Catalysis Today 145 (2009) 114–120

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Mechanistic study of the dry reforming of propane to synthesis gas over a Ni/Mg(Al)O catalyst

M.B. Jensen [a], L.B. Råberg [a], A. Olafsen Sjåstad [b,1], U. Olsbye [a,*]

[a] inGAP Center for Research-Based Innovation, Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway
[b] SINTEF Materials and Chemistry, P.O. Box 124 Blindern, N-0314 Oslo, Norway

ARTICLE INFO

Article history:
Available online 21 July 2008

Keywords:
Propane dry reforming
Methane dry reforming
Ni catalysts
Synthesis gas
Mechanistic study

ABSTRACT

The dry reforming of propane to synthesis gas over 2 wt.% Ni/Mg(Al)O has been investigated by means of partial pressure variation experiments, kinetic isotope effect and isotopic tracer studies, all at 600 °C. Partial pressure variation experiments gave reaction orders of 0.18 and 0.36 with respect to propane and carbon dioxide, respectively, indicating a high surface coverage under the chosen test conditions (C_3H_8:CO_2:H_2:N_2 (%) = 10:30:10:50, GHSV = 13333 ml/h g_{cat}). Switching to a deuterated feed did not induce any kinetic isotope effect, revealing that C–H bond rupture is not involved in the rate-limiting step. Isotopic tracer studies showed that the reverse water-gas shift reaction approaches equilibrium under the applied test conditions, demonstrating that CO_2 activation is fast. Temperature-programmed deuteration of a used catalyst showed that C_3 species dominate among the hydrocarbon species on the catalyst surface. Together, the above results led to the conclusion that C–C bond rupture is the rate-determining step of reaction. Isotopic tracer studies further showed (1) that methane is mainly formed as a primary product of reaction by propane dissociation followed by hydrogenation on Ni sites, and (2) the primary reaction selectivity favors C oxidation to CO over C hydrogenation to methane. Co-feeding methane and propane with CO_2 showed that propane is converted significantly faster than methane.

1. Introduction

Reforming of natural gas into synthesis gas (CO and H_2) is one of the “work-horses” of petrochemical industry. Supported Ni catalysts are the preferred choice as catalysts for these reactions, due to the low cost and easy availability of Ni metal [1]. Natural gas (NG) from the North Sea contains ca. 10 vol.% light alkanes (C_2–C_4). Light alkanes also have a high potential for use as fuel in modern compact fuel reformers. Overall detailed understanding of the catalytic reforming processes is required in order to develop high performance catalysts for such reactions, i.e., catalysts with a high activity and selectivity towards the target products, CO and H_2, and with a low selectivity for coke formation.

In this paper, we address the mechanism of dry reforming of propane to synthesis gas (CO and H_2) over Ni-based catalysts:

$$C_3H_8 + 3CO_2 \rightarrow 6CO + 4H_2 \qquad (1)$$

The mechanism of this reaction is only addressed in a few prior studies, in general using supported noble metal catalysts (Ru, Rh, Re) [2–4]. Sutton et al. [2] performed a kinetic study of the dry reforming of propane over a Ru/Al_2O_3 catalyst. They observed zero-order rate dependency in propane and a fractional dependence in CO_2 and concluded that CO_2 is involved in the rate-determining step of reaction (1). Solymosi et al. [3] used Fourier transform infrared (FT-IR) spectroscopy and reactor studies to investigate the dry reforming of propane over Rh on various supports. They reported the formation of propene and propylidyne species on the catalysts during the propane dissociation reaction even at low temperatures (−23 to 27 °C). Addition of CO_2 to the feed led to rapid reaction with either propane or propene on the catalyst, yielding synthesis gas as the major product. Partial pressure variations at 550–650 °C indicated that CO_2 is involved in the rate-determining step of the reaction. Solymosi et al. [4] have recently carried out similar studies over Re/Al_2O_3. As opposed to Rh, no strong interaction between propane and Re was found when using FT-IR. Co-adsorption of propane and CO_2 led to formation of formate species. Kinetic measurements showed zero-order dependency of propane and 0.6 order with the respect to CO_2, leading to the same conclusion as for the Rh catalysts regarding the rate-limiting step.

---

[*] Corresponding author. Tel.: +47 22855456; fax: +47 22855441.
E-mail address: unni.olsbye@kjemi.uio.no (U. Olsbye).

[1] Present address: Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo, Norway.

0920-5861/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2008.05.025

The main reaction (2) for synthesis gas production from natural gas, i.e., methane conversion via autothermal reforming, steam or dry reforming, or even partial oxidation, has been extensively studied, in particular during the past two decades [5]:

$$CH_4 + \text{“O”} \rightarrow CO + 2H_2 \quad (2)$$

Ni-based catalysts are most frequently used for the reforming reaction, and a sequence of elementary reaction steps has been proposed [6]:

$$CH_4 + 2* \rightarrow CH_3* + H* \quad (3)$$

$$CH_3* + * \rightleftharpoons CH_2* + H* \quad (4)$$

$$CH_2* + * \rightleftharpoons CH* + H* \quad (5)$$

$$CH* + * \rightleftharpoons C* + H* \quad (6)$$

$$H_2O + 2* \rightleftharpoons HO* + H* \quad (7)$$

$$HO* + * \rightleftharpoons H* + O* \quad (8)$$

$$C* + O* \rightleftharpoons CO* + * \quad (9)$$

$$CO* \rightleftharpoons CO(g) + * \quad (10)$$

$$2H* \rightleftharpoons H_2(g) + 2* \quad (11)$$

Over Ni (1 1 1) and (2 1 1) surfaces, Density-Functional Theory (DFT) studies have established that oxidation of adsorbed C species, reaction (9), has the highest enthalpy of activation. However, due to the entropy loss associated with adsorption of gas-phase species on a solid surface, the initial C–H bond rupture, reaction (3), has been singled out as the rate-determining step of reaction (2) [7]. Recently, experimental studies have verified that C–H bond rupture is indeed the rate-determining step of methane dry or wet reforming to synthesis gas over a Ni/MgO catalyst at 600 °C [8].

In our group, prior studies of methane dry reforming over Ni-based catalysts were recently extended to propane dry reforming [9–11]. By a combination of steady-state and transient catalytic experiments, using a Temporal Analysis of Products (TAP) reactor, and focusing on a Ni/Mg(Al)O catalyst, it was established that the slightly basic Mg(Al)O carrier material is able to adsorb CO_2 which is subsequently used as an oxidizing agent to produce Ni–O sites, contributing to the production of CO (and water) from propane, at 600 °C. It was also established that H_2 production is rapid compared to CO and methane production over Ni/Mg(Al)O at 600 °C [9].

In Ref. [11], 2 wt.% Ni/support catalysts with supports ranging from acidic to basic were compared as catalysts for the dry reforming of propane to synthesis gas reaction. It was observed that the reaction rate depends strongly on Ni particle size, similar to what previously reported for the methane dry and wet reforming reactions over Ni/MgO catalysts [8,12]. No direct correlation was observed between catalyst activity and support basicity. However, the methane selectivity was significantly lower over catalysts with more basic supports [Mg(Al)O, MgO, CaO] than over catalysts with acidic or amphoteric supports (SiO_2, Al_2O_3).

The present study is a continuation of the work described in Refs. [9–11]. The scope of this study is to elucidate the rate-determining step of the propane dry reforming to synthesis gas reaction over a Ni/Mg(Al)O catalyst, and to gain insight into the path of methane formation, which is an unwanted by-product in industrial pre-reforming reactors, due to the exothermicity of methane formation compared to synthesis gas [13]. Kinetic isotope effect (KIE) measurements for C–H bond rupture were performed over a number of Ni-based catalysts, while detailed mechanistic investigations were limited to a 2 wt.% Ni/Mg(Al)O catalyst.

2. Experimental methods

2.1. Catalyst preparation and activation

2 wt.% Ni/Mg(Al)O was synthesized according to the recipe reported for Ni–Mg(Al)O II in Ref. [11]. The catalyst was calcined and activated in one step, by fluidizing the corresponding hydrotalcite-like material in 10% H_2 in N_2 for 14 h at 650 °C before cooling to ambient temperature in the same atmosphere. The metallic nickel was finally passivated by passing 2% O_2 in N_2 over the material for 1 h. For performing catalytic experiments (see below), the catalyst was heated to 600 °C in 10% H_2 in N_2 before directly switching to reactant feed.

Samples of Ni/SiO_2, Ni/Al_2O_3 and Ni/CaO were prepared according to synthesis procedures described in detail in [11]. The calcined catalysts were activated *in situ* in a flow of 100 N ml/min 10% H_2 in N_2 for 14 h at 650 °C before cooling the system to 600 °C for performing catalytic experiments (see below). All samples contained approximately 2 wt.% Ni. Characterization details are reported in Ref. [11].

2.2. Partial pressure variation experiments, propane decomposition studies and kinetic isotopic effect (KIE) tests

Catalytic tests were performed at 600 °C in a tubular flow reactor with an inner diameter 6 mm. The temperature in the catalyst bed was measured by a thermocouple placed in a quartz well with an outer diameter of 3 mm inside the reactor. Water produced during reaction was collected in a water-trap after the reactor, and the dry effluent was analyzed by a three columns Agilent micro-GC with Thermal Conductivity Detectors (TCD).

Partial pressure variation experiments and KIE tests were performed with 0.45 g catalyst sieved to grain size range 0.18–0.30 mm. During partial pressure variation experiments, propane and CO_2 were individually varied in the range 0.02–0.19 and 0.21–0.32 bar, respectively. The partial pressure of H_2 (10 N ml/min) was kept constant, while N_2 was varied to keep a constant flow-rate of 100 N ml/min and $P(C_3H_8) = 0.1$ or $P(CO_2) = 0.3$ in the case of CO_2 or propane partial pressure variation experiments, respectively. The partial pressures were varied in a random manner. In order to correct for deactivation, the catalyst was returned to its reference test conditions [C_3H_8:CO_2:H_2:N_2 (%) = 10:30:10:50] between each partial pressure variation, and the ratio of reaction rates under two sets of conditions was taken as the ratio between the last measuring point of one set of conditions, and the first measuring point of the subsequent set of conditions, respectively. Previous studies of the temperature influence on propane reforming reaction over a 1.9 wt.% Ni/Mg(Al)O catalyst indicated that the reaction is not diffusion limited under the flow conditions used here [9].

Kinetic isotope effect measurements were performed by switching the feed gases from [C_3H_8:CO_2:H_2:N_2 (%) = 10:30:10:50] to [C_3D_8:CO_2:D_2:N_2 (%) = 10:30:10:50] after approximately 70 h on stream, at which point all catalysts had reached steady-state conversion levels (see Ref. [11]). The deuterated feed gases were kept for 20 min, before switching back to hydrogen-containing feed gases. The deactivation observed before and after switching flows was negligible in each experiment. The kinetic isotope effect was calculated as the ratio of propane conversion before and after switching to the deuterated flows, respectively.

Propane decomposition and isotopic tracer studies were carried out using 0.20 g catalyst. The gas composition was varied depending on the intention of the experiments. In the case of propane decomposition, the gas composition was C_3H_8:N_2 (%) = 18:82, with a total flow-rate of 27.5 N ml/min. The feed compositions in the tracer studies were: (1) C_3H_8:CO_2:D_2:N_2 (%) = 10:30:22:38, (2) $^{12}C_3H_8$:$^{13}CO_2$:H_2:N_2 (%) = 10:30:10:50, and (3) $^{13}CH_4$:$^{12}C_3H_8$:$^{12}CO_2$:H_2:N_2 (%) = 2.2:10:29.8:10:48 (total flow-rate of 45 N ml/min). The isotopic composition of each product in the reactor effluent was measured by GC–MS analysis, using a HP6890 GC with a GS-GASPRO 60 × 0.320 column and a HP6890 mass spectrometer analyzer.

The composition of adsorbates on the catalyst surface was elucidated by an experiment in which the catalyst was cooled to 25 °C in Ar after testing as a propane dry reforming catalyst at 600 °C, and then heated under a D_2 flow (5 N ml/min) to 600 °C (dT = 5 °C/min). The reactor effluent was analyzed on-line by a mass spectrometer (Pfeiffer Omnistar, 0–200 amu).

3. Results and discussion

3.1. General

All catalytic tests were carried out at relatively high conversion of propane and CO_2, ca. 20 and 40%, respectively. Such high conversions were partly chosen to achieve adequate amounts of products when performing isotope tracer studies. However, equally important was the endeavour to achieve realistic surface coverage of intermediates on the Ni catalyst. The conversions of propane and CO_2 were kept similar in all experiments to ensure that the results were comparable.

3.2. Surface coverage and reaction orders in propane and CO_2

Propane and CO_2 conversion curves versus time on stream, obtained during an experiment with partial pressure variation of propane, are presented in Fig. 1. Fig. 1 shows that when the propane partial pressure is reduced, all other conditions being unchanged, a gradual increase in propane and CO_2 conversion is observed with time on stream. A subsequent increase in propane partial pressure leads to the reverse situation, i.e., that the propane and CO_2 conversions gradually decrease with time on stream. This result indicates that the catalyst surface is partly covered by intermediates during testing, and that the composition and amount of these intermediates change depending on the gas composition. Following the propane and CO_2 conversions under reference conditions before, between and after the partial pressure variations, show that there is an overall gradual loss of activity with time on stream, which suggests that some of the intermediates present on the catalyst surface are gradually converted to carbonaceous deposits during the test. The amount of carbonaceous deposits on the catalyst after 1 week of testing under reference conditions was determined by combustion analysis, which showed that it contained 1.4 wt.% of carbon.

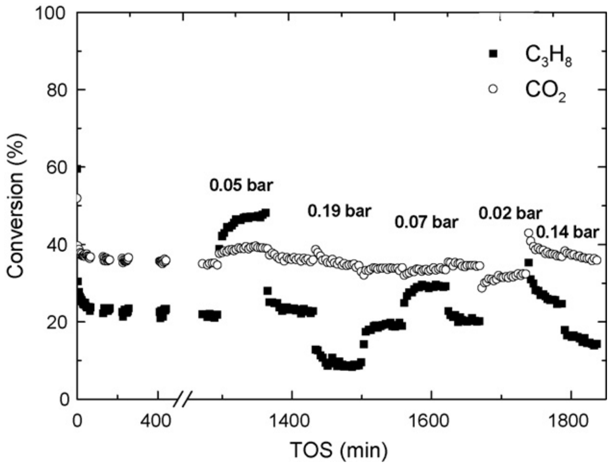

Fig. 1. Propane and CO_2 conversion versus time on stream during a propane partial pressure variation experiment. The propane pressure was varied in the range 0.05–0.19 bar, with a reference pressure of 0.10 bar initially and between each pressure change. T = 600 °C, Q = 100 N ml/min, GHSV = 13 333 ml/h g_{cat}.

The composition of adsorbates on the catalyst surface during testing as a propane dry reforming catalyst at 600 °C was elucidated by an experiment in which the catalyst was cooled to 25 °C in Ar, and then heated under a D_2 flow to 600 °C, after testing under reference conditions. The results of this experiment are shown in Fig. 2, as mass signal intensity versus time on stream. In Fig. 2A–D, signals which showed similar time dependency have been grouped together to facilitate the readability. As may be observed in Fig. 2A, the main signal evolving during heating is the $(m/e) = 3$ signal, corresponding to HD. The smaller $(m/e) = 2$ signal, corresponding to H_2, has the same time evolution as the $(m/e) = 3$ signal. Together, the two signals indicate that significant amounts of H species are adsorbed on the catalyst surface during testing. From Fig. 2B, it is observed that the signals for $(m/e) = 18$ and 16 closely follow each other, indicating that they represent water and oxygen, respectively, further suggesting the presence of OH groups on the surface during testing. The signals for $(m/e) = 17$ and 19 are shown in the same figure. These two signals follow each other closely, and have similarities with the $(m/e) = 16$ and 18 signal-versus-time curves, without being equal. This result could indicate that the $(m/e) = 17$ and 19 signals are composites of several products, such as OH and DHO, respectively, possibly overlapping with small amounts of protonated and deuterated methane/methyl species.

The signals for $(m/e) = 44$, 45 and 46 are shown in Fig. 2C. $(m/e) = 44$ is the major signal after hydrogen and water. $(m/e) = 44$ could represent several species, such as CO_2, C_3H_8 and $C_3H_4D_2$. If it were CO_2, one would expect a fragment signal at $(m/e) = 28$, representing CO, to follow the time dependence of $(m/e) = 44$. The observed time dependence of the $(m/e) = 28$ signal does not correspond to that of $(m/e) = 44$. However, the $(m/e) = 28$ signal (not shown) is always higher than the $m/e = 44$ signal, hence it is difficult to conclude whether CO_2 contributes to the $(m/e) = 28$ signal from this comparison. On the other hand, $(m/e) = 44$ corresponds perfectly well with the time dependency of the much smaller $(m/e) = 45$ and 46 signals; $(m/e) = 46$ being the most abundant of the two (Fig. 2C). This observation indicates that $(m/e) = 44$ represents a hydrocarbon, since CO_2 would not give a signal at $(m/e) = 46$ while deuteration of either propene or propane would indeed lead to a $(m/e) = 46$ signal. According to the library of the mass spectrometer in use, the main fragment of propane is $(m/e) = 29$, while that of propene is $(m/e) = 41$. The lesser amount of $(m/e) = 29$ (see Fig. 2D) compared to $(m/e) = 44$ (Fig. 2C) suggests that the main contributor to the $(m/e) = 44$ signal is propene, which is partly deuterated.

The signals for $(m/e) = 15$, 29, 42 and 43 are shown in Fig. 2D. All signals have the same intensity versus time pattern, with $(m/e) = 29$ being the most abundant signal among the four, and $(m/e) = 43$ the second most abundant; its peak height being approximately 20% of the $(m/e) = 29$ signal. The relative signal intensities of the four signals correspond perfectly well with the library spectrum for propane (taking into account that the $(m/e) = 44$ signal of propane is part of the $(m/e) = 44$ signal shown in Fig. 2C), and these signals were therefore assigned to propyl-like

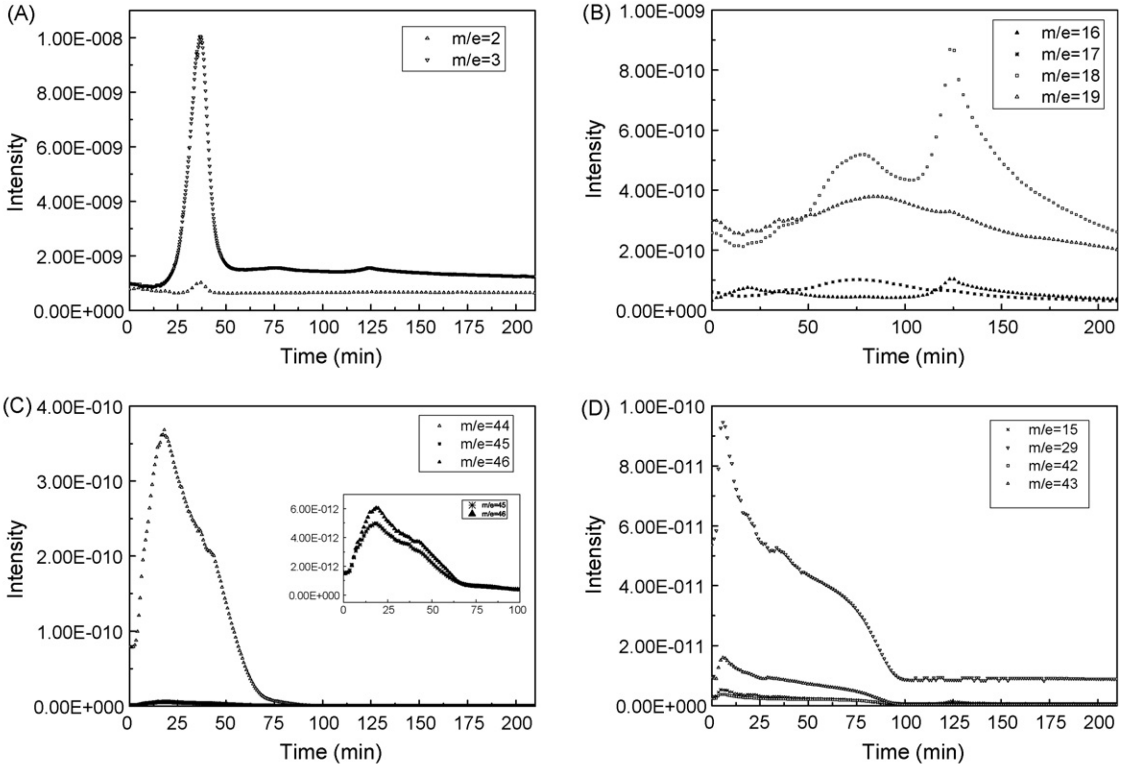

Fig. 2. Mass spectrometry signals versus time during temperature-programmed deuteration of a used propane dry reforming catalyst. $T = 25–600\,^{\circ}C$, $dT = 5\,^{\circ}C/min$, $Q(D_2) = 5$ N ml/min.

species on the surface, which recombine to form propane upon heating in D_2. It is surprising that the propyl species do not combine with D to form C_3H_7D in the excess D_2 fed in this experiment, and we are not in position to explain this observation. However, it may suggest that H is situated close to propyl on the catalyst surface, possibly because H diffusion is limited by a high surface coverage in hydrocarbon-derived adsorbates.

As an overall conclusion to the results in Figs. 1 and 2, the surface of the Ni/Mg(Al)O catalyst has a high coverage in H, OH and C_3H_6 or C_3H_5 species, with a smaller amount of C_3H_7 species. It is interesting to note that no indication of C_2H_x adsorbates, nor significant amounts of CH_x species, was found in this experiment.

The effect of varying propane and CO_2 partial pressures on the propane conversion rate is presented in Fig. 3. The reaction order is 0.18 and 0.36 with respect to C_3H_8 and CO_2, respectively. The low reaction orders for the reactants are in agreement with the significant surface coverage observed in the experiments presented in Figs. 1 and 2, and are a first indication that the initial steps of reaction, i.e., adsorption of reactants, are not the rate-determining step of the title reaction.

3.3. Decomposition of propane

Propane conversion versus time on stream when fed alone over the Ni/Mg(Al)O catalyst at 600 °C is shown in Fig. 4, and the product selectivities in Fig. 5. After significant initial deactivation during the first 5 min on stream, the conversion flattens and stabilizes at 5–6%. During the initial deactivation period, substantial amounts of methane and hydrogen are produced, together with trace amounts of propene, ethene, and ethane. This result demonstrates that the fresh catalyst is capable of forming various C_yH_x species without the presence of co-reactants, such as H_2O and CO_2. The initial main product, methane, might be formed through cracking of propane on acidic sites on the support into methane

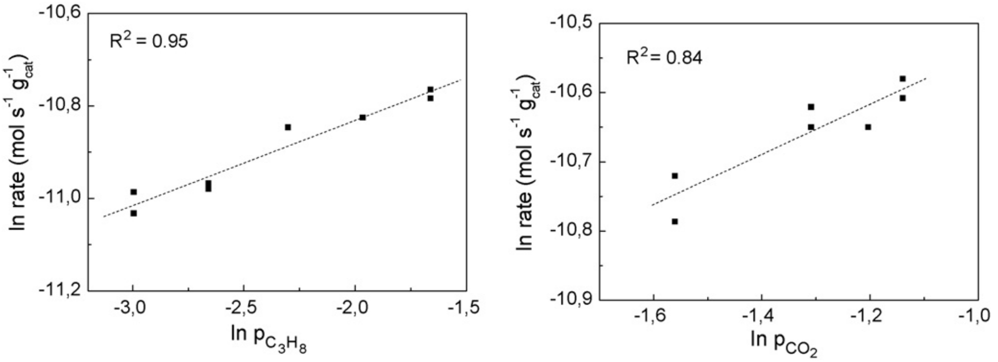

Fig. 3. Logarithmic reaction rate versus logarithm of partial pressure for propane and CO_2, respectively. The propane and CO_2 pressures were individually varied in the range 0.05–0.19 and 0.25–0.32 bar, respectively. $T = 600\,^{\circ}C$, $Q = 100$ N ml/min, GHSV = 13333 ml/h g_{cat}.

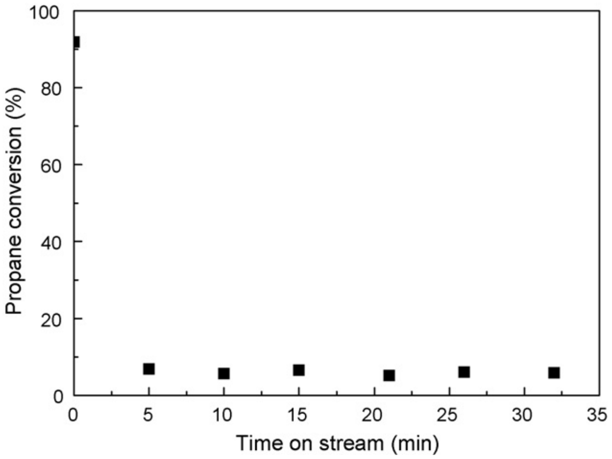

Fig. 4. Propane conversion versus time on stream (TOS) when feeding propane over Ni/Mg(Al)O. $T = 600\,^{\circ}\mathrm{C}$, $Q = 27.5$ N ml/min, $C_3H_8:N_2$ (%) = 18:82, GHSV = 6676 ml/h g_{cat}.

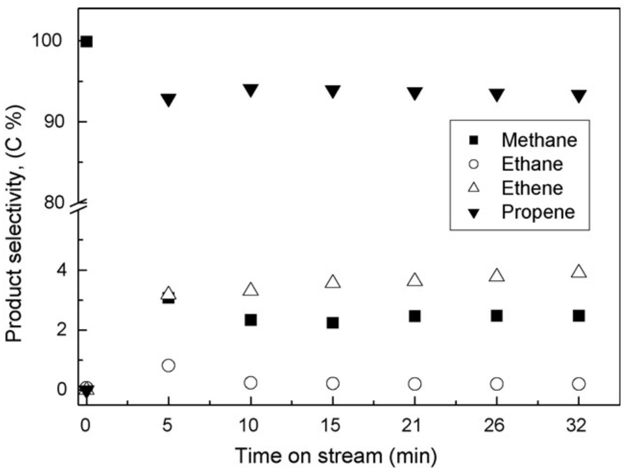

Fig. 5. Product selectivity versus time on stream when feeding propane over Ni/Mg(Al)O. $T = 600\,^{\circ}\mathrm{C}$, $Q = 27.5$ N ml/min, $C_3H_8:N_2$ (%) = 18:82, GHSV = 6676 ml/h g_{cat}. Note the axis break on the *y*-axis.

and ethene *or* by direct decomposition of propane on the nickel surface into CH_x which is subsequently hydrogenated into methane. The poor ethene/methane balance observed (see Fig. 5) clearly points to the latter. This conclusion was further supported by a blank test in which propane was fed over Mg(Al)O support, which gave <0.2% conversion under the same conditions.

After reaching steady-state, propene and hydrogen are the major products. This result strongly indicates that active sites for forming CH_x species are suppressed, presumably by coke formation, after which the Ni/Mg(Al)O catalyst functions more or less as a dehydrogenation catalyst.

In a previous study, pulses of propane alone were fed over a Ni/Mg(Al)O catalyst in a TAP reactor [9]. The amount of propane fed in each pulse was low (approximately 1/1000 compared to the number of Ni sites) and methane was the only carbon-containing product observed. A comparison between that test and the test reported above could suggest that the catalytic sites capable of C–C bond rupture preceding methane formation are the most active sites on this catalyst, while dehydrogenation may proceed (also) on less active sites.

3.4. *Kinetic isotopic effect (H–D exchange)*

Kinetic isotope effect measurements were performed to elucidate if C–H activation is involved in the rate-determining step of reaction. Because previous results have suggested that C oxidation over Ni/Mg(Al)O might be facilitated by CO_2 activation on the basic support, KIE measurements were carried out over a number of Ni/support materials to clarify whether such facilitation could possibly shift the rate-determining step of reaction. The results are presented in Table 1. The kinetic isotope effect is negligible for the propane dry reforming reaction over all materials. This result differs from what reported for methane dry or wet reforming over Ni/MgO at 600 °C, where a KIE of 1.62 was observed [8].

Table 1
Kinetic isotopic effect for the dry reforming of propane reaction over various catalysts

Catalyst	Conversion ratio of propane: C_3H_8/C_3D_8
Ni/Al_2O_3	0.99
Ni/SiO_2	1.00
Ni/Mg(Al)O	1.01
Ni/CaO	1.1, 1.0

$T = 600\,^{\circ}\mathrm{C}$, $Q = 100$ N ml/min, $C_3H_8:CO_2:H_2/D_2:N_2$ (%) = 10:30:10:50, GHSV = 13 333 ml/h g_{cat}.

This difference may be rationalized as follows: compared to methane, C–H bonds tend to weaken with an increasing number of carbon atoms in alkanes; the C–H bond being about 20 kJ/mol stronger for methane than for propane when considering the first C–H bond rupture [14]. The reduced bond energy will most likely lead to a lower activation energy, and this effect has previously been demonstrated for methane versus ethane steam reforming over a Ni/Mg–Al–O catalyst at 500 °C [15]. The KIE results are further consistent with the results presented in Section 3.2, where a low reaction order in propane was observed.

It may be argued that KIE measurements obtained at high conversion (in this case approximately 20 and 40%, respectively, for C_3H_8 and CO_2) may lead to erroneous conclusions, either due to the influence of reverse reactions or because the decrease in reactant partial pressures during reaction evens out the rate differences. However, propane reforming is not reversible under the applied conditions; hence the thermodynamic equilibrium conversion is 100% [16]. Further, simulation of the rate expression for propane dry reforming from 0 to 20% conversion, using the reaction orders found in Section 3.2, indicated that a kinetic isotope effect of 1.6 would decrease the propane conversion at the reactor outlet from 20 to 13% when switching from a hydrogenated to a deuterated feed, while in the experiments, no difference was observed between the two.

3.5. *Isotopic tracer studies*

3.5.1. *$C_3H_8 + CO_2 + D_2$//1:3:2.2*

H/D-exchange results obtained during a D_2 addition experiment under propane dry reforming conditions are reported in Table 2. The conversion of propane and CO_2 was approximately 20 and 40%, respectively, during the experiment.

As seen from Table 2, only limited H/D-exchange (1%) in propane is observed. This result is in line with what observed during heating of the used catalyst in D_2, reported in Section 3.2. Since no kinetic isotope effect was observed (see Section 3.4), we may conclude that dissociative adsorption of propane precedes the rate-determining step. A steady-state, highly reversible situation between propane and adsorbed propyl species is therefore expected. When only very limited amounts of deuterium was inserted into propane in the present experiment, one may again speculate whether propyl species on the surface preferably

Table 2
H/D-exchange in propane, propene, ethene, and methane when co-feeding the dry reforming of propane feed with D_2

Species	Relative amounts of deuterized species (%)					Total amount in effluent (%)
	Zero D	One D	Two D	Three D	Four D	
Propane	99	1	n.d.	n.d.	n.d.	8.9
Propene	85	15	n.d.	n.d.	n.d.	0.06
Ethene	97	1	1	1	n.d.	0.02
Methane	22	19	17	22	20	0.23

$T = 600\,^{\circ}C$, $Q = 45$ Nml/min, $C_3H_8:CO_2:D_2:N_2$ (%) = 10:30:22:38, GHSV = 13 500 ml/h g_{cat}. n.d.: not detected.

combines with adjacent H species on the surface, because H diffusion is hindered by high surface coverage by adsorbates.

Propene is detected in the effluent. The relatively high fraction of H/D-exchange in propene (Table 2) might point to significant retention time on the surface, suggesting a fairly strong interaction with Ni. Considering the excess of D_2 in the feed compared to H_2 (10 N ml/min D_2 and 3.8 N ml/min H_2 from propane at 21% conversion), full H/D-exchange is far from being observed even for propene.

The low H/D-exchange observed in ethene (see Table 2) can be rationalized by cracking of propane. However, the limited amount of ethene indicates that the cracking reaction is very modest. Methane, on the other hand, exists in far higher amounts than ethene. Further, a high degree of H/D scrambling is observed in methane. This is probably the result of hydrogenation/deuteration of strongly dehydrogenated CH_x species on the Ni surface. Another possible explanation could be fast methane reforming equilibration over the catalyst, and this point is addressed in Section 3.6.

3.5.2. $^{12}C_3H_8 + {}^{13}CO_2 + H_2//1{:}3{:}1$

$^{13}CO_2$ co-feed experiments were performed to elucidate relative rates of the reverse water-gas shift reaction (RWGS) (12):

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \tag{12}$$

and propane reforming reactions, as well as the influence of the methanation reaction [i.e., reverse reaction (2)] on methane formation. The conversion was 21 and 33% for propane and CO_2, respectively, and the amount of CH_4 in the effluent was 0.07%. The $^{12}C/^{13}C$ ratio in methane and carbon dioxide is reported in Table 3.

Under the assumption that breaking of C–C bonds in propane is non-reversible (see below), the content of ^{12}C in CO_2 ought to be 18% if the RWGS reaction is at equilibrium (at 21% propane conversion). As seen from Table 3, the ^{12}C fraction in CO_2 is about 14%, that is, close to the theoretical value of 18%. Further, the equilibrium conversion of CO_2 was calculated theoretically from thermodynamic data reported in the NIST Standard Reference Database 85 [16] where the RWGS reaction was included. The calculations were carried out assuming 21% propane conversion, and the result is in excellent agreement with the experimental value: 35% CO_2 conversion. These results clearly indicate that RWGS is close to equilibrium, which infers that the activation of CO_2 cannot be the rate-limiting step of the propane dry reforming reaction over the 2 wt.% Ni/Mg(Al)O catalyst.

Table 3
Carbon scrambling results of the $^{12}C_3H_8 + {}^{13}CO_2$ experiment

Species	^{12}C (%)	^{13}C (%)
CO_2	14	86
CH_4	76	24

$T = 600\,^{\circ}C$, $Q = 45$ N ml/min, $C_3H_8{:}13CO_2{:}H_2{:}N_2$ (%) = 10:30:10:50, GHSV = 13 390 ml/h g_{cat}.

Table 3 further shows that the isotopic composition of methane is altered towards ^{12}C, indicating that propane decomposition is the main route to methane formation under the present conditions. However, the ^{13}C content of methane is far from negligible, i.e., 24%, strongly indicating that the methanation reaction contributes significantly to methane formation at the appreciable propane and CO_2 conversions obtained in this experiment. The equilibrium pressure of methane was calculated under the same conditions as described above; being 1%, while the methane content in the effluent was 0.07%. Together these results suggest that hydrogenation of C species does indeed take place on the nickel surface, but the reaction is slow compared to oxidation of C atoms to CO. The latter conclusion is based on the low methane selectivity and the low ^{13}C content in methane; if the hydrogenation reaction was fast, the $^{12}C/^{13}C$ ratio would be closer to what observed in CO_2. Finally, no carbon scrambling was observed in propene, ethane or ethene, pointing to C–C rupture being irreversible.

3.6. Co-feeding of CH_4

$^{13}CH_4$ addition experiments were performed to elucidate whether the H–D scrambling observed for methane in Section 3.5.1 could be definitely linked to methane formation by propane decomposition on the Ni surface, or whether it could be an artifact due to rapid methane-surface reactions. The conversion of methane, propane, and CO_2 in this experiment was 6, 21, and 37%, respectively. The $^{12}C/^{13}C$ scrambling in methane and CO_2 is reported in Table 4.

The equilibrium conversion of methane and CO_2 was calculated under the assumption of 21% propane conversion [16]. The calculations suggest that methane is far from equilibrium (i.e., 6% methane conversion versus 42% methane conversion at thermodynamic equilibrium), while CO_2, as also seen in Section 3.5.2, is close to equilibrium conversion (43%). Assessing from literature reports that C–H bond rupture is the rate-determining step of methane reforming to synthesis gas, this result supports the conclusion in Section 3.5.1, that the H/D scrambling of methane is due to hydrogenation/deuteration of CH_x species formed by propane decomposition, rather than by rapid dissociative adsorption/associative desorption of methane.

A comparison between the methane and propane conversions obtained in this experiment clearly shows that propane is converted more rapidly than methane, in line with the lower C–H bond strength of propane (in gas phase), although surface stabilization of the adsorbates may alter the relative bond strengths [14]. However, this result is opposite to what observed when feeding either methane or propane alone with CO_2 and H_2 over the same catalyst [11]. The reason for this difference is likely to be a higher coverage of active sites by carbonaceous deposits during propane dry reforming compared to methane dry reforming, as indicated in Section 3.2.

Based on the experiments carried out in this study, we can rule out activation of CO_2 and C–H rupture in propane or subsequent species to be involved in any rate-limiting steps. The former is

Table 4
Carbon scrambling results of co-feeding the dry reforming of propane experiment with methane

Species	^{12}C (%)	^{13}C (%)
CO_2	98.6	1.4
CH_4	6.4	93.6

$T = 600\,^{\circ}C$, $Q = 47$ N ml/min, $^{13}CH_4{:}^{12}C_3H_8{:}^{12}CO_2{:}H_2{:}N_2$ (%) = 2.2:10:29.8:10:48, GHSV = 13 950 ml/h g_{cat}.

based on findings that the RWGS reaction approaches equilibrium, while the latter is a result of the absence of a kinetic isotopic effect. Thus, either C–C bond rupture in propane *or* oxidation of adsorbed CH_x species (x = 0–3) may be rate-determining steps. The results obtained during temperature-programmed deuteration of a used catalyst (Section 3.2) strongly points to C–C bond rupture as the rate-determining step, since C_3 species are the main hydrocarbon species present on the catalyst surface. This conclusion agrees well with our previous observation that the turn-over frequency of Ni/support catalysts for the propane dry reforming reaction is independent of the support, in spite of a higher oxygen concentration (and hence a higher CO selectivity) of the Ni/Mg(Al)O catalyst compared to e.g. Ni/SiO_2 and Ni/Al_2O_3.

The following reaction sequence may be proposed for the propane dry reforming reaction over a Ni/Mg(Al)O catalyst, based on the results presented above (* is the active site, n = 0–3):

$$C_3H_8(g) + 2* \rightleftharpoons C_3H_7* + H* \quad (13)$$

$$C_3H_7* + * \rightleftharpoons C_3H_6* + H* \quad (14)$$

$$C_3H_7* + (9-n)* \rightarrow 3CH_n* + (7-n)H* \quad (15)$$

$$CO_2(g) + 2* \rightleftharpoons CO* + O* \quad (16)$$

$$H_2O + 2* \rightleftharpoons HO* + H* \quad (17)$$

$$CH_n* + O* + n* \rightleftharpoons CO* + nH* + * \quad (18)$$

$$CH_n* + (4-n)H* \rightleftharpoons CH_4(g) + (5-n)* \quad (19)$$

$$CO* \rightleftharpoons CO(g) + * \quad (20)$$

$$2H* \rightleftharpoons H_2(g) + 2* \quad (21)$$

4. Conclusion

The results obtained in this study indicate that C–C bond rupture is the rate-determining step of propane dry reforming to synthesis gas over 2 wt.% Ni/Mg(Al)O at 600 °C. It has further been shown that methane is mainly formed as a primary product of reaction by propane dissociation followed by hydrogenation on Ni sites. The primary reaction selectivity favors C oxidation to CO over C hydrogenation to methane.

Acknowledgement

This project is supported by the Norwegian Research Council, under the KOSK program, contract no. 165830/V30. Ms. Sharmala Aravinthan, UiO, is acknowledged for assistance with the isotopic labelling experiments.

References

[1] J. Rostrup-Nielsen, in: J.R. Anderson, M. Boudart (Eds.), Catalysis—Science and Technology, vol. 5, Springer, Berlin, 1984.
[2] D. Sutton, J.F. Moisan, J.R.H. Ross, Catal. Lett. 75 (2001) 175.
[3] F. Solymosi, P. Tolmacsov, K. Kedves, J. Catal. 216 (1–2) (2003) 377.
[4] F. Solymosi, P. Tolmacsov, T.S. Zakar, J. Catal. 233 (2005) 51.
[5] L. Pinaeva, Y. Schuurman, C. Mirodatos, in: M. Maroto-Valer, C. Song, Y. Soong (Eds.), Environmental Challenges and Greenhouse Gas Control for Fossil Fuel Utilization in the 21st Century, Kluwer Academic/Plenum Publishers, 2002, p. 313.
[6] I. Chorkendorff, J.W. Niemantsverdriet, Concepts of Modern Catalysis and Kinetics, Wiley–VCH, Weinheim, Germany, 2003.
[7] H. Bengaard, J.K. Nørskov, J. Sehested, B.S. Molenbroek, J. Rostrup-Nielsen, J. Catal. 209 (2002) 265.
[8] J. Wei, E. Iglesia, J. Catal. 224 (2004) 370.
[9] A. Olafsen, Å. Slagtern, I.M. Dahl, U. Olsbye, Y. Schuurman, C. Mirodatos, J. Catal. 229 (2005) 163.
[10] A. Olafsen, C. Daniel, Y. Schuurman, L.B. Råberg, U. Olsbye, C. Mirodatos, Catal. Today 115 (1–4) (2006) 179.
[11] L.B. Råberg, M.B. Jensen, U. Olsbye, C. Daniel, S. Haag, C. Mirodatos, A. Olafsen Sjåstad, J. Catal. 249 (2007) 250.
[12] A. Parmaliana, F. Arena, F. Frusteri, S. Coluccia, L. Marchese, G. Martra, A.L. Chuvilin, J. Catal. 141 (1) (1993) 34.
[13] J.A. Moulijn, M. Makkee, A. Van Diepen, Chemical Process Technology, Wiley, New York, 2001.
[14] J. McMurry, Organic Chemistry, 6th edition, Thomson, USA, 2004.
[15] J.R. Rostrup-Nielsen, Steam Reforming Catalysts, Teknisk Forlag A/S, Copenhagen, 1975.
[16] NIST Standard Reference Database 85, NIST/TRC Table Database, WinTable, 2004.