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Temperature-Programmed Reduction and CO Hydrogenation of La_2O_3-Promoted Rh/SiO_2 Catalysts

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Rh/SiO_2-, Rh/La_2O_3-, and La_2O_3-promoted Rh/SiO_2 catalysts were investigated by temperature-programmed reduction (TPR) and CO hydrogenation. When the La_2O_3–Rh/SiO_2 catalysts were prepared by sequential impregnation with La impregnation as the final step, the Rh particles were partly covered by La_2O_3. When the impregnation sequence was reversed, and also when coimpregnation was applied, well dispersed Rh particles were formed, which showed a distinct interaction with the promoter but no covering. The presence of La_2O_3 shifted the TPR reduction of Rh_2O_3 to higher temperatures and enhanced the oxygenate selectivity in the CO hydrogenation. Catalysts exposed to air showed different TPR results and higher H_2 consumptions than *in situ* calcined catalysts due to the presence of La carbonate. After removal of carbonate, no H_2 consumption other than for the reduction of Rh^{3+} to Rh^0 was observed, demonstrating that no reduction of La_2O_3 takes place. © 1993 Academic Press, Inc.

INTRODUCTION

Rh is a versatile catalyst which can adsorb CO both associatively and dissociatively, and is thus able to hydrogenate CO to hydrocarbons as well as to C_1- and C_2-oxygenates. Supports and modifiers may change the balance between associative and dissociative chemisorption and can therefore play a crucial role in the catalytic performance of Rh. Many transition metal oxides have been observed to promote the activity of Rh and to change its selectivity (*1–6*). Amongst others, this behavior has been ascribed to the ability of CO to bind with its carbon atom to a Rh atom and with its oxygen atom to a neighboring transition metal cation (*7, 8*). In this way the CO bond weakens and dissociation is eased. After CO dissociation the oxygen atom is bonded to the transition metal cation and can in a subsequent step react with H_2 to H_2O, or with CO to CO_2. The transition metal cation formally undergoes a redox cycle, being oxidized by the oxygen atom and being reduced back by H_2 or CO. Although such a mechanism is conceivable for transition metals with several stable oxidation states, it seems questionable if a promoter like La can behave similarly, since only the La^{3+} state is known to be stable. Nevertheless, partial reduction of La_2O_3 in the presence of Rh and Pd to LaO_x has been described (*9*), and La_2O_3 has been observed to exert a large influence on Rh and Pd catalysts in the CO hydrogenation, mainly by enhancing the selectivity to alcohols (*2–4, 10–17*).

La_2O_3 is believed to partly reside on top of Rh crystallites (*10–12, 18–20*) and to reach this position in the course of reduction (*19*), although it has also been shown that such covering is facilitated by the redissolution of La_2O_3 during the impregnation with the Rh precursor (*10, 12*). Both the impregnation and the reduction processes can therefore contribute to the decoration of Rh (*20*). A major suppression of CO chemisorption relative to H_2 chemisorption on La_2O_3-supported Rh (*19, 20*) and Pd (*21*) as well as La_2O_3-promoted Rh/SiO_2 (*18*) has been cited as evidence for covering. In other studies the H_2 and CO adsorption data agreed rather well, however (*12, 22*). Negative shifts in the Pd and Rh $3d_{5/2}$ XPS lines have

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been attributed to coverage of the metal by partially reduced La_2O_3 (*19, 23*). The covering La_2O_3 was assumed to act analogously to the classical SMSI support TiO_2 (*24, 25*), in that the partly reduced LaO_x overlayer increases the electron density in the metal particle. This concept was further supported by the fact that the presence of La_2O_3 promoter or support increased the H_2 consumption during TPR of Pd (*9*) catalysts, suggesting that partial reduction of La_2O_3 had taken place. In this work the possible formation of La carbonate (*26, 27*) and its influence on the H_2 consumption were not taken into account, however.

In the present work we have addressed the question of the reducibility of La_2O_3 by means of temperature programmed reduction (TPR) studies of La_2O_3-promoted Rh/SiO_2 catalysts. The catalysts were prepared by wet impregnation varying the impregnation sequence of the precursor solutions, as well as by coimpregnation, and were compared with unpromoted Rh/SiO_2 and Rh/La_2O_3 catalysts. By calcining the catalysts *in situ*, as well as in air, the influence of La carbonate formation was studied. The TPR studies included a quantitative analysis of the H_2 consumption and were performed to investigate the reducibility of La_2O_3, the state of the components after preparation in the oxidized state, and the interaction between Rh and promoter. In addition, some activity and selectivity studies of CO hydrogenation were carried out. A comparison with former CO hydrogenation activity and selectivity and H_2 and CO chemisorption results (*12*), and with EXAFS results (*28*) is made.

EXPERIMENTAL

Catalyst Preparation

The silica support (CF Uetikon, Switzerland, Type C-560) was purified by washing it three times in 2*M* HNO_3 (360 K, 1 h) and twice in distilled water (360 K, 1 h), followed by calcination at 773 K. The resulting silica (460 m^2/g, 0.81 ml/g) was sequentially impregnated to incipient wetness with aqueous solutions of $La(NO_3)_3 \cdot 6H_2O$ (Fluka puriss. p.a.) and $Rh(NO_3)_3$ (Johnson Matthey, 5% solution in 1.7 *M* HNO_3, diluted to the required level). After each impregnation the catalysts were dried at 393 K for 3 h (2 K/min) and calcined in air at 773 K (3h, 5K/min), unless otherwise stated. The La/Rh atomic ratio γ was varied between 0 and 11.1, while the rhodium content was kept at about 1.4 wt% of the initial amount of support material. For one series of catalysts, referred to as LaRh, the impregnation sequence was $La(NO_3)_3$ followed by $Rh(NO_3)_3$, while for the other catalyst series, referred to as RhLa, the reverse sequence was applied. In that case a large batch of Rh/SiO_2 was prepared first and the required amount of La promoter was added to portions of this batch. For high La contents, two (γ = 5) or four (γ = 11.1) $La(NO_3)_3$ impregnation steps were necessary to reach the desired La loading for both series. Between these supplementary impregnations the samples were dried only.

A coimpregnated catalyst ($LaRh^{co}$) was prepared in one step with an equimolar rhodium–lanthanum solution, dried at 393 K and calcined at 773 K. Rh/La_2O_3 was prepared by impregnating La_2O_3 (Fluka, purum, ex La 99.98%, calcined at 1040 K, pore volume 0.28 ml/g) to incipient wetness with $Rh(NO_3)_3$, as for the silica-supported samples, but without calcination. All catalysts were stored in air.

Temperature-Programmed Reduction

The TPR experiments were carried out at ambient pressure in an apparatus as described by Huizinga *et al.* (*29*). The experimental parameters (flow rate, 11 ml/min; heating rate, 10 K/min; reducible material, ~20 mmol H_2-equivalents (~0.1 g of catalyst); H_2 concentration in reactant gas, 2.00 mmol/ml) were chosen such that *P*, a criterion introduced by Malet and Caballero (*30*), was lower than 10 K. Most TPR profiles were recorded between 200 and 1000 K, applying the procedures described by Vis *et al.* (*31*). For one series of experiments, an

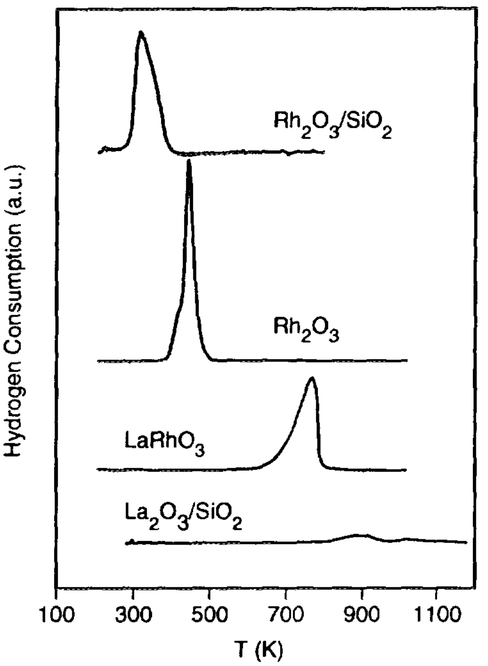

FIG. 1. TPR of Rh reference compounds

(additional) *in situ* calcination at 773 K (1 h, 10 K/min) preceded the first TPR. A second TPR was performed after recalcining the sample *in situ* at 773 K (1 h) with dry synthetic air, from which traces of CO_2 were removed by soda lime.

CO Hydrogenation

The syngas reactions were performed as described in Ref. (*7*). In brief, the catalysts were reduced at 723 K in H_2 before the temperature was lowered to 533 K. The pressure was raised to 4 MPa and the reaction was started by introducing CO to the flow reactor. The activities and selectivities were measured after 15 h on stream at a H_2/CO ratio of 3.

RESULTS

TPR of Reference Compounds

In Fig. 1 the TPR profiles of four reference compounds are presented, namely, (bulk) Rh_2O_3, silica-supported Rh_2O_3, silica-supported La_2O_3, and (bulk) $LaRhO_3$ (prepared according to Ref. (*32*)), a perovskite-type mixed oxide which has the strongest interaction possible between the oxides of Rh and La. An attempt to prepare silica-supported $LaRhO_3$ using a calcination temperature of 1023 K was not successful (*28*).

TABLE 1

TPR H_2 Consumptions

Sample	H/Rh	
	In situ calcined[a]	No pretreatment[b]
Rh/SiO_2	2.8	3.2
Rh_2O_3	n.a.	2.9
$LaRhO_3$	2.8	3.1
La_2O_3/SiO_2	≈0	0.1

[a] 773 K.

[b] Profiles in Fig. 1.

The TPR reduction of Rh_2O_3 dispersed on SiO_2 started already at room temperature, whereas bulk Rh_2O_3 reduced at a 130 K higher temperature. The reduction of $LaRhO_3$ started at about 600 K, when the reduction of both Rh_2O_3 samples was already completed. The peak maximum of 771 K for $LaRhO_3$ was 330 K higher than for Rh_2O_3. This large shift was not caused by a simultaneous reduction of the Rh^{3+} and La^{3+}, because the H_2 consumption (Table 1) corresponded to a complete reduction of the Rh only, leaving the La in its oxidation state of 3. La_2O_3/SiO_2 showed a small TPR peak if the sample had not been calcined *in situ*.

TPR of the LaRh and RhLa Catalysts

The catalysts of the LaRh series were analyzed by TPR in two different ways. In one type of experiment, the stored catalysts underwent the TPR reduction treatment without any further pretreatment. Although these experiments will be referred to as "not calcined" or "without pretreatment," it should be noted that the samples had been calcined in air after preparation, unless otherwise stated. The catalysts prepared by se-

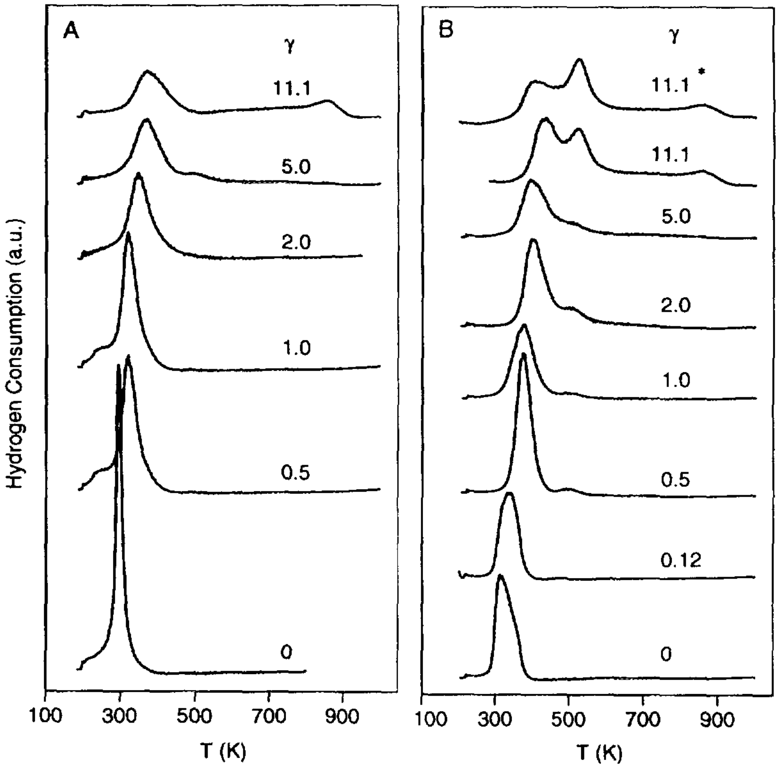

FIG. 2. TPR of LaRh catalysts: (A) calcined *in situ* and (B) no pretreatment. The γ = 11.1* sample was exposed to air for several hours before TPR.

quential impregnation had even undergone two calcinations, one after each impregnation step. In another type of experiment, the catalysts were additionally calcined in the TPR reactor prior to the TPR at the same temperature as after impregnation. Figure 2A shows the TPR profiles of the LaRh catalyst series after this *in situ* calcination. Rh/SiO$_2$ exhibited a sharp, narrow peak at 295 K. The peak became broader and more asymmetric with increasing La$_2$O$_3$ content and the peak maximum shifted about 80 K to higher temperatures. For the La5.0Rh catalyst a second, small peak with a maximum at 491 K could be seen. With La11.1Rh a continuous H$_2$ consumption up to 900 K was observed.

TPR runs of the LaRh catalysts which had not undergone an *in situ* calcination are shown in Fig. 2B. The influence of the promoter is again evident. The main peak shifted to higher temperatures with increasing promoter content of the catalyst. All peak maxima were more than 20 K higher than the corresponding ones in Fig. 2A. A peak at about 500 K, similar to the one observed for La5.0Rh in the calcined series, was present in all promoted samples with $\gamma \geq 0.5$. This peak depended on the extent of air exposure, as was demonstrated for the La11.1Rh catalyst. If the sample remained in air overnight before the TPR, the second peak became more intense than the first peak (topmost profile in Fig. 2B). The La11.1Rh catalyst had another maximum at about 850 K, as in the *in situ* calcined case.

The profiles for the *in situ* calcined catalysts of the RhLa series are plotted in Fig. 3A. The presence of La$_2$O$_3$ not only shifted the TPR peaks to higher temperature, but

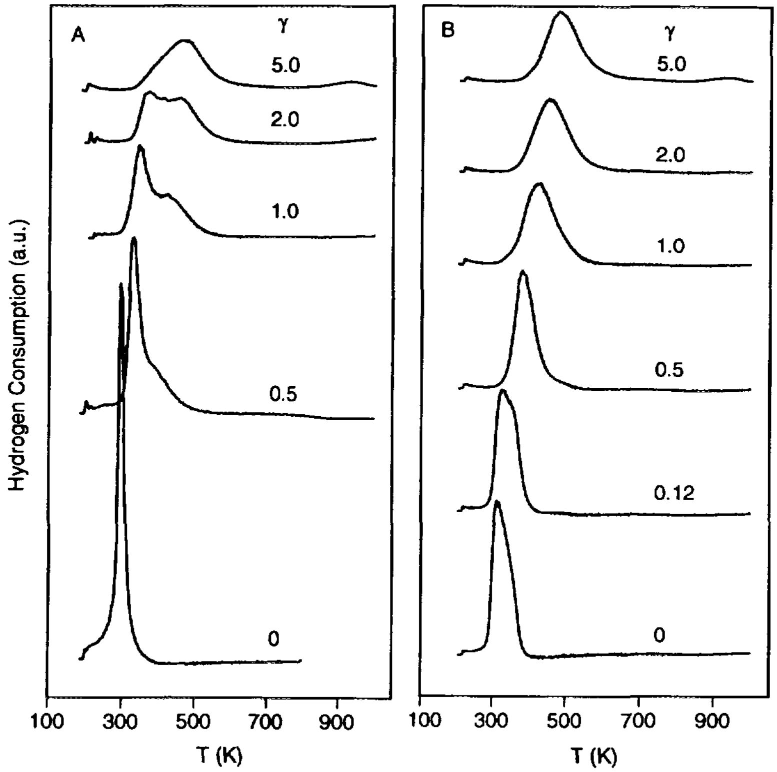

FIG. 3. TPR of RhLa catalysts: (A) calcined in situ and (B) no pretreatment.

also led to the appearance of a second peak which increased in intensity with increasing γ. Moreover, the peaks were much broader in the presence of the promoter. If no pretreatment was carried out with the RhLa catalysts, the reduction started at higher temperature compared to the *in situ* calcined samples (cf. Fig. 3B). Mainly one peak was observed, with a shoulder for the catalysts with $\gamma \leq 0.5$.

The results of the quantitative measurements of the H_2 consumption during TPR are presented in Table 2. The expected H_2 consumption for the reduction of Rh_2O_3 is three H atoms per Rh atom. Most LaRh and RhLa catalysts which had been calcined *in situ* indeed showed a H/Rh value of about 3. Only the La5.0Rh and La11.1Rh catalysts gave significantly higher values. If the catalysts had not been calcined *in situ*, however, the resulting H/Rh values were usually higher than 3. The effect was more pronounced for the LaRh series than for the RhLa series. Additional air exposure led to an enhanced H_2 consumption, as demonstrated for La11.1Rh. The Rh/La_2O_3 catalyst, which was only dried after preparation, consumed a large amount of H_2 due to the simultaneous decomposition of precursor salt and reduction of the anion.

For several catalysts a second TPR was performed. These catalysts were reoxidized after the first TPR with H_2O- and CO_2-free air in the same way as during the first *in situ* calcination. Thereafter the second TPR was performed. The LaRh and RhLa catalysts showed only one sharp peak in the second TPR. Its shape and peak temperature did not change when the first TPR was preceded by an *in situ* calcination. The H_2 consumption during the second TPR was always close to H/Rh = 3, and lower than during

TABLE 2

Catalyst Specifications, Hydrogen Consumptions, and Peak Maxima during TPR

Catalyst	γ	Rh content (wt %)[a]	H/Rh[b] First TPR isc[c]	H/Rh[b] First TPR np[d]	H/Rh[b] Second TPR
Rh/SiO_2	0	1.47	3.1	3.2	2.8
La0.12Rh	0.12	1.47	—	—	—
La0.5Rh	0.5	1.46	3.0	3.5	2.7
La1.0Rh	1.0	1.44	3.0	3.5	2.8
La2.0Rh	2.0	1.41	3.4	4.1	—
La5.0Rh	5.0	1.32	3.8	4.0	3.3[e]
La11.1Rh	11.1	1.08	4.9	8.9[f]	2.9
RhLa0.12	0.12	1.47	—	2.8	—
RhLa0.5	0.5	1.46	—	3.0	—
RhLa1.0	1.0	1.44	3.0	3.2	2.8
RhLa2.0	2.0	1.41	2.9	3.3	2.9
RhLa5.0	5.0	1.32	3.2	3.7	2.8
LaRh[co]	1.0	1.47	2.9	3.7	2.7
Rh/La_2O_3	50	1.26	19	27	3.3

[a] After calcination.

[b] H atoms consumed per total number of Rh atoms present.

[c] Additional *in situ* calcination.

[d] No extra pretreatment.

[e] Intermediate calcination performed with unpurified air (containing CO_2).

[f] Extended air exposure prior to TPR.

the first TPR (Table 2). If nonpurified air was used as an oxidizing agent prior to the second TPR, the H/Rh values were higher than with H_2O- and CO_2-free air. The influence of the promoter was smaller in the second TPR than in the first TPR, since the peak maximum temperature increased only slightly with γ from 305 K for Rh/SiO_2 to 321 K for La11.1Rh.

The TPR peak maxima as a function of γ are presented in Fig. 4. For the LaRh series, the nonpretreated catalysts had higher peak temperatures than their *in situ* calcined counterparts. At $\gamma = 5$, the maxima reached a constant level at 370 K for the *in situ* calcined series and about 400 K for the unpretreated series. In contrast to the main peaks, the temperature maxima of the second peaks of the unpretreated LaRh catalysts increased only slightly with γ. They represented only a minor H_2 consumption for $\gamma \leq 1.0$ (Fig. 2B). The catalysts of the RhLa

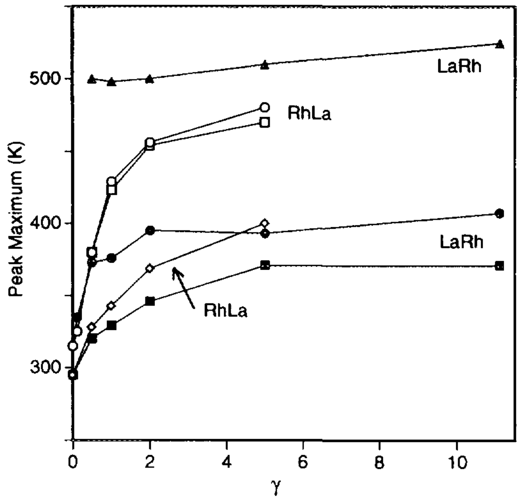

FIG. 4. TPR peak maxima for LaRh catalysts: (■) *in situ* calcined, (●) no pretreatment, first peak, (▲) no pretreatment, second peak; TPR peak maxima for RhLa catalysts: (◇) *in situ* calcined, first peak, (□) *in situ* calcined, second peak, and (○) no pretreatment.

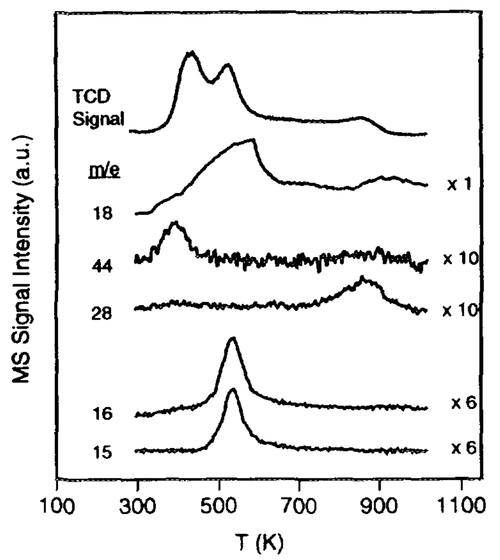

FIG. 5. Product gas composition during TPR of La11.1Rh.

series which had not been pretreated had a single peak maximum which was very sensitive to the promoter content, shifting from 315 K for Rh/SiO_2 to 480 K for RhLa5.0. The *in situ* calcination led to two peak maxima in the RhLa series. The first one was situated between the peak maxima of the LaRh series, while the second almost coincided with the peak maximum of the uncalcined samples. The TPR peak widths increased with γ from 10–30 K to 80-90 K in the first TPRs and from 20 to 40 K in the second TPRs.

A Balzers QMG 112 mass spectrometer, equipped with a faraday cap and operating at 5×10^{-4} Pa, was connected to the TPR system at the reactor outlet to measure the composition of the effluent gases of the unpretreated La11.1Rh catalyst under TPR conditions. The representative masses for CH_4, H_2O, CO and CO_2 are plotted together with the TCD signal in Fig. 5. The masses $m/e = 15$ and 16 behaved similarly and showed one maximum at about 535 K, which corresponded to the second TPR peak. The $m/e = 44$ signal showed a peak just below 400 K and a weak peak around 900 K. The $m/e = 28$ signal also had a peak in this area. The $m/e = 18$ signal mainly reflects the removal of adsorbed water which the sample had acquired during storage. A broad maximum was present between 300 and 600 K, and a weaker one around 900 K.

The influence of the promoter did not only depend on its content in the catalyst, but also on the way the catalyst was prepared, especially on the sequence of impregnation. Therefore, a coimpregnated catalyst was studied as well. The resulting TPR profiles of this catalyst as such, and after *in situ* calcination, are presented in Fig. 6, and the corresponding H_2 consumptions are presented in Table 2. For comparison also the profiles of the La1.0Rh and RhLa1.0 catalysts, which have the same Rh and La load-

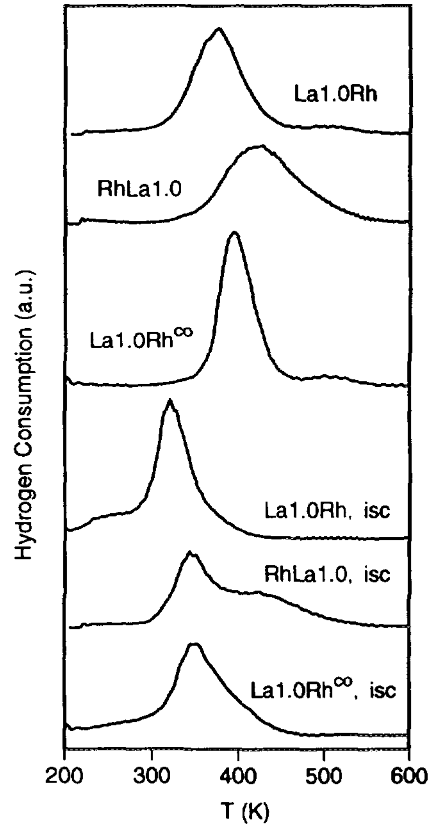

FIG. 6. TPR of coimpregnated and sequentially impregnated La_2O_3-promoted Rh/SiO_2 catalysts with La/Rh = 1, without and with *in situ* calcination (isc).

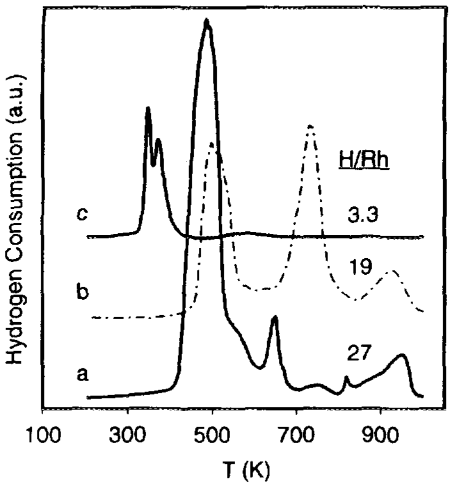

FIG. 7. TPR of Rh/La_2O_3: (a) no pretreatment, (b) calcined *in situ*, and (c) second TPR.

ings, are presented in Fig. 6. *In situ* calcination led to a peak shift to lower temperature for all three catalysts. The unpretreated coimpregnated catalyst had a narrower peak (40 K) than the sequentially impregnated ones (80 K).

TPR of Rh/La_2O_3

Rh/La_2O_3 was measured to compare the influence of the form in which the lanthana is present on the catalyst. Rh/La_2O_3, which was not calcined after preparation, was subjected to the same treatments as the promoted catalysts. The resulting TPR profiles are presented in Fig. 7. The maximum reduction rate was observed at 483 K for unpretreated Rh/La_2O_3, with several minor peaks at higher temperatures. *In situ* calcination led to peaks at 500 and 730 K and a smaller peak above 900 K. The second TPR showed two peaks at 350 and 370 K, and a small peak at 575 K. The H_2 consumption was very high for the unpretreated (because of reduction of the precursor anions) and the calcined catalyst (Table 2). It was only slightly above 3 for the second TPR, due to the peak at 575 K (Fig. 7).

CO Hydrogenation

All catalysts with a La : Rh atomic ratio of 1 were compared with Rh/SiO_2 and Rh/La_2O_3 regarding their performance in CO hydrogenation. The catalytic as well as the H_2 chemisorption results are given in Table 3. La1.0Rh produced preferentially methanol. The methanol selectivity was even more pronounced for $LaRh^{co}$. RhLa1.0 produced considerable amounts of C_2 oxygenates and had the highest TOF. The Rh/SiO_2 and Rh/La_2O_3 catalysts were the least active and produced mainly hydrocarbons. The selectivity for C_2 oxygenates was low for Rh/La_2O_3 and high for Rh/SiO_2, where acetaldehyde was the main oxygenate obtained.

DISCUSSION

TPR

The TPR results of the reference compounds demonstrate that La_2O_3 strongly hampers the reduction of Rh_2O_3 if intimate contact between these phases exists, as in $LaRhO_3$. The large shift in reduction temperature can not be attributed to a dispersion effect, because the maxima of dispersed Rh_2O_3 on SiO_2 and bulk Rh_2O_3 powder differ only by about 120 K (Fig. 1). After calcination of La_2O_3 dispersed on SiO_2 in CO_2-free air at 773 K, no hydrogen is consumed in TPR (Table 1). The small consumption with unpretreated La_2O_3/SiO_2 at 900 K must be attributed to the formation of carbonated La species, for example $LaCO_3(OH)$, during storage (*26*, *27*). As a matter of fact, SiO_2 should even be easier to reduce than La_2O_3, if the standard free energy changes of formation of the metal and water from the oxide and hydrogen are considered: 376 kJ/mol for Si and 497 kJ/mol for La (*33*). Taking into account also the absence of any stable compound with La in another oxidation state than 3, it is not surprising that no hydrogen consumption is observed for pure La_2O_3/SiO_2.

The higher peak temperatures with increasing La content in Figs. 2 and 3 show that La_2O_3 stabilizes Rh_2O_3 towards reduction by hydrogen, even at low La concentrations. Increasing the La content also leads to a higher hydrogen consumption, especially for the unpretreated samples (Table

TABLE 3

Catalyst Activities and Selectivities in CO Hydrogenation

Catalyst	H/Rh[a]	Act.[b]	TOF[c]	Selectivities in %[d]			
				CH_4	C_2^+	C_1-oxo	C_2-oxo
Rh/SiO_2	0.66	2.8	4.3	59	7	3	28
La1.0Rh	0.81	6.1	7.5	24	2	50	25
RhLa1.0	0.44	4.3	9.8	29	4	33	34
LaRh[co]	0.85	6.8	8.0	21	2	59	17
Rh/La_2O_3	0.38	1.0	2.5	46	8	41	4

[a] Chemisorption data.

[b] mmol CO converted/(mol Rh) · s.

[c] mmol CO converted/(mol surface Rh) · s.

[d] On a CO_2-free basis.

2). This might be explained by partial reduction of the La_2O_3 as proposed before by several authors (*9, 18, 19, 23, 34*). Our results do not support this explanation. First, *in situ* calcination leads to a reduction of the hydrogen consumption, or alternatively, air storage of $Rh–La_2O_3/SiO_2$ catalysts enhances the hydrogen consumption. As can be seen in Fig. 2B, air exposure leads to a considerable increase of the second peak of the La11.1Rh catalyst. Furthermore, a second TPR run after reoxidation gives normal hydrogen consumptions (H/Rh = 3) for the SiO_2-supported catalysts, except for the two samples which were not recalcined with CO_2-free air (H/Rh = 3.2). Third, the MS analysis of the La11.1Rh catalyst (Fig. 5) shows that the TPR peak above 500 K of the unpretreated LaRh catalysts (Fig. 2B) is connected with the evolution of CH_4 ($m/e = 15, 16$) around 540 K. Bernal *et al.* found that the carbonated phase on Rh/La_2O_3 is decomposed during reduction in two steps at 573 and 723 K, while carbonated La_2O_3 alone was transformed into La_2O_3 around 800 K (*27*). We therefore presume that the CH_4 in our case also originates from carbonated La_2O_3 species. Our TPR results show that La_2O_3 is not reduced below 1000 K, not even when it is in contact with Rh. Recently Shelef *et al.* came to the same conclusion in an XPS study of thin films of La_2O_3 and Pd (*35*).

Three different types of peaks were observed in the TPR profiles: one or two peaks in the 300–500 K region, a peak slightly above 500 K, and a peak above 850 K. The latter peak is only observed at the highest La loading and might be due to carbonated La_2O_3, remote from Rh, which decomposes around 850 K (*27*). The resulting CO_2 would then be reduced by H_2 on the Rh particles to CO and H_2O, which would explain the mass spectrometry results in Fig. 5. The peak above 500 K is mainly present in the unpretreated samples. Its intensity is greatly reduced by *in situ* calcination and the remaining peak(s) between 300 and 500 K can fully account for the reduction of Rh^{3+}. This and the mass spectrometry results for CH_4 (Fig. 5) prove that the 500 K peak is not due to the reduction of Rh species, but to the reduction of carbonate species.

The most intense TPR peak, which is the only one for Rh/SiO_2 and for most samples that have been calcined *in situ*, is located between 300 and 500 K and shifts to higher temperatures with increasing La content. This peak (or peaks) can be attributed to the reduction of Rh^{3+}, since it survives the *in situ* calcination and since the corresponding H_2 consumption is in all cases close to H/Rh = 3. The peak shift implies that the Rh_2O_3 particles are in contact with La_2O_3, even at low La_2O_3 loadings. The LaRh and RhLa catalysts display two types of 300–500 K

TPR peaks, one shifting mildly with γ from 300 to 360 or 390 K, and another shifting more strongly to 480 K (cf. Fig. 4). This suggests that two types of Rh_2O_3 particles may exist on these catalysts, one more easy to reduce than the other. The latter, more difficult to reduce Rh_2O_3 is only present in the RhLa catalysts. In a previous chemisorption study, we demonstrated that the Rh particles in the RhLa catalysts are partially covered by La_2O_3 moieties (*12*). The profiles of Fig. 3B suggest that for $\gamma \geq 0.5$ the Rh_2O_3 particles are fully covered when the catalysts were stored and not calcined *in situ*. The TPR peak of the RhLa catalysts therefore not only shifts to higher temperatures due to electronic influences, but also due to the protective layer of La species, and thus lies higher than the maxima for the LaRh catalysts. *In situ* calcination converts most of the carbonated and hydrated La_2O_3 into pure La_2O_3, as shown by the decrease of the H_2 consumption and of the peak above 500 K. The La_2O_3 islands shrink due to the loss of CO_2 and H_2O and uncover part of the Rh_2O_3 particles, which stay, however, in contact with La_2O_3. These Rh_2O_3 particles are responsible for the second peak in the TPR, at similar temperatures as the main peak in the LaRh series. Uncovering occurs to a lesser extent at high La loading as seen in the profiles of Fig. 3A, where the second peak grows at the expense of the first peak, which represents bare Rh_2O_3.

The hydrogen chemisorption and CO hydrogenation studies (*12*) showed that in the LaRh catalysts the Rh particles are mainly uncovered, also in the unpretreated catalysts. The corresponding Rh_2O_3 particles then account for the 300 to 360 or 390 K TPR peak. The lower temperatures for the *in situ* calcined samples are in agreement with the observation of Watson and Somorjai that it is easier to reduce dry Rh_2O_3 than hydrated Rh_2O_3 (*36*).

The shift of the TPR peak with γ for the LaRh series may be due to a change in Rh_2O_3 particle size. The chemisorption measurements showed that after reduction the dispersion of Rh increases with γ (*12*), which suggests that a high TPR peak temperature corresponds to small Rh_2O_3 particles. Apparently, small Rh_2O_3 particles interact stronger with La_2O_3 than large Rh_2O_3 particles. The particle sizes of the Rh_2O_3 particles in the RhLa catalysts in the oxidic state were constant, because all catalysts were taken from the same Rh/SiO_2 batch, and because no redissolution of Rh_2O_3 took place (*12*). The first TPR peak was attributed to Rh_2O_3 particles that are not covered by La_2O_3, as in the LaRh series. The increasing peak temperature with increasing γ may be explained by covering of the reduction nucleation centres on the Rh_2O_3 particles by La ions. The second peaks, as well as the peaks of the unpretreated RhLa catalysts, are very broad and they shift to much higher temperatures. Covering by the promoter oxide and diffusion limitations of H_2 through increasingly thicker La_2O_3 layers during TPR would explain this.

The coimpregnated $LaRh^{co}$ catalyst has a TPR peak maximum at 390 K when no pretreatment was applied, and a peak at 350 K with a shoulder at about 400 K in case an *in situ* calcination was applied before TPR (Fig. 6). These values, as well as the peak widths are close to those of the La2.0Rh catalyst which was prepared by sequential impregnation and calcination, and do not agree with values of RhLa catalysts. Also the occurrence of only a small shoulder around 400 K, instead of a substantial peak as in the RhLa catalysts with $\gamma \geq 0.5$ (cf. Fig. 3A), indicates that very little covering of Rh_2O_3 by La_2O_3 occurs. Apparently, after coimpregnation and calcination La_2O_3 is in contact with Rh_2O_3, but is not covering it.

The minor shift of the TPR peak with γ in the second TPR from 305 K for $\gamma = 0$ to 321 K for $\gamma = 11.1$, shows that the influence of La_2O_3 on Rh_2O_3 has severely decreased during the reduction up to 1000 K in the first TPR. Probably La^{3+} ions in contact with Rh_2O_3 particles in the LaRh catalysts, and La_2O_3 patches on top of Rh_2O_3 in the RhLa catalysts are removed from the Rh metal particles at high reduction temperature and do not move back during the calcination step at 773 K which precedes the second TPR. In this sense, La_2O_3–Rh/SiO_2 catalysts are different from Rh/La_2O_3 catalysts, in which there is always a contact between Rh and La_2O_3, whatever the pretreatment. In La_2O_3–Rh/SiO_2 catalysts on the other hand, La^{3+} ions can interact with the SiO_2 support and tend to move away from the metal to the support.

After *in situ* calcination of the Rh/La_2O_3 catalyst during one hour at 773 K, a substantial part of the La_2O_3 is not freed of carbonate, as shown by the H/Rh value of 19 (Table 2). Complete carbonate removal is achieved by TPR up to 1000 K, as demonstrated by the hydrogen consumption during the second TPR ($H/Rh = 3.3$). The slight excess of $H/Rh = 0.3$, due to the small peak at 575 K, could not be removed by repeated TPR-calcination cycles and can therefore not be attributed to carbonate. Trace amounts of rare earth metals in the La_2O_3 support may be responsible for this additional consumption. For instance, a 0.02% contamination of La by Ce would suffice to explain the additional consumption (10%) of hydrogen by reduction of Ce^{4+} to Ce^{3+}.

CO Hydrogenation

All La_2O_3-promoted 1.5% Rh/SiO_2 catalysts with $\gamma = 1$ have a high methanol selectivity, in contrast to Rh/SiO_2 which forms only tiny amounts of methanol. La_2O_3 suppresses the formation of acetaldehyde and enhances the formation of ethanol and its esters (mainly ethyl acetate) and ethers. Several authors have proposed that ethanal is a precursor of ethanol (*4, 37–40*), in line with our results, which showed that acetaldehyde was the major C_2-oxo component over pure Rh/SiO_2, while over all La_2O_3-promoted catalysts ethanol was the main component. The turnover frequencies for the different products (calculated from the product selectivities and the total TOF in Table 3) demonstrate that La_2O_3 mainly promotes the hydrogenation of undissociated CO and of acetaldehyde, and that the CO dissociation is hardly promoted. A key parameter in the promotion seems to be the size of the Rh–La_2O_3 interface, regardless of the relative position of the promoter. The interface could act as an area that enhances hydrogen bonding thereby increasing the hydrogen concentration. Levin *et al.* investigated Rh foil partially covered by TiO_x and found that CO chemisorption was suppressed at Rh sites adjacent to the TiO_x islands (*41*). Stevenson *et al.* (*42*) and Koerts and van Santen (*38*) argued that the promoter weakens the CO adsorption and, as a consequence, increases the surface hydrogen concentration during CO hydrogenation. This would increase the hydrogenation rate on the catalyst. One could envisage that the same holds for the Rh–La_2O_3 interface. Alternatively, spillover could also account for the increased methanol formation. CO on La_2O_3, either spilt over from Rh or directly adsorbed on the basic La_2O_3 surface, could react with OH^- to formate which is subsequently hydrogenated to methanol by spilt over hydrogen, as proposed by Kuznetsov *et al.* (*3*). An enhanced hydrogen concentration at the interface would lead to a higher activity in this model, too. In this relation it should be noted that Hattori and Wang observed the formation of reaction intermediates on La_2O_3 when La_2O_3 (without any metal present) saturated with CO was exposed to H_2 at synthesis gas reaction temperatures (*43*).

Coimpregnation leads to almost the same catalytic properties as the sequential impregnation in the LaRh series. This is supported by studies of redissolution, which showed that previously impregnated and calcined La_2O_3 could be dissolved by the Rh-precursor solution (*10, 12*), but that Rh_2O_3 was not dissolved by the La-precursor solution (*12*). Coimpregnation and sequential impregnation with La impregnation as the first step thus lead to very similar catalysts. The Rh–La_2O_3 interaction is still somewhat more efficient after coimpregnation as shown by the higher dispersions and activities of the coimpregnated samples and their product selectivities that lie between those of the La1.0Rh and the La2.0Rh catalysts (*12*).

Whereas La_2O_3 promotion increased the turnover frequency of the Rh/SiO_2 catalyst (Table 3), Rh/La_2O_3 had a lower TOF than Rh/SiO_2. This may be related to the difficulty of comparing the H_2 chemisorption value of a partially covered Rh surface in Rh/La_2O_3 with the bare Rh surface in Rh/SiO_2, although it is hard to believe that the conclusion can be reversed. Furthermore, Rh/La_2O_3 had a rather low methanol selectivity and a low C_2-oxo selectivity. It is not clear what the explanation for this is. It might have to do with strong adsorption of formate and acetate species (which are supposed to be precursors for methanol and ethanol), or of carbonate (compare the discussion by Walker *et al.* in Ref. (*44*)), on the La_2O_3 support. Nevertheless, the present results show that La_2O_3-supported Rh and La_2O_3-promoted Rh/SiO_2 behave differently.

CONCLUSIONS

The properties of coimpregnated LaRh catalysts are nearly the same as those of sequentially impregnated catalysts, in which La was impregnated prior to Rh (LaRh series). Small Rh particles interacting with La_2O_3, but not covered by the promoter are obtained. The selectivity to methanol in CO hydrogenation is strongly enhanced compared to Rh/SiO_2. When Rh is impregnated before La (RhLa series) the Rh particles are larger and they are partially covered by La_2O_3. The selectivity change is not as large as for the LaRh catalysts. The methanol selectivity is dependent on the amount of $Rh–La_2O_3$ interface area, which is higher in the LaRh catalysts, even though the Rh particles are not covered by La_2O_3. The main role of the interface is to enhance the availability of hydrogen, probably by spillover. This hydrogen could also be used to hydrogenate formate species on La_2O_3 to methanol.

The TPR results show that La_2O_3 can not be reduced below 1000 K, neither in pure form on SiO_2, nor in contact with Rh in a perovskite-type mixed oxide ($LaRhO_3$), nor dispersed on SiO_2 together with Rh. Therefore, partly reduced LaO_x can be ruled out as being responsible for the promoter effect in the CO–H_2 reaction.

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