Preparation and characterization of vanadium oxide promoted rhodium catalysts
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Published in:
Applied Catalysis

DOI:
10.1016/S0166-9834(00)80591-6

Published: 01/01/1987

Document Version
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

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PREPARATION AND CHARACTERIZATION OF VANADIUM OXIDE PROMOTED RHODIUM CATALYSTS


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(Received 29 December 1986, accepted 4 March 1987)

ABSTRACT

The location of the promoter element in rhodium on alumina and silica catalysts promoted by vanadium oxide has been studied by various techniques. Our results prove that an intimate contact between the active component, rhodium, and the promoter, vanadium oxide, is present in most catalysts studied.

For the silica-supported systems, temperature programmed reduction and diffuse reflectance infrared spectroscopy pointed to the formation of a mixed oxide (RhVO\(_x\)) during calcination. Reduction of this oxide phase resulted in a vanadium oxide layer on top of the metal particle, as could be concluded from carbon monoxide chemisorption experiments. CO chemisorption was suppressed in the Rh/V\(_2\)O\(_5\)/SiO\(_2\) catalysts, while transmission electron microscopy showed that the rhodium particle size was not influenced by the addition of vanadium oxide. This indicates that the suppression of CO chemisorption is not due to a decrease of metal particle size, but due to covering of the metal particle. Infrared spectroscopy showed that the amount of linearly bonded and bridge-bonded CO was almost completely suppressed, while the amount of gem-dicarbonyl species remained unaffected. No suppression of hydrogen chemisorption was observed. From this and TPD experiments it could be concluded that hydrogen adsorption occurs both on the exposed Rh atoms, as well as on the vanadium oxide patches partly covering the surface Rh atoms, pointing to the formation of hydrogen bronzes.

Temperature programmed reduction experiments showed that RhVO\(_4\) was not formed in Rh/V\(_2\)O\(_5\)/Al\(_2\)O\(_3\) during calcination. For V/Rh < 1.0, Rh\(_2\)O\(_3\) and V\(_2\)O\(_5\) particles exist separately on the support, due to the strong interaction between V\(_2\)O\(_5\) and Al\(_2\)O\(_3\). Only for catalysts with a V/Rh value around 7.0 (near-monolayer of vanadium oxide on alumina), oxidation at 898 K resulted in the formation of RhVO\(_4\). For these catalysts, Rh\(_2\)O\(_3\) might be positioned on top of the vanadium oxide layer after calcination. Almost all adsorbed CO was present in the form of the gem-dicarbonyl species and only a minor suppression of CO adsorption was observed.

INTRODUCTION

Much attention has been paid to the effect of various promoters and supports on the activity and selectivity of group VIII metals in the hydrogenation of carbon monoxide [1-3]. It has been reported that V\(_2\)O\(_3\) has a significant effect on this reaction. Kikuchi et al. [4] reported that V\(_2\)O\(_3\) supported Ru catalysts exhibited high turnover frequencies, high selectivities for heavier hydrocarbons and high
olefin/paraffin ratios relative to Ru/Al₂O₃ and other supported ruthenium catalysts. Mori et al. [5], using pulse surface reaction rate analysis, showed that addition of vanadium oxide greatly increased the rate of C-O bond dissociation of adsorbed CO in the methanation on Ru/Al₂O₃. Ichikawa et al. [6] and Van der Lee et al. [7] reported high selectivities to C₂-oxygenates using V₂O₃ supported Rh catalysts.

Like TiO₂-, Nb₂O₅- and Ta₂O₃-supported noble metal catalysts, V₂O₃-supported metal catalysts exhibit a significant suppression of hydrogen and carbon monoxide chemisorption after reduction at temperatures above 700 K [8-10]. Nowadays it is generally accepted that the high-temperature reduction causes the formation of a lower oxide that can diffuse onto the metal and spread over its surface (covering-model) [11-18]. These small patches of suboxide cause a suppression of the chemisorption capacity of the metal. Hicks et al. [19] studied the adsorption of H₂ and CO on La₂O₃-supported Pd catalysts and observed a suppression of the CO chemisorption after reduction at 573 K (low temperature reduction), even though La₂O₃ has not been reported as an SMSI support. In contrast to the CO chemisorption, the hydrogen chemisorption was not suppressed. The suppression of CO adsorption was attributed to patches of partially reduced support material, LaOₓ, already transferred to the surface of the Pd crystallites during catalyst preparation. The absence of a suppression of H₂ adsorption on Pd/La₂O₃ indicated that H₂ adsorption occurred on the exposed Pd surface atoms as well as on the LaOₓ patches covering the balance of the surface Pd atoms. Thus, in this case, the covering is not caused by the high reduction temperature, but by the fact that the overlayer of support oxide is already formed during catalyst impregnation.

In our laboratory we have studied the formation of C₂-oxygenates from synthesis gas at elevated pressures. Rh/V₂O₃ is of interest in this respect [6,7], but V₂O₃ has the disadvantage of a relatively low surface area (< 10 m² g⁻¹) and of a low mechanical and chemical stability. Therefore, we chose the route of promoting Rh/SiO₂ and Rh/Al₂O₃ systems with vanadium oxide in order to combine the good structural properties of Al₂O₃ and SiO₂ (high surface area, high pore volume, high mechanical and chemical stability) with the good selectivity properties of V₂O₃. In this publication we will describe the results of the characterization of the catalysts via a number of techniques, like temperature programmed reduction, hydrogen and carbon monoxide chemisorption, hydrogen desorption, transmission electron microscopy and infrared spectroscopy of adsorbed CO. In a subsequent paper [20] we will report the catalytic performance of the catalysts in the synthesis gas reaction.

**EXPERIMENTAL**

**Catalyst preparation**

As supports we used γ-Al₂O₃ (Ketjen, type 000-1.5E, surface area 200 m² g⁻¹,
pore volume 0.6 ml g\(^{-1}\)), SiO\(_2\) (Grace, type 113, surface area 360 m\(^2\) g\(^{-1}\), pore volume 1.1 ml g\(^{-1}\)) and V\(_2\)O\(_3\), obtained by reduction of V\(_2\)O\(_5\) (Merck, p.a.) at 1100 K in pure hydrogen for 2 h (heating rate 10 K min\(^{-1}\)) and subsequent passivation. This resulted in V\(_2\)O\(_3\) with a low surface area (3 m\(^2\) g\(^{-1}\), pore volume 0.32 ml g\(^{-1}\)). Vanadium oxide promoted SiO\(_2\) and Al\(_2\)O\(_3\) were prepared by incipient wetting these supports with an aqueous solution of NH\(_4\)VO\(_3\) (Merck, p.a.), drying at 395 K and calcining at 723 K (3 h). In this way, supports with a varying amount of vanadium oxide were obtained. We also tried to prepare a monolayer of vanadiumoxide on Al\(_2\)O\(_3\), as described in the literature for vanadium- and molybdenum-oxide monolayers on alumina [21-24], by batch adsorption of NH\(_4\)VO\(_3\). During the adsorption the pH was kept constant at 4 by adding H\(_2\)O\(_3\). In this way we made a V\(_2\)O\(_5\)/Al\(_2\)O\(_3\) support with 5.6 and 6.7 wt% V, the latter by two sequential adsorption steps. Drying and calcining were carried out as described above.

The catalysts were prepared by the incipient wetness method using an aqueous solution of Rh(NO\(_3\))\(_3\) (pH = 2.5, Drijfhout, Amsterdam), and were subsequently dried in air at 395 K for 16 h (heating rate 2 K min\(^{-1}\)). To remove nitrogenous residues from the precursor, the catalysts were calcined at 723 K for 3 h. Rhodium content was always around 1.5 wt%.

The following notations will be used: Rh/V\(_2\)O\(_3\)/SiO\(_2\) for silica supported rhodium catalysts promoted with vanadium oxide, Rh/V\(_2\)O\(_3\)/Al\(_2\)O\(_3\) for alumina supported rhodium catalysts promoted with vanadium oxide, and Rh/V\(_2\)O\(_3\) for vanadium oxide supported rhodium catalysts.

### Characterization techniques

Volumetric hydrogen and carbon monoxide chemisorption measurements were performed in a conventional glass system at 298 K as described in [25]. Before measuring the H\(_2\) and CO chemisorption the catalysts were reduced at 523 K or 723 K (heating rate 8 K min\(^{-1}\)) for 1 h and evacuated for 0.5 h, at the temperature indicated under RESULTS, to an ultimate vacuum of 10\(^{-2}\) Pa at the catalyst sample. The total amount of chemisorbed H atoms or CO molecules was obtained by extrapolating the linear part of the isotherm to zero pressure while correcting for the extrapolated chemisorption values of the bare support [26,27]. In a recent article we extensively discussed the method used (admission at 473 K, no distinction between reversibly and irreversibly adsorbed hydrogen, extrapolation to zero pressure) [28]. Al\(_2\)O\(_3\) and V\(_2\)O\(_3\)/Al\(_2\)O\(_3\) were found to adsorb CO, while SiO\(_2\), V\(_2\)O\(_3\)/SiO\(_2\) and V\(_2\)O\(_3\) did not adsorb CO. None of the supports adsorbed hydrogen.

The reduction behaviour of the supports and the reduction, oxidation and hydrogen desorption behaviour of the catalysts were studied by temperature programmed reduction (TPR), oxidation (TPO) and desorption (TPD), using the apparatus described extensively in ref. [29,30]. During TPR and TPO experiments, the heating rate was 5 K min\(^{-1}\), while during TPD experiments the heating rate was 15 K min\(^{-1}\). A final reduction temperature of 1073 K and 898 K
was used for the supports and catalysts, respectively. In a standard experiment, a catalyst was characterized by a TPR of the calcined catalyst, followed by a TPO of the reduced catalyst, followed by a TPR of the oxidized system. TPD experiments were always preceded by a TPR. We have described the sequence of experiments used during the temperature programmed reactions elsewhere [25,30].

Carbon monoxide adsorption was also studied by infrared spectroscopy. A self-supporting catalyst wafer was placed in an evacuable glass reactor (ultimate pressure 5 × 10⁻³ Pa). The catalyst was reduced in-situ at 543 K in flowing H₂ (heating rate 5 K min⁻¹) for 0.5 h and evacuated at this temperature for 1 h unless stated otherwise. All gases were purified over molecular sieves and a BTS column. After cooling down to room temperature, small doses of CO were introduced into the reactor, and the infrared spectrum was recorded after each dose. All spectra were recorded at 2 cm⁻¹ resolution using a Bruker IFS 113V Fourier transform infrared spectrometer, equipped with a HgCdTe detector. A satisfactory signal-to-noise ratio was obtained by adding 128 interferograms. From these spectra information about the relative amount of adsorbed carbon monoxide and the way in which CO is adsorbed on the metal particles was obtained.

Diffuse reflectance infrared spectroscopy was used to study V=O stretch bands. For that purpose, the Bruker IFS 113V Fourier transform spectrometer was equipped with a diffuse reflectance unit (Harrick). Spectra were recorded at 4 cm⁻¹ resolution and 8192 interferograms we added to obtain a satisfactory signal-to-noise ratio. The samples were carefully ground and diluted in KBr (1:10). The same amount of sample was used for each measurement.

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 prepared by putting a few droplets of a suspension of the catalyst in methanol on a 'holey' carbon coated Formfar film. Similar images were obtained when the suspension of the catalyst was put in an ultrasonic bath or by dry mounting of the catalyst. The specimens were examined with a Jeol 200CX, operating at 200 kV. Very small particles (<1 nm) could be observed best with an objective diaphragma of about 7 nm⁻¹ and a focus very close to zero. Especially when the support is crystalline, small metal particles are very difficult to see and to distinguish from artifacts, due to overlap of several support particles. In such cases only by comparison of images taken at different defocus values artifacts can be discriminated from metal particles.

The vanadium content of the supports was determined by means of atomic adsorption spectrometry, while the rhodium content was determined colorimetrically.
FIGURE 1: Temperature programmed reduction profiles of V$_2$O$_5$ (a), passivated V$_2$O$_3$ (b), Rh/V$_2$O$_3$ after drying at 395 K (c), and Rh/V$_2$O$_5$ after oxidation at 898 K (d). Note that the final reduction temperature for (a) and (b) was 1073 and for (c) and (d) was 898 K.

RESULTS

A. Rh/V$_2$O$_3$

In order to compare the results of vanadium oxide promoted Rh/SiO$_2$ and Rh/Al$_2$O$_3$ catalysts with Rh/V$_2$O$_3$, we started to study this system by temperature programmed reduction and hydrogen and carbon monoxide chemisorption.

In Figure 1a the reduction profile of V$_2$O$_5$ is presented. This profile is characterized by four different reduction peaks at 943, 973, 1013 and above 1073 K. These peaks are caused by the following reduction steps

$$V_2O_5 \rightarrow \frac{1}{3} V_6O_{13} \rightarrow V_2O_4 \rightarrow \frac{1}{3} V_6O_{11} \rightarrow V_2O_3$$

as shown by Bosch et al. [31] using X-ray diffraction. The final oxide formed in this reduction is V$_2$O$_3$, as can be calculated from the amount of hydrogen consumed during the reaction.

The reduction profile of reduced and passivated vanadium oxide, used as support for the vanadium oxide supported rhodium catalysts, shows one reduction peak around 923 K (cf. Figure 1b), caused by the reduction of the oxidized vanadium oxide surface layer, formed during the passivation and storage in air. Longer storage caused a deeper oxidized vanadium oxide layer (freshly prepared: 0.15 % V$^{5+}$, after one month storage: 2.2 % V$^{5+}$).

In Figure 1c the TPR profile of Rh/V$_2$O$_3$ is shown. This system is prepared by incipient wetting of the reduced and passivated vanadium oxide and by subsequent
drying at 395 K. The hydrogen consumption starts at 473 K and has a maximum at 553 K. Reduction is complete at 593 K. Assuming that rhodium is reduced from the 3+ valency to zero valency and that vanadium is reduced from V^{5+} to V^{3+}, one can calculate from the amount of hydrogen consumed that after drying about 10% of the vanadium was in the 5+ valency state.

The TPR profile after TPO (oxidation up to 898 K) is presented in Figure 1d. The Rh/V_2O_5 system starts to reduce at 493 K and has a maximum at 573 K. Reduction peaks are also observed above 673 K and these must be due to the reduction of the fully oxidized vanadium oxide support, as judged from the amount of hydrogen consumed during the reduction.

Hydrogen chemisorption measurement of 1.5 wt% Rh/V_2O_3, reduced and evacuated at 523 K, resulted in a very high H/Rh value (3.8). Reduction at a higher temperature resulted is a strong decrease of the H/Rh value, 0.09 and 0.00 after reduction and evacuation at 723 and 823 K, respectively. The CO/Rh value after reduction and evacuation at 523 K was 0.36.

B. Rh/V_2O_3/SiO_2

Temperature programmed reduction. TPR profiles of V_2O_5/SiO_2 supports (Figure 2a,b) show that the major part of the vanadium oxide is reduced more easily when supported on SiO_2 than when unsupported, and that the characteristic peaks of the unsupported V_2O_5 are not present (compare with Figure 1a). The reduction starts around 673 K, has a maximum hydrogen consumption at 773-823 K, and is (almost) complete at the end of the temperature ramp (1073 K). The amount of hydrogen consumed during the TPR (H_2/V = 1.0) indicates that also in the case of V_2O_5/SiO_2 supports, V^{5+} is reduced to V^{3+}. Almost no reduction was observed around 1073 K. This reduction behaviour indicates that no large crystalline V_2O_5 particles are formed, as is also supported by XRD. No crystalline V_2O_5 phase could be detected by this technique in the V_2O_5/SiO_2 samples.

Figures 2c-h show the TPR profiles of the Rh/V_2O_5/SiO_2 catalysts after calcination. A pronounced effect of the vanadium loading is observed. The Rh/SiO_2 system without vanadium (Figure 2c) starts to reduce at the beginning of the temperature ramp and has a maximum at 363 K. Reduction is complete at 463 K. A higher vanadium loading shifts the whole reduction profile. It causes an increase in the temperature at which the reduction is starting, a shift to higher temperatures of the peak maximum and an increase in the temperature at which the reduction is complete. For vanadium loadings above V/Rh = 1, an additional hydrogen consumption is observed above 573 K. Also in this case total hydrogen consumption matches the calculated values assuming the following reduction reactions: V^{5+} → V^{3+} and Rh^{3+} → Rh^{0}. Thus, for the silica supported catalysts, rhodium oxide and part of the vanadium oxide are reduced around 373 K, and part of the vanadium oxide content is reduced at higher temperatures (673-898 K).
FIGURE 2: Temperature programmed reduction profiles of the silica supported systems.

a. 0.8 wt% V$_2$O$_5$/SiO$_2$

b. 3.6 wt% V$_2$O$_5$/SiO$_2$

c-h. TPR after calcination of Rh/V$_2$O$_5$/SiO$_2$ catalysts

i-n. TPR after oxidation at 898 K of Rh/V$_2$O$_5$/SiO$_2$ catalysts.

Final reduction temperature 1073 K for a, and b. and 898 K for c-n.

The TPR profiles of the Rh/V$_2$O$_5$/SiO$_2$ catalysts after TPO (oxidation up to 898 K) are presented in Figure 2i-n. Also in this case, a shift of the reduction process to higher temperatures is observed when the vanadium loading is increased. In contrast to the TPR profiles after calcination at 723 K (Figure 2c-h), now several reduction peaks are observed. Rh/SiO$_2$ starts to reduce at the beginning of the temperature ramp and has a maximum hydrogen consumption at 323 K. The system with V/Rh = 0.12 is characterized by an additional peak around 387 K at the cost of the peak at 323 K. Further increase of the vanadium loading causes a further decrease of the hydrogen consumption at the beginning of the temperature ramp up to 323 K and a further increase of the hydrogen consumption between 373 and 473 K. In the TPR profiles of catalysts with V/Rh $>$ 1.0 a third hydrogen consumption peak is observed around 473 K. For these high vanadium loadings additional hydrogen consumption is measured above 673 K, with a peak around 773 K, like in V$_2$O$_5$/SiO$_2$ (cf. Figure 2b).
Temperature programmed desorption of hydrogen. Hydrogen TPD profiles for Rh/V₂O₅/SiO₂ catalysts with different V/Rh ratios are presented in Figure 3. After reduction at 523 K, hydrogen desorption is more difficult for catalysts with a high V/Rh ratio (see drawn line in Figure 3). From these TPD profiles we can conclude that after reduction and evacuation at 523 K all hydrogen will not be removed. Especially the catalysts with a high V/Rh ratio will still contain hydrogen. This has important implications for the H₂ and CO chemisorption measurements. Figure 3 shows that even evacuation at 723 K after reduction at 723 K will not remove all hydrogen (dashed line), because after a high reduction temperature part of the hydrogen is bonded strongly and only desorbs around 823 K. The high temperature desorption peak is most important for the highest vanadium loading (V/Rh = 4.5). The total amount of desorbed hydrogen was not influenced by the reduction temperature and the H/Rh ratio, calculated from these TPD profiles, slightly increased with increasing vanadium content.

H₂ and CO chemisorption measurements. Results of the hydrogen and carbon monoxide chemisorption measurements for the SiO₂ supported systems are presented in Figure 4. After reduction and evacuation at 523 K (low temperature reduction) the following features are observed (see Figure 4a1,b1). Up to V/Rh = 1.0, the hydrogen and carbon monoxide chemisorption capacity is strongly suppressed by addition of vanadium oxide. Further addition of vanadium oxide does not change the CO/Rh values and causes a gradual increase in the H/Rh values. After reduction and evacuation at a higher temperature (723 K), a similar behaviour is observed (see Fig. 4a2,b2), the suppression of H/Rh and CO/Rh being even larger.
FIGURE 4: H₂ and CO chemisorption measurements of the 1.5 wt% Rh/V₂O₃/SiO₂ catalysts after several pretreatment procedures, as a function of the V/Rh ratio.

a1. H/Rh after reduction at 523 K and evacuation at 523 K
a2. H/Rh after reduction at 723 K and evacuation at 723 K
a3. H/Rh after reduction at 523 K and evacuation at 723 K
b1. CO/Rh after reduction at 523 K and evacuation at 523 K
b2. CO/Rh after reduction at 723 K and evacuation at 723 K
b3. CO/Rh after reduction at 523 K and evacuation at 723 K

However, as shown by the TPD experiments, during the evacuation at the reduction temperature preceding the chemisorption measurements (at 523 K as well as 723 K), the hydrogen put on the catalyst during reduction is not removed completely and this effect is most important for the catalysts with high V/Rh ratio. The observed decrease of the H/Rh and CO/Rh values with increasing V/Rh ratio (cf. Figure 4a,b) might be caused by this effect. We therefore performed chemisorption measurements after reduction at 523 K and evacuation at 723 K. The H/Rh and CO/Rh values obtained after this pretreatment are presented in Figures 4a3 and 4b3. H/Rh was more or less constant up to V/Rh = 1.0, and then increased with increasing vanadium content. However, the CO chemisorption still decreased with increasing V/Rh up to V/Rh = 1.0, although not to the same extent as in the case of evacuation at the reduction temperature.

Of course, it is important to check whether oxidation has taken place during the evacuation at a temperature above the final reduction temperature. During the high temperature evacuation, water formed by dehydration of the silica
support might oxidize the rhodium and cause an increased hydrogen chemisorption, because in that case part of the hydrogen will be used to re-reduce the rhodium oxide. Therefore, after reduction at 523 K and evacuation at 723 K, oxygen was added to the catalyst at 723 K. The amount of oxygen consumed was 1.52 O/Rh for 1.5 wt% Rh/SiO₂, proving that Rh was in the zero valent state after reduction at 523 K and evacuation at 723 K.

The hydrogen and carbon monoxide chemisorption measurements thus demonstrate that the vanadium oxide suppresses the carbon monoxide chemisorption, while it promotes the hydrogen chemisorption. Because suppression of CO/Rh can be caused by either an increase of the particle size or by an influence of the vanadium oxide on the chemisorption capacity of the rhodium metal (by a covering and/or electronic effect), we examined the rhodium particle size by TEM.

Transmission electron microscopy. Figure 5 presents the metal particle size distribution for several Rh/V₂O₅/SiO₂ catalysts. A comparison of the Rh/V₂O₅/SiO₂ catalysts with different V/Rh ratios showed that all catalysts exhibited rhodium particles with an average particle size of 20 ± 2 Å. These data should be treated with some caution since electron microscopy, by its nature, sees only a limited part of the total catalyst surface. However, after analyzing several micrographs of each system, we feel confident that the systems studied do not differ significantly in their particle size distribution (cf. Figure 5). Spacings are observed in some of the particles and they point to the existence of Rh metal. The reduced and passivated catalysts, used for the TEM measurements, can easily be re-reduced (TPR peak around 353 K) by the electron beam in the microscope.

Thus, the observed decrease in CO/Rh with increasing V/Rh ratio cannot be caused by differences in metal particle size.

Infrared spectroscopy of adsorbed CO. Chemisorption of carbon monoxide at 298 K was also studied by infrared spectroscopy, in order to determine the binding sites for CO and to measure the CO adsorption capacity of the exposed rhodium. Spectra for CO adsorbed at 298 K on 1.5 wt% Rh/SiO₂, reduced in-situ at 523 K and evacuated at 673 K (maximum temperature of the cell) are shown in Figure 6. Each spectrum was recorded after adding a dose of CO to the sample chamber containing the catalyst disc. Estimates of the amounts of CO in the cell, relative to the amount of rhodium are presented in the caption to Figure 6. The infrared spectrum of CO adsorbed on Rh/SiO₂ (T_ad = 298 K, CO/Rh = 250, Figure 6f) exhibited bands at 2092, 2068, 2022 and 1859 cm⁻¹. Following the original assignments of Yang and Garland [32], the band at 1859 cm⁻¹ is attributed to bridge-bonded CO (B), the band at 2068 cm⁻¹ to linearly bonded CO (L), and the bands at 2022 (T₁) and 2092 cm⁻¹ (T₂) to the symmetric and antisymmetric stretchings of the gem-dicarbonyl species (two CO molecules bonded to one rhodium cation). Recently, the existence and behaviour of these different structures for several supported Rh catalysts have been studied [32-40].
FIGURE 5: Rhodium particle size distributions for Rh/V₂O₅/SiO₂ catalysts with varying V/Rh ratio. N = number of particles used to determine particle size distribution. D = mean metal particle size.

FIGURE 6: Infrared spectra of CO adsorbed on 1.5 wt% Rh/SiO₂ at 298 K, using an increasing dose of CO. (Reduction temperature 523 K, evacuation temperature 673 K). The approximate amounts of CO expressed as CO/Rh were: 0.05 (a), 0.2 (b), 0.8 (c), 2 (d), 20 (e) and 250 (f).

As is shown in Figure 6, the first aliquot of CO causes the B and L band to appear at 1800 and 2043 cm⁻¹, respectively. Addition of more CO leads to a large increase of the B and L band, and to the appearance of the shoulders at 2024 and 2090 cm⁻¹ originating from the twin-species (T₁ and T₂). Only a modest increase in the band frequencies of the B and L bands is observed: ΔO_B = 59 cm⁻¹ and ΔO_L = 25 cm⁻¹. This increase has been ascribed to the fact that at higher CO coverage there is an increase in the dipole-dipole coupling between CO molecules and consequently an increase in the CO stretching frequency [41]. The shifts in band frequencies of the twin species T₁ and T₂ were negligible, as to be expected for CO molecules bonded to isolated Rh⁺ cations.

The infrared spectrum of CO adsorbed on Rh/V₂O₅/SiO₂ was dramatically influenced by the presence of vanadium oxide, as shown in Figure 7. With increasing vanadium content, the amounts of bridge-bonded and linearly bonded CO, B and L respectively, strongly decreased and almost disappeared for V/Rh = 4.5. The bands, due to the dicarbonyl species, T₁ and T₂, remain about constant.

In order to compare the amounts of adsorbed CO for the systems with different...
FIGURE 7: The infrared spectra of CO adsorbed on 1.5 wt% Rh/V$_2$O$_5$/SiO$_2$ catalysts with varying V/Rh ratios (adsorption at 298 K, P$_{CO} = 10$ Torr, reduction temperature 523 K, evacuation temperature 673 K).

V/Rh ratios, the adsorbance spectra were integrated:

$$A = \frac{1}{w_c} \int_{1500}^{2200} 10 \log (I_0/I) \, d\nu$$

where $10 \log (I_0/I)$ is the adsorbance and $w_c$ is the amount of catalyst present in the cross-section of the beam. The A-values were normalized to the A-value of the Rh/SiO$_2$ catalyst (V/Rh = 0). The results are presented in Figure 8. A decrease of the A-value with increasing V/Rh ratio is observed. Of course, CO/Rh values cannot be calculated from these A-values because of differences in absorption coefficients for the different adsorption forms of carbon monoxide. Duncan et al. [42] reported the following infrared absorption coefficients for Rh/AI$_2$O$_3$: $\varepsilon$(L) = 26 $10^6$, $\varepsilon$(B) = 85 $10^6$, $\varepsilon$(T$_1$,symm) = 74 $10^6$ and $\varepsilon$(T$_2$,asymm) = 128 $10^6$ cm mol$^{-1}$ for the linearly bonded and bridge-bonded CO, and symmetrical twin and asymmetrical twin structure, respectively. We could not determine the integrated areas of the adsorption bands separately and therefore can only use the A-values qualitatively. At high V/Rh values, the gem-dicarbonyl structure is the most predominant form, and this structure has the highest $\varepsilon$-value. Therefore the real decrease in the CO/Rh ratio is higher than the observed decrease in the relative A-value (see Figure 8). The trend is similar to the trend observed for the CO chemisorption measurements (Figure 4). Thus, infrared spectroscopy shows that CO/Rh decreases along with increasing vanadium oxide content and that this decrease originates mainly from a decrease of the amount of linearly bonded and bridge-bonded CO. The amount of CO bonded in the twin structure remains almost constant.

Diffuse reflectance infrared spectrometry. The diffuse reflectance infrared spectra of V$_2$O$_5$, V$_2$O$_5$/SiO$_2$ (2.2 wt% V) and Rh/V$_2$O$_5$/SiO$_2$ (2.2 wt% V, 4.5 wt% Rh, calcined at 723 K) in the region of V-O stretching frequencies are presented in
FIGURE 8: Relative integrated areas of the infrared absorbance spectra of the vanadium oxide promoted 1.5 wt% Rh/SiO₂ catalysts relative to that of unpromoted 1.5 wt% Rh/SiO₂
a. after reduction at 523 K and evacuation at 523 K
b. after reduction at 523 K and evacuation at 673 K.

FIGURE 9: Diffuse reflectance infrared spectra (Kubelka-Munk units versus wavenumber) of V₂O₅ (a), V₂O₅/SiO₂, 2.2 wt% V (b) and Rh/V₂O₅/SiO₂, 2.2 wt% V, 4.5 wt% Rh, calcined at 723 K (c).

Figure 9. For V₂O₅/SiO₂ and V₂O₅ bands around 1010 and 920 cm⁻¹ are observed. The band around 1010 cm⁻¹ is ascribed to the V-O stretching vibration of V₂O₅, the band at 920 cm⁻¹ might be due to reduced vanadium oxide species like V₂O₄ [43,44]. Partial reduction of V₂O₅ at the surface of the sample was observed by a change in colour, and was a result of the fact that the infrared spectra were recorded in vacuum. For the Rh/V₂O₅/SiO₂ sample, the intensity of the band at 1010 cm⁻¹ dramatically decreased and the band at 920 cm⁻¹ completely disappeared, although the same amount of catalyst was present in the sample holder.
C. Rh/V₂O₅/Al₂O₃

Temperature programmed reduction. We attempted to prepare a monolayer of vanadium oxide on the alumina support by adsorbing metavanadate at pH = 4 (using HNO₃). This resulted in a 5.6 wt% V loading. Calcination of this system followed by a second adsorption step resulted in a 6.7 wt% V loading. Assuming an area of 10.3 Å² per VO₂.₅ unit [4b], one can calculate that 6.7 wt% V only occupies about 40% of the support surface. An explanation for a sub-maximum coverage is that during the preparation step the metavanadate is only adsorbed on one type of OH-group of the alumina. Evidence for this will be presented in a subsequent paper [20]. In Figure 10a the TPR profile of the 6.7 wt% V₂O₅/Al₂O₃ support after calcination is presented. The reduction of the vanadium oxide already starts around 573 K, and has a maximum around 773 K. Some extra hydrogen consumption is observed around 1023 K. With XRD no crystalline V₂O₅ phase could be detected in this support.
FIGURE 11: H₂ (●) and CO (○) chemisorption measurements of the 1.5 wt% Rh/V₂O₃/Al₂O₃ catalysts after reduction at 523 K and evacuation at 723 K, as a function of the V/Rh ratio.

FIGURE 12: Infrared spectrum of adsorbed CO on 1.5 wt% Rh/Al₂O₃ (a), and 1.5 wt% Rh/V₂O₃/Al₂O₃ (V/Rh = 7.0) (b), after reduction at 523 K and evacuation at 673 K (P₉₀ = 10 Torr, adsorption at 298 K).

The reduction profiles of the Rh/V₂O₃/Al₂O₃ catalysts after calcination (Figure 10b-e) are all similar. Hydrogen consumption starts at the beginning of the temperature ramp (298 K) and has a maximum at 415-442 K. The amount of hydrogen consumed during the TPR run matches the theoretical value when assuming reduction of Rh³⁺ to Rh⁰ and of V⁵⁺ to V³⁺. For the systems with a high vanadium oxide loading, hydrogen consumption is also observed at temperatures above 673 K, the temperature region where reduction is observed for V₂O₅/Al₂O₃ (cf. Figure 10a). In contrast with the first TPRs (Figure 10b-e), in the TPR profiles obtained after oxidation up to 898 K during TPO (Figure 10f-h), an influence of the vanadium loading on the reduction temperature is observed for catalysts with a high V/Rh ratio. The systems with a higher vanadium loading exhibit a higher reduction temperature, as was also observed for the silica-supported systems after calcination.

H₂ and CO chemisorption, infrared of adsorbed CO. The results of the hydrogen and carbon monoxide chemisorption measurements of the Rh/V₂O₃/Al₂O₃ systems are presented in Figure 11. CO/Rh values decreased only slightly with increasing vanadium content, in contrast to those for the Rh/V₂O₃/SiO₂ catalysts. The H/Rh ratio is constant up to V/Rh = 1.0, but systems with high V/Rh ratios exhibit very high H/Rh ratios, as was also measured for the Rh/V₂O₃ catalyst.
after a low temperature reduction. Rhodium particles were not observed by TEM in any catalyst, pointing to a particle size less than 8 Å. The infrared spectra of Rh/Al₂O₃ and Rh/V₂O₅/Al₂O₃ with V/Rh = 7.0 are presented in Figure 12. Also in this case, the bridge-bonded and linearly bonded CO were suppressed by the presence of vanadium oxide, while the twin species were favoured. The Rh/Al₂O₃ catalyst already had more twin-adsorbed CO than the Rh/SiO₂ catalyst. A minor peak at 2181 cm⁻¹ was observed for the vanadium oxide promoted system and may be attributed to CO bonded to Rh(III) [36].

DISCUSSION

Temperature programmed reduction.

The TPR profiles of silica- and alumina-supported vanadium oxide exhibited only one prominent hydrogen consumption maximum. This contrasts with the reduction behaviour of bulk V₂O₅, where several reduction steps can be distinguished [31]. Single peaks were also observed for titania-supported monolayers of V₂O₅ by Van Hengstum et al. [46] and Bond et al. [47], and for silica- and alumina-supported vanadium oxide by Kijenski et al. [48] and Roozeboom et al. [49]. The appearance of only one reduction peak suggests the presence of small amorphous vanadium oxide particles. In such particles no shear structures like V₆O₁₃ and V₆O₁₁ can be formed and therefore the reduction process proceeds in one step. However, taking into account the limited resolution of TPR measurements in the systems under study, the appearance of only one reduction peak does not decisively prove that the reduction occurs in a single step [48]. Nevertheless, it can be concluded that the supported vanadium oxide exhibits a completely different reduction behaviour than bulk V₂O₅. Combining this with the results of XRD measurements, we can confidently conclude that large crystalline V₂O₅ particles are absent.

Temperature programmed reduction profiles of the calcined Rh/V₂O₅ and Rh/V₂O₅/SiO₂ systems suggest that an intimate contact exists between the vanadium oxide promoter and the rhodium metal particles even at a low V/Rh ratio. The rhodium facilitates the reduction of the vanadium oxide, i.e. the reduction shifts to a lower temperature, and vanadium oxide hampers the reduction of rhodium oxide, i.e. its reduction temperature shifts to a higher value. The first effect could be explained by hydrogen spillover. However, the second cannot be explained by hydrogen spillover and proves that rhodium and vanadium oxide are in intimate contact in the Rh/V₂O₅/SiO₂ catalysts after calcination at 723 K. This effect is even more pronounced in the profiles of the second TPR (after oxidation at 898 K). In the profiles of the catalysts with low V/Rh values, one can even distinguish a peak due to the reduction of "free" rhodium oxide and a peak due to the reduction of rhodium oxide and vanadium oxide in close contact. The peak of the free rhodium oxide diminishes with increasing V/Rh ratio.

All this can be understood by assuming that a mixed oxide is formed. A mixed oxide of Rh₂O₃ and V₂O₅, RhVO₄, is known to exist and can be formed by heating
Rh$_2$O$_3$ and V$_2$O$_5$ under oxygen atmosphere at 923 K [50]. This temperature is higher than our calcination temperature (723 K), but surface reactions are known to proceed at lower temperatures than bulk reactions. This also clarifies the difference between the first TPR after calcination at 723 K and the second TPR after oxidation at 898 K. During the high temperature oxidation well defined phases of Rh$_2$O$_3$ and RhVO$_4$ are formed, reflected by distinct reduction peaks in the second TPR. For V/Rh > 1.0 a third hydrogen consumption peak around 453 K and a fourth consumption peak around 773 K can be observed. The third peak might be caused by the reduction of a mixed oxide with V/Rh > 1.0, like Rh$_2$V$_4$O$_{13}$, or by V$_2$O$_5$ layers positioned on top of the RhVO$_4$. The fourth reduction peak occurred around the temperature where V$_2$O$_5$/SiO$_2$ reduces (cf. Figure 2a,b) and must be caused by the reduction of V$_2$O$_5$ that is not in intimate contact with rhodium.

Although the assumption of the formation of a mixed oxide seems plausible, on the basis of the TPR profiles we cannot exclude that V$_2$O$_5$ is positioned on the nucleation sites of the reduction process of Rh$_2$O$_3$, or that V$_2$O$_5$ totally covers the Rh$_2$O$_3$. Furthermore we also cannot exclude that part of the V$_2$O$_5$ is positioned between the Rh$_2$O$_3$ particle and the SiO$_2$ support. However, additional evidence for the formation of a mixed oxide is obtained from the diffuse reflectance infrared spectrometry measurements. In the IR spectrum of Rh/V$_2$O$_5$/SiO$_2$ (calcined at 723 K, V/Rh = 0.9) almost no V-O stretching bands were observed (Figure 9c), pointing to the absence of "free" V$_2$O$_5$. This suggests that V$_2$O$_5$ and Rh$_2$O$_3$ formed a chemical compound. Bands of RhVO$_4$ have been reported below 900 cm$^{-1}$ [50]. In this frequency region it was impossible to measure the infrared spectrum because of the strong absorption bands of SiO$_2$ and the insensitivity of the detector.

The present study clearly showed that after calcination at 723 K an intimate contact exists between the V$_2$O$_5$ promoter and the Rh$_2$O$_3$ particle, most probably in the form of a mixed oxide (RhVO$_4$). A schematic representation of this situation is presented in Figure 13a. For V/Rh < 1, after calcination and oxidation distinct Rh$_2$O$_3$ and RhVO$_4$ particles exist. For V/Rh > 1, V$_2$O$_5$ and mixed oxide particles like RhVO$_4$ are present on the support.

For the 1.5 wt% Rh/V$_2$O$_5$ catalyst, the first reduction peak is shifted to even higher temperatures than in the case of Rh/V$_2$O$_5$/SiO$_2$. This might be due to a covering of RhVO$_4$ by several layers of V$_2$O$_5$.

The first TPRs of the alumina-supported vanadium oxide promoted systems show that rhodium facilitates the reduction of vanadium oxide, but that the reduction of rhodium is not hampered by the presence of vanadium oxide. For the Rh/V$_2$O$_5$/Al$_2$O$_3$ catalysts with V/Rh < 1, even after oxidation at 898 K no hampering of the reduction of Rh$_2$O$_3$ was observed. We conclude that in this case the intimate contact between Rh$_2$O$_3$ and V$_2$O$_5$ in the form of a mixed oxide does not exist. Hydrogen spillover can explain the co-reduction of Rh$_2$O$_3$ and V$_2$O$_5$. In agreement with this, the influence of V$_2$O$_5$ on the catalytic activity of Rh/Al$_2$O$_3$ for catalysts with V/Rh < 1 was negligible [20]. Thus, at least for V/Rh < 1, V$_2$O$_5$
FIGURE 13: 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).

and Rh$_2$O$_3$ particles exist separately on the Al$_2$O$_3$ support. During the impregnation of vanadium and rhodium, ammonium metavanadate and rhodium nitrate complexes rapidly adsorb on distinct sites on the alumina surface and, after calcination, these will result in Rh$_2$O$_3$ and V$_2$O$_5$ particles. The NH$_4$VO$_3$ and Rh(NO$_3$)$_3$ complexes do not adsorb on SiO$_2$ and therefore a mixed oxide can be formed on that support.

For Rh/V$_2$O$_5$/Al$_2$O$_3$ with V/Rh = 7.0 and 8.4, there clearly is an influence of the V$_2$O$_5$ on the reduction behaviour of Rh$_2$O$_3$, the reduction of Rh$_2$O$_3$ is shifted to a higher temperature in the second TPR, pointing to the formation of a mixed oxide. For these catalysts also an influence of the V$_2$O$_5$ on the catalytic behaviour is observed [20] and probably the Rh$_2$O$_3$ is (partly) positioned on top of the V$_2$O$_5$ layer. The mixed oxide (RhVO$_4$) can be formed only after oxidation at 898 K, because of the strong interaction between the V$_2$O$_5$ layer and the Al$_2$O$_3$ support. For the Rh/V$_2$O$_5$/Al$_2$O$_3$ catalysts with high V/Rh values, hydrogen consumption above 573 K is observed during the first and second TPR. This consumption must be due to the reduction of V$_2$O$_5$ positioned far away from the rhodium particles, so that hydrogen spillover cannot facilitate its reduction.

The resulting model which describes the state of the Rh/V$_2$O$_5$/Al$_2$O$_3$ catalysts is presented in Figure 13b. For V/Rh < 1, separate Rh$_2$O$_3$ and V$_2$O$_5$ particles exist on the support, with no interaction. For the catalysts with V/Rh = 7.0 and 8.4, part of the Rh$_2$O$_3$ is positioned on V$_2$O$_5$ and only after oxidation at 898 K a mixed oxide is formed.

Hydrogen and carbon monoxide chemisorption.

For the Rh/V$_2$O$_3$/SiO$_2$ catalysts, hydrogen and carbon monoxide chemisorption after reduction and evacuation at 523 K or 723 K showed a decrease of the H/Rh and CO/Rh values with increasing vanadium oxide content. However, from the temperature
Programmed desorption experiments we learned that the suppression of the hydrogen chemisorption is not real but is caused by incomplete desorption at the reduction and evacuation temperature. This effect aggravates with increasing vanadium content. After reduction at 723 K, part of the hydrogen is bonded even stronger (desorption peak at 823 K), and therefore also reduction and evacuation at 723 K is not sufficient to remove all hydrogen.

Considering the TPD results, reduction at 523 K and evacuation at 723 K seems to be the right pretreatment preceding hydrogen and carbon monoxide chemisorption. Using this pretreatment, CO/Rh still decreases with increasing vanadium content. This suppression of carbon monoxide chemisorption cannot be caused by a larger particle size since TEM measurements show that the rhodium particle size is not dependent on the vanadium content. The suppression of carbon monoxide chemisorption by promoters has also been reported by Van den Berg et al. [51] for Mo and Mn promoted Rh/SiO₂, by Ichikawa et al. [52] for Fe and Zr promoted Rh/SiO₂, and by Hicks et al. [19] for Pd/La₂O₃. The suppression of CO chemisorption proves that the promoter oxide partially covers the metal particle. In fact, one can calculate that in order to decrease the CO chemisorption by a factor of 3, (as was measured by carbon monoxide chemisorption and infrared spectroscopy) at a V/Rh ratio of 1.0, the vanadium oxide has to be spread over the rhodium surface as a near-monolayer. These results point to a model as depicted in Figure 13c.

The idea of the spreading of an oxidic overlayer over a noble metal received considerable support in recent work on the so-called strong metal-support interaction (SMSI). The support (e.g. TiO₂) is converted to a suboxide (e.g. Ti₄O₇) after high temperature reduction, and there is strong experimental evidence that this suboxide spreads over transition metals forming incomplete overlayers [11-18]. However, the observed covering effect for the Rh/V₂O₃/SiO₂ system does not originate from the high temperature reduction, but already exists after reduction at 523 K. The suppression in this case is caused by V₂O₃ layers, formed during the reduction of RhVO₄, which was generated during calcination (Figure 13a,c).

For the alumina-supported catalysts, only a minor suppression of the CO chemisorption is observed, suggesting that covering by vanadium oxide did not occur. In this case, no mixed oxide is formed after calcination (see TPR results). For low V/Rh values, the vanadium oxide does not cover the rhodium metal particle but is positioned on separate locations on the Al₂O₃ surface. For V/Rh >> 1, part of the rhodium particles might be positioned on vanadium oxide (Figure 13d).

Infrared spectroscopy of adsorbed CO.

The infrared spectra of the Rh/V₂O₃/SiO₂ catalysts support and specify the conclusion from the CO chemisorption measurements (Figure 9). Bridge-bonded and linearly bonded carbon monoxide are almost completely suppressed, the twin structure of adsorbed CO is (almost) unaffected by the presence of vanadium
oxide (Figure 7). Thus, the remarkable fact that the CO/Rh value is not completely suppressed above V/Rh = 1.0 is due to the absence of suppression of the gem-dicarbonyl species. As shown by EXAFS, in the gem-dicarbonyl species two CO molecules are bonded to a Rh\(^{+}\) cation, formed by oxidation (using OH-groups of the support) of small Rh metal particles during CO adsorption [40]. Of course, this highly dispersed rhodium can not be seen by TEM. Apparently, particles covered by vanadium oxide still can provide Rh atoms which can be oxidized by OH-groups during adsorption of carbon monoxide, forming the Rh(CO)\(^2\)\(^+\) species. The same behaviour is seen for the Rh/V\(_2\)O\(_3\)/Al\(_2\)O\(_3\) systems with V/Rh = 7.0. In that case, the linearly bonded and bridge-bonded CO are also suppressed, suggesting that the rhodium particles are partially covered by vanadium oxide. The twin structure even increases when vanadium oxide is present. This may be caused by a better adsorption of the rhodium precursor on the vanadium oxide monolayer than on the bare alumina support, resulting in a smaller particle size in the vanadium oxide promoted system. In the future, we will further study these systems by EXAFS.

Hydrogen ad- and desorption studies.

In the case of Rh/V\(_2\)O\(_3\)/SiO\(_2\), the hydrogen chemisorption is not suppressed, H/Rh is constant up to V/Rh = 1. However, the CO chemisorption results pointed to a partial coverage of the metal particles. This suggests that hydrogen will adsorb not only on the exposed rhodium atoms, but also on the surface of the V\(_2\)O\(_3\) patches covering the metal particle. Such an adsorption has been reported before by Hicks et al. for Pd/La\(_2\)O\(_3\) systems [19]. Evidence for the adsorption of hydrogen on V\(_2\)O\(_x\) patches is obtained from the desorption profiles after reduction at 723 K (Figure 3b,c,d, dashed profiles). We think that the first desorption area between 298 and 623 K is due to the desorption of hydrogen bonded to Rh, and that the second desorption area (673-973 K) is due to the desorption of hydrogen from the vanadium oxide, because the first peak decreases and the second peak increases with increasing vanadium oxide content.

The silica- and alumina-supported systems with V/Rh > 1.0, as well as the Rh/V\(_2\)O\(_3\) systems, exhibit (very) high H/Rh ratios. These high ratios can not be explained by the assumption that all hydrogen is bonded to the metal. For instance, the 1.5 wt% Rh/V\(_2\)O\(_3\) catalyst has a H/Rh value of 3.8, but TEM showed that the average particle size was 35 Å. Calculations based on half spherical metal particles indicate that the fraction of exposed metal atoms is 0.36 for an average particle size of 35 Å [25,28], in good agreement with the CO chemisorption measurement for this catalyst. However, a H/Rh value of 3.8 with all hydrogen bonded to the metal, would result in a H/Rh\(_{\text{surface}}\) stoichiometry of about 10, which is impossible. This must mean that the hydrogen is not only adsorbed on the metal but also on the support. However, vanadium oxide itself did not adsorb hydrogen. Thus, the presence of the metal is necessary to reach such high H/Rh values. From the chemisorption measurement of the silica-supported catalysts it
can also be concluded that the extra hydrogen must be positioned on/in the vanadium oxide. Hydrogen chemisorption of these systems show that with equal rhodium particle size, the addition of an excess of vanadium oxide (V/Rh > 1) results in a strong increase of the H/Rh value.

An explanation for the hydrogen atoms located in or on vanadium oxide might be the formation of bronzes. Recently, Tinet et al. [53,54] and Bond et al. [55] reported the formation of hydrogen bronzes like $H_2xV_2O_5$ ($x = 0-1.7$) at about 338 K from a $V_2O_5$ microcrystalline powder, coated with small Pt particles, in contact with gaseous molecular hydrogen, through hydrogen spillover. It is essential that hydrogen is provided in atomic form by dissociation on a noble metal. The hydrogen atoms then can insert in the host lattice, $V_2O_5$. It has been shown that the proton is localized, creating $V^{4+}$ and $V^{3+}$ paramagnetic centers [54]. Thus, in our catalysts hydrogen adsorbs on exposed rhodium atoms, dissociates, and diffuses to vanadium oxide on the metal particle or support (by spillover), forming the hydrogen bronzes.

Recently, Lin et al. [56] proposed a similar spillover process from the rhodium metal to the vanadium oxide followed by hydrogen bronze formation. They observed a slow hydrogen adsorption rate and an increase in uptake with increasing pressure. Since we admitted hydrogen at 473 K at a relatively high pressure (around 80 kPa), the spillover and bronze formation will be more extended in our measurements. Lin's results also pointed to the importance of the impregnation and drying steps in the catalysts preparation.

CONCLUSIONS

Temperature programmed reduction studies showed that after calcination at 723 K, Rh facilitates the reduction of $V_2O_5$, and $V_2O_5$ hampers the reduction of rhodium oxide in the case of Rh/$V_2O_5$/SiO$_2$ systems. Diffuse reflectance infrared spectrometry showed that a Rh/$V_2O_5$/SiO$_2$ catalyst with V/Rh = 0.9 did not contain "free" $V_2O_5$. These results suggest the formation of the mixed oxide RhVO$_4$.

For Rh/$V_2O_5$/Al$_2$O$_3$ systems with V/Rh < 1, no evidence is found for an intimate contact between Rh$_2$O$_3$ and $V_2O_5$. Separate Rh$_2$O$_3$ and $V_2O_5$ particles will exist on the Al$_2$O$_3$ support due to the strong interaction between the $V_2O_5$ and the Al$_2$O$_3$ support. For Rh/$V_2O_5$/Al$_2$O$_3$ catalysts with high V/Rh values (7.0 and 8.4) the formation of RhVO$_4$ was observed only after oxidation at 898 K. For these catalysts, Rh$_2$O$_3$ is believed to be partially positioned on top of a $V_2O_5$ layer. A higher oxidation temperature is required to form RhVO$_4$, because of the stronger interaction between $V_2O_5$ and Al$_2$O$_3$.

CO chemisorption showed that CO/Rh was suppressed by the presence of vanadium oxide, proving a (partial) coverage of the rhodium metal by vanadium oxide in the Rh/$V_2O_3$/SiO$_2$ catalysts. TEM showed that the rhodium particle size was not influenced by the addition of vanadium oxide. Almost no suppression of CO chemisorption was observed for the Rh/$V_2O_3$/Al$_2$O$_3$ systems. Infrared spectroscopy
showed that the linearly bonded and bridge-bonded CO were almost completely suppressed by vanadium oxide, especially present in the Rh/V_2O_3/SiO_2 systems, whereas the twin structure was unaffected.

Hydrogen chemisorption experiments showed that hydrogen is not only adsorbed by exposed rhodium atoms but also by vanadium oxide patches covering the rhodium. The systems with a high V/Rh ratio exhibit very high H/Rh values (up to H/Rh = 3.0), caused by the formation of hydrogen bronzes.

Our results prove that for the Rh/V_2O_3/SiO_2 catalysts an intimate contact between the active component, rhodium, and the promoter, vanadium oxide, is present. The weak interaction between V_2O_5 and SiO_2, and the strong interaction between Rh_2O_3 and V_2O_5, result in the formation of a mixed oxide (RhVO_4) during catalyst preparation (calcination), which after reduction results in a vanadium oxide layer on top of the metal particle. On the other hand, for the Rh/V_2O_3/Al_2O_3 catalysts, a strong interaction between V_2O_5 and the Al_2O_3 support prevents mixed oxide formation, and Rh_2O_3 and V_2O_5 particles exist separately on the Al_2O_3 support. Only for Rh/V_2O_5/Al_2O_3 catalysts with a high V/Rh ratio (near mono-layer coverage of vanadium oxide), rhodium particles might be positioned on top of the V_2O_5 layer, after oxidation at 898 K leading the formation of RhVO_4.

ACKNOWLEDGMENTS

This study was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

The authors wish to thank the coworkers of the Centre for Electron Microscopy of Antwerp (RUCA) for the use of the JEOL 200 CX, ir. F. Dirne, H. Saeijs and P. Couwenberg for performing part of the experimental work, and dr. J.P. Weterings for helpful discussions.

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