (C_{ads}) and CO_{ads} in isotopic labeling experiments [51] and the high concentration of CO_{ads} observed in IR spectroscopy [12,52,53]. Adsorbed, "spectator" CO might then be related to the presence of carbon species Cα. Further investigations will be required to verify this hypothesis.

It is noteworthy that the only catalyst that had been prepared by means of impregnation, viz. I267, was found to display a clearly deviating behavior in terms of the methanation activity: we calculated a TON of about 1.4×10^{-3} methane molecules per site per second. The reason for this relatively high methanation activity is unclear, yet, but it may be related to the presence of several monolayers of carbon on this sample.

Based on the combined body of results it can be expected that the preparation method, the pretreatment procedure, and the support employed (affecting the degree of reduction of the metal phase, TiO_{2-x} species on the metal surface etc.) may affect the reactivity of the carbon-containing species deposited on the catalyst. This complicating factor should be born in mind when discussing crystallite size effects in reactions in which the reactivity of the carbidic intermediates is of importance.

4. Conclusions

A pronounced variation of the reactivity of submonolayers of carbon-containing species deposited from synthesis gas with the nickel crystallite size is observed. Differences in the reactivity of the carbon-containing ad-layer seem to induce variations in the methanation activity with the nickel crystallite size.

Acknowledgement

We thank GASTEC N.V. (Apeldoorn, The Netherlands) for its financial support.

References

[1] H. Pichler, Adv. Catal. 4 (1952) 271.
[2] J.H. Sinfelt, Z.H. Hurwitz and J.C. Rohrer, J. Catal. 1 (1962) 481.
[3] W.M.H. Sachtler, Faraday Disc. Chem. Soc. 72 (1981) 7.
[4] F.G. Gault, Adv. Catal. 30 (1981) 1.
[5] G.A. Somorjai and D.W. Blakely, Nature 258 (1975) 580.
[6] H.P. Bonzel and H.J. Krebs, Surf. Sci. 91 (1980) 499.
[7] M.Yu. Smirnov, V.V. Gorodetskii, A.R. Cholach and D.Yu. Zemlyanov, Surf. Sci. 311 (1994) 308.

[8] C.H. Bartholomew, Catal. Rev. Sci. Eng. 24 (1982) 67.
[9] P.R. Wentrcek, B.J. Wood and H.J. Wise, J. Catal. 43 (1976) 366.
[10] M. Araki and V. Ponec, J. Catal. 44 (1976) 439.
[11] D.W. Goodman, R.D. Kelley, T.E. Madey and J.T. Yates, J. Catal. 63 (1980) 226.
[12] P. Biloen and W.M.H. Sachtler, Adv. Catal. 30 (1981) 165.
[13] V. Ponec, Catalysis 5 (1981) 48, and references therein.
[14] B.W. Wojeciechowski, Catal. Rev. Sci. Eng. 30 (1988) 629.
[15] T. Koerts and R.A. van Santen, J. Mol. Catal. 70 (1991) 119.
[16] W.A.A. van Barneveld and V. Ponec, Ind. Eng. Chem. Prod. Res. Dev. 18 (1979) 268.
[17] R.A. van Santen, A. de Koster and T. Koerts, Catal. Lett. 7 (1991) 1.
[18] L. Guczi, R.A. van Santen and K.V. Sarma, Catal. Rev. Sci. Eng. 38 (1996) 249, and references therein.
[19] R. van Hardeveld and A. van Montvoort, Surf. Sci. 15 (1969) 189.
[20] F. Labohm, C.W.R. Engelen, O.L.J. Gijzeman, J.W. Geus and G.A. Bootsma, J. Chem. Soc. Faraday Trans. I 78 (1982) 2435.
[21] F.C. Schouten, O.L.J. Gijzeman and G.A. Bootsma, Bull. Soc. Chem. Belg. 88 (1979) 541.
[22] W. Erley and H. Wagner, Surf. Sci. 74 (1978) 333.
[23] W. Erley, H. Ibach, S. Lehwald and H. Wagner, Surf. Sci. 83 (1979) 585.
[24] A. Berko and H.P. Bonzel, Surf. Sci. 251/252 (1991) 1112.
[25] E.G.M. Kuijpers, A.K. Breedijk, W.J.J. van der Wal and J.W. Geus, J. Catal. 81 (1983) 429.
[26] J.H. Onuferko, D.P. Woodruff and B.W. Holland, Surf. Sci. 87 (1979) 357.
[27] H. Yang and J.L. Whitten, Surf. Sci. 255 (1991) 193.
[28] L.C. Isset and J.M. Blakely, Surf. Sci. 58 (1976) 397.
[29] L.A. Hermans and J.W. Geus, in: *Scientific Bases for the Preparation of Heterogeneous Catalysts*, eds. B. Delmon, P. Grange, P. Jacobs and G. Poncelet (Elsevier, Amsterdam, 1979).
[30] J.G. McCarty and H. Wise, J. Catal. 57 (1979) 406.
[31] V. Stuchlý and K. Klusáček, J. Catal. 139 (1993) 62.
[32] K.B. Kester and J.L. Falconer, J. Catal. 89 (1984) 380.
[33] R.Z.C. van Meerten, A.H.G.M. Beamont, P.F.M.T. van Nisselrooij and J.W.E. Coenen, Surf. Sci. 135 (1983) 565.
[34] M.P. Kaminsky, N. Winograd, G.L. Geoffroy and M.A. Vannice, J. Am. Chem. Soc. 108 (1986) 1315.
[35] H. He, J. Nakamura and K. Tanaka, Surf. Sci. 283 (1983) 117.
[36] J. Happel, I. Suzuki, P. Kokayeff and V. Fthenakis, J. Catal. 65 (1980) 59.
[37] J.A. Rabo, A.P. Risch and M.L. Poutsma, J. Catal. 53 (1978) 295.
[38] J.A. Rabo and L.F. Elek, in: *Proc. 7th Int. Congr. on Catalysis*, Tokyo, P A33 (1980) p. 490.
[39] P. Biloen, J.N. Helle, F.G.A. van den Berg and W.M.H. Sachtler, J. Catal. 81 (1983) 450.
[40] P. Winslow and A.T. Bell, J. Catal. 94 (1985) 385.
[41] J.W.E. Coenen, W.M.T.M. Schats and R.Z.C. van Meerten, Bull. Soc. Belg. 88 (1979) 435.
[42] R.Z.C. van Meerten, J.G. Vollenbroek, M.H.J.M. de Croon, P.F.M.T. van Nisselrooij and J.W.E. Coenen, Appl. Catal. 3 (1982) 29.
[43] E.G.M. Kuijpers, A.K. Breedijk, W.J.J. van der Wal and J.W. Geus, J. Catal. 72 (1981) 210.
[44] R. van Hardeveld and A. van Montvoort, Surf. Sci. 4 (1966) 396.
[45] R. van Hardeveld and F. Hartog, in: *Proc. 4th Int. Congr. on Catalysis*, P. 70 (1968) p. 295.
[46] J.W.E. Coenen, Appl. Catal. 54 (1989) 65.
[47] C.T. Campbell and D.W. Goodman, Surf. Sci. 123 (1982) 413.
[48] T. Mori, A. Miyamoto, N. Takahashi, M. Fukagaya, T. Hattori and W. Murakami, J. Phys. Chem. 90 (1986) 5197.
[49] C.H. Bartholomew and C.K. Vance, J. Catal. 91 (1985) 78.
[50] M.E. Levine, M. Salmeron, A.T. Bell and G.A. Somorjai, J. Catal. 106 (1987) 401.
[51] P. Biloen, J.N. Helle and W.M.H. Sachtler, J. Catal. 58 (1979) 95.
[52] G. Blyholder and L.D. Neff, J. Catal. 2 (1963) 138.
[53] R.A. Della Betta and M. Shelef, J. Catal. 48 (1977) 111.