Hydrogenation of carbon monoxide over vanadium oxide-promoted rhodium catalysts

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HYDROGENATION OF CARBON MONOXIDE OVER VANADIUM OXIDE-PROMOTED RHODIUM CATALYSTS

B.J. Kip, P.A.T. Smeets, J. van Grondelle and R. Prins.

Laboratory of Inorganic Chemistry and Catalysis,

Eindhoven University of Technology,

P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

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ABSTRACT

The effect of vanadium oxide as support and promoter on supported rhodium catalysts on the CO hydrogenation has been investigated at 0.15 and 4.0 MPa. Rh/V₂O₃ reduced at 723 K has a good selectivity toward oxygenated products, especially C₂-oxygenates, but has a low activity and stability. Vanadium oxide added as a promoter to catalysts consisting of rhodium supported on silica and alumina showed a remarkable effect on the activity of these systems. For the silica-supported systems the activity increased by a factor of 40, the deactivation of these catalysts was low (2 % h⁻¹) and the oxo-selectivity was very high (70 %). Although the vanadium oxide blocks part of the active metal surface, as became evident from a suppressed chemisorption capacity, it also enhances the rate of CO dissociation in those locations where reaction is still possible. The enhancement prevails over the blocking in the case of silica- and alumina-supported vanadium oxide-promoted catalysts, while blocking dominates for the vanadium oxide-supported catalyst after high temperature reduction. Experiments in which ethylene was added to a working catalyst, provided indications that the main promoter action of the vanadium oxide is to increase the CO dissociation, thereby increasing the activity of the catalyst.

For the alumina-supported catalysts, most of the vanadium oxide is scavenged by the support and only at a high V/Rh ratio, the activity of the Rh/Al₂O₃ catalyst is increased. The addition of vanadium oxide to the alumina-supported catalysts caused a suppression of the formation of ethers. The vanadium oxide probably covers the acidic ether-forming sites of the alumina support. During the first hours of reaction no acetic acid was observed for the alumina-supported catalysts due to a chromatographic effect. Initially, the acetic acid that was produced was adsorbed by basic sites of the support and only after prolonged reaction was acetic acid observed at the reactor outlet.

INTRODUCTION

The hydrogenation of carbon monoxide over rhodium catalysts produces a variety of products. The product distribution can be influenced by using different supports or promoters [1-11]. Since C₂-oxygenates are desirable products from an economic point of view [12], much attention has been paid to improve catalyst activity and selectivity to C₂-oxygenates. Vanadium oxide used as a support [9] or as a promoter [5,13,14] is reported to be of interest in this respect.

In the preceding paper we reported the synthesis and characterization of such V₂O₃-promoted Rh/SiO₂ and Rh/Al₂O₃ systems [15]. For the Rh/V₂O₃ catalyst, a

complete suppression of hydrogen chemisorption was observed after high temperature reduction, as previously reported by Tauster and Fung [16] for Ir/V₂O₃. They called this effect Strong Metal Support Interaction (SMSI). The now generally accepted explanation for the SMSI effect is that during high-temperature reduction a lower oxide is formed (for TiO₂ this suboxide is for instance Ti₄O₇) and that this oxide spreads over the metal particle, leading to a suppression of hydrogen and carbon monoxide chemisorption [16-22]. For the vanadium oxide-promoted Rh/SiO₂ catalysts, temperature programmed reduction experiments showed that rhodium facilitates the reduction of vanadium oxide and that vanadium oxide hampers the reduction of rhodium oxide, indicating that an intimate contact exists between rhodium and vanadium oxide. These and diffuse reflectance infrared spectroscopy experiments suggest the formation of RhVO₄ [15]. Carbon monoxide chemisorption was suppressed by the presence of vanadium oxide, but metal particle size was not influenced by the presence of vanadium oxide, as determined by TEM. This points to covering of the rhodium particles by patches of vanadium oxide. In this case, covering is not caused by reduction at high temperatures as normally in SMSI systems, but is due to the formation of RhVO₄ during the calcination step. Infrared spectroscopy of adsorbed carbon monoxide showed that only the linearly bonded and bridge-bonded CO were suppressed and that the amount of the gem-dicarbonyl species slightly increased with increasing V/Rh ratio [15]. Since absorption bands were not found at low wave numbers (around 1500 cm⁻¹), we did not find evidence for a weakening of the C-O band by the promoter, as suggested by Sachtler et al. [23-25] and Ichikawa et al. [11]. The measurements, described above suggest a model for the Rh/V₂O₃/SiO₂ systems as shown in Figure 1A and C.

FIGURE 1: Schematic illustration of the model for the silica- and alumina-supported, vanadium oxide-promoted rhodium catalysts after calcination at 723 K (A and B) and after reduction at 523 K (C and D).

For the vanadium oxide-promoted $\text{Rh}/\text{Al}_2\text{O}_3$ systems, indications for an intimate contact between the vanadium oxide and the rhodium were found only for catalysts with a high V/Rh ratio (around 7). For these catalysts only after oxidation at 898 K a mutual affection of the reduction of rhodium and vanadium oxide was observed in TPR, suggesting the formation of RhVO_4 . For these catalysts, rhodium might be positioned on V_2O_5 layers and after reduction some vanadium oxide might be located on top of the rhodium particles. For $\text{V}/\text{Rh} < 1$, no indication for an intimate contact was present. Rh_2O_3 and V_2O_5 are believed to be present as separate particles on the alumina support due to the strong interaction between vanadium oxide and the alumina support. The model for the $\text{Rh}/\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ catalysts is summarized in Figure 1B,D.

In this study we report the results of the H_2/CO reaction over $\text{Rh}/\text{V}_2\text{O}_3$ and vanadium oxide-promoted Rh/SiO_2 and $\text{Rh}/\text{Al}_2\text{O}_3$. Attention will be paid to the role of the promoter element. Ethylene addition is carried out on a working catalyst with and without promoter in order to compare the in situ rate of hydrogenation and CO insertion.

EXPERIMENTAL

Catalyst preparation and characterization.

Since the catalysts used in this study were the same as those used in the characterization studies reported earlier [15], we refer to that study for information on catalyst preparation. The following notations will be used in the present article: $\text{Rh}/\text{V}_2\text{O}_3/\text{SiO}_2$ for silica-supported vanadium oxide-promoted rhodium catalysts, $\text{Rh}/\text{V}_2\text{O}_3/\text{Al}_2\text{O}_3$ for alumina-supported vanadium oxide-promoted rhodium catalysts, and $\text{Rh}/\text{V}_2\text{O}_3$ for vanadium oxide-supported rhodium catalysts.

The results of the characterization of the catalysts by temperature programmed reduction, hydrogen and carbon monoxide chemisorption, transmission electron microscopy, hydrogen desorption and IR studies of adsorbed carbon monoxide have been reported before [15]. The results are summarized in Table 1.

Transmission electron microscopy was used to study the metal particle size before and after the syngas reaction. The catalysts were examined with a Jeol 200 CX, operating at 200 kV.

CO hydrogenation

A continuous flow stainless-steel high pressure reactor, lined with copper to prevent metal carbonyl formation, was used to study the hydrogenation of carbon monoxide. The catalysts were reduced in situ in this reactor in pure hydrogen at 0.1 MPa, using a temperature ramp of 5 K min^{-1} between 298 and 723 K (unless stated otherwise), and holding the final temperature for 1 h. The reactor was subsequently cooled to reaction temperature and pressurized with H_2 to the desired level. After stabilization an additional CO flow was started. Flows were regulated accurately by means of thermal mass flow controllers. All catalysts were measured

TABLE 1

Results and characterization of vanadium oxide-supported or-promoted 1.5 wt% Rh catalysts.

Systems	V/Rh ^a	H/Rh ^b	CO/Rh ^b	D(Å) ^c
Rh/V ₂ O ₃ ^d	--	3.8	0.36	52
Rh/SiO ₂	0	0.72	0.71	20
Rh/V ₂ O ₃ /SiO ₂	0.13	0.71	0.70	22
,,	0.50	0.73	0.56	18
,,	1.0	0.76	0.27	22
,,	2.0	0.86	0.32	n.m. ^e
,,	4.5	1.89	0.36	19
Rh/Al ₂ O ₃	0	1.6	1.3	n.o. ^e
Rh/V ₂ O ₃ /Al ₂ O ₃	0.13	1.4	n.m.	n.m.
,,	1.0	1.6	1.1	n.o.
,,	7.0	3.3	1.2	n.o.
,,	8.4	3.1	1.1	n.m.

a) atomic ratio, b) determined after reduction at 523 K and evacuation at 723 K by back extrapolation of the desorption isotherm to room temperature, c) mean diameter of rhodium particles, determined by TEM, d) Rh/V₂O₃ system in non-SMSI state, after reduction at 523 K. H/Rh was 0.09 and 0.00 after reduction at 723 and 823 K, respectively, e) n.m. is not measured, n.o. is not observable (diameter less than 8 Å).

under the same reaction conditions (GHSV = 4000 l l⁻¹ h⁻¹, H₂/CO = 3, P = 0.15 or 4.0 MPa, catalyst bed 1 ml). The reaction temperature was adjusted so that conversion of CO was around 2%. The product stream was fed to a GC system via a heated sampling line and analyzed on-line. A capillary column (crosslinked 5% phenyl methyl silicone, film thickness 1.0 μm, internal diameter 0.31 mm, length 50 m, split ratio 1:36) enabled us to determine accurately the amount of saturated and unsaturated hydrocarbons up to C₈, alcohols up to C₇, aldehydes up to C₅, ethers, esters and acetic acid in 16 min. Peak area integration was carried out with a Nelson Analytical Interface-IBM PC configuration. The integrated product signals were converted into volume percentages using experimental (methane, ethane, methanol and ethanol) and theoretical calibration factors. Conversion and selectivity were calculated on carbon basis.

RESULTS

Rh/V₂O₃

Table 2 summarizes the results of the hydrogenation over vanadium oxide-supported rhodium catalysts at 4.0 MPa. As vanadium oxide is a SMSI support, we

TABLE 2: Results of H_2 -CO reaction for 1.5 wt% Rh/ V_2O_3 systems after 15 h time on stream, $H_2/CO = 3$, GHSV = $4000\text{ l l}^{-1}\text{ h}^{-1}$.

Reduction temp. (K)	523	723	823	723
P (MPa)	4.0	4.0	4.0	0.15
React. temp. (K)	513	543	543	513
Activity ^a	3.4	0.8	0.8	0.6
corr. act. ^b	2.1	0.1	0.1	0.4
sel. (%) ^c				
CH ₄	75.8	16.8	11.3	28.2
C ₂ + ^d	10.6	12.9	8.4	33.6
C ₁ OH _{tot} ^e	6.8	25.1	23.2	0.3
C ₂ OH _{tot} ^f	5.4	26.1	28.6	6.9
C ₂ =O ^g	0.4	6.4	10.3	27.9
C ₂ OOH ^h	0.5	2.8	4.0	1.8
C ₃ O+ ⁱ	0.6	4.6	14.6	1.3
oxo. sel. ^j	13.6	70.3	80.3	38.2
Deact. (% h ⁻¹)	4.0	2.9	11.1	8.4
C ₂ =/C ₂	0.1	0.2	0.4	5.9
C ₃ =/C ₃	0.2	0.7	2.1	10
C ₄ =/C ₄	0.4	1.2	1.9	10.0

a) activity in mmol converted CO (mol Rh)⁻¹ s⁻¹, b) calculated activity at 503 K using $E_{act} = 100\text{ kJ mol}^{-1}$, c) selectivities expressed as %C efficiency, d) hydrocarbons containing two or more C atoms, e) total amount of methanol, ethers and esters included, f) total amount of ethanol, ethers and esters included, g) acetaldehyde, h) acetic acid, esters included, i) oxygenated products containing three or more C atoms, j) total oxo-selectivity.

reduced the Rh/ V_2O_3 system in situ at 523, 723 and 823 K. The influence of the reduction temperature is clearly observed. The higher reduction temperature caused a strong decrease in activity. Therefore the catalysts reduced at a high temperature had to be tested at a higher reaction temperature, in order to obtain a conversion high enough to enable accurate measurements. To compare activities for all catalysts studied in this paper, the activities were corrected for differences in temperature, and calculated at 503 K, using $E_{act} = 100\text{ kJ mol}^{-1}$. This activation energy was measured for the catalyst Rh/ V_2O_3 /SiO₂ with V/Rh = 4.5.

Not only was the activity influenced by the reduction temperature, but also the selectivity changed markedly. Oxo-selectivity increased dramatically with increasing reduction temperature, from 13.6 to 70.3 and 80.3 % when using $T_{red} = 523, 723$ and 823 K, respectively, and so did the proportion of unsaturated hydrocarbons.

TABLE 3: Results of H_2 -CO reaction after 15 h time on stream for vanadium oxide-promoted 1.5 wt% Rh/SiO₂ systems reduced in situ at 723 K. For definitions see Table 2. Experimental conditions: GHSV = 4000 1 1⁻¹ h⁻¹, $H_2/CO = 3.0$.

V/Rh ^a	0	0.12	0.5	1.0	2.0	2.0	2.0	4.5	0	0.5	2.0
P (MPa)	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	0.15	0.15	0.15
React. temp. (K)	600	546	523	503	504	503	501	501	591	523	504
activity	2.8	1.7	1.6	1.8	2.9	2.5	3.0	1.8	2.4	1.8	1.8
corr. act.	0.06	0.3	0.6	1.8	2.7	2.5	3.3	0.05	1.0	1.7	1.7
sel. (%)											
CH ₄	33.2	20.3	21.8	20.3	20.4	31.6	19.5	85.4	36.2	26.5	26.5
C ₂ ⁺	2.3	2.2	5.2	8.8	9.9	11.1	12.4	13.5	28.1	37.8	37.8
C ₁ OH _{tot}	29.1	27.8	20.4	25.1	27.5	15.3	27.2	0.5	0.8	2.5	2.5
C ₂ OH _{tot}	20.5	20.2	24.2	25.9	26.9	20.9	25.9	0.2	23.2	26.4	26.4
C ₂ =O	4.3	7.6	7.6	3.7	1.2	6.3	1.1	0.4	10.2	6.4	6.4
C ₂ OOH	10.2	20.6	17.1	10.0	8.7	9.4	7.0	0.0	0.8	0.7	0.7
C ₃ O ⁺	0.6	1.4	3.7	6.2	5.4	5.4	6.9	0.0	0.7	2.1	2.1
oxo. sel.	64.5	77.5	73.0	70.9	69.7	57.3	68.1	1.1	35.7	35.7	35.7
Deact. (% h ⁻¹)	1.7	3.5	3.8	2.6	1.9	2.0	1.8	n.m.	3.8	3.0	3.0
C ₂ =/C ₂	0.0	0.2	0.2	0.5	0.4	n.m.	0.6	0.0	0.9	1.1	1.1
C ₃ =/C ₃	0.0	1.1	1.8	2.1	2.1	n.m.	2.7	0.0	10	10	10
C ₄ =/C ₄	0.0	0.2	1.2	1.6	1.3	n.m.	1.7	0.0	3.8	3.8	3.8

a) V/Rh, atomic ratio, b) reduced at 523 K.

We also performed an experiment at low pressure (0.15 MPa) after a high temperature reduction. In that case activity was low too. The methanol selectivity was below 1.0 % because of thermodynamic limitations. The total amount of other oxygenates was comparable to that obtained in the high pressure experiment. The relative amount of unsaturated hydrocarbons was high and considerable amounts of longer hydrocarbons were measured. A high acetaldehyde selectivity was observed (28%).

In all cases the deactivation was high (3–11 % h⁻¹). The selectivity changed markedly as a function of time on stream, especially after reduction at high temperature. Methanol and ethanol selectivities increased and hydrocarbon selectivity decreased with reaction time. The total oxo-selectivity increased from 29% after 0.5 h to 81% after 16 h time on stream for the Rh/V₂O₃ catalyst reduced at 823 K.

Thus, Rh/V₂O₃ catalyst reduced at high temperature (> 723 K) exhibits a relatively high oxo-selectivity, but a low activity and strong deactivation. During high temperature reduction the rhodium particles become covered by V₂O₃, as suggested by Van der Lee et al. [9]. The V₂O₃ patches covering the Rh particles will be partly removed by water (formed as a product during the syngas reaction), but the remaining vanadium oxide still has an effect on activity and selectivity. This was also shown by Lin et al. [26]. They reported that a few pulses of CO + H₂ reversed the SMSI-state for Rh/TiO₂ reduced at high temperatures, whereas this was not the case for Rh/V₂O₃ after high temperature reduction.

However, the activity and stability of these catalysts is low and V₂O₃ has bad structural properties (low surface area, low pore volume, relatively high solubility in water). Rh/Al₂O₃ exhibits a high activity and stability [3,27,28], and SiO₂ and Al₂O₃ are stable supports with good structural properties (high surface area, high pore volume). We therefore tried to combine the selectivity properties of Rh/V₂O₃ reduced at a high temperature and the activity and stability properties of alumina- and silica-supported systems by promoting Rh/Al₂O₃ and Rh/SiO₂ with varying amount of vanadium oxide. Especially, we attempted to prepare a monolayer of vanadium oxide on alumina, so that the resulting catalyst would have the good structural properties of alumina, and the described promoter activity of vanadium oxide.

Rh/V₂O₃/SiO₂

Influence of V/Rh ratio. As shown above, the influence of the reduction temperature on the catalytic performance of Rh/V₂O₃ was significant. However, for the Rh/V₂O₃/SiO₂ systems, the reduction temperature had a minor influence. The Rh/V₂O₃/SiO₂ system with V/Rh = 2, was reduced at 523 and 723 K (cf. Table 3). In comparison with the catalyst reduced at high temperature, the catalyst reduced at low temperature showed a slightly higher selectivity to methane and acetaldehyde and a lower selectivity to methanol and ethanol. Total oxo-selectivity after

reduction at 523 K was 57 %, whereas this selectivity was 70 % after reduction at 723 K. We used the reduction at 723 K as a standard for all catalysts.

Table 3 summarizes the effect of vanadium oxide promotion on Rh/SiO₂ at 4.0 and 0.15 MPa. In the high pressure case, a sharp increase in activity with increasing V/Rh ratio was observed. Using an activation energy of 100 kJ mol⁻¹, as was measured for Rh/V₂O₃/SiO₂ with V/Rh = 4.5, it is calculated that the vanadium oxide-promoted Rh/SiO₂ catalysts with V/Rh = 4.5 is 40 times more active than the unpromoted Rh/SiO₂ catalyst, and almost 20 times more active than Rh/V₂O₃ reduced at 723 K. The extent of deactivation of these catalysts was considerably lower than that of Rh/V₂O₃. Clearly the promoted catalysts were considerably more active than the unpromoted catalyst.

The total oxo-selectivity slightly decreased with increasing V/Rh ratio, mainly due to a decreased methanol and acetic acid selectivity, but still was around 70%, comparable to those obtained for the Rh/V₂O₃ systems reduced at high temperature. The increase of the relative amount of unsaturated hydrocarbons with increasing V/Rh ratio up to V/Rh = 1 must be due to differences in reaction temperature.

To exclude the influences of temperature on selectivity, we tested Rh/SiO₂ and Rh/V₂O₃/SiO₂ (V/Rh = 1.0) at the same temperature (548 K). In order to measure at the same conversion level (about 3 %), we adjusted the GHSV for these systems by changing the amount of catalyst and the total gas flow. The results are presented in Table 4. Activities and selectivities for the different product groups are compared. Clearly the formation rate of all products is increased by the presence of vanadium oxide, but the rates for hydrocarbons and C₃O⁺ formation are increased most, while the formation rate of methanol is only increased by a factor of six.

In the low pressure case (P = 0.15 MPa, see Table 3), of course, almost no methanol was formed due to thermodynamic limitations. However, relatively high oxo-selectivities were measured (up to 36 %) because of a high selectivity to ethanol and acetaldehyde. During the low pressure experiments, the deactivation and the proportion of unsaturated hydrocarbons were high. The presence of vanadium oxide had a remarkable influence on the total oxo-selectivity. The unpromoted Rh/SiO₂ catalysts had a total oxo-selectivity of 1 %, whereas the promoted Rh/SiO₂ catalysts had a total oxo-selectivity of 36 %.

A separate experiment was conducted to investigate the CO hydrogenation activity of the vanadium oxide itself. A V₂O₃/SiO₂ catalyst containing 1.6 wt % V was tested at 591 K, but no products could be detected.

Rhodium particles size. Rhodium particle size can have a significant influence on the activity of Rh/SiO₂ catalysts in the synthesis gas reaction [27,29]. Therefore the improvement of the activity by addition of vanadium oxide might be caused by a decrease in particle size. But as shown in Table 1, rhodium particle size did not differ significantly for the silica-supported systems with or without vanadium oxide. The average particle size was 20 ± 2 Å. Particle size can be increased by

TABLE 4: Rh/SiO₂ and Rh/V₂O₃/SiO₂ (V/Rh = 1.0) catalyst tested at the same reaction temperature (548 K), GHSV for Rh/SiO₂ = 660 l l⁻¹ h⁻¹, GHSV for Rh/V₂O₃/SiO₂ = 8000 l l⁻¹ h⁻¹, P = 4.0 MPa, H₂/CO = 3.0.

	Selectivity (%C)		Activity (mmol converted CO (mol Rh) ⁻¹ s ⁻¹)		factor of increase of formation
	Rh/SiO ₂	Rh/V ₂ O ₃ /SiO ₂	Rh/SiO ₂	Rh/V ₂ O ₃ /SiO ₂	
CH ₄	11.6	30.7	0.051	3.75	74
C ₂ +	1.4	10.9	0.006	1.33	222
C ₁ OH _{tot}	57.2	12.4	0.252	1.51	6
C ₂ OH _{tot}	13.7	25.2	0.060	3.07	51
C ₂ =O	0.0	6.9	0.000	0.84	∞
C ₂ OOH	14.7	10.5	0.065	1.28	20
C ₃ O+	1.4	3.4	0.006	0.41	68
C ₂ oxo	28.4	42.6	0.125	5.20	42
total oxo	87.0	58.4	0.383	7.12	19
Total activity			0.440	12.2	28

sintering due to adsorption of CO [30] or syngas reaction [31]. The metal particle size distribution of Rh/V₂O₃/SiO₂, V/Rh = 1.0 had not changed at all during reaction. The unpromoted catalyst showed some larger particles (25-35 Å), but the majority of the particles remained unchanged. The presence of some larger particles will originate from a more pronounced sintering process at the higher reaction temperature needed for the Rh/SiO₂ catalyst. Thus, the observed higher activity for the promoted catalyst cannot be caused by the presence of larger particles in this catalyst.

Performance as a function of time on stream. The catalytic performance of Rh/SiO₂ and Rh/V₂O₃/SiO₂ (V/Rh = 2.0) at 4.0 MPa as a function of time on stream is presented in Figure 2A and B, respectively. Clearly, for Rh/SiO₂ the moderate decrease in overall activity (1.7 % h⁻¹) is mainly correlated with the decrease in activity to methane (3.6 % h⁻¹). The formation rate of methanol was almost constant, while the other products showed an intermediate deactivation. For the Rh/V₂O₃/SiO₂ (V/Rh = 2.0) catalyst, a similar behaviour of activity versus time on stream is observed. After several hours on stream an almost constant formation rate of methanol and a slight deactivation for the other products is observed. This deviating deactivation behaviour of methanol can be explained by the assumption that methanol is formed on sites different from those for the other products, such as metal ions [32-34].

During the first hours of reaction, the amount of methanol and ethanol increased for the unpromoted but decreased for the promoted catalyst. This might

FIGURE 2: Formation rates of several products as a function of time on stream ($P = 4.0$ MPa, GHSV = $4000 \text{ l l}^{-1} \text{ h}^{-1}$, $\text{H}_2/\text{CO} = 3.0$), expressed in mmol converted CO $(\text{mol Rh})^{-1} \text{ s}^{-1}$.

A. 1.5 wt% Rh/SiO₂, $T_{\text{react}} = 600$ K

B. 1.5 wt% Rh/V₂O₃/SiO₂, V/Rh = 2.0, $T_{\text{react}} = 504$ K.

be a result of changes in the catalyst systems during reaction, especially for the promoted catalyst. A partial removal of the covering by V₂O₃ due to water formed during the syngas reaction might occur.

Influence of H_2/CO and Temperature. In Figure 3a and b, the influence of the H_2/CO ratio and the reaction temperature on the activity for Rh/SiO₂ and Rh/V₂O₃/SiO₂, V/Rh = 4.5 is presented. From the temperature dependence of the activity, activation energies can be calculated. For the promoted system a total activation energy of 100 kJ mol^{-1} was measured. The activation energies for methane, methanol and ethanol were 135, 65 and 105 kJ mol^{-1} , respectively. For the unpromoted system, the total activation energy and the activation energy for methane were 89 and 160 kJ mol^{-1} , respectively. As can be seen in Figure 3b, the formation rate of methanol and ethanol cannot be described by an Arrhenius equation. This might be due to successive reactions, to thermodynamic limitations (in the case of methanol), or to changes in the catalyst (e.g. less rhodium ions at high temperatures). In all cases the total activity and the formation rates to CH₄, C₁OH and C₂OH increased with increasing H_2/CO ratio. Only for the promoted system, the formation rate of methanol became almost constant above $\text{H}_2/\text{CO} = 1.0$. Note that the measurements of the promoted and unpromoted catalysts took place at different temperatures. In Table 5, the selectivity data for the promoted system as a function of temperature and H_2/CO ratio are given. Clearly, an increase in temperature and a decrease in H_2/CO ratio induced a higher C₂-oxygenate selectivity and a lower methanol selectivity. The methane selectivity increased with increasing temperature and H_2/CO ratio. A low H_2/CO ratio resulted in a high acetic acid selectivity.

FIGURE 3: Influence of H_2/CO and reaction temperature on formation rates of the most important products after 15 h on stream,

- influence of H_2/CO ratio on overall reaction rate (a1), methane formation rate (a2), methanol formation rate (a3) and ethanol formation rate (a4)
- influence of reaction temperature on overall reaction rate (b1), methane formation rate (b2), methanol formation rate (b3) and ethanol formation rate (b4).

Activities are expressed in mmol converted CO (mol Rh) $^{-1}$ s $^{-1}$. Drawn lines represent data of Rh/SiO $_2$, dotted lines of Rh/V $_2$ O $_3$ /SiO $_2$, V/Rh = 4.5. Reaction conditions: GHSV = 4000 l l $^{-1}$ h $^{-1}$, P = 4.0 MPa, reaction temperature for a-series: 593 K for Rh/SiO $_2$ and 503 K for Rh/V $_2$ O $_3$ /SiO $_2$, H_2/CO for b-series = 3.0.

TABLE 5: Influence of temperature and H_2/CO ratio on syngas reaction at 4.0 MPa over $Rh/V_2O_3/SiO_2$ ($V/Rh = 4.5$), $GHSV = 4000 \text{ l l}^{-1} \text{ h}^{-1}$.

T (K)	Temperature influence				H_2/CO influence			
	483	495	510	524	503	503	503	503
H_2/CO	3.0	3.0	3.0	3.0	0.5	1.0	2.0	3.0
Act.	1.3	2.4	4.9	8.9	1.4	2.2	3.0	3.6
SeI (%C)								
CH_4	14.0	17.4	21.7	27.9	10.1	11.6	19.4	22.3
C_2^+	9.7	9.7	10.6	12.3	12.1	9.3	12.4	11.6
C_1OH_{tot}	36.6	31.5	25.2	17.4	25.1	33.7	25.3	22.9
C_2OH_{tot}	26.1	27.7	28.4	28.9	27.9	25.2	27.2	28.5
$C_2=O$	0.4	0.2	0.7	1.5	3.0	2.8	1.0	0.9
C_2OOH	7.2	7.4	7.6	7.3	13.8	10.3	8.9	7.9
C_3O^+	6.1	6.1	5.8	4.7	8.1	7.1	6.6	5.9
C_2oxo	33.7	35.3	36.7	37.7	44.7	38.3	37.1	37.3
tot oxo	76.4	72.9	67.7	59.8	77.9	79.1	69.0	66.1

Flory-Schulz distribution. From a detailed analysis of the products, Flory-Schulz distributions were obtained for the unpromoted and promoted catalysts, presented in Figure 4A and B, respectively. No straight lines were found in the Flory-Schulz plots and therefore chain-growth probabilities for low and high carbon numbers (n) were calculated. For the promoted catalyst ($V/Rh = 4.5$), the chain-growth probability for hydrocarbons α_{C_n} ranged from 0.4 ($n = 3-8$) to 0.6 ($n = 5-8$). The chain-growth probability for oxygenates α_{C_nO} ranged from 0.3 ($n = 1-5$) to 0.4 ($n = 4-7$). Thus we observed a significantly higher α -value for the hydrocarbons than for the oxygenates. Since the most accepted mechanism for the formation of oxygenates is the insertion of CO in a growing alkylgroup, hydrocarbons with n and oxygenates with $n+1$ C-atoms were taken together to calculate the total chain-growth probability. The total chain-growth probability $\alpha_{C_n+C_{n+1}O}$ was 0.4 ($n = 3-6$). The following chain-growth probabilities were measured for the unpromoted Rh/SiO_2 catalyst: α_{C_n} ranged from 0.3 ($n = 3-4$) to 0.5 ($n = 4-7$), α_{C_nO} was 0.2 ($n = 3-5$) and $\alpha_{C_n+C_{n+1}O}$ was 0.3 ($n = 2-4$). Furthermore, in both cases an overshoot of C_2 -oxygenated products and a deficit of C_2 -hydrocarbons was observed, compared with the expected amounts based on the Flory-Schulz plots. In the experiments at low pressure, a higher chain-growth probability was observed for $Rh/V_2O_3/SiO_2$, $V/Rh = 4.5$: $\alpha_{C_n} = 0.6$ ($n=3-5$), $\alpha_{C_nO} = 0.4$ ($n=3-6$) and $\alpha_{C_n+C_{n+1}O} = 0.5$ ($n=3-5$).

FIGURE 4: Flory-Schulz distribution for hydrocarbons (□), oxygenates (●) and the sum of hydrocarbons and oxygenates, counted as $C_n + C_{n+1}O$ (○) after 15 h on stream.

A. Rh/SiO_2 B. $\text{Rh/V}_2\text{O}_3/\text{SiO}_2$, $\text{V/Rh} = 4.5$.

$\text{Rh/V}_2\text{O}_3/\text{Al}_2\text{O}_3$

The results for the vanadium oxide-promoted alumina-supported rhodium catalysts are presented in Table 6. In the low as well as the high pressure cases, 0.15 and 4.0 MPa respectively, an increase in activity was observed with increasing V/Rh ratio. However, the increase in activity was not as pronounced as in the case of vanadium oxide promotion of the Rh/SiO_2 catalyst. Low amounts of vanadium oxide ($\text{V/Rh} < 1$) had a negligible influence on the activity, in contrast to the silica-supported catalysts. For the catalysts with $\text{V/Rh} = 7.0$ and 8.4 , the catalysts with a near mono-layer of vanadium oxide on the alumina surface, the vanadium oxide caused an increase of the activity by a factor of three and increased selectivities to C_2 -oxygenates and longer hydrocarbons, whereas the selectivities to methane and methanol were diminished. The total oxo-selectivity was slightly increased by the presence of vanadium oxide (up to 52 %), but was considerably lower than for the $\text{Rh/V}_2\text{O}_3/\text{SiO}_2$ (70 %) and $\text{Rh/V}_2\text{O}_3$ (70-80%) catalysts. The deactivation was low and increased slightly with increasing V/Rh ratio.

A noteworthy effect of the vanadium oxide content on the formation of dimethyl ether was observed (see Table 6). Dimethyl ether is thought to be formed on acidic sites of the Al_2O_3 by dehydration of methanol [28]. The low dimethyl ether concentrations for $\text{V/Rh} = 7.0$ and 8.4 suggest that there are almost no free acidic sites available in these systems, otherwise the ether formation would not be suppressed that much. We conclude that the vanadium oxide has covered the alumina sites responsible for the dehydration of methanol.

The rate of formation of acetic acid changed markedly as a function of time on stream (see Figure 5). For the alumina and low-vanadium oxide loaded alumina-supported catalysts, the acetic acid concentration started to increase after about 12 h time on stream, whereas in the case of high vanadium oxide loaded aluminas, the increase in acetic acid formation took place after about 5 h time on

TABLE 6: Results of H_2 -CO reaction after 15 h time on stream for vanadium oxide promoted 1.5 wt% Rh/ Al_2O_3 systems reduced in situ at 723 K. For definitions see Table 2. Experimental conditions: GHSV = $4000\ l\ l^{-1}\ h^{-1}$, $H_2/CO = 3.0$.

V/Rh ^a	0.0	0.12	1.0	7.0	8.4	0.12	1.0	7.0
P (MPa)	4.0	4.0	4.0	4.0	4.0	0.15	0.15	0.15
React. temp. (K)	501	493	493	493	493	503	493	493
activity	1.6	1.0	1.3	3.8	3.6	0.8	0.8	2.8
corr. act.	1.8	1.7	2.1	6.2	5.9	0.8	1.3	4.5
sel. (%)								
CH ₄	46.3	39.5	39.7	37.5	36.2	54.1	48.8	39.1
C ₂ ⁺	6.6	8.8	8.2	11.8	11.6	21.1	27.0	35.6
C ₁ OH _{tot}	22.4	29.3	23.9	15.6	16.0	15.4	10.2	3.6
C ₂ OH _{tot}	19.1	17.0	19.9	21.2	21.4	7.6	10.8	18.1
C ₂ =O	1.6	1.4	1.7	1.6	1.6	0.0	0.6	1.0
C ₂ OOH	0.9	0.9	3.6	7.3	7.5	0.2	0.3	1.0
C ₃ O ⁺	3.1	3.1	3.0	5.0	5.7	1.6	2.3	1.5
oxo. sel.	47.1	51.7	52.1	50.7	52.2	24.8	24.2	25.2
Deact. (% h ⁻¹)	0.4	0.5	0.7	1.9	1.7	3.0	3.3	2.3
ether formation ^b	.51	.39	.23	.02	.01	.32	.15	0.0

a) V/Rh, atomic ratio, b) $2 \cdot COC / (C_1OH + 2 \cdot COC)$.

FIGURE 5: Formation rate of acetic acid (in $mmol\ C_2OOH / (mol\ Rh)^{-1}\ s^{-1}$) as a function of time on stream. For reaction conditions see Table 2 and 3.

a. Rh/ Al_2O_3

b. Rh/ V_2O_3/Al_2O_3 , V/Rh = 1

c. Rh/ V_2O_3/Al_2O_3 , V/Rh = 7.0

d. Rh/ V_2O_3/SiO_2 , V/Rh = 2

stream. The silica-supported systems (with or without vanadium oxide) started to produce acetic acid during the first hour of reaction. We think that the fact that acetic acid is only observed after prolonged reaction on the alumina-supported catalysts, is due to a chromatographic effect. Already during the first hours acetic acid or its reaction-intermediate is formed, but is bonded by basic sites on the support. When these sites are filled, acetic acid can leave the catalyst surface and be detected as one of the products in the gas stream. The following experiment proved this chromatographic effect. Downstream of the Rh/Al₂O₃ catalyst bed an additional bed of 1 ml of Al₂O₃ was placed. The amount of acetic acid that could be adsorbed during the first hours of reaction thus was doubled, and indeed acetic acid appeared in the product stream only after 23 h time on stream. Since acetic acid is observed almost immediately after the start of the reaction, these adsorption sites will not be available on SiO₂. In the case of the alumina-supported catalysts with high V/Rh ratios, the quicker breakthrough of acetic acid (cf. Figure 5c) is caused by the higher formation rate of acetic acid. The amount of acetic acid which stays adsorbed on the catalyst can be estimated from Figure 5 assuming that the formation rate of acetic acid in the beginning is the same as after prolonged reaction. The amounts of adsorbed acetic acid are 0.20, 0.28 and 0.34 mmol C₂OOH (g Al₂O₃) for Rh/Al₂O₃, Rh/V₂O₃/Al₂O₃ (V/Rh=1) and Rh/V₂O₃/Al₂O₃ (V/Rh=7.0), respectively.

Ethylene addition

In order to study the reaction mechanism and the role of the vanadium oxide promoter, we examined the influence of ethylene addition to a working catalyst as has been done before for other catalyst systems [35-37]. Since addition of a gas is not easy in high pressure experiments, and since oxo-selectivity is relatively high in the low pressure experiment with the vanadium oxide-promoted catalysts, we used the Rh/V₂O₃/SiO₂ (V/Rh = 1.0) catalyst in the low pressure syngas reaction (0.15 kPa) for this experiment. We added 0.3 vol% C₂H₄ to the catalyst after prolonged reaction (23 h) at 503 K and stopped addition 3 h later. Subsequently, after another 2.5 h we again added ethylene, now in a concentration of 0.95 vol%, and after another 2.5 h we stopped this addition. While most of the added ethylene remained in the C₂-hydrocarbon fraction, part of it was hydrogenated to ethane. The hydrogenation activity was 1.0 mmol H₂ (mol Rh)⁻¹ s⁻¹, irrespective of the amount of ethylene added to the syngas. The normal Fischer Tropsch activity of this catalyst was 2.85 mmol CO (mol Rh)⁻¹ s⁻¹. The amount of propanol and propanal increased dramatically and was dependent on the amount of added ethylene (see Table 7). None of the other products was influenced by this addition.

Ethylene addition was also studied for the unpromoted Rh/SiO₂ catalyst (see Table 8). During reaction at 593 K, no extra propanol and propanal were found after addition of ethylene. All added ethylene was hydrogenated, even after addition of 0.83 vol% C₂H₄. We also studied addition of ethylene at 503 K, the

TABLE 7: Effect of ethylene addition to $H_2 + CO$ reaction over $Rh/V_2O_3/SiO_2$ ($V/Rh = 1$) catalyst. Reaction conditions: $P = 0.15$ MPa, $GHSV = 4000 \text{ l l}^{-1} \text{ h}^{-1}$, $H_2/CO = 3.0$, $T_{\text{react}} = 503$ K. All data are expressed in 10^{-2} vol%. (so not as selectivities, but as volume percentages of the gas stream).

Addition of	CH_4	C_2H_4	C_2H_6	C_3H_6-8	C_3OH	$C_3=O$
---	8.06	1.15	0.71	1.56	0.15	0.06
0.30 vol% C_2H_4	7.34	15.8	16.4	1.45	1.21	0.43
---	7.03	1.10	0.49	1.33	0.16	0.05
0.95 vol% C_2H_4	6.51	76.2	13.7	1.34	3.16	1.02
---	6.09	0.95	0.37	1.10	0.17	0.04

TABLE 8: Effect of ethylene addition to $H_2 + CO$ reaction over Rh/SiO_2 catalyst. Reaction conditions: $P = 0.15$ MPa, $GHSV = 4000 \text{ l l}^{-1} \text{ h}^{-1}$, $H_2/CO = 3.0$. All data are expressed in 10^{-2} vol%.

Temperature (K)	Addition of	CH_4	C_2H_4	C_2H_6	C_3H_6-8	C_3OH	$C_3=O$
593	---	19.6	0.0	0.53	0.39	0.0	0.0
593	0.24 vol% C_2H_4	18.8	0.0	24.4	0.42	0.0	0.0
593	0.83 vol% C_2H_4	19.2	0.0	83.1	0.55	0.0	0.0
503	---	0.16	.014	.008	0.01	0.0	0.0
503	0.27 vol% C_2H_4	0.16	13.6	11.6	0.01	0.83	1.16

temperature used for the experiments with the promoted catalyst ($Rh/V_2O_3/SiO_2$ ($V/Rh = 1.0$)). At this temperature the normal syngas reaction rate was very low. However, addition of ethylene now caused the formation of a remarkable amount of propanol and propanal and the hydrogenation activity was rather high. Half of the amount of added ethylene was hydrogenated.

DISCUSSION

$Rh/V_2O_3/SiO_2$

Influence of promoter on activity. In a previous study [15], we already discussed the location of the vanadium oxide promoter in $Rh/V_2O_3/SiO_2$ catalysts. Results of temperature programmed reduction and diffuse reflectance spectroscopy measurements suggest the formation of a mixed oxide ($RhVO_4$) during calcination of the catalyst. Reduction of this oxide phase resulted in a decoration of the rhodium metal particles by patches of vanadium oxide during the reduction, causing a suppression of the CO chemisorption. Thus, intimate contact between the promoter and the active metal exists. In the syngas reaction further evidence is found for this. Even small amounts of vanadium oxide added to Rh/SiO_2 cause a large increase in activity pointing to an intimate contact. Thus, although it is not known if the covering, which exists after reduction, is continued during syngas reaction

FIGURE 6: Schematic model of the elementary steps for the synthesis of hydrocarbons and oxygenates during carbon monoxide hydrogenation:

- (1) CO dissociation, followed by the formation of an CH_x group,
- (2) CO insertion in C_xH_y group forming acyl species that is the precursor for C_2 -oxygenates,
- (3) H addition and β -H elimination of surface C_xH_y group forming hydrocarbons,
- (4) growth of hydrocarbon chain,
- (5) CO insertion into metal-H, resulting in methanol.

conditions (since water formed during the reaction may undo the covering), there must be intimate contact between metal and promoter after prolonged reaction.

Clearly, the addition of vanadium oxide to Rh/SiO_2 dramatically enhances the activity of the catalyst system. First we want to exclude a trivial effect that could cause this increase in activity. Rhodium particle size can dramatically affect the activity [27,29]. However, after analyzing several micrographs of promoted and unpromoted catalysts before and after synthesis gas reaction, we feel confident that the systems studied did not differ significantly in their rhodium particle size. Thus, the increase in activity due to promotion cannot be caused by an increase in particle size as reported by Arakawa et al. [29] but must originate from the interaction between vanadium oxide and rhodium, influencing the rate determining step of the reaction and/or creating more reactive sites.

Figure 6 represents a mechanism for the formation of oxygenates and hydrocarbons as proposed by several groups [10,11,23]. The main initiating steps in this mechanism are believed to be the dissociation of CO and the hydrogenation of the resulting carbon atoms to CH_x species ($x = 1-3$). Once formed, these CH_x species can undergo a number of competing reactions, such as hydrogenation to methane, addition to an alkyl-group to cause chain-growth, and CO insertion to form intermediates for oxygenated hydrocarbons.

For a number of catalyst systems, it has been possible to conclude that CO dissociation is not the rate determining step under reaction conditions. For nickel catalysts it was found that the slowest step in the methanation reaction was the hydrogenation of CH_x species [38] and that the concentration of adsorbed hydrogen atoms on the surface is the limiting factor [39]. On iron catalysts, CO dissociation is rapid compared with the rate of the overall reaction as reported by Van Dijk et al. [40]. Using transient isotope techniques, Biloen et al. [41] obtained evidence showing that CO dissociation is rapid over nickel, cobalt and ruthenium. This observation led Van den Berg et al. [10] to assume that the hydrogenation of surface carbon is the rate determining step in the hydrogenation of CO over rhodium catalysts. The role of their promoter, MnO and MoO_2 , is then to increase the rate of hydrogenation. Ellgen et al. [42] studied the kinetics of the CO/H_2 reaction and reported a decrease in the H_2 pressure dependence by adding a Mn promoter, indicating that the concentration of hydrogen adsorbed on the catalyst has indeed become less limiting.

Two reasons were mentioned by Van den Berg et al. for the increase in the hydrogenation rate by promoting [10]. Firstly, the promoter oxides can act as a hydrogen reservoir via spillover of adsorbed hydrogen and/or formation of hydroxyl groups. Secondly, the function of the promoter might be to decrease the heat of adsorption of CO via the formation and stabilization of rhodium ions. Since the surface of the catalyst is practically completely covered with CO under reaction conditions, a small change in the heat of chemisorption of CO, leading to a small decrease in θ_{CO} (e.g. from 0.999 to 0.990), could result in a 10-fold increase in θ_{H} and therefore a 10-fold increase in activity. Thus, Van den Berg et al. proposed that the role of MoO_2 and MnO is to change the relative surface concentration of CO and H_2 , thereby accelerating the rate-determining step.

However, our ethylene-addition experiments are in contradiction with this conclusion in the case of vanadium oxide promotion. Conclusions from addition of reactive compounds must be considered with care. As noted by Chuang et al. [35], the added and adsorbed ethylene is not equivalent to the precursor for ethylene formed during the CO hydrogenation reaction. This is obvious since the chance for the added ethylene to enter chain-growth rather than to be hydrogenated to ethane is significantly different from that for the C_2H_x surface intermediates formed during CO hydrogenation. This effect was also seen for the promoted and unpromoted catalysts used in this study. The amount of ethylene incorporated in high hydrocarbons was negligible compared with the chain-growth probability of C_2H_x intermediates formed during CO hydrogenation. However, the added ethylene can serve as a probe to determine hydrogenation and CO insertion activities under reaction conditions.

From Table 7 and 8 the following picture emerges. If $\text{Rh}/\text{V}_2\text{O}_3/\text{SiO}_2$ and Rh/SiO_2 are tested at the same temperature (503 K), the reaction rate for $\text{Rh}/\text{V}_2\text{O}_3/\text{SiO}_2$ is very much higher than that of Rh/SiO_2 . However, under these reaction conditions,

the amount of ethylene converted to ethane is about the same for these two systems and therefore their hydrogenation rates are comparable. Thus, the fact that Rh/SiO₂ has a low activity at 503 K can not be due to a low hydrogenation activity. The same conclusion can be drawn from the experiments in which the H₂/CO ratio is varied (Figure 3a). The increase in activity with increasing H₂/CO ratio is comparable for the two systems. Therefore, the hydrogenation rate is not rate determining for the Rh/SiO₂ catalyst. A further indication that the presence of hydrogen is not rate limiting is the fact that during reaction over Rh/SiO₂ at 591 K, the amount of unsaturated hydrocarbons is very low, indicating a high hydrogenation activity.

The other possibility is that the CO dissociation is the rate determining step. Mori et al. [14] have used a combination of pulse surface reaction rate analysis and emissionless diffuse reflectance infrared spectrometry to measure the rate constants for C-O bond dissociation (k_{CO}) and methane formation (k_{HC}) separately. The influence of several promoters, e.g. V, Mo, W and Re, on a Ru/Al₂O₃ catalyst was studied. They reported that vanadium oxide enhanced the CO dissociation (k_{CO} increased), while the influence of the vanadium oxide on the hydrogenation was small (k_{HC} decreased by addition of vanadium oxide). Furthermore, k_{HC} was much higher than k_{CO} and an IR absorption band at 2926 cm⁻¹ was observed for the V-promoted catalysts only. Mori et al. assigned this band to the C-H stretching vibration of the CH_x species. These results suggest that the main role of the vanadium oxide promoter is to enhance the rate of dissociation of CO. We will pursue this suggestion by further studying the vanadium oxide promotion of Rh catalysts by means of ¹³C-NMR.

The promoter effect of vanadium oxide on the activation of the CO band can be caused by an interaction of the oxygen atom of the chemisorbed CO with a positively charged promoter centre (V³⁺), as was proposed by Sachtler et al. [24] for promoted systems in general. Burch et al. [43] and Bell et al. [44] proposed a similar activation of CO by an ion of the support for Pd catalysts. Sachtler et al. studied a Mn-promoted Rh catalyst with IR spectroscopy (CO adsorbed at 298 K) and observed a CO band at low frequency, around 1530 cm⁻¹ [23-25]. Ichikawa et al. [11] reported the existence of a similar band for Mn-promoted rhodium catalysts. The band at 1530 cm⁻¹ is ascribed to C- and O-bonded carbon monoxide and a model was proposed in which ions of an electropositive metal (promoter) on the surface of the rhodium metal particle provide sites at which CO may be "C"-bonded to a metal surface and "O"-bonded to a promoter ion [23-25,11]. Recently, Sachtler and Ichikawa [25] reported that the band position of the bridge-bonded CO for the vanadium oxide-promoted Rh/SiO₂ was shifted to lower wavenumbers compared with the unpromoted Rh/SiO₂ catalyst (Rh-V/SiO₂ had a broad strong band at 1760 cm⁻¹, and a shoulder at 1650 cm⁻¹, while Rh/SiO₂ had a strong band at 1880-1900 cm⁻¹). They ascribed this shift also to a tilted mode of CO adsorbed on Rh and the promoter, resulting in a weakened C-O bond. As a result, C-O bond dissociation is

facilitated. For our catalysts, the shift of the bridge-bonded CO due to the promotion of vanadium oxide was less (shift of 50 cm^{-1} to lower wavenumbers) [15] and can also be caused by the lower CO coverage, as vanadium oxide decreases the amount of CO adsorbed in the bridged form. Therefore, it is questionable whether shifts in this order of magnitude point to the formation of C- and O-bonded CO. However, it is still possible that these species are formed under reaction conditions.

Mori et al. [14] proposed a mechanism in which a CO molecule adsorbs on the metal and is transformed into a M-CHOH intermediate. An adjacent V^{3+} -ion pulls the oxygen atom away from this hydroxycarbene intermediate, and forms a transition state that promotes the dissociation of CO into $(CH_x)_{ad}$ and $(OH)_{ad}$. Simultaneously V^{3+} is oxidized to V^{4+} . The vanadium oxide promoter catalyzes the CO dissociation by an oxidation/reduction cycle.

From our measurements we can not exclude one of the described models for the promoter action.

Influence of promoter and reaction conditions on selectivity. At first sight, the influence of the promoter on the selectivity is high. While the Rh/SiO₂ catalyst has a high selectivity to methanol and methane, the Rh/V₂O₃/SiO₂ catalysts have a relatively high selectivity to C₂-oxygenates and higher hydrocarbons. However, this can be caused by the differences in reaction temperature. As can be seen in the ethylene addition experiment, ethylene is completely hydrogenated at the reaction temperature necessary for Rh/SiO₂ to obtain sufficient conversion (593 K) and no insertion of CO in ethylene took place to form propionaldehyde or propanol. However, ethylene addition at 503 K showed that, although the activity for CO hydrogenation is very low at that temperature for Rh/SiO₂, CO insertion takes place with approximately the same reaction rate as on the Rh/V₂O₃/SiO₂ catalyst. This proves that the presence of vanadium oxide is not necessary for the CO insertion reaction in ethylene. To exclude temperature influences, we tested Rh/SiO₂ and Rh/V₂O₃/SiO₂ (V/Rh = 1.0) at the same temperature (see Table 4). The difference is even more pronounced. Rh/SiO₂ produced mainly methanol (57 %), and C₂-oxygenates (28 %) at 548 K. At the same temperature the promoted system had a relatively low methanol selectivity (9 %), and produced much methane (29 %), C₂-oxygenates (42 %) and heavier products. From the formation rates of the different products at 548 K, we can conclude that the methanol formation rate is only increased by a factor of six, while the formation rate to the other product groups is increased by a factor of forty to two hundred. The higher formation rates of the products, except for methanol, can be understood by the assumption that vanadium oxide enhances the dissociation of CO and increases the chain-growth probability.

Vanadium oxide not only enhanced the dissociative path leading to hydrocarbons and higher oxygenated products, but also the associative pathway leading to methanol, as methanol has been proven to be formed non-dissociatively [45]. As

methanol is thought to be formed over metal ions [32-34], this suggests that the presence of vanadium oxide increased the amount of rhodium ions. Unfortunately, we do not have information about the amount of rhodium ions in our catalysts. However, temperature programmed reduction studies showed that in vanadium oxide-promoted catalysts, the reduction of rhodium oxide is shifted to higher temperatures [15]. Thus, it is plausible to assume that in the vanadium-promoted catalyst the amount of rhodium ions is higher than in the unpromoted Rh/SiO₂ catalysts. The amount of metal ions does not influence the formation rate of C₂-oxygenates, as proved by Van der Lee et al. [9].

Not only did the amount of vanadium oxide influence the selectivity pattern during syngas reaction, but also the reaction conditions (temperature, pressure and H₂/CO ratio) had an important effect. For the vanadium promoted catalyst, an increase in temperature caused a decrease in methanol selectivity, while the methane selectivity increased and the C₂-oxygenate selectivity increased slightly (see Table 5 and Figure 3b). Temperatures above 573 K disfavour the formation of oxygenates, as can be seen in Figure 3b for the unpromoted Rh/SiO₂ catalyst (compare the increase in activity to C₁OH (3b3) and C₂OH (3b4) with the increase in activity to methane (3b1)). Probably, CH_x species, once formed, are readily hydrogenated to methane, and do not have the chance to grow to longer carbon chains or undergo a CO insertion reaction. This was also concluded from the ethylene addition experiments at 593 K.

A higher H₂/CO ratio caused an increase in the formation rates of all products (see Figure 3a and Table 5). The C₂-oxygenate and methanol selectivity are higher at low H₂/CO ratios. The methanol formation rate of the promoted catalyst was almost constant above H₂/CO = 1.0.

For the promoted catalyst, the pressure mainly affected the formation rate of methanol. At 0.15 MPa, the formation of methanol is thermodynamically unfavourable. A remarkably high selectivity to C₂-oxygenates is observed at 0.15 MPa. For the unpromoted Rh/SiO₂, the major product at 0.15 MPa is methane. A high pressure (4.0 MPa) results in a better total oxo-selectivity due to an increased methanol and C₂-oxygenate selectivity. Thus, at a high reaction temperature, the increase in pressure is positive for C₁- and C₂-oxygenates, while for low temperatures, a higher pressure mainly affects the methanol selectivity. Therefore, if one is interested in a high total oxo-selectivity, the best reaction conditions for the promoted catalyst are a low reaction temperature, a low H₂/CO ratio and a high pressure. If one is only interested in a high C₂-oxygenate selectivity, a low H₂/CO ratio and a higher reaction temperature are required, while a high pressure is not necessary.

Besides influencing the selectivity pattern of catalysts via differences in reaction kinetics, successive reaction and/or thermodynamic limitations, the reaction conditions (pressure, H₂/CO, temperature and GHSV) can also affect the catalyst system itself. For instance the extent of covering by V₂O₃ and/or the

amount of rhodium ions will be influenced by the reaction conditions. The surface concentration of oxygen, formed by dissociation of CO, and the amount of water are affected by the reaction parameters and will play an important role. Low conversions, as a result of a low temperature, and a high GHSV will result in relatively low water vapour pressures. This will in turn result in a relatively low amount of rhodium ions. A high pressure will result in a high water vapour pressure, which can result in a relatively high amount of metal ions. The water vapour pressure also can influence the extent of coverage by vanadium oxide, as the SMSI state is known to be reversed by water or oxygen.

From the detailed study of the products and the Flory-Schulz distributions we can conclude that the chain-growth probability for hydrocarbons is higher than for the oxygenated products. This is in contrast to the measurements reported by Van den Berg and Sachtler [24,46]. Studying a Rh-Mn-Mo/SiO₂ catalyst at 10 MPa, they showed that the Flory-Schulz distributions of hydrocarbons and oxygenates exhibit the same chain-growth probability and from this fact they concluded that the chain-growth mechanisms for hydrocarbons and oxygenates are identical. However, this is not a necessary condition. Assuming an identical chain-growth mechanism for hydrocarbons and oxygenates, we must conclude from our measurements that the CO insertion rate is dependent on the chain-length of the carbon fragment into which it inserts. In agreement with several groups [24,46,47] we observed an undershoot of C₂-hydrocarbons and an overshoot of C₂-oxygenated products in the Flory-Schulz plots.

Rh/V₂O₃/Al₂O₃

Although not to the same extent, the vanadium oxide promoter also caused an increase in the activity for Rh/Al₂O₃ catalysts. Small amounts of vanadium oxide (up to V/Rh = 1.0) did not influence the activity. This confirms the conclusion from the characterization studies that rhodium and vanadium oxide particles exist separately on the alumina support. The Rh/V₂O₃/Al₂O₃ catalysts with a high V/Rh ratio (7.0 and 8.4) had an activity three times larger than the unpromoted Rh/Al₂O₃ catalyst. Clearly, large amounts of vanadium oxide are required to promote the Rh/Al₂O₃ catalyst. This is due to the strong interaction between vanadium oxide and alumina, the first amount of vanadium oxide is scavenged by the alumina support. This also explains why the vanadium oxide promoter in the study of Mori et al. [14] only had a limited positive effect on their Ru/Al₂O₃ catalyst. The rate of formation of C₂-oxygenates and hydrocarbons containing two or more carbon atoms is increased to a higher extent than the formation rate of methanol and methane, causing a shift in the selectivity pattern to heavier products.

The alumina-supported catalysts produced more methanol than the silica-supported ones. As could be concluded from chemisorption and TEM measurements, the rhodium particle size of the alumina-supported catalysts is much smaller than the particle size of the silica-supported catalysts. This might

result in a higher amount of rhodium ions, thus causing a higher methanol formation rate.

Two interesting, special features were observed for the $\text{Rh}/\text{V}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts. Firstly, part of the alcohols formed are converted into ethers over acidic sites of the alumina in the case of $\text{Rh}/\text{Al}_2\text{O}_3$ [28]. In the present study we found that the amount of ether formed from alcohols decreased with increasing vanadium content. For the high vanadium oxide loaded catalysts, the amount of dimethylether was negligible. This suggests that the sites responsible for the ether formation are covered completely by vanadium oxide. It also offers an explanation for the fact that in the preparation of the catalysts we did not succeed in the formation of a 100% monolayer coverage. The maximum V/Rh ratio of 8.4 (6.7 wt% V) which we obtained corresponds to a coverage of 40 % of the surface area of the Al_2O_3 used in this study, assuming that all vanadium oxide is present as a monomolecular layer on the support. The catalytic results suggest that during preparation of the monolayer of vanadium oxide on alumina the ammonium metavanadate ions adsorb only on the sites which are responsible for ether formation during Fischer Tropsch reaction. Apparently, at $\text{V}/\text{Rh} = 8.4$, these sites are all filled with vanadium oxide, therefore no more ether formation takes place and there are no further sites available for adsorption of vanadium, leading to a maximum coverage of 40 %.

The second feature is related to other, non acidic sites on the alumina support. Studying the catalytic activity as a function of time on stream, a chromatographic effect was observed for acetic acid. For $\text{Rh}/\text{Al}_2\text{O}_3$, only after prolonged reaction (12 h) was acetic acid detected, whereas for $\text{Rh}/\text{V}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{V}/\text{Rh} = 7.0$, acetic acid was already found after 5 h time on stream. However, the amount of strongly adsorbed acetic acid increased slightly with increasing V/Rh ratio (in a shorter time more acetic acid is formed in the promoted case due to a higher formation rate). The chromatographic effect is due to adsorption of acetic acid or of a precursor of acetic acid on basic sites on the support, as was proven by the experiment in which an additional amount of alumina was placed downstream of the catalyst bed. Once the adsorption sites are filled, acetic acid appeared as products in the gas stream at the reactor outlet. These type of sites increased with increasing V/Rh ratio, suggesting that the addition of vanadium oxide converts sites responsible for ether formation (acid sites) into sites responsible for adsorption of acetic acid (basic sites).

Using the surface model for $\gamma\text{-Al}_2\text{O}_3$ proposed by Knözinger and Ratnasamy [48], one can understand the coexistence of acidic and basic sites on an alumina surface. Under syngas reaction conditions (water is formed and the temperature is relatively low), the alumina surface will be hydroxylated to a high extent. Knözinger and Ratnasamy expect a maximum of five different OH configurations, their actual occurrence and relative concentration depending on the relative contributions of the different crystal faces. The OH-groups in the various

configurations bear slightly different net charges, and as a consequence have slightly different properties. One would expect an OH-group which is coordinated to three cations in octahedral interstices (Type III according to Knözinger and Ratnasamy, with a net positive charge of + 0.5) to be the most acidic, since abstraction of a proton would lead to an oxygen atom bearing a net negative charge of only -0.5, which is close to the value of zero necessary for electroneutrality. By the same arguments, OH-groups with a more negative net charge, like an OH-group coordinated to a single tetrahedral Al^{3+} cation (Type IA, net charge -0.25) or an OH-group coordinated to a single cation in an octahedral interstice (Type IB, net charge -0.5) have a higher basicity. Thus, the model proposed by Knözinger and Ratnasamy allows us to suggest that, while sites with a more basic character and sites with a more acidic character coexists on the alumina surface, the acidic ones are responsible for the ether formation and the basic ones responsible for the adsorption of acetic acid.

Rh/V₂O₃

The activity and the selectivity of the CO hydrogenation over 1.5 wt% Rh/V₂O₃ catalysts depend critically on the reduction temperature. After reduction at 823 K, the oxo-selectivity was very high (80%), but the activity was low. We also saw a complete suppression of hydrogen chemisorption after high temperature reduction [15]. These results point to a covering of the metal particles as in the SMSI systems [16-22]. Van der Lee et al. [9] also observed similar effects of the reduction temperature. Using a 4.5 wt% Rh/V₂O₃ catalyst, they reported that a high reduction temperature was always beneficial for the selectivity to oxygenates, and that a more extended covering of the metal particles induced by a reduction at higher temperature sometimes caused a decrease and sometimes caused an increase in activity. Probably, the vanadium oxide promoter induces two counteracting effects [9]. Firstly, the vanadium oxide blocks a part of the active metal surface and selectively suppresses reactions which need a large ensemble of metal atoms. This blocking also results in suppressed hydrogen and carbon monoxide chemisorption. Secondly, the vanadium oxide patches enhance the rate of CO dissociation at the metal-vanadium oxide interface, that is at the perimeter of the V₂O₃ patches on the Rh particles (see also Rh/V₂O₃/SiO₂ catalysts). In a recent study Levin et al. [49] reported the influence of TiO_x and AlO_x submonolayers deposited on a polycrystalline Rh foil. AlO_x deposition suppressed the rate of CO hydrogenation in direct proportion to the AlO_x coverage, but the product distribution and kinetics were unaffected, indicating that the only effect of AlO_x is to block Rh sites. With increasing TiO_x coverage, the methanation rate passed through a maximum at a TiO_x coverage of 0.15 monolayer. Kinetics and catalyst selectivity were also changed by the TiO_x layer. They attributed the unusual behaviour of TiO_x-promoted Rh to the occurrence of highly active catalytic sites near the perimeter of the TiO_x islands making up the overlayer. Thus, also

in the case of TiO_x -promotion, the effect of blocking of sites and the creation of highly active sites compete. Which effect prevails is strongly dependent on the extent and structure of the overlayer and explains why covering in the case of $\text{Rh/V}_2\text{O}_3/\text{SiO}_2$ resulted in an increased activity (the second effect is stronger), and covering in the case of our 1.5 wt% $\text{Rh/V}_2\text{O}_3$ catalyst caused a decrease in activity (the blocking effect is stronger). Similar explanations can be given for the difference in the influence of vanadium oxide promotion of $\text{Ru/Al}_2\text{O}_3$. As already mentioned, Mori et al. [14] reported an increase in activity, whereas Enomoto et al. [50] showed that the activity in carbon monoxide hydrogenation decreased after vanadium oxide promotion.

In contrast to the SMSI-state of Rh/TiO_2 , obtained after high temperature reduction, the SMSI-state of $\text{Rh/V}_2\text{O}_3$ is maintained during the syngas reaction and is not reversed by water formed during the reaction, as has also been reported by Lin et al. [26].

Our results, as well as the results of Van der Lee et al. [9] and Levin et al. [49] suggest that the vanadium oxide patches which cover the metal particle not only have a positive effect on the CO dissociation, but also have a positive effect on the formation of oxygenated intermediates. Furthermore, the extent of covering seems to affect the hydrogenation activity. The 1.5 wt% $\text{Rh/V}_2\text{O}_3$ catalyst reduced at 523 K has a high hydrogenation activity, low amounts of unsaturated hydrocarbons are formed and the ethanol/acetaldehyde ratio is high (ethanol is thought to be formed by hydrogenation of acetaldehyde). This catalyst has a high methane selectivity, probably caused by the high hydrogenation rate. Once C_1 -intermediates are formed, they are readily hydrogenated to methane before CO can insert (which results in C_2 -oxygenates), or before the C_1 -intermediate can grow to longer hydrocarbon chains. Reduction at a high temperature (723 or 823 K) resulted in a lower activity (due to site blocking), a lower methane and higher oxygenate selectivity. This will be due to a lower hydrogenation rate, as is also reflected in a higher acetaldehyde/ethanol ratio and a higher amount of unsaturated hydrocarbons. This also explains the high deactivation of this catalysts. Due to the low hydrogenation activity long unsaturated hydrocarbons can accumulate on the surface leading to coke formation. For the $\text{Rh/V}_2\text{O}_3/\text{SiO}_2$ catalysts, the lower amount of unsaturated hydrocarbons and acetaldehyde and the lower deactivation point to a relatively high hydrogenation rate. This is consistent with the model described before in which the covering by vanadium oxide was less in these systems, compared with the $\text{Rh/V}_2\text{O}_3$ catalyst reduced at a high temperature.

CONCLUSIONS

Addition of vanadium oxide to Rh/SiO_2 and $\text{Rh/Al}_2\text{O}_3$ caused an important increase in the activity. The results suggest that the rhodium particles are partially covered by vanadium oxide and that the role of the vanadium oxide promoter is to

enhance the CO dissociation. The results of Rh/V₂O₃ show that this rate enhancing can be dominated by the blocking of reaction sites by patches of vanadium oxide present on the metal particles. There will be an optimum positive influence of the vanadium oxide promoter on the activity and this optimum will depend on the impregnation, drying, calcination and reduction steps. The oxo-selectivities were high for the Rh/V₂O₃/SiO₂ and Rh/V₂O₃ catalysts. The insertion reaction of CO into ethylene was not influenced by the presence of vanadium oxide patches in the Rh/V₂O₃/SiO₂ catalysts.

For the alumina-supported vanadium oxide-promoted catalysts, high V₂O₃ loadings are required to improve the activity. In these catalysts, the vanadium oxide covered the acidic sites on the alumina support and this resulted in a complete suppression of the ether formation. Furthermore, a chromatographic effect for acetic acid was observed for these catalysts. During the first hours of reaction the formed acetic acid is adsorbed on the support. Only after prolonged reaction time acetic acid is found in the gas stream.

So, Rh/V₂O₃/SiO₂ is the better catalyst system. Because of a stronger interaction between V₂O₃ and Rh₂O₃ than between V₂O₃ and the SiO₂ support, Rh₂O₃ and V₂O₃ are in intimate contact. After reduction V₂O₃ partially covers the Rh particles, resulting in a relatively high activity and oxo-selectivity (70 %). For the Rh/V₂O₃ catalyst, reduced at a high temperature, the covering of the Rh particles by V₂O₃ is substantial. In this case, blocking of active sites dominates the promoting effect of V₂O₃ on the CO dissociation, resulting in a relatively low activity. Oxo-selectivity is high for this system (70-80 %). Because of the strong interaction between V₂O₃ and Al₂O₃ most of the V₂O₃ is scavenged by the Al₂O₃ support, and a high V₂O₃ loading is required to affect the activity of Rh/Al₂O₃. For this system, the oxo-selectivity is relatively low (50 %).

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