PREPARATION AND CHARACTERIZATION OF VANADIUM OXIDE PROMOTED RHODIUM CATALYSTS

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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_4) 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 $\text{Rh/V}_2\text{O}_3/\text{SiO}_2$ 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 $\text{Rh/V}_2\text{O}_3/\text{Al}_2\text{O}_3$ during calcination. For $\text{V/Rh} < 1.0$, Rh_2O_3 and V_2O_5 particles exist separately on the support, due to the strong interaction between V_2O_5 and Al_2O_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_2O_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_2O_3 has a significant effect on this reaction. Kikuchi et al. [4] reported that V_2O_3 supported Ru catalysts exhibited high turnover frequencies, high selectivities for heavier hydrocarbons and high

olefin/paraffin ratios relative to $\text{Ru}/\text{Al}_2\text{O}_3$ 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 $\text{Ru}/\text{Al}_2\text{O}_3$. Ichikawa et al. [6] and Van der Lee et al. [7] reported high selectivities to C_2 -oxygenates using V_2O_3 supported Rh catalysts.

Like TiO_2 -, Nb_2O_5 - and Ta_2O_5 -supported noble metal catalysts, V_2O_3 -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 H_2 and CO on La_2O_3 -supported Pd catalysts and observed a suppression of the CO chemisorption after reduction at 573 K (low temperature reduction), even though La_2O_3 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, LaO_x , already transferred to the surface of the Pd crystallites during catalyst preparation. The absence of a suppression of H_2 adsorption on $\text{Pd}/\text{La}_2\text{O}_3$ indicated that H_2 adsorption occurred on the exposed Pd surface atoms as well as on the LaO_x 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 C_2 -oxygenates from synthesis gas at elevated pressures. $\text{Rh}/\text{V}_2\text{O}_3$ is of interest in this respect [6,7], but V_2O_3 has the disadvantage of a relatively low surface area ($< 10 \text{ m}^2 \text{ g}^{-1}$) and of a low mechanical and chemical stability. Therefore, we chose the route of promoting Rh/SiO_2 and $\text{Rh}/\text{Al}_2\text{O}_3$ systems with vanadium oxide in order to combine the good structural properties of Al_2O_3 and SiO_2 (high surface area, high pore volume, high mechanical and chemical stability) with the good selectivity properties of V_2O_3 . 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 $\gamma\text{-Al}_2\text{O}_3$ (Ketjen, type 000-1.5E, surface area $200 \text{ m}^2 \text{ g}^{-1}$,

pore volume 0.6 ml g^{-1}), SiO_2 (Grace, type 113, surface area $360 \text{ m}^2 \text{ g}^{-1}$, pore volume 1.1 ml g^{-1}) and V_2O_3 , obtained by reduction of V_2O_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_2O_3 with a low surface area ($3 \text{ m}^2 \text{ g}^{-1}$, pore volume 0.32 ml g^{-1}). Vanadium oxide promoted SiO_2 and Al_2O_3 were prepared by incipient wetting these supports with an aqueous solution of NH_4VO_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_2O_3 , as described in the literature for vanadium- and molybdenum-oxide monolayers on alumina [21-24], by batch adsorption of NH_4VO_3 . During the adsorption the pH was kept constant at 4 by adding HNO_3 . In this way we made a $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ 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 $\text{Rh}(\text{NO}_3)_3$ (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 nitrogeneous 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: $\text{Rh}/\text{V}_2\text{O}_3/\text{SiO}_2$ for silica supported rhodium catalysts promoted with vanadium oxide, $\text{Rh}/\text{V}_2\text{O}_3/\text{Al}_2\text{O}_3$ for alumina supported rhodium catalysts promoted with vanadium oxide, and $\text{Rh}/\text{V}_2\text{O}_3$ 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_2O_3 and $\text{V}_2\text{O}_3/\text{Al}_2\text{O}_3$ were found to adsorb CO, while SiO_2 , $\text{V}_2\text{O}_3/\text{SiO}_2$ and V_2O_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 $5 \cdot 10^{-3}$ Pa). The catalyst was reduced in-situ at 543 K in flowing H_2 (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 $V=0$ 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 were 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 Formvar 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 ($<1 \text{ nm}$) could be observed best with an objective diaphragm 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_2O_5 (a), passivated V_2O_3 (b), Rh/V_2O_3 after drying at 395 K (c), and Rh/V_2O_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_2O_3

In order to compare the results of vanadium oxide promoted Rh/SiO_2 and Rh/Al_2O_3 catalysts with Rh/V_2O_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_2O_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

as shown by Bosch et al. [31] using X-ray diffraction. The final oxide formed in this reduction is V_2O_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_2O_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 in 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 /SiO₂

Temperature programmed reduction. TPR profiles of V_2O_5 /SiO₂ supports (Figure 2a,b) show that the major part of the vanadium oxide is reduced more easily when supported on SiO₂ 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 /SiO₂ 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 /SiO₂ samples.

Figures 2c-h show the TPR profiles of the Rh/ V_2O_5 /SiO₂ catalysts after calcination. A pronounced effect of the vanadium loading is observed. The Rh/SiO₂ 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: $V^{5+} \rightarrow V^{3+}$ and $Rh^{3+} \rightarrow Rh^0$. 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_2O_5/SiO_2

b. 3.6 wt% V_2O_5/SiO_2

c-h. TPR after calcination of $Rh/V_2O_5/SiO_2$ catalysts

i-n. TPR after oxidation at 898 K of $Rh/V_2O_5/SiO_2$ catalysts.

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

The TPR profiles of the $Rh/V_2O_5/SiO_2$ 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_2O_5/SiO_2 (cf. Figure 2b).

FIGURE 3: Temperature programmed desorption of hydrogen for $\text{Rh}/\text{V}_2\text{O}_3/\text{SiO}_2$ systems, reduced at 523 K (—) and reduced at 723 K (----).

Temperature programmed desorption of hydrogen. Hydrogen TPD profiles for $\text{Rh}/\text{V}_2\text{O}_3/\text{SiO}_2$ 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 H_2 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.

H_2 and CO chemisorption measurements. Results of the hydrogen and carbon monoxide chemisorption measurements for the SiO_2 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: H_2 and CO chemisorption measurements of the 1.5 wt% $Rh/V_2O_3/SiO_2$ 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 preceeding 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/V₂O₃/SiO₂ catalysts. A comparison of the Rh/V₂O₃/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 (T_1) and 2092 cm⁻¹ (T_2) 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/V₂O₃/SiO₂ catalysts with varying V/Rh ratio. N = number of particles used to determine particle size distribution. $\bar{D}$ = 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: $\Delta\sigma_B = 59$ cm⁻¹ and $\Delta\sigma_L = 25$ 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/V₂O₃/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/V₂O₃/SiO₂ 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:

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

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/SiO₂ 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/Al₂O₃: $\epsilon(L) = 26 \cdot 10^6$, $\epsilon(B) = 85 \cdot 10^6$, $\epsilon(T_{1,\text{symm}}) = 74 \cdot 10^6$ and $\epsilon(T_{2,\text{asymm}}) = 128 \cdot 10^6 \text{ cm mol}^{-1}$ 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 ϵ -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 V₂O₅, V₂O₅/SiO₂ (2.2 wt% V) and Rh/V₂O₅/SiO₂ (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.

FIGURE 10: Temperature programmed reduction profiles of alumina supported 1.5 wt% Rh catalysts .

a. 6.7 wt% V_2O_5/Al_2O_3

b-e. Rh/ V_2O_5/Al_2O_3 catalysts after calcination

f-h. Rh/ V_2O_5/Al_2O_3 catalysts after oxidation at 898 K.

Final reduction temperature 1073 K for a. and 898 K for b-h.

c. Rh/ V_2O_5/Al_2O_3

Temperature programmed reduction. We attempted to prepare a monolayer of vanadium oxide on the alumina support by adsorbing metavanadate at pH = 4 (using HNO_3). 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 $10.3 \text{ \AA}^2$ per $VO_{2.5}$ unit [45], 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% V_2O_5/Al_2O_3 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 V_2O_5 phase could be detected in this support.

FIGURE 11: H_2 (•) and CO (o) chemisorption measurements of the 1.5 wt% $\text{Rh}/\text{V}_2\text{O}_3/\text{Al}_2\text{O}_3$ 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% $\text{Rh}/\text{Al}_2\text{O}_3$ (a), and 1.5 wt% $\text{Rh}/\text{V}_2\text{O}_3/\text{Al}_2\text{O}_3$ (V/Rh = 7.0) (b), after reduction at 523 K and evacuation at 673 K ($P_{\text{CO}} = 10$ Torr, adsorption at 298 K).

The reduction profiles of the $\text{Rh}/\text{V}_2\text{O}_3/\text{Al}_2\text{O}_3$ 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 Rh^{3+} to Rh^0 and of V^{5+} to V^{3+} . 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 $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ (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.

H_2 and CO chemisorption, infrared of adsorbed CO. The results of the hydrogen and carbon monoxide chemisorption measurements of the $\text{Rh}/\text{V}_2\text{O}_3/\text{Al}_2\text{O}_3$ systems are presented in Figure 11. CO/Rh values decreased only slightly with increasing vanadium content, in contrast to those for the $\text{Rh}/\text{V}_2\text{O}_3/\text{SiO}_2$ 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 $\text{Rh}/\text{V}_2\text{O}_3$ 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 $\text{Rh}/\text{Al}_2\text{O}_3$ and $\text{Rh}/\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ with $\text{V}/\text{Rh} = 7.0$ 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 $\text{Rh}/\text{Al}_2\text{O}_3$ catalyst already had more twin-adsorbed CO than the Rh/SiO_2 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 V_2O_5 , where several reduction steps can be distinguished [31]. Single peaks were also observed for titania-supported monolayers of V_2O_5 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 V_6O_{13} and V_6O_{11} 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 V_2O_5 . Combining this with the results of XRD measurements, we can confidently conclude that large crystalline V_2O_5 particles are absent.

Temperature programmed reduction profiles of the calcined $\text{Rh}/\text{V}_2\text{O}_5$ and $\text{Rh}/\text{V}_2\text{O}_5/\text{SiO}_2$ 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 $\text{Rh}/\text{V}_2\text{O}_5/\text{SiO}_2$ 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 Rh_2O_3 and V_2O_5 , RhVO_4 , is known to exist and can be formed by heating

Rh_2O_3 and V_2O_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_2O_3 and RhVO_4 are formed, reflected by distinct reduction peaks in the second TPR. For $\text{V/Rh} > 1.0$ 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 $\text{V/Rh} > 1.0$, like $\text{Rh}_2\text{V}_4\text{O}_{13}$, or by V_2O_5 layers positioned on top of the RhVO_4 . The fourth reduction peak occurred around the temperature where $\text{V}_2\text{O}_5/\text{SiO}_2$ reduces (cf. Figure 2a,b) and must be caused by the reduction of V_2O_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_2O_5 is positioned on the nucleation sites of the reduction process of Rh_2O_3 , or that V_2O_5 totally covers the Rh_2O_3 . Furthermore we also cannot exclude that part of the V_2O_5 is positioned between the Rh_2O_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 $\text{Rh}/\text{V}_2\text{O}_5/\text{SiO}_2$ (calcined at 723 K, $\text{V/Rh} = 0.9$) almost no V-O stretching bands were observed (Figure 9c), pointing to the absence of "free" V_2O_5 . This suggests that V_2O_5 and Rh_2O_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_2O_5 promoter and the Rh_2O_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 $\text{V/Rh} < 1$, after calcination and oxidation distinct Rh_2O_3 and RhVO_4 particles exist. For $\text{V/Rh} > 1$, V_2O_5 and mixed oxide particles like RhVO_4 are present on the support.

For the 1.5 wt% $\text{Rh}/\text{V}_2\text{O}_5$ catalyst, the first reduction peak is shifted to even higher temperatures than in the case of $\text{Rh}/\text{V}_2\text{O}_5/\text{SiO}_2$. This might be due to a covering of RhVO_4 by several layers of V_2O_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 $\text{Rh}/\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ catalysts with $\text{V/Rh} < 1$, even after oxidation at 898 K no hampering of the reduction of Rh_2O_3 was observed. We conclude that in this case the intimate contact between Rh_2O_3 and V_2O_5 in the form of a mixed oxide does not exist. Hydrogen spillover can explain the co-reduction of Rh_2O_3 and V_2O_5 . In agreement with this, the influence of V_2O_5 on the catalytic activity of $\text{Rh}/\text{Al}_2\text{O}_3$ for catalysts with $\text{V/Rh} < 1$ was negligible [20]. Thus, at least for $\text{V/Rh} < 1$, V_2O_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_2O_3 particles exist separately on the Al_2O_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_2O_3 and V_2O_5 particles. The NH_4VO_3 and $\text{Rh}(\text{NO}_3)_3$ complexes do not adsorb on SiO_2 and therefore a mixed oxide can be formed on that support.

For $\text{Rh}/\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ with $\text{V}/\text{Rh} = 7.0$ and 8.4 , there clearly is an influence of the V_2O_5 on the reduction behaviour of Rh_2O_3 , the reduction of Rh_2O_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_2O_5 on the catalytic behaviour is observed [20] and probably the Rh_2O_3 is (partly) positioned on top of the V_2O_5 layer. The mixed oxide (RhVO_4) can be formed only after oxidation at 898 K, because of the strong interaction between the V_2O_5 layer and the Al_2O_3 support. For the $\text{Rh}/\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ 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_2O_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 $\text{Rh}/\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ catalysts is presented in Figure 13b. For $\text{V}/\text{Rh} < 1$, separate Rh_2O_3 and V_2O_5 particles exist on the support, with no interaction. For the catalysts with $\text{V}/\text{Rh} = 7.0$ and 8.4 , part of the Rh_2O_3 is positioned on V_2O_5 and only after oxidation at 898 K a mixed oxide is formed.

Hydrogen and carbon monoxide chemisorption.

For the $\text{Rh}/\text{V}_2\text{O}_3/\text{SiO}_2$ 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 $Rh/V_2O_3/Al_2O_3$ 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 $Rh/V_2O_3/SiO_2$, 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_2O_3 patches covering the metal particle. Such an adsorption has been reported before by Hicks et al. for Pd/La_2O_3 systems [19]. Evidence for the adsorption of hydrogen on V_2O_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_2O_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_2O_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_{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 $H_{2x}V_2O_5$ ($x = 0-1.7$) 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 $Rh/V_2O_5/Al_2O_3$ systems with $V/Rh < 1$, no evidence is found for an intimate contact between Rh_2O_3 and V_2O_5 . Separate Rh_2O_3 and V_2O_5 particles will exist on the Al_2O_3 support due to the strong interaction between the V_2O_5 and the Al_2O_3 support. For $Rh/V_2O_5/Al_2O_3$ 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_2O_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_2O_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 $Rh/V_2O_3/Al_2O_3$ systems. Infrared spectroscopy

showed that the linearly bonded and bridge-bonded CO were almost completely suppressed by vanadium oxide, especially present in the Rh/V₂O₃/SiO₂ 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/V₂O₃/SiO₂ catalysts an intimate contact between the active component, rhodium, and the promoter, vanadium oxide, is present. The weak interaction between V₂O₅ and SiO₂, and the strong interaction between Rh₂O₃ and V₂O₅, result in the formation of a mixed oxide (RhVO₄) 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/V₂O₅/Al₂O₃ catalysts, a strong interaction between V₂O₅ and the Al₂O₃ support prevents mixed oxide formation, and Rh₂O₃ and V₂O₅ particles exist separately on the Al₂O₃ support. Only for Rh/V₂O₅/Al₂O₃ catalysts with a high V/Rh ratio (near mono-layer coverage of vanadium oxide), rhodium particles might be positioned on top of the V₂O₅ layer, after oxidation at 898 K leading the formation of RhVO₄.

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