Reaction routes for methane conversion on transition metals at low temperature

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REACTION ROUTES FOR METHANE CONVERSION ON TRANSITION METALS AT LOW TEMPERATURE

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Abstract

Two new metal catalysed routes for methane conversion are discussed: methane oligomerization and methane addition to olefins. These reactions are realized in a reaction cycle consisting of several steps. In both reaction sequences methane is first dissociatively adsorbed on a reduced transition metal catalyst between 500 and 800 K resulting in surface carbon and hydrogen. A particular highly reactive surface carbonaceous intermediate is found to produce C_2^+ hydrocarbons upon hydrogenation between 300 and 400 K. The maximum yield for higher hydrocarbons is 13 % obtained on a Ru/SiO_2 catalyst. When olefins are co-adsorbed together with surface carbon generated from methane, more C_2^+ hydrocarbons are produced. Experiments with ^{13}C labelled CH_4 and unlabelled olefins demonstrate that surface carbon from methane is incorporated into the co-adsorbed olefins.

INTRODUCTION

Methane conversion to higher hydrocarbons is of world wide interest. Up to now only indirect routes via synthesis gas have been commercialized. Hydrocarbons are formed from synthesis gas via methanol and the MTG process [1] or via the Fischer-Tropsch reaction [2,3] and the SMDS [4,5] process. Direct methane conversion using pyrolysis, resulting in acetylene and benzene, can only operate at temperatures above 1200 K [6]. Oxidative coupling of methane to ethylene has been proposed as a promising alternative route [7-12] and proceeds at temperatures between 850 and 1200 K.

In the Fischer-Tropsch reaction it has been shown that carbidic C_1 species are the reaction intermediates initiating chaingrowth upon hydrogenation [49,50]. These C_1 reaction intermediates can also be formed from other molecules than CO. Petit and Brady [13,14] used CH_2N_2 as a source for surface carbon, Cavalcanti et al [15,16] used CH_3NO_2, Van Barneveld and Ponec [17] used $CH_{(4-x)}Cl_x$ and Williams et al [18] demonstrated that also surface carbon generated from methyliodide could be incorporated into C_2^+ hydrocarbons during CO hydrogenation.

Recent experiments demonstrate that also hydrocarbon formation from surface carbon from methane is possible when methane is activated. Shelimov and Kazanski [19] activated methane by photo energy. Ceyer and co-workers [20,21] activated methane under UHV conditions by a krypton bombardment. During subsequent temperature desorption benzene appeared in the gas phase from the recombination of surface CH_x fragments. Tanaka et al [22] generated CH_2 species from methane on cobalt and demonstrated their reactivity to ethene. Belgued et al [23] created CH_x surface species on platinum and demonstrated C_2^+ hydrocarbons in a hydrogen flow. Here we present a cyclic reaction path for the formation of C_2^+ hydrocarbons on transition metal catalyst in which methane is thermally activated. In the first step methane is dissociatively adsorbed on a reduced group VIII metal between 500 and 800 K. Subsequently higher hydrocarbons are formed upon exposure to hydrogen at a lower temperature. The ability of the C_1 intermediates to form carbon-carbon bonds can also be used to add these species to other co-adsorbed molecules. This is demonstrated for the alkylation of ethene, acetylene and propene using methane, according to a cyclic route. To distinguish methane addition from olefin disproportionation [24-26], experiments with $^{13}CH_4$ were performed.

Thermodynamic consideration

The oligomerization of methane to alkanes is not thermodynamically allowed in one step. However, using two steps occurring at different conditions, this reaction can be made feasible. This is shown for the reaction of methane to ethane and hydrogen using bulk cobalt carbide as a reaction intermediate (see Fig 1).

$$2\,CH_4 + 6\,Co \rightarrow 2\,Co_3C + 4\,H_2 \quad (1)$$

$$2\,Co_3C + 3\,H_2 \rightarrow C_2H_6 + 6\,Co \quad (2)$$

$$\text{---------------------------} \quad +$$

$$2\,CH_4 \rightarrow C_2H_6 + H_2 \qquad\qquad (3)$$
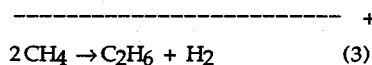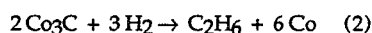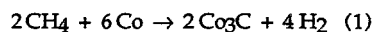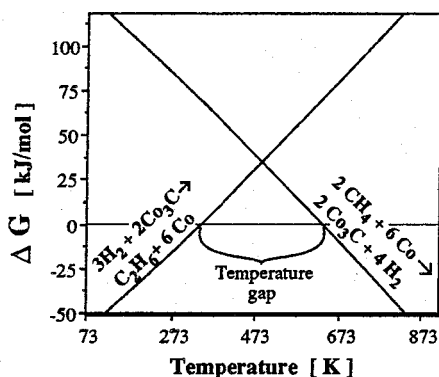
$$\Delta G_{sum(1000\ K)} = 71.0\ kJ/mol$$

Figure 1 y-axis: ΔG [kJ/mol], values 100, 75, 50, 25, 0, -25, -50. X-axis: Temperature [K], values 73, 273, 473, 673, 873. Curve labels: $3H_2 + 2Co_3C$, $C_2H_6 + 6Co$, $2CH_4$, $2Co_3C + 4H_2$, $2CH_4 + 6Co$. "Temperature gap".

Figure 1. Gibbs free energies as a function of the temperature for the decomposition of methane on cobalt (1) and the hydrogenation of cobalt carbide to ethane (2).

Figure 1 shows that there is no common temperature where the two reactions steps are both negative. To perform the two reaction steps ($\Delta G<0$) a temperature gap of nearly 300 K at standard conditions, has to be overcome. The size of this temperature gap is rather insensitive to the metal-carbon bond strength. Instead of working with a temperature swing it is also possible to use a pressure swing as recently demonstrated by Belgued et al [23].

The alkylation of ethene and propene to form propane and butane respectively, is thermodynamically possible in one step below 725 K [32] and is possible using super acids [28-31]. However, on transition metals this reaction has not yet been realized. This is due to the fact that the sticking coefficient for dissociative methane adsorption is much smaller than that of ethene and propene, preventing the co-adsorption of methane with an olefin. To realize this co-adsorption, a reaction cycle is proposed in which methane and the olefin are adsorbed separately at different temperatures.
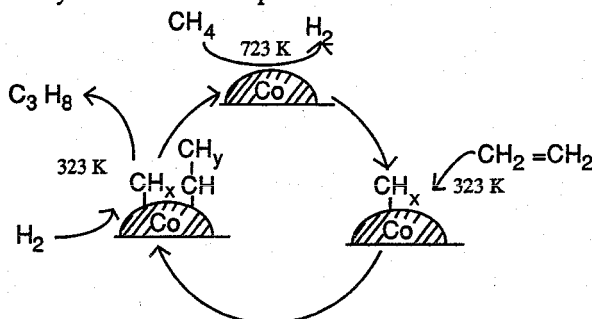
Reaction cycle diagram: CH_4, H_2, 723 K, Co; C_3H_8, 323 K, CH_y, CH_xCH, Co; H_2; CH_x, Co, $CH_2=CH_2$, 323 K.

Figure 2. Reaction cycle for the conversion of methane and ethene to propane.

After the co-adsorption of the carbonaceous intermediates they are hydrogenated to higher hydrocarbons.

EXPERIMENTAL

Catalysts

Transition-metal catalysts were prepared by incipient wetness impregnation of preshaped silica (Grace 332, surface area=300 m^2/g, mesh 100) with an aqueous solution of the metal nitrates or chlorides. The catalysts were dried at 110 °C. The catalysts were characterized with Transmission Electron Microscopy and CO chemisorption.

Method.

The reactions were performed in a micro reactor which consisted of a quartz tube with an internal diameter of 10 mm. For each experiment 300 mg of the catalyst was placed in the reactor and was reduced in situ between 673 and 823 K. Methane decomposition was performed from a flow of 45 ml/min of diluted methane. Typically a pulse of 1.5 or 3 minutes of 0.5 % methane in helium was given at 723 K. After methane decomposition, the catalyst was cooled in 100 seconds below 473 K to avoid 'ageing' of the surface carbon species. After cooling, surface carbon was hydrogenated to higher hydrocarbons in a flow of 22.4 ml/min of hydrogen at 1 atm, typically at 368 K. At the alkylation experiments, olefins were co-adsorbed from pulses of 1.4 μmol, at 372 K.

Product analysis was performed on line with a quadruple mass spectrometer (type: PGA 100 from Leybold) or with a gas chromatograph (CP 9000 from Chrompack) using a widebore column (plot Q) of 25 meters. 15 loops of 0.2 ml of the reaction gasses could also be stored in a multi position valve and analysed afterwards. For the experiments with labelled methane the widebore column was (splitless) connected with a capillary which ended in the ionization chamber of a high resolution mass spectrometer.

RESULTS AND DISCUSSION

Methane decomposition on reduced transition metal catalyst can result in three different kinds of carbonaceous surface species as identified with NMR [33] and AES [34,35]. They can be distinguished by their different hydrogenation temperatures as shown in Figure 3.
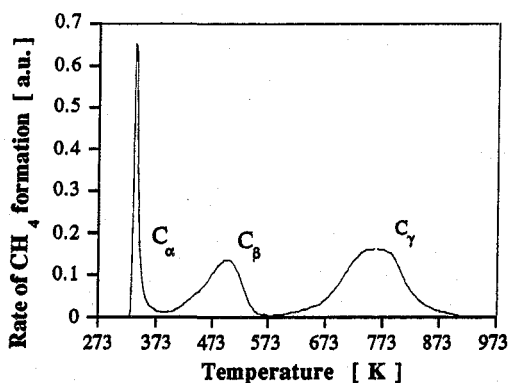
Carbidic (C_α) surface carbon can be hydrogenated below 400 K and is most suitable for the formation of C_2^+ hydrocarbons. A less reactive amorphous carbonaceous layer (C_β) is hydrogenated around 500 K and produces only traces of C_2^+ hydrocarbons. Unreactive graphitic carbon (C_γ) reacts above 650 K to produce only methane. For C_2^+ hydrocarbon formation it is important to have a high selectivity for C_α carbon formation. This is achieved at low carbon surface coverages.

The temperature of hydrogenation of surface carbon from methane, is important to the amount and selectivity of hydrocarbons formed (see Fig 4).
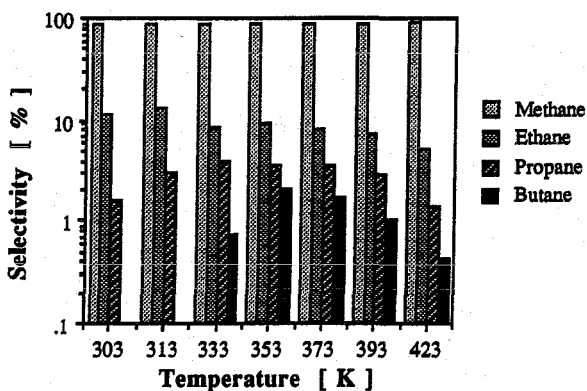
Figure 4. Product distribution as a function of the hydrogenation temperature of surface carbon, deposited from methane at 723 K on a 10 wt.% Co/SiO_2.

The optimum chaingrowth selectivity upon hydrogenation, is reached around 370 K. At higher temperature less reactive C_β becomes hydrogenatable, reducing the selectivity for C_2^+ hydrocarbons. Different metals were tested in their affinity to form C_2^+ hydrocarbons upon hydrogenation at 368 K of surface carbon from methane (see Fig.5).
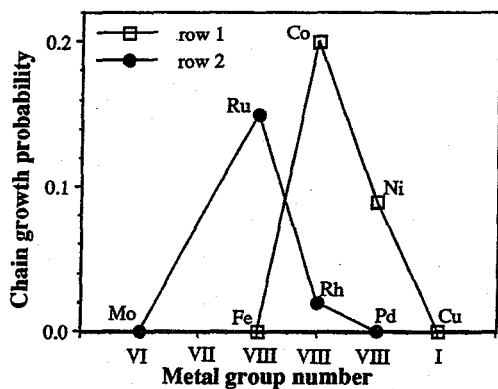
Figure 5. Chaingrowth probability α, upon hydrogenation at 368 K of surface carbon generated from a pulse of 3 min. of methane at 723 K on transition metal catalysts.

As shown in Figure 5 the chance for carbon-carbon bond formation versus methanation goes through a maximum as a function of the place in the periodic table. Earlier we have indicated that this relates to the metal-carbon bond strength [36-39]. Stronger bonded surface carbon has a higher chance for carbon-carbon bond formation. However, when the metal-carbon bond-strength is too large (Fe and W), stable carbides are formed that can not produce any hydrocarbons upon hydrogenation at low temperature ($\alpha=0$ in Fig. 5). Ruthenium and cobalt show optimum intermediate performance. In the third row platinum behaves exceptional, due to its high selectivity for ethane formation.

The maximum overall yield to C_2^+ hydrocarbons is dependant on the methane conversion in the adsorption step, the fraction of C_α carbon formed and the chaingrowth probability during methane conversion. These are a function of the carbon surface coverage remaining after methane adsorption. Different carbon surface coverages were created by varying the methane adsorption time.
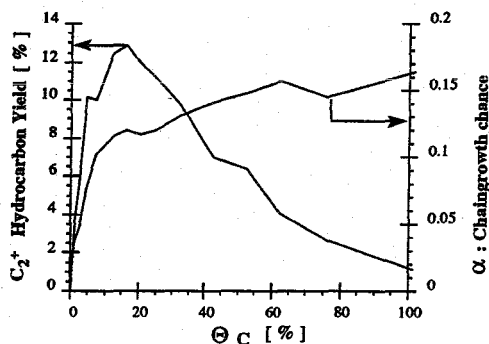
Figure 6. The overall yield and chaingrowth propagation during hydrogenation, in the step wise conversion of methane to C_2^+ hydrocarbons as a function of the carbon surface coverage, on a 5 wt.% Ru/SiO_2 catalyst.

The optimum yield on the ruthenium catalyst is 13% reached at a carbon surface coverage of only 18%. At lower carbon surface coverage the chaingrowth selectivity decreases, while at higher coverage the selectivity for C_α carbon decreases and the conversion during methane desorption becomes less than 100 %.

The mechanism of carbon-carbon bond formation is very similar to that occurring in the Fischer-Tropsch reaction in which also mainly linear hydrocarbons are formed [40,41]. During CO hydrogenation, ethene addition experiments have been performed [42,45], showing enhanced rates for higher hydrocarbon formation. From these experiments it was suggested that the initiation of chain growth is one of the slow steps in the formation of hydrocarbons [46,47]. After the formation of a C_2 fragment the insertion of the subsequent CH_x units would be more easy. A similar principle is applied here, to add surface carbon from methane to co-adsorbed ethene or other olefins (see Fig 7). To realize methane and ethylene co-adsorption, their adsorptions were carried out at different temperature according to the reaction cycle in Figure 2.
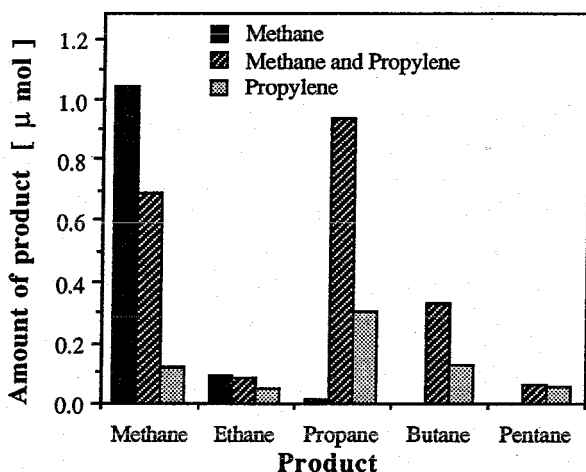
Figure 7. Product formation upon hydrogenation at 313 K of adsorbed methane (T_{ads}=723 K), adsorbed propene (1 pulse at 313 K) and their co-adsorption, on a 10 wt.% cobalt catalyst.

Figure 7 compares the amount of products formed during hydrogenation, after separate methane and propene adsorption and their co-adsorption. Surface carbon from methane alone can be hydrogenated to C_2^+ hydrocarbons [48]. However, most of the dissociatively adsorbed methane reacts back towards methane. When propene is co-adsorbed, the amount of methane formed is reduced and butane formation becomes significant. This indicates a reaction between adsorbed C_1 species from methane and co-adsorbed propene, forming butane. When separately adsorbed propene is hydrogenated, also butane formation is found to occur. To distinguish methane incorporation into propene from propene auto homologation, experiments were performed with ^{13}C labelled methane. The results are shown in table 1.

Table 1. Fraction of single labelled product formed upon hydrogenation at 323 K of surface carbon generated from methane (adsorbed at 723 K, 6.7 μmol) and olefin (adsorbed at 323 K from 3 pulses of 1.4 μmol).

Reaction	Catalyst	
	5% Ru/SiO$_2$	10% Co/SiO$_2$
$^{13}CH_4 + C_2H_4 \rightarrow {}^{13}C^{12}C_2H_8$	62 %	58 %
$^{13}CH_4 + C_2H_2 + H_2 \rightarrow {}^{13}C^{12}C_2H_8$	47 %	51 %
$^{13}CH_4 + C_3H_6 \rightarrow {}^{13}C^{12}C_3H_{10}$	47 %	73 %

Table 1 shows that the homologated product is both formed by methane incorporation and by hydrogenolysis and self homologation. Both reactions occur with about the same rate because equal molar amounts of methane and propane react at the conditions used. This result is in agreement with that obtained by Rodriguez et al [24,25] who indicated that the mechanism of homologation is related to that occurring in the Fischer-Tropsch reaction.

CONCLUSIONS

The use of a non steady state reaction cycle, as suggested here, provides two new reactions routes for the conversion of methane to higher hydrocarbons on transition metal catalysts: First methane oligomerization and second alkylation of olefins using methane. In the first reaction, the temperature cycle is able to overcome the positive change in Gibbs free energy of the overall reaction. In the second reaction, methane and olefin co-adsorption is realized, necessary for olefin alkylation. The interesting features of these conversion routes are the relative low temperatures applied and the absence of oxidants.

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DISCUSSION

Q: J. R. H. Ross (Ireland)

I believe that the y axis of your Figure 1 should read ΔG_0. Assuming that is so, these values must indicate the possibility of carrying out the two steps of your reactions even if ΔG_0 is greater than zero. Have you looked at the possibility of operating within your "temperature gap"?

A: R. van Santen

The y-axis of Figure 1 indeed is ΔG_0. Within the temperature gap, one can drive the reaction by a pressure swing.

Q: F. Solymosi (Hungary)

First, I would like to mention that we obtained almost exactly the same TPR curves for the $H_2 + C/Rh$ system some years ago, when the surface carbon was produced by CO dissociation.

Secondly, I mention that recently we performed with Dr. Erdőhelyi a comparative study on the decomposition of CH_4 on supported Pt metals. Surprisingly, Rh/SiO_2 was the most active and Pt/SiO_2 was the least active. But as regards the formation of ethane, both behaved similarly. As regards the hydrogenation of surface carbon, Pt/SiO_2 different from the others, as even C_6 hydrocarbon was produced. We made a great attempt to detect CH_x fragments on catalysts by sensitive FTIR spectroscopy without any positive results. Did you try Amount of C_2H_6 and H_2 formed in the decomposition of CH_4 on supported metals at 523 K in 10 min.
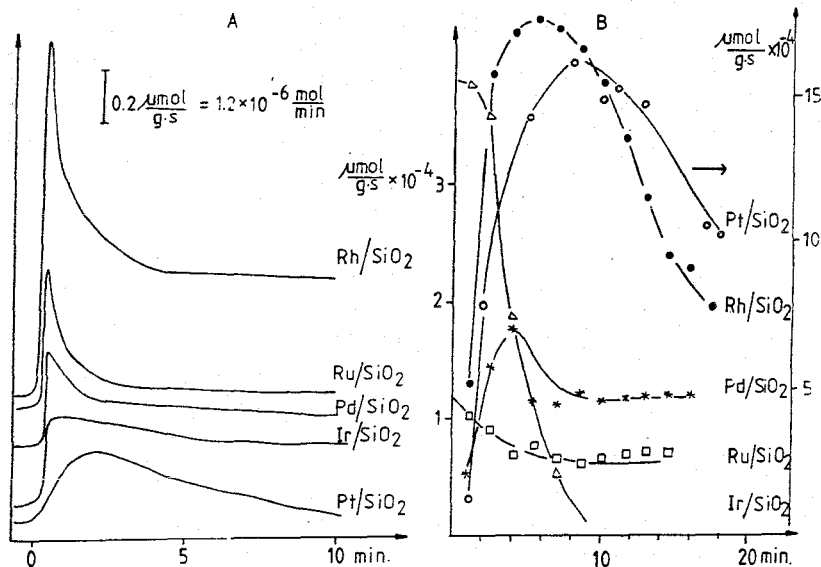
Rates of H_2 and C_2H_6 formation in the decomposition of CH_4 on silica supported metals at 523 K. Flow rate of N_2+CH_4 (12.5 %): 40 cm^3/min

Catalyst	D %	C_2H_6 μmol/g	C_2H_6/M[a]	H_2 μmol/g	H_2/M[a]
5 % Ru/SiO$_2$	3.1	0.05	3.30	72.2	4.70
5 % Ru/SiO$_2$	23.3	0.22	1.94	340.0	3.05
5 % Pd/SiO$_2$	10.7	0.08[b]	1.64	73.3	1.45
5 % Pt/SiO$_2$	23.4	0.69	11.50	83.3	1.38
5 % Ir/SiO$_2$	22.9	0.11	1.76	165.0	2.76

[a]The amount of C_2H_6 or H_2 is related to the number of surafce atoms.
[b]Sum of ethane and ethylene

A: R. van Santen

We find very similar reactivity differences between Pt and Rh. Characterization studies of the partially hydrogenated carbonaceous intermediates are in progress.

Q: R. B. Moyes

My comment is in relation to the title of this paper. The authors draw attention to the need for reaction of methane in a lower temperature regime where control is more likely, and phase changes better known. In Hull we (R. B. Moyes, D. A. Whan and G. Bond) have been experimenting with microwave heating for methane reactions and have been able to achieve coupling at temperatures 300 ^{0} to 400 ^{0}C lower than by conventional heating.

The familiar selectivity pattern, in which CO_x is the major product at 600 ^{0}C on oxide catalysts changes to C$_2$ yields as the temperature this towards 850 ^{0}C is maintained. This pattern (with some minor differences) is also obtained by microwave heating but the onset of C$_2$ production is at 250 ^{0}C or so, depending on the catalyst - reaction conditions, and call oxygen is being consumed when the temperature is in the 400-550 ^{0}C region.

The apparatus is the conventional differential flow reactor with the catalyst - at the focal point - of a single mode microwave cavity. Temperature measurement and control are not easy, but we are confident that they can be achieved. The heating effect-requires a microwave-coupling material in the reactor such as the rare earth oxides, or an inert material such as carbide to heat the catalyst - mass. The increased activity is ascribed to readier radical production due to surface interaction with the microwave field, and the rapid quenching since only the catalyst mass is heated, and not the surroundings.

A: R. van Santen

The reactivity of C-species generated by CO dissociation has inspired us to start our CH$_4$ studies. As mentioned elsewhere (J. Catal. to be appeared) we reproduced the earlier finding [1, 2].

[1]   F. Solymosi and A. Erdöhelyi, *Surf. Sci.*, **110**, L630 (1987)
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Q: M. M. Bhasin ((USA)

What is the stoichiometry of the reaction, particularly with respect to paraffin and H_2 produced ? How do you rationalize such stoichiometry with your hypothesis that carbidic carbon is the active species ? Do you think that surface or sub-surface H-species are present and participating in the reaction ? What kind of mechanistic picture do you purpose to explain your observations ?

A: R. van Santen

We propose that on 3rd and 4th row transition metals in a first step of the reaction methane dissociatively adsorbs and produces a CH_x intermediates, with x being 1 or 2 or 0.

Hydrogen is necessary for the subsequent reaction to higher alkanes. Chain growth proceeds very similar to the propagation reaction in the Fischer-Tropsch reaction.

In such a mechanism propagation occurs by insertion of a CH_x species into the growing hydrocarbon chain. This is why graphitization has to be prevented.

Q: S. I. Woo (Korea)

Chain growth probability of Fe on shown in figure 5 is zero. However, in the Fischer-Tropsch reaction, Fe can produce ethane, ethylene, and higher hydrocarbons. This indicates that the chain growth mechanism of the carbides formed on Fe clusters by methane should differ greatly from that of Fe clusters in the F-T reaction. What do you think about this difference ?

A: R. van Santen

Hydrogenation of adsorbed carbonaceous intermediates has been studied on well reduced iron catalysts. Because of carbide formation at low temperatures surface carbon has such a low reactivity that it will not react. In the Fischer-Tropsch synthesis reaction the active form of iron is a carbidic form to which surface carbonaceous intermediates are much more weak bonded than to well reduced iron.

Q: R. van Hardeveld (The Netherlands)

On your catalyst three types of carbon are formed, carbidic, amorphous, and graphitic, of which only the amorphous carbon products C_2 and higher products. The ratio in which these three forms of carbon are formed is most important for the yield of desired products. The plane exposition of your catalyst will be very important in this respect, since the low index planes are active to formation of graphitic carbon and the higher index planes to formation of amorphous carbon. hence, a particle size effect is expected. It is estimated that the yield of C_{2+} products will be optimal for 5-10 nm particles. Hence catalyst preparation will be very important to optimize the yield.

Furthermore, one might expect that if the catalyst is properly alloyed to prevent or decrease the formation of a graphitic overlayer (ensemble effect), the larger crystal will also show increased selectivity. Can you comment on these remarks ?

A: R. van Santen

These are very worthwhile suggestions.

Q: D. Wang (China)

Work from our laboratory (Wang et al., Catal. Lett (1989)) shows that, on Ru(001), carbidic carbon polymerizes to graphitic carbon between 600 K and 700 K. Is there an upper temperature limit for the deposition of carbidic carbon atoms from methane above which they immediately transform to unreactive carbon overlayers with your catalysts ? Is there any temperature dependence, with respect to the temperature at which you decompose methane, and the resulting selectivity on hydrogenation ?

A: R. van Santen

Yes, there is a relation between temperature of dissociative methane adsorption and selectivity for oligomerization. Generally, a lower deposition temperature favours the selectivity.

Q: A. Machocki (Poland)

How do you estimate the perspectives and chances for practical utility of your method for higher hydrocarbon production from methane ?

A: R. van Santen

Yields as well as heat balance have to be improved before practical application becomes worthwhile.

Q: K. Foger (Australia)

1) Which of the identified carbon species reacts ?

2) Do you have any higher hydrocarbon in the methane feed ?

A: R. van Santen

1) The selective adsorbed carbon species on transition metals of the 3rd and 4th row is the C_a species, that probably is a surface carbidic carbon.

2) We have used CH_4 of high purity, but trace amounts of higher hydrocarbons cannot be excluded.

Therefore we consider as a crucial experimental result the finding that when 100 % of the methane present in the reactant pulse becomes adsorbed, it is found that over 10 % of the carbon-atoms deposited become incorporated in higher alkanes.

Q: J. G. Goodwin (USA)

What were the deactivation characteristics of the catalyst during the reaction of CH_4 with olefins in the absence of H_2 ?

A: R. van Santen

We perform the reaction in the sequence:

(1) methane adsorption; (2) olefin adsorption; (3) hydrogenation. Usually each step is done at a different temperature.

Q: A. Sárkány (Hungary)

My question is related to the product distribution. Did you calculate the equilibrium conversion and distribution ? How far are your product distributions from equilibrium ones ? Could you tell us haw fast the transformation of alpha form to beta one is ?

A: R. van Santen

Each separate step has been chosen to occur at a condition far from equilibrium.

The rate of transformation of C_a to C_b depends strongly on temperature.