Hydrogenation of carbon monoxide over rhodium/silica catalysts promoted with molybdenum oxide and thorium oxide

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Hydrogenation of Carbon Monoxide over Rhodium/Silica Catalysts Promoted with Molybdenum Oxide and Thorium Oxide

B.J. KIP*, E.G.F. HERMANS, J.H.M.C. VAN WOLPUT, N.M.A. HERMANS, 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 promotion of silica-supported rhodium catalysts in the hydrogenation of carbon monoxide by molybdenum oxide and thorium oxide has been examined. Temperature programmed reduction studies indicated the formation of rhodium molybdates, while no evidence was found for the formation of such mixed oxides in the thorium oxide-promoted catalysts. Hydrogen and carbon monoxide chemisorption were suppressed by the presence of molybdenum oxide, pointing to a coverage of the rhodium particles by this promoter oxide. The catalysts with Mo:Rh ratios exceeding one even exhibited an almost complete suppression of the rhodium chemisorption capacity. In the thorium oxide-promoted catalysts the chemisorption of hydrogen and carbon monoxide were not suppressed. Infrared spectroscopy of adsorbed carbon monoxide showed that molybdenum oxide completely suppressed bridge-bonded and linearly bonded carbon monoxide, as well as the gem-dicarbonyl species. Thorium oxide addition resulted in a minor decrease of the linearly bonded carbon monoxide, while the bridge-bonded carbon monoxide was suppressed to a greater extent. The IR spectra of the thorium oxide-promoted catalysts also exhibited a broad absorption band between 1300 and 1750 cm^{-1} , which is thought to be due to carbon monoxide bonded with the carbon atom to the metal and with the oxygen atom to the promoter ion.

Carbon monoxide hydrogenation was greatly enhanced by the presence of both molybdenum oxide and thorium oxide. Thorium oxide-promoted catalysts had a high selectivity to C_2 -oxygenates, while the molybdenum oxide-promoted catalysts exhibited a high methanol selectivity. Ethylene addition to a working catalyst showed that the carbon monoxide insertion reaction, which is thought to be responsible for the formation of oxygenates, was not enhanced by molybdenum oxide, nor by thorium oxide. The ethylene addition experiments indicated that the role of the promoter is to enhance carbon monoxide dissociation. The results can be understood by assuming that side-bonded carbon monoxide, with its weakened C–O bond, is responsible for the higher carbon monoxide dissociation activity.

INTRODUCTION

In a previous study [1,2] we observed a sharp increase in the activity of carbon monoxide hydrogenation when vanadium oxide was added to silica- and

alumina-supported rhodium catalysts. The major role of the vanadium oxide promoter was to enhance the carbon monoxide dissociation, and thus to increase the activity. The increase in activity was also observed by Mori et al. [3,4] for vanadium oxide-promoted $\text{Ru}/\text{Al}_2\text{O}_3$ catalysts. A high oxo-selectivity was measured for the V_2O_3 -promoted Rh/SiO_2 catalyst [2]. The carbon monoxide insertion reaction, which is thought to be an important step in the formation of oxygenated hydrocarbons, was not influenced by the presence of vanadium oxide, as could be concluded from ethylene addition experiments.

Temperature programmed reduction and diffuse-reflectance infrared measurements of calcined vanadium oxide-promoted silica-supported rhodium catalysts indicated that during the calcination a mixed oxide of rhodium oxide and vanadium oxide (RhVO_4) was formed. The size of the rhodium particles formed after reduction was not influenced by the presence of the promoter oxide. Suppression of carbon monoxide chemisorption after reduction at 523 K proved that the rhodium particles were (partly) covered by vanadium oxide patches. The absence of hydrogen chemisorption suppression was explained by the adsorption of hydrogen by vanadium oxide via the formation of vanadium hydrogen bronzes.

From these observations we concluded that on the one hand the vanadium oxide blocks part of the active metal surface, resulting in a suppressed chemisorption capacity, while on the other hand, the vanadium oxide patches enhance the rate of carbon monoxide dissociation along their perimeter. This enhancement effect is most important for silica-supported vanadium oxide-promoted rhodium catalysts. For vanadium oxide-supported rhodium catalysts, however, the covering and blocking effect dominates after high temperature reduction.

Mori et al. [4] proposed a catalytic redox cycle to explain the role of the vanadium oxide promoter in their V_2O_3 -promoted $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst. They postulated a hydroxycarbene intermediate ($\text{M}=\text{CHOH}$) and in their model V^{3+} pulls the oxygen atom away from this intermediate. During this step, V^{3+} is oxidized to V^{4+} and subsequently reduced by hydrogen, reforming V^{3+} . In this way, the oxidation-reduction cycle of the promoter oxide may explain the dissociation of the C-O bond during the hydrogenation of carbon monoxide.

In the present paper we will extensively study two other promoters, molybdenum oxide and thorium oxide. Ellgen and coworkers [5,6] and Van den Berg et al. [7] examined the promotive effect of molybdenum oxide and observed a positive effect on the activity and oxo-selectivity. Jackson et al. [8] reported that the activity of a Rh/MoO_3 catalyst was twenty times higher than the activity of Rh/SiO_2 . Ichikawa et al. [9] reported an enhanced formation rate of C_2 -oxygenates by the addition of thorium oxide. Rare earth oxides have also been reported to influence the hydrogenation of carbon monoxide over Rh. Underwood and Bell reported large differences between Rh supported on silica and Rh supported on La_2O_3 , Nd_2O_3 and Sm_2O_3 [10]. Kiennemann et al. [11] reported CeO_2 to be very effective for the promotion of ethanol formation. The

molybdenum oxide promotion has a similarity with vanadium oxide promotion. The MoO_3 can be reduced under our reduction conditions and rhodium oxide can form rhodium molybdates with MoO_3 [12]. On the contrary, thorium oxide can not be reduced under normal conditions and no thorium rhodates have been reported [13]. However, for the promoter influence on the carbon monoxide dissociation as described by Mori et al. [4] one needs a reduction-oxidation cycle. For these reasons we studied the promotion of Rh/SiO_2 by molybdenum oxide and thorium oxide using a number of characterization techniques like temperature programmed reduction, hydrogen and carbon monoxide chemisorption, transmission electron microscopy, infrared spectroscopy of adsorbed carbon monoxide and carbon monoxide hydrogenation at elevated pressure.

EXPERIMENTAL

Catalyst preparation

As supports we used silica (Grace, type 113, surface area $360 \text{ m}^2 \text{ g}^{-1}$, pore volume 1.1 ml g^{-1}), ThO_2 (Merck, surface area $3.9 \text{ m}^2 \text{ g}^{-1}$, pore volume 0.11 ml g^{-1}) and MoO_3 (Merck, surface area $4.0 \text{ m}^2 \text{ g}^{-1}$, pore volume 0.13 ml g^{-1}). Molybdenum oxide- and thorium oxide-promoted silica were prepared by incipient wetting the silica support with an aqueous solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Merck, p.a.) and $\text{Th}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$ (Merck, p.a.) respectively, drying at 395 K and calcining at 723 K (3 h). In this way, supports with a varying amount of molybdenum and thorium oxide were obtained. The catalysts were prepared by the incipient wetness method using an aqueous solution of $\text{Rh}(\text{NO}_3)_3$ ($\text{pH}=2.5$, Drijfhout, Amsterdam, The Netherlands), and were subsequently dried in air at 395 K for 16 h (heating rate 2 K min^{-1}). To remove nitrogeneous residues from the precursor, the catalysts were calcined at 723 K for 3 h. Rhodium content was always around 1.5 wt. %.

Characterization techniques

Volumetric hydrogen and carbon monoxide chemisorption measurements were performed as described elsewhere [1,14]. Catalysts were reduced at 723 K (heating rate 8 K min^{-1}) for 1 h and evacuated for 0.5 h at 723 K before the chemisorption experiment.

The reduction behaviour of the supports and the reduction, oxidation and hydrogen desorption behaviour of the catalysts were studied by temperature programmed reduction (TPR) and oxidation (TPO), using the apparatus described extensively in refs. 15 and 16. During TPR and TPO experiments the heating rate was 5 K min^{-1} .

Carbon monoxide adsorption was also studied by infrared spectroscopy. The

glass reactor and spectrometer were described in ref. 1. The catalysts were reduced in situ at 543 K in flowing hydrogen (heating rate 5 K min^{-1}) for 0.5 h and evacuated at 543 K for 1 h. The IR spectrum was obtained by adding 512 interferograms. From these spectra information about the relative amount of adsorbed carbon monoxide and the way in which carbon monoxide is adsorbed on the metal particles was obtained.

In order to get information about the metal particle size transmission electron microscopy (TEM) was used. Catalysts were pretreated by reduction at 523 K and subsequent passivation. The specimens were examined with a Jeol 200CX, operating at 200 kV.

Carbon monoxide hydrogenation

The high-pressure reactor and analysis system were described in detail elsewhere [2]. The catalysts were reduced in situ in pure hydrogen at 0.1 MPa, using a temperature gradient of 5 K min^{-1} between 298 and 723 K and holding the final temperature for 1 h. All catalysts were measured under the same reaction conditions (gas hourly space velocity, GHSV = $4000\text{ l l}^{-1}\text{ h}^{-1}$, hydrogen:carbon monoxide ratio = 3, $P = 0.15$ or 4.0 MPa). The reaction temperature was adjusted so that conversion of carbon monoxide was around 2%.

RESULTS

Temperature programmed reduction

Thorium oxide promotion

TPR profiles of the thorium oxide-promoted rhodium catalysts are presented in Fig. 1. For ThO_2 and $\text{ThO}_2/\text{SiO}_2$ no measurable amount of hydrogen consumption was found up to 898 K. For the 1.5 wt.% Rh/ ThO_2 catalysts calcined at 723 K, the major part of the hydrogen consumption (about 70%) was found before the start of the temperature gradient (cf. Fig. 1a). Hydrogen consumption maxima were found at 346 and 502 K. The TPR profile of this catalyst after oxidation at 898 K (the TPR after a TPO experiment) exhibited a minor hydrogen consumption before the start of the temperature gradient (about 13%) and two consumption maxima at 325 and 410 K (Fig. 1b). Similar TPR profiles were observed by Vis et al. [17] for Rh/ TiO_2 catalysts after oxidation at 873 K. They found two reduction maxima at 330–340 and 385–400 K, respectively, and ascribed the two peaks to two different kinds of Rh/ Rh_2O_3 particles. The first kind was easy to reduce and consisted of flat, raftlike particles, the second was harder to reduce and consisted of spherical particles. In our case, this second Rh_2O_3 phase was only observed for 1.5 wt.% Rh/ ThO_2 and not for 1.5 wt.% Rh/ SiO_2 , indicating that for Rh/ ThO_2 , the particle size

Fig. 1. Temperature programmed reduction profiles of ThO_2 -promoted catalysts; a: 1.5 wt.% Rh/ ThO_2 , after calcination at 723 K, b: 1.5 wt.% Rh/ ThO_2 , after oxidation at 898 K, c: 1.5 wt.% Rh/ SiO_2 , after calcination at 723 K, d: 1.5 wt.% Rh/ $\text{ThO}_2/\text{SiO}_2$ (Th/Rh = 1.0), after calcination at 723 K, e: 1.5 wt.% Rh/ $\text{ThO}_2/\text{SiO}_2$ (Th/Rh = 1.0), after oxidation at 898 K.

was larger. Hydrogen chemisorption measurements also pointed to a larger particle size for the Rh/ ThO_2 catalyst (*vide infra*).

The amounts of hydrogen consumed during the TPR runs matched the values calculated for reduction of Rh^{3+} to Rh^0 . Within the experimental error (5%) it can be concluded that no Th^{4+} was reduced.

Only a minor influence of ThO_2 on the reduction behaviour of Rh/ SiO_2 was seen. For the calcined samples (Figs. 1c, d) the major peak was found between 353 and 378 K. Some hydrogen consumption was observed around 473 K, and its amount increased with increasing thorium oxide content. This extra peak is ascribed to carbon dioxide adsorbed to thorium oxide during catalyst preparation [18]. In the TPR profile after oxidation at 898 K (Fig. 1e) no influence of the thorium oxide on the reduction behaviour was found at all. The amount of hydrogen consumed during the TPR runs of the calcined and oxidized Rh/ $\text{ThO}_2/\text{SiO}_2$ catalysts pointed to the reduction of Rh^{3+} to Rh^0 . Within the experimental error no thorium oxide was reduced.

The TPR results do not present evidence for an intimate contact between the thorium oxide promoter and the rhodium metal. Thorium oxide itself cannot be reduced, not even with the use of the rhodium metal.

Fig. 2. Temperature programmed reduction profiles of MoO_3 -promoted catalysts; a: MoO_3 , b: 1.5 wt.% Rh/MoO_3 , after calcination at 723 K, c: 1.5 wt.% Rh/MoO_3 , after oxidation at 898 K, d: $\text{MoO}_3/\text{SiO}_2$ (1.4 wt.% Mo), after calcination at 723 K, e-f: 1.5 wt.% $\text{Rh}/\text{MoO}_3/\text{SiO}_2$ after calcination at 723 K, e: $\text{Mo}/\text{Rh}=0$, f: $\text{Mo}/\text{Rh}=1.0$, g-j: 1.5 wt.% $\text{Rh}/\text{MoO}_3/\text{SiO}_2$ after oxidation at 898 K, $\text{Mo}/\text{Rh}=0, 0.12, 1.0$ and 4.0 for g, h, i and j, respectively.

Molybdenum oxide promotion

In Fig. 2a the TPR profile of molybdenum oxide is presented. The reduction started at 853 K and had a maximum at 993 K. At 1073 K, the maximum reduction temperature obtainable in our apparatus, the average oxidation state was close to Mo^{4+} . Arnoldy et al. [19] showed that the reduction of MoO_3 is highly dependent on the water content of the reducing mixture. They reported reduction of MoO_3 to Mo between 600 and 1100 K. In our case the MoO_3 reduction is more difficult because of the low hydrogen concentration (5% H_2/Ar versus 67% H_2/Ar) and a high sample size:flow-rate ratio (4 mg $\text{MoO}_3/(\text{ml}$

min^{-1}) versus $0.5 \text{ mg MoO}_3/(\text{ml min}^{-1})$ used by Arnoldy et al.). This results in a relatively high water:hydrogen ratio during our reduction process.

Clearly, rhodium facilitated the reduction of molybdenum oxide in the 1.5 wt.% Rh/MoO₃ catalyst, calcined at 723 K (Fig. 2b). The major hydrogen consumption for this catalyst took place below 573 K. Two peaks were observed at 428 and 478 K. A broad hydrogen consumption maximum was found between 573 and 873 K, caused by the reduction of molybdenum trioxide not in direct contact with rhodium. In the TPR profile after oxidation at 898 K, only the peak at 478 K and the broad hydrogen consumption area between 573 and 873 K were present (Fig. 2c). The amount of hydrogen consumed during the TPR (after calcination at 723 K and oxidation at 898 K) pointed to the reduction of Rh³⁺ to Rh⁰ and of Mo⁶⁺ to Mo²⁺. Apparently, the low hydrogen concentration and high sample weight:flow-rate ratio resulted in a relatively high water vapour pressure causing thermodynamical limitations for a complete reduction of the MoO₃ to Mo.

The reduction of MoO₃/SiO₂ started slowly around 573 K and had a maximum around 773 K (Fig. 2d). The amount of hydrogen consumed pointed to the reduction reaction Mo⁶⁺ to Mo²⁺. Arnoldy et al. [20] reported for 11.7 wt.% MoO₃/SiO₂ a hydrogen consumption maximum around 750 K and a second maximum around 920 K. The position of the second maximum was highly dependent on the water vapour pressure and shifted to 1050 K if a water-hydrogen-argon mixture was used. They reported that the total hydrogen consumption (first and second peak together) pointed to the complete reduction of MoO₃ to Mo. As already pointed out before, our experimental conditions result in a relatively high water:hydrogen ratio, which can explain the differences between the observed TPR profiles in this study and the TPR profiles observed by Arnoldy et al. [19,20].

The TPR profiles of calcined Rh/MoO₃/SiO₂ catalysts (Figs. 2e, f) show that rhodium enhanced the reduction of MoO₃. Almost all hydrogen consumption took place below 573 K and the amount of hydrogen consumed in this temperature region pointed to the reduction of Rh₂O₃ (Rh³⁺ to Rh⁰) and MoO₃ (Mo⁶⁺ to Mo²⁺). Only for catalysts with high molybdenum:rhodium ratios hydrogen consumption was seen above 573 K. On the other hand, MoO₃ slightly hampered the reduction of Rh₂O₃. A shift to higher reduction temperatures was observed for the main TPR peak when the molybdenum:rhodium ratio was increased and also the start of the reduction occurred at a higher temperature. These effects were more pronounced for the oxidized catalysts (Figs. 2g-j), different peaks could even be observed. Higher molybdenum:rhodium ratios caused a decrease of the amount of hydrogen consumed before the temperature gradient, and of the peak around 323 K, and an increase of the hydrogen consumption peak between 373 and 473 K. From the TPR profiles it can be concluded that rhodium facilitated the reduction of MoO₃ and that MoO₃ hampered the reduction of Rh₂O₃.

Thus, the TPR profiles of calcined and oxidized Rh/MoO₃/SiO₂ clearly provide evidence for a mutual affection of the active metal (rhodium) and the promoter (MoO₃).

Hydrogen and carbon monoxide chemisorption

In Fig. 3 the hydrogen and carbon monoxide chemisorption measurements for the ThO₂- and MoO₃-promoted catalysts are presented. For the Rh/MoO₃/SiO₂ catalysts, reduced and evacuated at 573 K, a suppression of the hydrogen:rhodium and carbon monoxide:rhodium ratios by the presence of MoO₃ was observed (Figs. 3a2 and 3b2, respectively). Reduction and evacuation at 723 K resulted in an even higher suppression of the chemisorption capacity (Figs. 3a3 and 3b3, respectively). At high molybdenum:rhodium ratios (Mo:Rh=4.0) a slight increase of the hydrogen:rhodium and carbon monoxide:rhodium ratios was observed.

The 1.5 wt.% Rh/ThO₂/SiO₂ catalysts did not exhibit any suppression of the chemisorption capacity, their hydrogen:rhodium and carbon monoxide:rhodium values did not vary with increasing Th/Rh ratio (Figs. 3a1 and 3b1).

The chemisorption capacity of the 1.5 wt.% Rh/ThO₂ catalyst was low. Hydrogen:rhodium was equal to 0.19 and carbon monoxide:rhodium was equal to 0.18. This was also concluded from the TPR profile after TPO, where the presence of a reduction peak at 410 K pointed to the presence of large spherical particles [17].

For the 1.5 wt.% Rh/MoO₃ catalyst, very high hydrogen:rhodium and carbon monoxide:rhodium values were observed, pointing to an anomalous effect. After reduction and evacuation at 723 K, the hydrogen:rhodium and the carbon monoxide:rhodium ratios were 2.2 and 5.2, respectively.

Transmission electron microscopy

The decrease of the chemisorption capacity for the Rh/MoO₃/SiO₂ catalysts can be caused by an increased metal particle size, or by a more direct influence of the promoter on the chemisorption capacity of the rhodium metal particles due to a covering and/or electronic effect. To exclude the first explanation TEM measurements were performed. The addition of the MoO₃ promoter did not significantly change the rhodium particle size: $D(\text{Rh}/\text{SiO}_2) = 20 \text{ \AA}$ and $D(\text{Rh}/\text{MoO}_3/\text{SiO}_2) = 21 \text{ \AA}$ (Mo/Rh = 1.0). Molybdenum oxide particles were not seen by TEM, because molybdenum oxide is not a well defined oxide under TEM conditions. For the Rh/ThO₂/SiO₂ catalyst (Th/Rh = 1.0) particles with a diameter of around 30 Å were observed. However, the characteristic spacings of Rh metal (2.1 and 2.6 Å), present in the particles of Rh/SiO₂ and Rh/Mo/SiO₂, were not seen in most of the particles of the Rh/ThO₂/SiO₂. On

Fig. 3. Hydrogen and carbon monoxide chemisorption measurements of the 1.5 wt. % Rh/ $\text{ThO}_2/\text{SiO}_2$ and Rh/ $\text{MoO}_3/\text{SiO}_2$ catalysts as a function of the Th:Rh and Mo:Rh ratio. Evacuation was performed at the reduction temperature; a1: H/Rh after reduction at 723 K for ThO_2 -promoted catalysts, a2: H/Rh after reduction at 523 K for MoO_3 -promoted catalysts, a3: H/Rh after reduction at 723 K for MoO_3 -promoted catalysts, b1: CO/Rh after reduction at 723 K for ThO_2 -promoted catalysts, b2: CO/Rh after reduction at 523 K for MoO_3 -promoted catalysts, b3: CO/Rh after reduction at 723 K for MoO_3 -promoted catalysts.

the contrary, spacings of about 3.1 Å were seen which originated from ThO_2 particles.

Thus, the suppression of the chemisorption capacity for the MoO_3 -promoted rhodium catalysts is not due to a decreased metal particle size.

Infrared spectroscopy of adsorbed carbon monoxide

Chemisorption of carbon monoxide at 298 K was also studied by infrared spectroscopy, in order to determine the binding sites for carbon monoxide and to measure the carbon monoxide adsorption capacity of the exposed rhodium. In a recent study, we already showed that vanadium oxide had a remarkable influence on the infrared spectrum of adsorbed carbon monoxide. The addition of vanadium oxide only suppressed the linearly bonded and bridge-bonded carbon monoxide, while the amount of carbon monoxide present in the gem-dicarbonyl form remained about constant [1].

Fig. 4. Infrared spectra of carbon monoxide adsorbed at 298 K ($P_{\text{CO}} = 10$ Torr (1.33 kPa), reduction and evacuation temperature 523 K) for 1.5 wt.% Rh/SiO₂ catalysts; a: Rh/SiO₂, b-f: Rh/MoO₃/SiO₂, g-i: Rh/ThO₂/SiO₂.

Fig. 5. Relative integrated areas of infrared absorbance spectra of the MoO_3 -promoted Rh/SiO_2 catalysts relative to the unpromoted Rh/SiO_2 catalyst using the integrated infrared spectra of Fig. 4 (a) and relative carbon monoxide:rhodium ratios from carbon monoxide chemisorption measurements (b).

In Fig. 4 the IR spectra of carbon monoxide adsorbed on Rh/SiO_2 catalysts, promoted with a varying amount of molybdenum oxide and thorium oxide, are presented. The infrared spectrum of carbon monoxide adsorbed on Rh/SiO_2 was dramatically influenced by the presence of molybdenum oxide. With increasing molybdenum oxide content, the amount of linearly bonded and bridge-bonded carbon monoxide, as well as the number of gem-dicarbonyl species strongly decreased and almost disappeared for $\text{Mo}:\text{Rh} = 4.0$. For the catalysts with $\text{Mo}:\text{Rh} > 1.0$, an additional peak around 1890 cm^{-1} is observed. The intensity of this peak decreased less than the intensity of the other peaks. In order to compare the amounts of adsorbed carbon monoxide for the systems with different $\text{Mo}:\text{Rh}$ ratios, the absorbance spectra were integrated as described before [1], resulting in an integrated absorption value (A -value) for every $\text{Mo}:\text{Rh}$ ratio. These A -values were normalized to the A -value of the Rh/SiO_2 catalyst ($\text{Mo}:\text{Rh} = 0$). The relative A -values for the MoO_3 -promoted catalysts are presented in Fig. 5, together with the relative carbon monoxide:rhodium values (compared with Rh/SiO_2) obtained by carbon monoxide chemisorption. Of course, the A -values can not be used to calculate the carbon monoxide:rhodium values because of differences in absorption coefficients for the different absorption forms of carbon monoxide, as reported by Duncan et al. [21]. However, from the trends observed in Fig. 5, one can conclude that the carbon monoxide adsorption sites on rhodium measured by IR are suppressed

completely, whereas carbon monoxide chemisorption showed that for Mo:Rh ratios > 1.0 , there still is a small chemisorption of carbon monoxide. We think that this carbon monoxide is adsorbed on the molybdenum oxide promoter. However, this kind of adsorbed carbon monoxide should also have been seen by IR spectroscopy. This difference between the IR results and the chemisorption results will be a result of differences in carbon monoxide pressure. During chemisorption measurements, the carbon monoxide pressure was in the 100–600 Torr range (13–78 kPa), whereas during IR measurements, 10 Torr (1.3 kPa) of carbon monoxide was introduced into the cell and subsequently, the cell was evacuated to 10^{-3} Torr (0.13 Pa), in order to remove gas phase carbon monoxide. This evacuation was harder for catalysts with a high Mo:Rh ratio, suggesting that additional carbon monoxide was weakly adsorbed on the molybdenum oxide promoter.

The position of the gem-dicarbonyl species was unaffected by the presence of MoO_3 . The position of the linearly bonded carbon monoxide shifted to lower wavenumbers with increasing MoO_3 content ($\Delta\sigma L = 20 \text{ cm}^{-1}$). The shift of the bridge-bonded carbon monoxide to lower wavenumbers with increasing MoO_3 content was around 70 cm^{-1} . No bands at lower wavenumbers ($< 1800 \text{ cm}^{-1}$) were observed. The shifts of the linearly bonded and bridge-bonded carbon monoxide were comparable with the shifts found when increasing the amount of carbon monoxide adsorbed on Rh/SiO_2 ($\Delta\sigma L = 25 \text{ cm}^{-1}$ and $\Delta\sigma B = 59 \text{ cm}^{-1}$) [1].

The influence of thorium oxide on the IR spectrum of adsorbed carbon monoxide is shown in Figs. 4g–i. The amount of linearly adsorbed carbon monoxide for the catalyst with Th:Rh = 0.5 was slightly lower than that for the unpromoted catalyst. Further addition of thorium oxide did not result in a further decrease of the amount of linearly adsorbed carbon monoxide and also the position of this band was not influenced by ThO_2 promotion. The amount of bridge-bonded carbon monoxide was considerably lower for the ThO_2 -promoted catalysts than for the unpromoted catalyst and decreased with increasing Th:Rh ratio. The position of the bridge-bonded carbon monoxide band for the ThO_2 -promoted catalysts was shifted to lower wavenumbers by the presence of ThO_2 compared with the unpromoted catalyst ($\Delta\sigma B = 51 \text{ cm}^{-1}$). For the ThO_2 -promoted catalysts, also a band around $1650\text{--}1700 \text{ cm}^{-1}$ was observed and between 1300 and 1650 cm^{-1} still absorption was seen. The integrated areas of the ThO_2 -promoted catalysts amounted to about 75% of the integrated area of the Rh/SiO_2 catalyst and did not decrease with increasing Th:Rh ratio. This is in contrast with the chemisorption measurements which showed that the carbon monoxide:rhodium value was not influenced by the addition of ThO_2 . However, the carbon monoxide causing the broad low-frequency absorption bands will have a relatively low extinction coefficient (see Discussion) and therefore will result in an underestimation of the amount of adsorbed carbon monoxide.

Hydrogenation of carbon monoxide

Thorium oxide and molybdenum trioxide promotion

In Table 1 the results of the $\text{CO} + \text{H}_2$ reaction over ThO_2 -promoted and MoO_3 -promoted catalysts are presented. The results are given after 15 h time-on-stream, when a constant small decrease of the activity is reached. The selectivity patterns were constant at that time. The catalysts were compared at a similar conversion level in order to obtain differential reaction conditions (conversion $< 5\%$) and to obtain accurate measurement of the different products by gas chromatography (GC) (conversion $> 1\%$). Therefore the reaction temperature was adjusted. The other reaction conditions, hydrogen:carbon monoxide ratio, P and GHSV were held constant. In order to compare activities at the same temperature (523 K), the measured activities were corrected for temperature differences using an activation energy of 100 kJ mol^{-1} , as was measured for $\text{Rh}/\text{ThO}_2/\text{SiO}_2$ at $\text{Th}/\text{Rh} = 1.0$. Of course, the different systems have different activation energies, and therefore the calculated activities are only an estimate of the activity at that temperature.

The 1.5 wt.% Rh/ThO_2 catalyst had a moderate activity and a reasonably high C_2 -oxygenate selectivity (41%). Compared with 1.5 wt.% Rh/SiO_2 , the activity of the ThO_2 -supported catalyst was five times larger. The ThO_2 -promoted silica-supported catalysts had high selectivities to C_2 -oxygenates (48–57%), more than half of it being ethanol. Thorium oxide also had a remarkable effect on the activity of the Rh/SiO_2 catalysts. The activity sharply increased with increasing Th:Rh ratio up to Th:Rh = 0.5. Further addition of ThO_2 only resulted in a slight increase of the activity. The activity of the Rh/SiO_2 catalyst was increased 36 times for the catalyst with Th:Rh = 4.0, which is similar to the increase in activity observed for V_2O_3 promotion [2]. The methanol selectivity is rather low (7–17%). The deactivation for the ThO_2 -promoted catalysts was lower than for the Rh/ThO_2 catalyst ($2\% \text{ h}^{-1}$ versus $4\% \text{ h}^{-1}$).

Carbon monoxide hydrogenation at 0.15 MPa for 1.5 wt.% Rh/SiO_2 and 1.5 wt.% $\text{Rh}/\text{ThO}_2/\text{SiO}_2$ (Th:Rh = 1.0) shows that the promotive effect of thorium oxide was also present at low pressure, the activity of the promoted catalyst was 38 times larger than that of the unpromoted catalyst. In the low pressure experiments the methane selectivity was high and the methanol selectivity was low. However, also the C_2 -oxygenate selectivity was considerably lower than in the high pressure case (21.5 versus 51.8%). This is different from V_2O_3 -promotion, where high C_2 -oxygenate selectivities were also measured in the low pressure experiment. It is remarkable that the increase in pressure did not result in an increased activity for these systems. This points to changes in the catalyst system due to the increased pressure, probably because of an increased water vapour pressure.

The 1.5 wt.% Rh/MoO_3 catalyst had a low C_2 -oxygenate (2%) and methanol

TABLE 1

Results of hydrogen-carbon monoxide reaction after 15 h time-on-stream for ThO_2 - and MoO_3 -promoted 1.5 wt. % catalysts reduced in situ at 723 KExperimental conditions: GHSV = $4000 \text{ l l}^{-1} \text{ h}^{-1}$, hydrogen: carbon monoxide = 3.0

	Rh/ThO ₂	Rh/MoO ₃	Rh/SiO ₂	Rh/ThO ₂ /SiO ₂			Rh/MoO ₃ /SiO ₂								
Prom./Rh ^a	—	—	0	0.12	0.5	1.0	4.0	1.0	0.12	0.5	1.0	2.0	4.0	1.0	
P (MPa)	4.0	4.0	4.0	4.0	4.0	4.0	4.0	0.15	4.0	4.0	4.0	4.0	4.0	0.15	
React. Temp (K)	535	508	600	535	528	528	507	528	544	508	508	508	500	503	
Activity ^b	1.2	2.8	2.8	2.3	3.9	5.7	2.4	6.1	2.9	7.9	9.9	7.7	4.7	1.7	
Corr. Act. ^c	0.7	5.6	0.14	1.4	3.1	4.6	5.0	4.9	1.1	15.7	19.7	15.3	13.6	2.5	
Sel. (%C) ^d															
CH ₄	35.6	52.2	33.2	85.4	25.5	30.8	32.3	26.4	53.8	17.2	12.4	14.1	16.5	19.4	30.5
C ₂ ^e	7.3	31.0	2.3	13.5	2.1	4.5	5.8	5.8	23.9	4.5	8.1	11.0	12.3	18.4	25.4
C ₁ OH ^f	11.6	13.3	29.1	0.5	14.3	11.0	7.7	16.9	0.7	38.0	51.7	53.1	52.3	43.6	27.3
C ₂ OH ^g	16.7	1.6	20.5	0.2	31.3	30.6	30.7	30.4	16.9	25.8	18.0	13.8	12.4	12.3	12.7
C ₂ =O ^h	12.8	0.0	4.3	0.4	7.1	5.4	6.5	2.8	4.1	0.0	0.0	0.0	0.0	0.0	0.0
C ₂ OOH ⁱ	11.5	0.5	10.2	0.0	18.4	15.6	14.6	14.8	0.5	10.5	1.5	0.9	0.3	0.4	0.2
C ₃ O ^{-j}	4.6	1.4	0.6	0.0	1.3	2.1	2.4	3.0	0.2	4.0	8.4	7.1	6.2	6.0	3.9
C ₂ oxy ^k	41.0	2.1	35.0	0.6	56.8	51.6	51.8	48.0	21.5	36.3	19.5	14.7	12.7	12.7	12.9
Oxo. sel. ^l	57.2	16.8	64.5	1.1	72.4	64.7	61.9	67.9	22.3	78.3	79.6	74.9	71.2	62.3	44.1
Deact. (% h ⁻¹)	3.8	1.2	0.9	n.m.	1.7	2.1	2.4	1.4	n.m.	1.1	1.1	0.9	<0.5	<0.5	1.0

n.m.: Not measured.

^aTh/Rh and Mo/Rh, atomic ratio.^bActivity in mmol converted carbon monoxide (mol Rh)⁻¹ s⁻¹.^cCalculated activity at 523 K using $E_{\text{act}} = 100 \text{ kJ mol}^{-1}$.^dSelectivities expressed as %C efficiency.^eHydrocarbons containing two or more carbon atoms.^fTotal amount of methanol, ethers and esters included.^gTotal amount of ethanol, ethers and esters included.^hAcetaldehyde.ⁱAcetic acid, esters included.^jOxygenated products containing three or more carbon atoms.^kC₂-oxygenate selectivity.^lTotal oxo-selectivity.

(13%) selectivity. The catalyst showed a substantial activity and a moderate deactivation. These results were comparable with the results of Jackson et al. [8].

From the TPR experiments we concluded that after reduction at 898 K, molybdenum was in the 2+ state. However, we do not have information about the valency of the molybdenum under reaction conditions. Nevertheless we will use the following notation for the silica-supported molybdenum oxide-promoted systems: Rh/MoO/SiO₂.

Promotion of 1.5 wt.% Rh/SiO₂ by molybdenum oxide considerably increased the activity, even more than promotion by thorium and vanadium oxide. A maximum increase in activity was observed for a Mo:Rh ratio of 1.0. Compared with the unpromoted 1.5 wt.% Rh/SiO₂, the activity of the Rh/MoO/SiO₂ (Mo:Rh=1.0) catalyst was increased by a factor of 141. For Mo:Rh ratios > 1.0 the activity decreased with increasing Mo:Rh ratio. The molybdenum oxide-promoted catalysts had a high methanol selectivity (around 50%) and a relatively low C₂-oxygenate selectivity (12–20%). Total oxo-selectivity was high (60–80%), and deactivation was low (around 1% h⁻¹).

The effect of molybdenum oxide promotion was less effective in the low pressure experiment (0.15 MPa). The activity of the promoted catalyst (Mo:Rh=1.0) was nineteen times larger than the activity of the unpromoted catalyst. Total oxo-selectivity was lower than in the high pressure case (44 versus 75%), mainly due to a decreased methanol selectivity.

For the molybdenum oxide-promoted catalysts a lower deactivation was observed than for the thorium oxide-promoted catalysts (1.0 and 2.0% h⁻¹, respectively). The decrease of the methanol formation rate was lower (< 0.5% h⁻¹) than the decrease of the formation rate of the other products (2–3% h⁻¹) for both catalysts. The low overall deactivation of the molybdenum oxide-promoted catalysts is therefore a result of the high selectivity to methanol. The different deactivation behaviour for methanol compared with the other products, suggests that methanol is formed on other sites than the other products. This suggestion has been made before by Poels and coworkers [22,23] and Hindermann et al. [24]. They proposed that methanol is formed over metal ions, while the other products are formed over well-reduced metal particles.

From Table 1 it can be concluded that the addition of molybdenum oxide and thorium oxide to a 1.5 wt.% Rh/SiO₂ catalyst resulted in an increased activity. Thorium oxide resulted in a high C₂-oxygenate selectivity, while molybdenum oxide led to a high methanol selectivity. However, different reaction temperatures were used to test the several catalyst systems and this may have influenced the selectivity patterns. Therefore, we tested the unpromoted 1.5 wt.% Rh/SiO₂ and promoted 1.5 wt.% Rh/promoter/SiO₂ catalysts (promoter = ThO₂, MoO₃ and V₂O₃, promoter:Rh = 1.0) at the same temperature, i.e. 548 K. The GHSV was adjusted in such a way that the conversion level was around 2%. The results of these measurements are presented in Table 2. The

TABLE 2

Hydrogen-carbon monoxide reaction over Rh/SiO₂ and Rh/promoter/SiO₂ (promoter=ThO₂, MoO and V₂O₃, promoter:Rh = 1.0) catalysts at 548 K

Reaction conditions: hydrogen:carbon monoxide = 3.0 and $P = 4.0$ MPa. GHSV for Rh/SiO₂ 660, for Rh/ThO₂/SiO₂ 8000, for Rh/MoO/SiO₂ 64000 and for Rh/V₂O₃/SiO₂ 16000 l l⁻¹ h⁻¹. For definitions see Table 1.

	Selectivity (%C)				Activity*				Factor of increase**		
	Unprom.	Mo	Th	V	Unprom.	Mo	Th	V	Mo	Th	V
CH ₄	11.6	15.4	42.8	29.1	0.051	11.5	5.91	5.22	225	116	102
C ₂ -	1.4	8.6	3.3	14.0	0.006	6.4	0.46	2.52	1067	77	426
C ₁ OH	57.2	57.7	4.1	9.5	0.252	43.2	0.57	1.71	171	3	7
C ₂ OH	13.7	13.3	25.0	23.9	0.060	10.0	3.45	4.30	167	58	72
C ₂ =O	0.0	0.0	11.1	9.7	0.000	0.0	1.53	1.75	0	∞	∞
C ₂ OOH	14.7	0.7	11.4	8.8	0.065	0.5	1.57	1.58	8	24	24
C ₃ O ⁺	1.4	4.3	2.0	5.0	0.006	3.2	0.28	0.90	537	47	150
C ₂ oxy	28.4	14.0	47.5	42.4	0.125	10.5	6.56	7.63	84	52	61
Tot. oxo	87.0	76.0	53.6	56.9	0.383	56.9	7.40	10.24	149	19	27
Total act.					0.440	74.9	13.8	17.98	170	31	41
CO dissociation***					0.126	26.4	10.0	12.46	210	79	99

*Formation rate of several product groups expressed as mmol carbon monoxide converted (mol Rh)⁻¹ s⁻¹.

**Effect of promoter on formation rates of several product groups related to the unpromoted catalyst.

***Carbon monoxide dissociation rate is total activity minus formation rate of methanol minus half of formation rate of C₂-oxygenates.

selectivity pattern is greatly influenced by the promoter used. The molybdenum oxide-promoted catalysts had a high methanol selectivity, while thorium oxide and vanadium oxide resulted in a high C₂-oxygenate selectivity. (The results of the V₂O₃-promoted catalysts differ slightly from the results reported in [2] due to a different Rh(NO₃)₃ batch.) Furthermore, one can see that longer chain products like C₂⁺ and C₃O⁺ are favoured by the presence of vanadium oxide.

These observations might lead us to the conclusion that molybdenum oxide promotes the formation of methanol, and thorium oxide and vanadium oxide promote the formation of C₂-oxygenates. However, it is better to compare formation rates for the different product groups. In Table 2 these formation rates of several product groups and the influence of the promoter oxides on these formation rates, expressed as a factor of increase of the formation rates to the several products groups relative to the unpromoted catalyst, are presented. From these factors of increase (F) a clear picture of the role of the promoter emerges. The formation rate of methanol is mostly enhanced by the molybdenum oxide promoter ($F_{\text{Mo}}:F_{\text{Th}}:F_{\text{V}} = 171:3:7$). The formation rate of methane is increased by ThO₂ and V₂O₃ by a factor of about 100 and for MoO

promotion by a factor of 225. The formation rate of C_2 -oxygenates is increased by roughly the same factor for all three promoters ($F_{Mo}:F_{Th}:F_V=84:52:61$). The lower selectivity to C_2 -oxygenates for the molybdenum oxide-promoted catalysts therefore does not originate from a low formation rate of C_2 -oxygenates, but from a high methanol formation rate. Because methanol is most probably formed by a completely different mechanism as the rest of the products (hydrogenation of associatively adsorbed carbon monoxide versus hydrogenation of dissociatively adsorbed carbon monoxide [25]), the factor of increase of the formation rate of all products except methanol was also calculated. The effect of V_2O_3 and ThO_2 on this combined product group was approximately the same, $F_{Th}=70$ and $F_V=87$. Molybdenum oxide promotion resulted in a higher increase factor ($F_{Mo}=169$). The increase factor for the longer chain products (C_{2+} and C_3O^+) decreased in the order $F_{Mo}>F_{Th}>F_V$.

Ethylene addition

As shown by Chuang et al. [26,27], Jordan and Bell [28], Ichikawa et al. [29], Van den Berg et al. [30,31], Sachtler [32] and Pijolat and Perrichon [33] ethylene addition to a working catalyst is a very powerful method to study the mechanism of carbon monoxide hydrogenation. Possible reactions of ethylene are the formation of methane, hydrogenation to ethane, chain-growth reaction forming propane and propylene and the carbon monoxide insertion reaction forming propanol and propionaldehyde. The latter reaction is thought to be responsible for the formation of C_{2+} -oxygenates [26-33]. In this study we examined the influence of the promoter on these specific reaction steps in order to investigate the role of the promoter in the carbon monoxide hydrogenation.

Since addition of a gas is not easy in a high pressure experiment and the promoter effect was also present in the reaction at low pressure, we studied ethylene addition at 0.15 MPa. Ethylene was added after prolonged reaction (15 h time-on-stream). The results for Rh/SiO₂ and Rh/promoter/SiO₂, promoter:Rh=1.0 (promoter=MoO, ThO₂ and V₂O₃) are presented in Table 3.

In order to compare the results of ethylene addition for the different catalysts at identical conditions, we calculated the vol.% of the several products formed after addition of 0.30 vol.% ethylene at 503 K, assuming first order kinetics in ethylene. The amount of ethylene hydrogenated to ethane increased in the order unpromoted < V₂O₃ < ThO₂ < MoO (0.13:0.16:0.20:0.27). The amount of carbon monoxide inserted into added ethylene forming C₃-oxygenates increased in the order V₂O₃ < ThO₂ < MoO < unpromoted (0.014:0.015:0.017:0.022). The chain-growth for the unpromoted and V₂O₃-promoted catalysts was negligible, while thorium oxide exhibited a small incorporation of ethylene and molybdenum oxide considerably enhanced the incorporation of ethylene.

These results prove that carbon monoxide insertion is not increased by the

TABLE 3

The effect of ethylene addition to hydrogen-carbon monoxide reaction over Rh/SiO₂ and promoted Rh/promoter/SiO₂ (promoter = MoO, ThO₂, or V₂O₃, promoter:Rh = 1.0) catalysts

Reaction conditions: $P = 0.15$ MPa, hydrogen:carbon monoxide = 3.0 and GHSV = 4000 l l⁻¹ h⁻¹. All data are expressed in 10⁻² vol.% compound

Promoter	Temperature (K)	Added C ₂ H ₄ (10 ⁻² vol.%)	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆₋₈	C ₃ OH	C ₃ =O
—	503	—	0.16	0.01	0.01	0.01	0.00	0.00
—	503	27	0.16	13.6	11.6	0.01	0.83	1.16
—	593	—	19.6	0.0	0.53	0.39	0.00	0.00
—	593	24	18.8	0.0	24.4	0.42	0.00	0.00
—	593	83	19.2	0.0	83.1	0.55	0.00	0.00
MoO	503	—	7.84	0.36	1.52	0.64	0.16	0.06
MoO	503	33	6.84	1.42	29.8	2.35	1.91	0.14
MoO	503	78	6.16	4.14	67.2	3.93	5.22	0.31
MoO	528	—	26.8	0.66	6.23	2.15	0.12	0.14
MoO	528	35	25.4	0.00	39.9	4.27	0.19	0.14
ThO ₂	503	—	9.72	0.29	0.30	0.64	0.02	0.00
ThO ₂	503	25	8.64	8.6	16.3	0.66	1.03	0.23
ThO ₂	503	66	7.56	20.2	42.8	0.76	2.60	0.53
ThO ₂	503	—	8.55	0.29	0.32	0.54	0.15	0.02
ThO ₂	528	—	48.7	0.52	2.39	2.90	0.17	0.05
ThO ₂	528	29	45.4	1.35	29.5	2.96	0.82	0.16
V ₂ O ₃	503	—	8.06	1.15	0.71	1.56	0.15	0.06
V ₂ O ₃	503	30	7.34	15.8	16.4	1.45	1.21	0.43
V ₂ O ₃	503	—	7.03	1.10	0.49	1.33	0.16	0.05
V ₂ O ₃	503	95	6.51	76.2	13.7	1.34	3.16	1.02
V ₂ O ₃	503	—	6.09	0.95	0.37	1.10	0.17	0.04

presence of the promoter oxide. A higher temperature disfavoured the carbon monoxide insertion reaction. Furthermore, the hydrogenation reaction of ethylene is not the rate limiting step in the carbon monoxide hydrogenation, because part of the added ethylene is hydrogenated without a significant decrease of the carbon monoxide hydrogenation reaction rate. The hydrogenation rate is higher for the MoO- and ThO₂-promoted catalysts than for the V₂O₃-promoted and unpromoted catalysts. Incorporation of ethylene into a growing chain, resulting in an increased amount of C₃-hydrocarbons, is present for Rh/SiO₂ tested at 593 K, for MoO-promoted catalysts tested at 503 K and only in a modest way for ThO₂. The ethylene incorporation reaction was absent for the V₂O₃-promoted catalyst and for Rh/SiO₂ tested at 503 K.

DISCUSSION

Temperature programmed reduction

Temperature programmed reduction studies of the Rh/MoO₃/SiO₂ catalysts after calcination at 723 K showed that there is an intimate contact between the MoO₃ promoter and Rh₂O₃. The reductions of Rh₂O₃ and MoO₃ can not be distinguished in the TPR profile. The reduction of MoO₃ is facilitated by the presence of rhodium metal, the reduction of MoO₃ shifts to a lower temperature, and the reduction of Rh₂O₃ is hampered by the presence of MoO₃, the reduction peak of Rh₂O₃ shifts to a higher temperature. This effect is more pronounced in the TPR profiles of the samples oxidized at 898 K. The easier reduction of the MoO₃ points to an intimate contact between Rh₂O₃ and MoO₃, but can also be explained by assuming hydrogen spillover. Once Rh₂O₃ is reduced to rhodium metal, hydrogen molecules can dissociate on the rhodium metal and the hydrogen atoms formed can spillover and reduce the MoO₃, resulting in a lower reduction temperature of MoO₃. However, the hampered reduction of Rh₂O₃ proves that there must be an intimate contact between Rh₂O₃ and MoO₃ in the Rh/MoO₃/SiO₂ catalysts after calcination at 723 K and oxidation at 898 K.

The hampered reduction of Rh₂O₃ can be understood by assuming that a mixed oxide of Rh₂O₃ and MoO₃ is formed, or that the Rh₂O₃ particles are completely covered with a layer of MoO₃, preventing the hydrogen molecules from reaching the Rh₂O₃ at a low temperature. A mixed oxide of Rh₂O₃ and MoO₃, Rh₂MoO₆, is known to exist and can be formed by heating RhCl₃ and MoO₃ in a molar ratio of 2:1 in air for 60 h at 773 K and for 48 h at 923 K [12,13]. This temperature is higher than the calcination temperature used for the Rh/MoO₃/SiO₂ catalysts, but surface reactions are known to proceed at lower temperatures than bulk reactions. This also clarifies the difference between the TPR profiles after calcination at 723 K and after oxidation at 898 K. The latter profiles show distinct reduction peaks which may be due to better defined distinct phases, "free" Rh₂O₃ and Rh₂MoO₆.

Similar influences of the promoter oxide on the reduction behaviour of Rh₂O₃ were observed for V₂O₅-promoted Rh/SiO₂ catalysts [1]. In Fig. 6 the influences of V₂O₅ and MoO₃ on the TPR profile of Rh/SiO₂ after oxidation at 898 K are compared. For promoter:Rh = 0.5 the amount of "free" Rh₂O₃, reducing below 373 K, almost completely vanished in the MoO₃-promoted catalysts (Fig. 6b), while this amount was only decreased by a factor of two for the V₂O₅-promoted catalyst (Fig. 6c, the amount of "free" Rh₂O₃ can be calculated by estimating the amounts of hydrogen consumed in the first and second peak).

Fig. 6. Temperature programmed reduction profiles after oxidation at 898 K; a: 1.5 wt.% Rh/SiO₂, b: 1.5 wt.% Rh/MoO₃/SiO₂, Mo:Rh=0.5, c: 1.5 wt.% Rh/V₂O₅/SiO₂, V:Rh=0.5, d: 1.5 wt.% Rh/TiO₂/SiO₂, Th:Rh=0.5.

This supports the assumption of the formation of mixed oxides, because for MoO₃ a mixed oxide with Rh:Mo=2 is most stable (Rh₂MoO₆), while for V₂O₅ a mixed oxide with Rh:V=1 is most stable (RhVO₄). The same amount of promoter thus decreases the amount of “free” Rh₂O₃ twice as much for MoO₃-promotion, than for V₂O₅-promotion. However, this phenomenon does not completely exclude the possibility of covering of the Rh₂O₃ by MoO₃ and V₂O₅. Molybdenum trioxide may spread better over Rh₂O₃ and may form a more complete layer of oxide and thus may shield Rh₂O₃ better at a lower promoter:Rh ratio. However, for V₂O₅-promoted systems, diffuse-reflectance infrared spectroscopy showed that the V=O stretching band which was present in the V₂O₅/SiO₂ system, was not present in the Rh/V₂O₅/SiO₂ (V:Rh=0.9) catalyst after calcination, indicating that no “free” V₂O₅ was present. This strongly suggests that Rh₂O₃ and V₂O₅ are not present in a “free” form and therefore must have formed a compound. By analogy, we assume that this is also the case for the Rh/MoO₃/SiO₂ catalysts. Of course, these measurements are not a direct evidence for the formation of a mixed oxide. In near future, we will study these systems in more detail using extended X-ray absorption fine structure measurements (EXAFS) and we hope to obtain a direct evidence for the formation of the mixed oxides in the V₂O₅- and MoO₃-promoted catalysts.

For Mo:Rh ratios > 1.0, hydrogen consumption is also observed at temperatures between 573 and 873 K, i.e. the temperature region where reduction was

found for $\text{MoO}_3/\text{SiO}_2$. Thus for this system, part of the MoO_3 is not in intimate contact with Rh_2O_3 .

From the TPR profiles of the ThO_2 -promoted catalysts, we can not conclude whether or not there is an intimate contact between the promoter oxide and Rh_2O_3 . Thorium oxide did not reduce at all and the reduction profile of Rh_2O_3 after calcination was only slightly influenced by the presence of ThO_2 , due to carbon dioxide adsorbed on ThO_2 . The TPR profiles of the oxidized samples were not at all influenced by the presence of ThO_2 . In the literature, no information is available about the formation of a mixed oxide of ThO_2 and Rh_2O_3 [13].

Hydrogen and carbon monoxide chemisorption

Hydrogen and carbon monoxide chemisorption measurements showed a decrease of hydrogen:rhodium and carbon monoxide:rhodium for the molybdenum oxide-promoted catalysts with increasing Mo:Rh ratio. For the thorium oxide-promoted catalysts, such a suppression of hydrogen and carbon monoxide chemisorption was not observed.

The decrease of the hydrogen:rhodium and carbon monoxide:rhodium ratios with increasing promoter:Rh ratio was also seen for vanadium oxide-promoted catalysts and may originate from an increased rhodium metal particle size or from an influence of the promoter oxide on the chemisorption capacity of the rhodium metal (electronic or covering effect). A TEM study showed that the rhodium metal particle size was not influenced by the promoter oxide (MoO and V_2O_3). A similar suppression of chemisorption was observed for noble metals supported on transition metal oxides like TiO_2 and V_2O_3 after reduction at higher temperatures ($T_{\text{red}} > 723 \text{ K}$) [34–36]. The almost generally accepted explanation for this so-called Strong Metal Support Interaction (SMSI) effect is the covering of the metal particle by suboxides of the support (like Ti_4O_7) formed during the high-temperature reduction [37–44]. However, for the MoO - and V_2O_3 -promoted catalysts, the suppression of carbon monoxide and hydrogen chemisorption was already present after reduction at a much lower temperature (523 K). The suppression was more pronounced after reduction at 723 K. We think that also in our case the rhodium metal particles are covered with molybdenum and vanadium oxide, even after a low temperature reduction. Hicks et al. [45] reported similar results for La_2O_3 -supported palladium catalysts. They observed a suppression of the carbon monoxide chemisorption after reduction at 573 K (low temperature reduction) and attributed this suppression to patches of partially reduced support material, LaO_x , already transferred to the surface of the palladium crystallites during catalyst preparation.

For Mo:Rh ratios > 1.0 , a slight increase of the hydrogen:rhodium and carbon monoxide:rhodium ratios with increasing Mo:Rh ratio was observed,

pointing to adsorption of hydrogen and carbon monoxide on the molybdenum oxide. In recent studies, Tatsumi et al. [46] and Concha et al. [47] reported carbon monoxide hydrogenation over silica-supported molybdenum oxide catalysts at 573 K and 1.6 MPa and at 623 K and 0.14 MPa, respectively. Of course, for this reaction to occur, molybdenum oxide must be able to adsorb both hydrogen and carbon monoxide. Hall and coworkers [48,49] reported that reduced alumina-supported molybdenum oxides chemisorbed carbon monoxide and hydrogen. The very high hydrogen:rhodium and carbon monoxide:rhodium ratios found for 1.5 wt. % Rh/MoO₃ also point to the adsorption of both hydrogen and carbon monoxide on MoO_x.

So, for the MoO₃-promoted catalysts, hydrogen and carbon monoxide chemisorption and TEM pointed to a coverage of the rhodium particles by patches of molybdenum oxide, even after low temperature reduction. For the thorium oxide-promoted catalysts, the hydrogen and carbon monoxide chemisorption measurements did not indicate any coverage of the metal particles.

Infrared spectroscopy

The IR spectra of carbon monoxide adsorbed on Rh/MoO/SiO₂ catalysts prove that MoO completely suppressed the carbon monoxide chemisorption capacity of rhodium. For Mo:Rh > 1.0, almost no carbon monoxide adsorbed on rhodium in the bridge-bonded, linearly bonded or gem-dicarbonyl form. The carbon monoxide bonded to the MoO_x is not seen in the IR studies, due to the evacuation after carbon monoxide admission.

An increasing Mo:Rh ratio resulted in shifts to lower wavenumbers of the bands of the linearly bonded and bridge-bonded carbon monoxide. We do not think that this is caused by an electronic effect of the promoter on the rhodium metal, but ascribe this effect to the lower carbon monoxide coverage, resulting in a decrease of the dipole-dipole coupling between carbon monoxide molecules and consequently a decrease in the carbon monoxide stretching frequency [50]. This conclusion is supported by the observation that the shifts of the linearly bonded and bridge-bonded carbon monoxide with increasing carbon monoxide pressure and thus increasing carbon monoxide coverage, observed for the unpromoted Rh/SiO₂ catalysts, were similar.

For the ThO₂-promoted catalysts, the amount of linearly adsorbed carbon monoxide was slightly lower for the promoted catalysts and the corresponding absorption band shifts to slightly lower wavenumber. The amount of bridge-bonded carbon monoxide decreased with increasing Th:Rh ratio and shifted to lower wavenumbers, which can be a result of a decreased dipole-dipole coupling caused by the decreased carbon monoxide coverage. Also a broad absorption band between 1300 and 1800 cm⁻¹ and a band maximum around 1680 cm⁻¹ were observed. The origin of this band is ascribed to carbon and oxygen

bonded carbon monoxide (see the discussion about the carbon monoxide hydrogenation reaction).

From the IR study we conclude that MoO_3 dramatically suppressed all forms of carbon monoxide adsorbed on rhodium, while ThO_2 mainly influenced the bridge-bonded carbon monoxide and caused the appearance of a broad absorption band between 1300 and 1800 cm^{-1} .

Carbon monoxide hydrogenation reaction

From the results presented in Table 2 we conclude that the total activity of the Rh/SiO_2 catalyst was greatly enhanced by the presence of the promoter oxides used in this and the preceding study: MoO , ThO_2 and V_2O_3 . The increase of the total activity was largest for the molybdenum oxide-promoted catalysts. The large increase in activity by the presence of the promoter oxides points to an intimate contact between the promoter oxide and the rhodium metal. For MoO and V_2O_3 , hydrogen and carbon monoxide chemisorption measurements and IR spectroscopy pointed to a covering of the rhodium metal particle by patches of MoO and V_2O_3 . During carbon monoxide hydrogenation, this covering can be removed by water, one of the products of the carbon monoxide hydrogenation reaction, as has been reported for TiO_2 -supported Rh and Pt catalysts [51]. The highest activity was measured for the $\text{Mo}:\text{Rh}=1.0$ catalyst and further addition of MoO caused a decrease in activity. We think that this is due to two counteracting effects. Firstly, the MoO patches block part of the active metal surface and selectively suppress reactions which need a large ensemble. This blocking also results in a suppressed hydrogen and carbon monoxide chemisorption. Secondly, the molybdenum oxide patches enhance the carbon monoxide hydrogenation reaction at the metal-molybdenum oxide interface, that is at the perimeter of the molybdenum oxide patches on the Rh particle. The latter effect prevails for $\text{Mo}:\text{Rh} < 1$ and the first dominates for $\text{Mo}:\text{Rh} > 1$. This explanation was also proposed for the V_2O_3 promotion effect [2].

Hydrogen and carbon monoxide chemisorption measurements indicate that within the experimental error of the measurements (5%), for the $\text{Rh}/\text{ThO}_2/\text{SiO}_2$ catalysts no covering of the rhodium metal particles by ThO_2 occurred. However, it is still possible that a limited number of ThO_2 molecules is positioned on top of the Rh particles. This would explain the small influence of ThO_2 on the IR spectra of adsorbed carbon monoxide. Other possible locations for the thorium oxide are the perimeter of the rhodium particle, or the area between the rhodium particle and the silica support. It is also possible that the major part of the thorium oxide is not in contact with the rhodium metal particle at all. However, TEM studies showed that almost no distinct rhodium particles (characteristic spacing of 2.1 and 2.6 Å) were present in the

Rh/ThO₂/SiO₂ catalyst, suggesting that the major part of the rhodium particles was in intimate contact with the ThO₂ particles.

In order to further study the position of the ThO₂ promoter, a 0.5 wt.% Rh/ThO₂/SiO₂ (Th:Rh=3.0) catalyst was made. The hydrogen:rhodium chemisorption value was 0.87 and the carbon monoxide:rhodium value was 0.97. This catalyst contained the same amount of ThO₂ as the 1.5 wt.% Rh/ThO₂/SiO₂ catalyst with Th:Rh=1.5. One can calculate that in this catalyst roughly twice as many rhodium atoms should be positioned at the perimeter of the rhodium particles as in the 1.5 wt.% Rh/TiO₂/SiO₂ catalysts (H:Rh=0.64) [14,52]. If ThO₂ is positioned at the perimeter of the rhodium metal particles and if furthermore, ThO₂ is promoting the carbon monoxide hydrogenation just at these locations, then the 0.5 wt.% Rh/ThO₂/SiO₂ catalyst should have an activity twice as large as the 1.5 wt.% Rh/ThO₂/SiO₂ catalyst. This was not the case. Within the experimental error (10%) the catalysts had the same activity. We therefore conclude that the ThO₂-promoted sites are not solely located at the perimeter of the rhodium particles, but must also be positioned on top of the rhodium metal particles.

We conclude that MoO and V₂O₃ are positioned on top of the rhodium metal particles, while only a small part of the ThO₂ promoter is positioned on top of the rhodium particle.

The promoter oxides not only influenced the activity but also changed the selectivity pattern. As shown in the Results section, the selectivity differences between the catalysts tested were mainly a result of differences in methanol formation rate. Molybdenum oxide greatly enhanced the formation of methanol and therefore exhibited high oxo-selectivities. The increase of the methanol formation rate was only modest for the V₂O₃- and ThO₂-promoted catalysts and much lower than the increase of the formation rate of the other products, resulting in a relatively low methanol selectivity. In contrast to the other products of carbon monoxide hydrogenation, methanol is thought to be formed non-dissociatively [25] over metal ions [22-24]. It is possible that the Rh/MoO/SiO₂ catalysts contain more Rh⁺ ions, stabilized by the MoO, and in this way increase the methanol formation rate. We do not have any information about the amount of rhodium ions, but it is not likely that the increase of methanol formation by a factor 171 can be ascribed to a higher amount of Rh⁺ ions. From TPR we can conclude that the reducibility of Rh/V₂O₃/SiO₂ and Rh/MoO₃/SiO₂ is comparable, while the factors of increase of the methanol formation rates were 7 and 171, respectively. The carbon monoxide chemisorption measurements combined with IR spectroscopy showed that carbon monoxide can be adsorbed on MoO and not on the other promoter oxides. Considering the results of Poels and coworkers [22,23] and Hindermann et al. [24] that methanol is formed over metal ions, we think that the carbon monoxide adsorbed on Moⁿ⁺ ions is hydrogenated to methanol by hydrogen

atoms, formed over rhodium metal. Thus, in this case, the catalytic reaction is taking place on the promoter oxide.

Because the carbon monoxide insertion reaction is thought to be responsible for oxygenate formation [30–32,53,54], this reaction needs closer attention. The increase of the formation of C_2 -oxygenates due to the addition of the promoter oxides was in all cases lower than the increase of the activity for all other products, except methanol (see Table 2, methanol is excluded because it is thought to be formed via another mechanism [25]). This suggests that the addition of promoter oxides does not increase the carbon monoxide insertion reaction. Ethylene addition to a working catalyst at 0.15 MPa and 503 K clearly supports this suggestion. The increase of C_3 -oxygenates formed by carbon monoxide insertion into ethylene, was slightly lower for the promoted catalysts than for the unpromoted catalyst. Assuming first order kinetics in ethylene, the amount of carbon monoxide inserted into ethylene when 0.30 vol.% ethylene was added at 503 K to the synthesis gas mixture ($H_2:CO=3.0$, $P=0.15$ MPa) was 0.022, 0.017, 0.015 and 0.014 vol.% for the unpromoted, MoO-, ThO_2 - and V_2O_3 -promoted Rh/SiO₂ catalysts, respectively. It is clear that the addition of the promoter oxides did not enhance the rate of carbon monoxide insertion.

The formation rate of longer chain products (C_{2+} and C_3O^+) varied for the promoters studied and increased in the order unpromoted $< ThO_2 < V_2O_3 \ll MoO$. This points to a higher chain-growth probability for the MoO-promoted catalysts. Ethylene addition experiments pointed to the same conclusion. For the MoO-promoted catalyst, the amount of C_3 -hydrocarbons increased, indicating the incorporation of ethylene into a C_1 fragment. For the ThO_2 -promoted catalyst only a minor increase of C_3 -hydrocarbons was observed, while for the V_2O_3 -promoted catalyst no increase of C_3 -hydrocarbons was found.

Ethylene addition was also used to study the hydrogenation rate of a working catalyst. Assuming first order kinetics, the amount of ethylene hydrogenated during carbon monoxide hydrogenation at 503 K (0.30 vol.% added ethylene) was found to be 0.13, 0.16, 0.20, and 0.27 vol.% for the unpromoted, ThO_2 -, V_2O_3 - and MoO-promoted catalyst, respectively. Thus, the hydrogenation activity of the promoted catalysts was somewhat higher than that of the unpromoted catalyst. Nevertheless, from the ethylene addition experiments it can be concluded that the hydrogenation is not rate limiting. Although the hydrogenation of ethylene proceeds well over a Rh/SiO₂ catalyst at 503 K, its activity for carbon monoxide hydrogenation at that temperature was low. The ethylene hydrogenation reaction rates for the promoted catalysts were in the same order of magnitude as that of the unpromoted catalysts, but the carbon monoxide hydrogenation was enhanced by a factor of 30 to 170. This suggests that carbon monoxide dissociation, instead of hydrogenation, is the rate limiting step in the hydrogenation of carbon monoxide and that the main role of

Fig. 7. Model for the promotion mechanism for the C–O bond dissociation in the carbon monoxide hydrogenation; A: model according to Mori et al. [4] requiring a reduction–oxidation cycle of the promoter, B: model according to Burch et al. [68,69], Bell et al. [70,71] and Sachtler et al. [30–33,54,72], in which carbon monoxide is carbon bonded to the rhodium metal and oxygen bonded to the promoter ion.

the promoter oxide is to enhance this dissociation reaction. Mori et al. [4] studied promotion of Ru/Al₂O₃ by oxides of V, Nb, Mo, W and Re using pulse surface reaction rate analysis (PSRA). In this technique the rate of carbon monoxide dissociation and subsequent hydrogenation to methane can be determined separately, be it under non-steady-state conditions. Based on their experiments, they concluded that the role of the promoter is to enhance carbon monoxide dissociation, while the influence of the promoter oxide on the hydrogenation was small.

Possible reasons for the enhancement of carbon monoxide bond dissociation by adding a promoter oxide are: an electronic effect of the promoter oxide on the rhodium particle, or a direct effect of the promoter on the carbon monoxide bond strength, a participation of the promoter oxide in the dissociation of carbon monoxide.

In case of an electronic effect, the addition of the promoter will increase or decrease the electron density on the active metal and in this indirect way change the catalytic behaviour of the active metal. Especially in the case of alkali addition, this effect is invoked by numerous authors [55–63]. Addition of alkali is known to result in an increased electron density on the metal [62–64]. However, in our case, the shifts of the bands in the IR spectra were small and could be explained by the decrease of the dipole–dipole coupling due to a decreased carbon monoxide coverage. For ThO₂, the band of the linearly bonded carbon monoxide did not shift at all. These results suggest that there is not an electronic effect of the promoter oxides on the metal particles.

Mori et al. [4,64] proposed a mechanism as shown in Fig. 7A, in which the promoter oxide plays an active role in the carbon monoxide dissociation. They postulated an hydroxycarbene (M=CHOH) intermediate for C–O bond dissociation, based on an observed inverse H₂–D₂ isotope effect for carbon monoxide dissociation. A carbon monoxide molecule is adsorbed on the metal, forming the M=CHOH intermediate. A V³⁺-ion adjacent to the metal atom, to which the hydroxycarbene is attached, pulls the oxygen atom away from the

M=CHOH fragment, and forms a transition state that promotes the dissociation of carbon monoxide to $(\text{CH}_x)_{\text{ad}}$ and $(\text{OH})_{\text{ad}}$. Simultaneously V^{3+} is oxidized to V^{4+} . The $(\text{OH})_{\text{ad}}$ species on V^{4+} can be hydrogenated, forming water and V^{3+} . In this way the vanadium oxide promoter catalyzes the carbon monoxide dissociation by an oxidation–reduction cycle. A similar cycle is possible for the MoO-promoted catalysts.

For this model, it is necessary that the promoter oxide is positioned on top or at the perimeter of the rhodium metal particle and that a reduction–oxidation cycle is possible. For the ThO_2 -promoted catalysts, temperature programmed reduction studies did not provide any evidence for a reduction–oxidation cycle. Therefore the mechanism proposed by Mori et al. can not explain the promoter effect of ThO_2 .

The postulation of a hydroxycarbene fragment contrasts with conclusions drawn by Araki and Ponc [65,66]. They studied methanation over a Ni film. From ^{13}CO measurements they concluded that carbon monoxide methanation occurs by dissociation of carbon monoxide via a C_1 -intermediate. Isotopic transient measurements of Biloen et al. [67] also suggested that the intermediates in hydrogenation of carbon monoxide over Co, Ni and Ru catalysts have a carbidic character.

Burch and coworkers [68,69], Rieck and Bell [70,71] and Sachtler and coworkers [30,54,72] proposed a model based on the activation of carbon monoxide by the interaction of a promoter ion with the oxygen atom of a chemisorbed carbonyl (see Fig. 7B). The ions of an electropositive metal (the promoter ion) on the surface of a metal particle might provide sites at which carbon monoxide may be bonded with its carbon atom to a metal atom and with its oxygen atom to the promoter ion. This results in a weakened C–O bond, which shows up as a lowering of the carbon monoxide stretching frequency in IR spectroscopy. Frequency decreases in the order of 100 to 300 cm^{-1} are common for carbon- and oxygen-bonded carbonyl compounds and must be compared with frequencies at 1950–2130 cm^{-1} (linearly bonded carbon monoxide), 1850–1950 cm^{-1} (bridge-bonded carbon monoxide) and 1750–1900 cm^{-1} (C-bridging three metal atoms). Ichikawa et al. [53] and Sachtler [32] reported a band around 1530 cm^{-1} for carbon monoxide adsorbed on Mn^{2+} promoted rhodium catalysts, suggesting that carbon- and oxygen-bonded carbon monoxide is present. Of course, the vanadium and molybdenum ions can also pass through the reduction–oxidation cycle in this mechanism. The oxygen atom bonded to vanadium or molybdenum ions can oxidize these promoter ions after the carbon monoxide dissociation, and the oxidized promoter ion can be reduced by hydrogen atoms dissociated on the rhodium metal. However, such a reduction–oxidation cycle is not necessary.

For the ThO_2 -promoted catalysts a broad IR band between 1300 and 1750 cm^{-1} and a shoulder around 1700 cm^{-1} were seen, pointing to carbon- and oxygen-bonded carbon monoxide. Small amounts of ThO_2 positioned on the

rhodium metal particle will be responsible for this effect since the carbon monoxide:rhodium ratio did not decrease with increasing ThO_2 content. Kiennemann et al. [11] reported an absorption band at 1725 cm^{-1} for CeO_2 -promoted Rh/SiO_2 catalysts and assigned it to side-on adsorbed carbon monoxide.

No bands in the region below 1700 cm^{-1} were found in the infrared spectra of the MoO - and V_2O_3 -promoted catalysts used in this study. This does not fully exclude the model proposed by Sachtler et al. for these catalysts. The extinction coefficient for a carbon- and oxygen-bonded carbon monoxide molecule will be very small because such a carbon monoxide molecule is positioned (almost) parallel to the metal surface. As discussed by Pearce and Sheppard [73], the vibrations of a dipole parallel to the metal surface will be annihilated by its mirror image in the surface and therefore will have a very small extinction coefficient. Furthermore, the IR spectra have been measured after admission of only 10 Torr (1.3 kPa) carbon monoxide at room temperature and therefore we do not have information of the side-on bonded carbon monoxide under reaction conditions. Thirdly, Erley et al. [74] also observed the 1530 cm^{-1} band for carbon monoxide on a stepped nickel surface and showed that an increase in temperature to only 310 K resulted in a complete disappearance of the 1530 cm^{-1} band, indicating the rapid dissociation of this form of adsorbed carbon monoxide. The temperature in our FTIR apparatus is about 300–310 K and this might explain why we did not observe the side-bonded carbon monoxide for the MoO - and V_2O_3 -promoted catalysts.

CONCLUSIONS

Temperature programmed reduction studies showed that the molybdenum oxide and vanadium oxide promoters are coreduced with rhodium oxide. The results suggest the formation of a mixed oxide for these promoter oxides (Rh_2MoO_6 , RhVO_4). The TPR profiles of the ThO_2 -promoted catalysts show that ThO_2 can not be reduced under the conditions used. No indication has been found for the formation of a mixed rhodium thorium oxide, nor for any interaction between ThO_2 and Rh_2O_3 or rhodium.

Hydrogen and carbon monoxide chemisorption measurements indicated the coverage of the rhodium metal particles by patches of V_2O_3 and MoO . At higher promoter:rhodium ratios, hydrogen is also adsorbed on V_2O_3 and MoO and carbon monoxide is only adsorbed on MoO . For ThO_2 -promoted catalysts, no indication of a covering of the rhodium metal particle by patches of promoter oxide is found from the chemisorption measurements.

IR spectroscopy measurements showed that V_2O_3 decreased the amount of bridge-bonded and linearly bonded carbon monoxide, while MoO suppressed all forms of carbon monoxide adsorption. Thorium oxide mainly decreased the amount of bridge-bonded carbon monoxide. No indication of carbon- and oxygen-bonded carbon monoxide (carbon to metal and oxygen to promoter ion)

was found for the V_2O_3 - and MoO-promoted catalysts. IR spectra of the ThO_2 -promoted catalysts exhibited bands below 1750 cm^{-1} pointing to the formation of side-on bonded carbon monoxide.

All promoter oxides enhanced the carbon monoxide hydrogenation rate. The methanol formation rate was increased by MoO to a greater extent, probably via an intermediate bonded on molybdenum ions. Ethylene addition at 503 K and 0.15 MPa showed that the carbon monoxide insertion rate into ethylene decreased in the order unpromoted $> MoO > ThO_2 > V_2O_3$, while hydrogenation decreased in the order $MoO > ThO_2 > V_2O_3 > unpromoted$. The results suggest that carbon monoxide dissociation is rate limiting and that the main role of the promoter is to enhance the dissociation of carbon monoxide.

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