The Formation of ThRh Hydride and the Synthesis of Methane by its Reaction with CO

By

H. Berner, H. Oesterreicher[1], K. Ensslen

Fakultät für Physik, Universität Konstanz, D-7750 Konstanz, West Germany

and

L. Schlapbach

Laboratorium für Festkörperphysik, ETH, CH-8093 Zürich, Switzerland

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The compound ThRh forms $ThRhH_{3.1}$ under 1 bar H_2 pressure at room temperature. Thermodynamic analysis yields $\Delta H^\circ = -58.7$ kJ/mole H_2 and $\Delta S^\circ = -128$ J/K · mole H_2. A methanation reaction is observed when $ThRhH_{3.1}$ is exposed to CO. A preferential reaction of CO with the hydrogen stored in the metal hydride rather than with the hydrogen in the ambient gas phase is shown by use of hydrogen-isotopes. XPS experiments of ThRh and $ThRhH_z$ demonstrate surface segregation into ThO_2 and Rh clusters, when exposed to O_2 or CO.

Die intermetallische Verbindung ThRh bildet bei einem H_2-Gleichgewichtsdruck von 1 bar und Zimmertemperatur das Hydrid $ThRhH_{3.1}$, dessen Bildungsenthalpie $\Delta H^\circ = -58.7$ kJ/mol H_2 und Bildungsentropie $\Delta S^\circ = -128$ J/K · mol H_2 beträgt. Wird $ThRhH_{3.1}$ einer CO-Atmosphäre ausgesetzt, ist die Entstehung von Methan nachzuweisen. Mit Hilfe von Wasserstoffisotopen wird gezeigt, daß bei dieser Reaktion der Wasserstoff, der im Metallhydrid gespeichert ist, gegenüber dem Wasserstoff aus der Gasphase bevorzugt eingebaut wird. XPS-Untersuchungen von ThRh und $ThRhH_z$ zeigen bei Zugabe von O_2 bzw. CO eine Oberflächenzersetzung, bei der ThO_2- und Rh-Teilchen entstehen.

Introduction

Metals and intermetallic compounds consisting of rare earths or actinides in combination with transition metals can absorb large amounts of hydrogen.

One step of this process is the dissociation of the H_2 molecule at the surface. As shown by the example of LaNi$_5$ [1] a segregation of the rare earth element at the surface takes place, binding the oxidizing impurities and keeping the transition metal in the metallic state. In this way sites are created, which are able to dissociate molecules. On the other hand these compounds can deliver large quantities of atomic hydrogen from the bulk. They therefore should be good candidates as catalysts for hydrogenation reactions.

Wallace *et al.* [2 – 4] investigated various compounds of this type in their unhydrided state with regard to their catalytic activity in the NH_3 and CH_4 synthesis. They found, that under the synthesis gas CO and H_2 the compounds decompose into crystallites consisting of the transition metal and of an oxide of the rare earth/actinide which showed at least in one case higher activity than a conventional oxide supported catalyst of the same elements. Soga *et al.* [5] studied the hydrogenation of ethylene over LaNi$_5$ and found, that the rate of hydrogenation over the hydride was larger than over the unhydrided material. Oesterreicher *et al.* [6] showed the catalytic formation of water, when hydrides of intermetallic compounds were exposed to air.

In this work we studied the CH_4 synthesis from carbon monoxide over ThRh hydride. We choose ThRh as a model compound type "rare earth or actinide/transition metal" for several reasons:

a) the material is expected to form a hydride, which is even stable at temperatures of 200 – 300 °C.

b) Rhodium could become catalytically active in clustersize on the surface, if the expected segregation of Thorium occurs.

c) Thorium is reported [4] to form a more active support than La, U or Zr.

In addition to a study of the hydriding behaviour of ThRh and the reaction of ThRh hydride with CO, XPS was used to help understanding of the surface processes.

Experimental details and results

1. Material

ThRh was prepared by melting the components together on a water cooled copper hearth of an arc furnace under argon atmosphere. The button was flipped and remelted several times to improve homogeneity.

The orthorhombic crystal structure [7] was verified by analysis of X-ray powder diagrams (Guinier camera, Cu-$K\alpha$ radiation). There was also evidence of ThO_2 presence, but not of Th or Rh.

2. Hydriding

ThRh was hydrided in the reactor of a high-pressure stainless steel apparatus with various reservoirs of known volume and facilities to work at different pressure ranges. The temperature was monitored by a NiCr – Ni thermocouple in the reactor bed. For the variation of the temperature, an external heater was used.
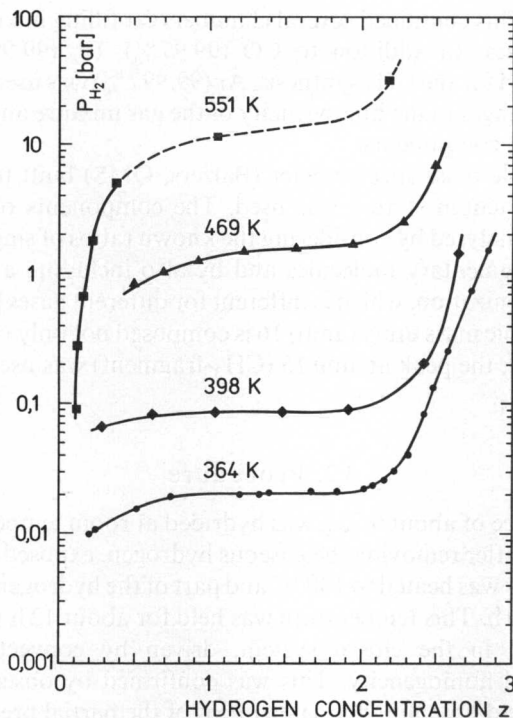
Fig. 1. Pressure-composition-diagram for desorption isotherms of ThRhH$_z$, measured on two samples (sample 1: 398 K, sample 2: 551 K, 469 K, 364 K)

The sample was exposed to H$_2$ gas (99.999 %), additionally purified from O$_2$ and H$_2$O by chemisorption and molecular sieve filtration, respectively, accomplished by passing the gas through a commercially available cartridge (Oxisorb, Messer Griessheim). The amount of absorbed hydrogen was calculated from the pressure drop. The first reaction with H$_2$ (28 bar) occurred spontaneously at room temperature without previous activation. At this temperature and 1 bar equilibrium H$_2$ pressure the hydride ThRhH$_{3.1}$ is formed. The pressure-composition isotherms, shown in Fig. 1 were measured for four temperatures by monitoring the equilibrium H$_2$ pressure starting from a point, where ThRh is in the hydride phase and pumping out known quantities of hydrogen gas. Three of these desorption isotherms show plateaus, associated with the transformation of the hydride (β) phase into the solid solution (α) phase. Thermodynamic parameters derived from a logarithmic plot of plateau pressure vs. reciprocal temperature are $\Delta H° = -58.7$ kJ/mole H$_2$ and $\Delta S° = -128$ J/K · molr H$_2$. The X-ray pattern of the ThRh hydride could not be indexed by enlarging the orthorhombic cell of ThRh, nor by the presence of ThH$_2$ or Th$_4$H$_{15}$.

3. Catalysis

3.1. Apparatus

The catalysis experiments were performed in the hydriding apparatus by use of corresponding parts of it as a single pass reactor (volume 5 cm^3) or as a

closed system. This contained several chambers for filling in known amounts of different gases. In addition to CO (99.97%), H_2 (99.999%) and D_2 (99.4%) required for the CH_4 synthesis, Ar (99.997%) was used as a reference gas to check changes in the homogeneity of the gas mixture and in the partial pressures of the components.

A quadrupole mass spectrometer (Balzers, QMS) built together with a separate high vacuum station was used. The components of the gas were quantitatively analysed by considering the known ratios of singly and doubly ionized and fragmentary molecules and by also including a factor for the probability of ionization, which is different for different gases [8, 9]. Since the peak at the atomic mass unity (amu) 16 is composed not only of CH_4 but also of CO and H_2O, the peak at amu 15 (CH_3-fragment) was used to detect the presence of CH_4.

3.2. Procedure

A ThRh piece of about 0.75 g was hydrided at room temperature, cooled to $-50°C$ and after removing the gaseous hydrogen, exposed to CO and Ar. Then the reactor was heated to $100°C$ and part of the hydrogen in the hydride allowed to desorb. This temperature was held for about 12 h while the gases were circulated in the closed system, driven by convection, to reach equilibrium and homogeneity. This was confirmed by observing constant total pressure and obtaining the same ratios of the partial pressures as those ratios determined from the filled in quantities. Either the closed system was used during the whole experiment or the reactor was switched over to a single pass reactor and the gases passed over the ThRh hydride at a constant feed rate of 1 ml gas/min (standard pressure). This rate was limited by the mass spectrometer, which was run at $1 \cdot 10^{-4}$ mbar. At the end of each single experiment the reactor was evacuated, the gas further analysed by mass spectrometry and the hydride was outgassed at $200°C$ for about 1 h. This procedure was repeated several times with the same ThRh sample.

3.3. Results

In all experiments with exposing ThRh hydride to CO, CH_4 was the only detectable product. The presence of H_2O was not detected either during the experiment or during evacuation at the end of the experiment. Further a progressive decrease of the hydrogen storage capacity was observed. This fact, together with the absence of oxygen containing gaseous products and the recorded pressure decrease during CH_4 synthesis suggest, that the ThRh sample became more and more oxidized.

In each successive experiment the time and the temperature, at which the beginning of the CH_4 synthesis could be detected, was lower than in the previous experiment. We took the detection of 1% of CH_4 relative to the total
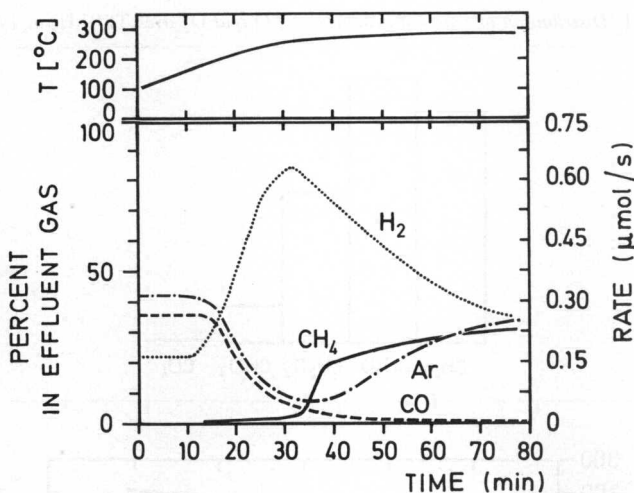
Fig. 2. Rate of CH_4 formation from CO over $ThRhH_z$ during increase of the temperature. H_2 evolves from the hydride. Ar is used as a "feed rate" reference

amount of the analysed gas as a measure for the onset. In the virgin hydrogenation cycle of ThRh the onset is found after 12 h at 100°C plus 3.5 h at 200°C. In the 8th catalysis cycle it could be already seen after 12 h at 95°C. The total pressure was 1.1 and 1.2 bar, respectively.

We studied more detailed the influence of the desorption of the hydrogen from the metal hydride on the CH_4 formation. In Fig. 2 the gas mixture and temperature course in a single pass experiment are shown. A temperature increase leads to increased hydrogen desorption, initiating instantaneously a higher rate of CH_4 formation compared with the fraction of argon, which is a reference of the feed rate during desorption. To show the preference in the methane synthesis between the hydrogen evolved from the hydride and the ambient H_2 gas, an isotope experiment was carried out. ThRh was hydrided and after removing most of the gaseous hydrogen, exposed to carbon monoxide and deuterium in the closed system. During evacuation of the reactor the mass spectrum showed peaks at amu 2, 3 and 4 in the ratio 7 : 6 : 8 arising from H_2, HD and D_2 and peaks at amu 12 to 20, which refer to several C–H–D compounds listed in Table 1. Although the presence of more D_2 gas than H_2 gas is evident, CH_4 and CH_3D are dominant over CD_4. From these results we conclude, that in forming methane, hydrogen from the hydride is preferred over hydrogen from the gas phase.

After 7 experiments with CO and 10 hydriding cycles, the ThRh piece had disintegrated to powder and had increased its weight by 7%. X-ray diffraction analysis showed ThO_2, $ThRh_3$ and Rh. This sample was then exposed to oxygen at 200°C for 12 h and the result of the subsequent catalysis

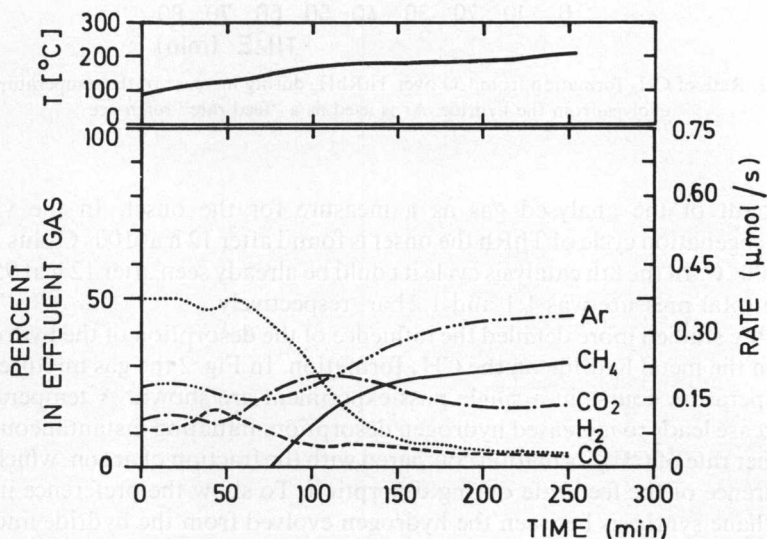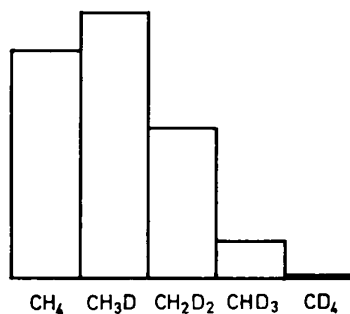Table 1. *Distribution of reaction products of* CO *and* D_2 *over* $ThRhH_z$ *at* 171 °C

CH$_4$ CH$_3$D   CH$_2$D$_2$ CHD$_3$ CD$_4$

Fig. 3. Formation of CH_4 and CO_2 from CO and H_2 over the oxidized ThRh sample during increase of the temperature. H_2O is also formed (see text). Ar is used as a "feed rate" reference

experiment is shown in Fig. 3. Hydrogen was admitted in the gaseous state, because the material did not take up any more hydrogen. The decrease of CO combined with the increase in CH_4 implies, that CH_4 is formed from CO and not from CO_2, which was also produced. Water was detected in larger amounts during evacuation and therefore not marked in the figure. The X-ray diffraction analysis showed that the material consists of ThO_2 and Rh.

The last experiment carried out without the ThRh sample or its decomposed products confirmed, that no products at reaction conditions were formed by experimental artefacts.

4. Surface analysis

The ThRh surface was studied by X-ray photoemission spectroscopy with a VG-Escalab-Spectrometer using Mg-$K\alpha$ radiation ($hv = 1\,253.6\,eV$; Au $4f_{7/2}$ at $83.9\,eV$, FWHM $1.2\,eV$). The ThRh was cleft under UHV conditions $(2-4\cdot10^{-10}\,mbar)$ and after analysing the clean surface the samples were exposed in situ to increasing doses of O_2 and CO, respectively. The photoelectron energy distribution curves of the core levels Th $4f_{7/2, 5/2}$, Rh $3d_{5/2, 3/2}$, O $1s_{1/2}$ and C $1s_{1/2}$ were measured to evaluate the chemical state and the concentration ratios within the escape depth of the photoelectrons ($\sim 20\,\text{Å}$). The chemical state was determined by comparison to known spectra. The concentration ratio was calculated from the integrated peak height divided by theoretical cross sections [10].

In Fig. 4 the spectra of cleft ThRh before and after oxygen treatment are shown. The clean sample contains metallic Th [11, 12] and metallic Rh [13, 14]. With increasing amounts of oxygen, increasing intensity of the chemically shifted Th $4f$ peaks is observed. This is explained by formation of ThO_2 [12] in agreement with the increase and position of the oxygen peak. The Rh peak shifts $0.2\,eV$ to lower binding energies, which could be explained by the formation of small Rh clusters with a high amount of top surface atoms. The C spectra do not change during exposure to O_2. The concentration Th : Rh changes from 1.6 : 1 of the cleft sample to 2.7 : 1 after 100 L O_2 ($1\,L = 1$ Langmuir $= 1\cdot10^{-6}\,Torr\cdot s$). Therefore O_2 exposure leads to enrichment of Th at the surface in the form of ThO_2. The Rh remains metallic.
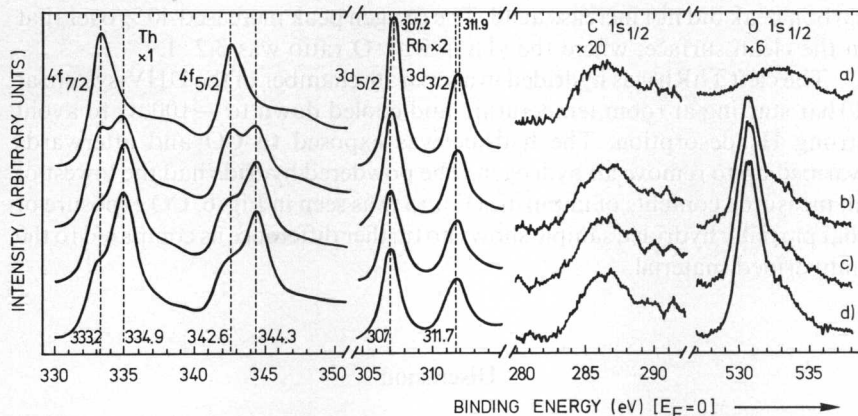

Fig. 4. XPS spectra of cleft ThRh exposed to O_2 at $20\,°C$: (a) cleft sample, Th : Rh = 1.6 : 1; (b) exposed to 1 L O_2, Th : Rh = 2.1 : 1; (c) exposed to 10 L O_2, Th : Rh = 2.5 : 1; (d) exposed to 100 L O_2, Th : Rh = 2.7 : 1
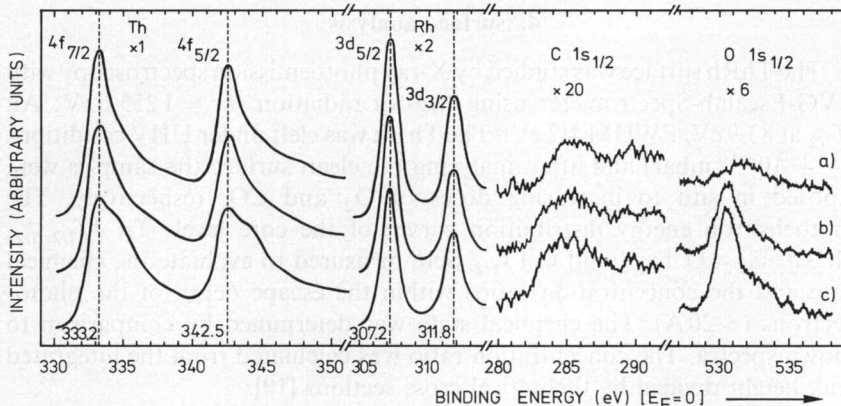
Fig. 5. XPS spectra of cleft ThRh exposed to CO at 200 C: (*a*) cleft sample, Th : Rh = 1.5 : 1;
(*b*) exposed to 10 L CO, Th : Rh = 1.6 : 1; (*c*) exposed to 1 000 L CO, Th : Rh = 1.8 : 1

Further the spectra of ThRh were recorded before and after CO exposure
at room temperature and at 200°C. Some of them are shown in Fig. 5. The
same effect − enrichment of Th as ThO_2 and metallic Rh − as after O_2
exposure is seen. However, it takes 1 000 L CO to produce the same amount of
ThO_2 as with only 1 L O_2. The C spectra show new small contributions at
energies between 282 and 285 eV, especially at 200°C, which could originate
from dissociated CO [15]. The ratio C : O however changes from 1 : 0.5 for the
cleft sample to 1 : 1.2 after 1 000 L CO, so that not all of the oxygen can be
derived from dissociated CO. To analyse the amount of surface coverage by
oxygen, which diffuses from the bulk to the surface, we followed the surface
concentration of O and C of a freshly cleft sample at 200°C over 2 h. The
carbon peak did not increase at all. The oxygen peak increased 40 % over that
in the clean surface, where the (Th + Rh) : O ratio was 3.2 : 1.

The cleft ThRh was hydrided in a separate chamber of the UHV-system at
20 bar starting at room temperature and cooled down to − 100°C to avoid
strong H_2 desorption. The hydride was exposed to CO and afterwards
warmed up to remove all hydrogen. The powdered hydride had the lowest of
all measured contents of impurities C and O as seen in Fig. 6. CO exposure of
that partially hydrided sample shows no further difference as compared to the
unhydrided material.

Discussion

The derived thermodynamic properties of ThRh hydride, $\Delta H° =$
$− 58.7$ kJ/mole H_2 and $\Delta S° = − 128$ J/K · mole H_2, are comparable to those
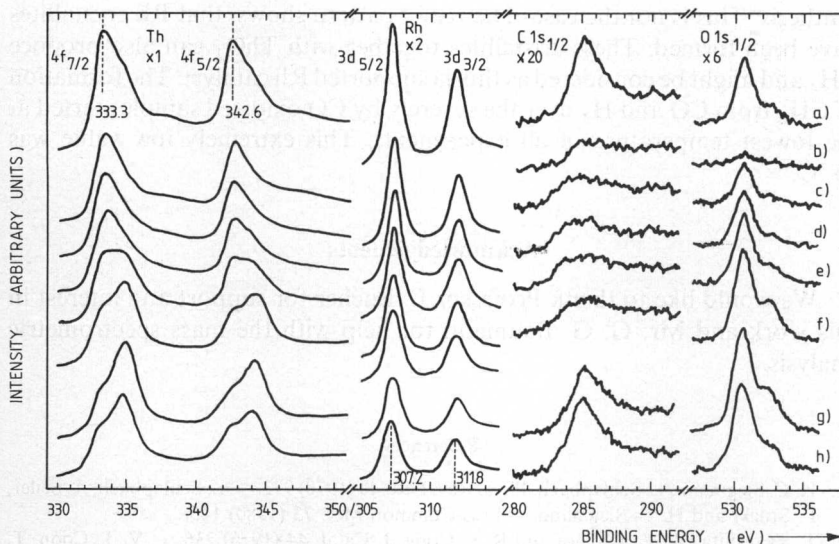of similar hydrides such as ThNi and ThCo, which are reported in the

Fig. 6. XPS spectra of cleft ThRh and of ThRhH$_z$ exposed to CO: (a) cleft sample at 20°C, Th:Rh = 1.6:1; (b) hydrided, cooled to −100°C, Th:Rh = 1.4:1; (c) hydride exposed to 10 L CO, Th:Rh = 1.5:1; (d) hydride exposed to 100 L CO, Th:Rh = 1.5:1; (e) hydride exposed to 1000 L CO, Th:Rh = 1.6:1; (f) hydride exposed to 10000 L CO, Th:Rh = 1.8:1; (g) hydride warmed up to 20°C, Th:Rh = 2.5:1; (h) completely dehydrided, Th:Rh = 2.4:1

literature [16]. Thus ThRh hydride is stable enough to be handled without strong desorption at temperatures up to 200°C. This temperature range is necessary to study CH$_4$ synthesis from CO over the metal hydride.

With the enrichment of Th as ThO$_2$ on the surface and the formation of metallic Rh, when exposed to O$_2$, ThRh has the expected surface properties anticipated from similar experiments with LaNi$_5$ [1], where oxidized La and metallic Ni are found in the ratio 1:1 on the surface.

When ThRh hydride is exposed to CO, CH$_4$ is formed below temperatures of 200°C. The hydrogen evolving from the hydride is preferred in forming CH$_4$, compared to the hydrogen in the gas phase, as shown in the isotope experiment. This fact makes evident that the origin and state of the hydrogen is very important. This preference appears to be caused by the large supply of atomic hydrogen by the hydride. In addition new clean, i.e. catalytically active surfaces may be created during hydriding and dehydriding of the intermetallic compound by progressive disintegration or segregation.

However the oxygen of the carbon monoxide is used subsequently for oxidation of Th, although a "reducing atmosphere" is formed by dehydriding. But if the CH$_4$ synthesis from CO would work only on the basis of oxidation of Th, the completely oxidized sample would not show any CH$_4$

synthesis. This is not the case. The X-ray pattern shows, that Rh crystallites have been formed. These cristallites together with ThO_2 can also produce CH_4 and might be considered as thoria supported Rh catalyst. The formation of CH_4 from CO and H_2 over the severely by CO oxidized sample started at the lowest temperature of all experiments. This extremely low value was 95°C.

Acknowledgements

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