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ZrO_2-Promoted Rh/SiO_2 Catalysts in CO Hydrogenation and Temperature-Programmed Reduction

A. L. Borer, C. Brönnimann, and R. Prins

Laboratorium für Technische Chemie, Eidgenössische Technische Hochschule, 8092 Zürich, Switzerland

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The hydrogen chemisorption, high-pressure CO hydrogenation, and temperature-programmed reduction of ZrO_2-promoted Rh/SiO_2 catalysts were studied. The promoter decreased the adsorption capacity of the catalysts by covering the metal surface. The covering of Rh by ZrO_2 seemed to occur during reduction. At low ZrO_2 loadings this covering created new active sites for CO hydrogenation, while at higher ZrO_2 loadings both activity and turnover frequency were decreased. The impregnation sequence in the pore volume impregnation had no influence on the catalytic behavior. By applying different calcination procedures, however, the interactions between ZrO_2 and the SiO_2 support, as well as between ZrO_2 and Rh_2O_3, could be intensified and the catalytic behavior altered. When ZrO_2 is in contact with Rh, it can be partly reduced and forms Zr^{3+} ions. Thus, the interaction between Rh and ZrO_2 is similar to the strong metal–support interaction.

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INTRODUCTION

CO can adsorb associatively and dissociatively on a metal like Rh and can therefore be hydrogenated to methanol, as well as to hydrocarbons and C_2 oxygenates such as acetaldehyde, ethanol, and acetic acid (1, 2). Oxophilic promoters such as TiO_2, ZrO_2, and La_2O_3 were found to markedly increase the yields of ethanol and other C_2 oxygenates (3), whereas basic promoters such as ZnO, MgO, and CaO enhanced the methanol yield (2, 4). The influence of the promoter on the CO hydrogenation has been ascribed to direct contact between metal and promoter (5–7), as well as to remote control by promoter material which is not in direct contact with the metal (8). Evidence for promotion by direct contact comes from IR observations that the IR frequency of the bridge-bonded CO is shifted to lower wavenumbers by certain promoters, which was explained by the ability of CO to bind with its C atom to a metal atom and with its O atom to a neighboring promoter cation (9). Other evidence is that the CO hydrogenation activity goes through a maximum with increasing promoter loading (10–12). At low promoter loadings the interface between metal and promoter increases, thus enabling more CO molecules to bind across the interface and be activated for dissociation, insertion, and hydrogenation, while at high promoter loadings too much metal surface is covered by the promoter, so that the size of the interface decreases again.

When after CO dissociation the O atom is bonded to the promoter cation this cation formally undergoes an oxidation, while during the subsequent removal of the O atom by H_2 or CO the promoter cation is formally reduced back to its original oxidation state (13). This suggests that metal cations that can undergo redox cycles might be good promoters for CO hydrogenation. Indeed many transition metal oxides promote the CO hydrogenation, but La_2O_3, ZrO_2, and ThO_2 are also efficient promoters, although it has been questioned if two stable oxidation states exist for La, Zr, and Th. A recent study (12) showed that a former proof (7) for the reducibility of La_2O_3 to LaO_x ($x < 1.5$) was incorrect, since the reduction of carbonate present at the surface of La_2O_3 had been taken for the reduction of La_2O_3 itself. After proper removal of carbonate no evidence for La_2O_3 reduction could be found. It therefore seemed of interest to extend the study of promoter reducibility to ZrO_2.

In the present work we report a temperature programmed reduction (TPR) and high pressure CO hydrogenation study of ZrO_2-promoted Rh/SiO_2 catalysts. Like La_2O_3, ZrO_2 is of interest because it is sometimes regarded as nonreducible under usual conditions and should therefore not promote CO hydrogenation by assisting in a redox cycle as proposed by Mori *et al.* for V_2O_5 (13). On the other hand, it is known from solid state chemistry that ZrO_x with $x < 2$ exists, which indicates that ZrO_2 can be reduced. The work on La_2O_3-promoted Rh/SiO_2 has revealed that TPR experiments can provide valuable information on the reducibility of the promoter (14). We have used Cl-free Rh and Zr precursors in the preparation of the catalyst samples, because of the effect which Cl can have on the catalytic behavior of Rh (15, 16). We have varied the impregnation sequence and the promoter loading, since this proved effective in the study of La_2O_3-promoted Rh/SiO_2 (12, 14, 17).

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TABLE 1

Catalyst Specifications

Notation	Zr/Rh	Rh content (wt %)[a]	H/Rh
Rh/SiO_2	0	1.47	0.57
Zr0.12Rh	0.12	1.47	0.47
Zr0.5Rh	0.5	1.46	0.40
Zr1.0Rh	1.0	1.45	0.45
Zr2.0Rh	2.0	1.42	0.45
Zr5.0Rh	5.0	1.35	0.40
RhZr0.12	0.12	1.47	0.44
RhZr0.5	0.5	1.46	0.42
RhZr1.0	1.0	1.45	0.45
RhZr2.0	2.0	1.42	0.37
RhZr5.0	5.0	1.35	0.30
RhZr5.0*	5.0	1.35	0.32
Zr55Rh	55	0.15	
ZrO_2/SiO_2		8.25[b]	

[a] After calcination.
[b] Zr content.

EXPERIMENTAL

The same catalyst preparation method as described in Ref. (14) was applied. Thoroughly washed silica (C-560 from CF Uetikon) was impregnated to incipient wetness with aqueous solutions of $ZrO(NO_3)_2 \cdot xH_2O$ (Aldrich) and $Rh(NO_3)_3$ (Johnson Matthey, 5% solution in 1.7 *M* HNO_3, diluted to the required level). The Zr-content of $ZrO(NO_3)_2 \cdot xH_2O$ was determined gravimetrically from the weight loss that occurred when the nitrate was calcined to the oxide at 773 K for 3 h. One impregnation step was sufficient to obtain an Rh loading of 1.5%. Because of the limited solubility of $ZrO(NO_3)_2$, two or five impregnation steps were necessary to obtain a Zr/Rh atomic ratio (γ) of 2 or 5, respectively. Each impregnation step was followed by drying the sample at 393 K (heating rate 2 K/min) and calcining it in air at 773 K (3 h, 5 K/min). Two series of catalysts, denoted ZrRh and RhZr, were prepared, with γ varying between 0 and 5. In the ZrRh catalysts Zr was impregnated first, while for the RhZr catalysts Rh was impregnated first. No calcination, only drying at 393 K, was applied between the Zr impregnations of the RhZr5.0* and Zr55Rh catalysts. A calcination was only applied after the last Zr impregnation and after the Rh impregnation. The Zr55Rh catalyst contains only 0.15 wt% Rh, but the same amount of ZrO_2 as in the Zr5.0Rh and RhZr5.0 catalysts with $\gamma = 5$. All catalyst samples were stored in air and their specifications are listed in Table 1.

Equipment and procedure for volumetric H_2 adsorption measurements have been described in Ref. (12). About 0.1 g of catalyst was reduced at 723 K (1 h, 5 K/min) and evacuated at 673 K for 30 min to a pressure below 10^{-4} Pa. After cooling under vacuum to 293 K the adsorption isotherm was recorded between 10 and 40 kPa. The amount of chemisorbed H_2 was obtained by extrapolating the isotherm to zero pressure.

The procedure described in detail in Ref. (12) was followed for the high pressure CO hydrogenation experiments. In short: After reduction at 723 K in H_2 for 1 h the temperature was set to 530 K, the pressure was raised to 4 MPa and the reaction was started by introducing CO to the reactor at a H_2/CO flow ratio of 3. The activity and selectivity data to be presented were obtained after 15 h. The experimental details of the TPR experiments have been outlined in Ref. (14). In essence, the TPR experiments were carried out at ambient pressure in a horizontally placed quartz tube with 5% H_2 in Ar, and the changes in H_2 concentration were monitored by a TCD. Best resolution was obtained by proper choice of experimental parameters (18, 19). Most TPR profiles were recorded between 200 and 1000 K, applying the procedure of Vis *et al.* (20). Before TPR the samples were calcined *in situ* with dry air at 773 K, unless otherwise stated.

RESULTS

Hydrogen Chemisorption

The hydrogen chemisorption on the freshly reduced catalysts decreased with increasing ZrO_2 loading in both ZrRh and RhZr series (Table 1). At low Zr loadings the differences between the series were small, but at high loadings the H_2 chemisorption decreased stronger for the RhZr series. In the ZrRh series the H/Rh values levelled off at a value of about 0.42 with increasing γ, while in the RhZr series it reached a value of 0.30, which is a reduction of about 50% of the value of Rh/SiO_2. The percentage of exposed Rh obtained from hydrogen chemisorption was used to determine the turnover frequencies in Table 2.

CO Hydrogenation

ZrO_2 had a large influence on activity and turnover frequency, as is evident from Fig. 1 and Table 2. The activity and the turnover frequency increased up to $\gamma = 0.5$ and decreased thereafter, so that the Zr5.0Rh catalyst was even less active than the unpromoted Rh/SiO_2 catalyst. It was more advantageous to impregnate Rh before Zr, since the catalysts of the RhZr series were more active and showed higher turnover frequencies than their ZrRh counterparts. The best catalysts of the ZrRh and the RhZr series were several times more active than Rh/SiO_2.

The selectivities to hydrocarbons, C_1 oxygenates (methanol and its esters and ethers), C_2 oxygenates (ethanol, derived esters and ethers, and acetaldehyde), and

TABLE 2

CO Hydrogenation Results over ZrO_2-Promoted Rh/SiO_2

Catalyst	Zr/Rh	Activity[a]	TOF[b]	Selectivities in %[c] CH_4	C_{2+}	MeOH	C_1 E/E[d]	EtOH	C_2 E/E[d]	AcH
Rh/SiO_2	0	2.5	4.4	59	7	4	1	7	5	13
ZrRh	0.12	7.1	15.1	49	8	6	2	22	9	3
	0.5	7.2	18.0	43	7	11	2	23	10	2
	1.0	6.6	14.7	38	7	13	3	25	11	2
	2.0	4.0	8.9	32	8	22	3	20	10	2
	5.0	1.0	2.5	23	15	41	4	10	7	0
RhZr	0.12	7.5	17.0	53	10	4	1	18	9	4
	0.5	9.3	22.1	43	8	9	2	23	11	2
	1.0	8.9	19.8	40	8	10	3	24	12	2
	2.0	6.0	16.2	34	8	15	3	26	11	2
	5.0	3.5	11.7	72	5	10	1	7	3	2
RhZr5.0*	5.0	4.3	13.4	30	8	19	4	23	12	3

[a] mmol CO converted/(molRh) · s.
[b] mmol CO converted/(mol surface Rh) · s.
[c] On a CO_2-free basis.
[d] Esters and ethers.

total oxygenates were calculated from the product selectivities given in Table 2 and are plotted in Figs. 2 and 3. Since only traces of C_{3+} oxygenates were formed they were not taken into account. For $\gamma \leq 1$ the selectivities of the RhZr and ZrRh series are virtually equal, while small differences are observed for higher Zr/Rh ratios, most clearly in the C_1 and C_2 oxygenates selectivities for $\gamma = 5$. A monotonic increase of the total oxygenates selectivity with increasing γ was measured for the ZrRh series (Fig. 2A). This was due to an increase in the C_1 oxygenate selectivity as shown in Fig. 3A, while the C_2 oxygenate selectivity went through a maximum. The selectivity data for RhZr5.0* were similar to those of RhZr2.0, rather than to those of RhZr5.0. To alter the Rh-Zr interaction, the RhZr5.0* catalyst was prepared using less calcination steps. As a consequence, the selectivity data for the RhZr5.0* catalyst, rather than those of the RhZr5.0 catalyst, matched very well with the selectivities of the other RhZr catalysts as a function of γ (Figs. 2B and 3B).

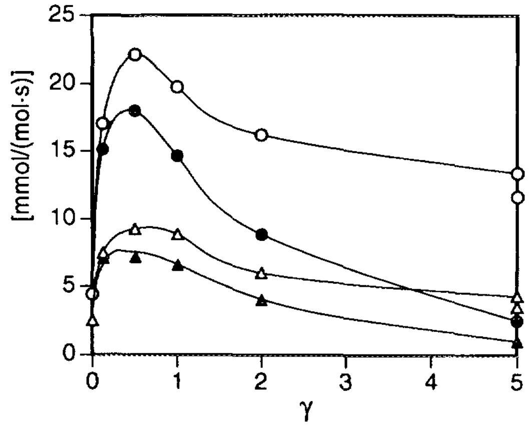

FIG. 1. Activities and turnover frequencies (TOF) of the catalysts of the ZrRh and the RhZr series as a function of the Zr/Rh atomic ratio (γ). Activities: (▲) ZrRh, (△) RhZr. TOF: (●) ZrRh, (○) RhZr (the additional points for the RhZr series at $\gamma = 5$ belong to RhZr5.0, while those on the lines belong to RhZr5.0*).

The turnover frequencies for methane, C_{2+} hydrocarbons, and C_1 and C_2 oxygenates, obtained by multiplying the overall turnover frequency with the corresponding selectivities (Table 2), are presented in Fig. 4. Like the total turnover frequency (Fig. 1), the turnover frequencies of all products went through a maximum at $\gamma = 0.5$, except for the C_1 oxygenates in the RhZr series. In both series, for $\gamma \geq 0.5$, the turnover frequencies for C_1 oxygenates and C_{2+} hydrocarbons changed much less than those of methane and C_2 oxygenates.

The CO hydrogenation experiments on the 8.25% ZrO_2/SiO_2 catalyst showed an erratic behavior. Although the same general trend (as presented below) was observed in all cases, the absolute values of the activities and the rate of activity decrease were different from experiment to experiment. The results of a typical experiment are listed in Table 3 as a function of time on stream. The Zr loading of the Zr/SiO_2 catalyst was the same as those of the Zr5.0Rh and RhZr5.0 catalysts, and the test conditions were the same as for the ZrO_2-promoted Rh/SiO_2 cata-

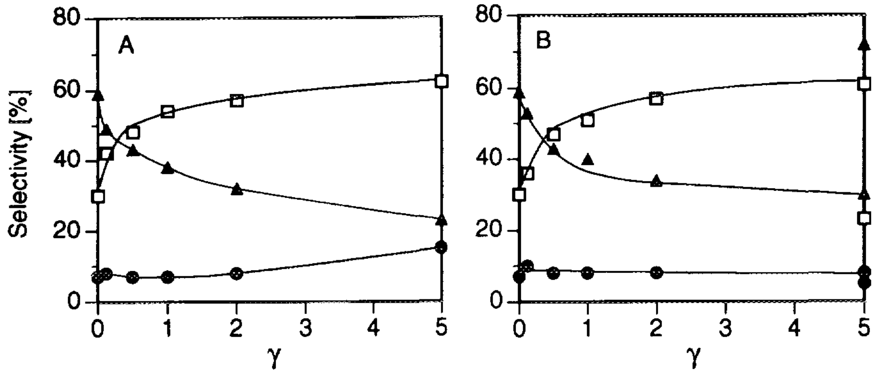

FIG. 2. Selectivities to CH_4 (▲), C_{2+} hydrocarbons (●), and all oxygenates (□) as a function of the Zr/Rh atomic ratio (γ). (A) ZrRh series, (B) RhZr series (the additional points for the RhZr series at γ = 5 belong to RhZr5.0, while those on the lines belong to RhZr5.0*).

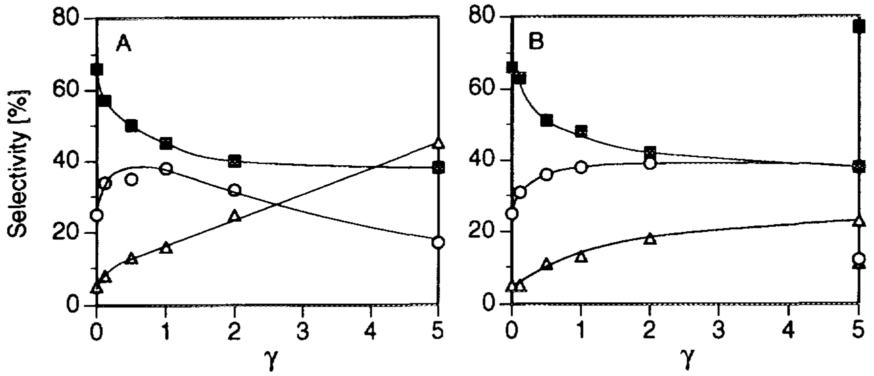

FIG. 3. Selectivities to C_1 oxygenates (△), C_2 oxygenates (○), and all hydrocarbons (■) as a function of the Zr/Rh atomic ratio (γ). (A) ZrRh series, (B) RhZr series (the additional points for the RhZr series at γ = 5 belong to RhZr5.0, while those on the lines belong to RhZr5.0*).

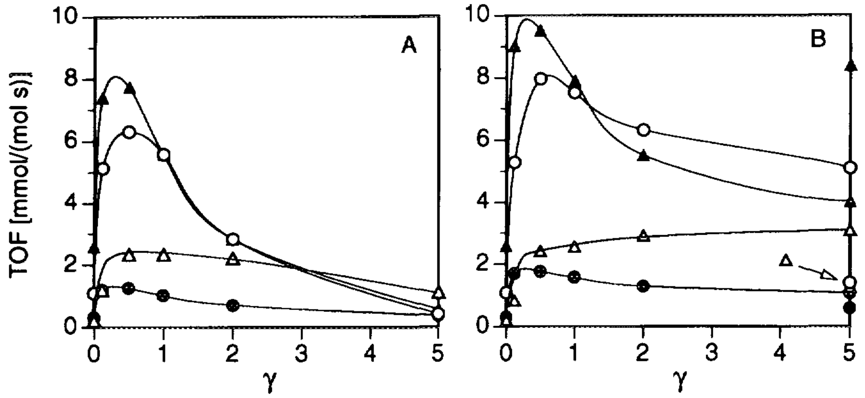

FIG. 4. Turnover frequencies for CH_4 (▲), C_{2+} hydrocarbons (●), C_1 oxygenates (△), and C_2 oxygenates (○) as a function of the Zr/Rh atomic ratio (γ). (A) ZrRh series, (B) RhZr series (the additional points for the RhZr series at γ = 5 belong to RhZr5.0, while those on the lines belong to RhZr5.0*).

TABLE 3

CO Hydrogenation over 8.25% ZrO_2/SiO_2

t (min)	α[a] [%]	Act[b] ×100	Selectivity [%]		
			C_1 Oxo	C_2 Oxo	HC[c]
10	0.13	3.9	58	22	20
40	0.05	1.4	30	20	50
70	0.03	1.0	11	1	88
100	0.03	0.9	0	0	100

[a] CO conversion.

[b] Activity (mmol CO converted/(molZr) · s).

[c] Hydrocarbons (almost exclusively CH_4).

lysts, to compare the intrinsic CO hydrogenation activity of the promoter with that of Rh. Initially a low activity was observed, which decreased in time. Because of the very low signal-to-noise ratio of the GC signal the accuracy of these measurements was low. The selectivity to oxygenates was high in the beginning, but vanished after a certain period. The activity values in these experiments were two orders of magnitude lower than those of the Rh catalysts.

TPR of the ZrRh and the RhZr Catalysts

The reduction profiles of the catalysts of the ZrRh series are plotted in Fig. 5A. The presence of a small amount of ZrO_2 ($\gamma = 0.12$) had no effect on the reduction behavior, but small shifts of the TPR peak were observed for the Zr0.5Rh and Zr1.0Rh samples, although the peak shape stayed the same. The catalysts with higher Zr loadings showed broader peaks and the maximum was shifted to higher temperature. Thus the peak of Zr5.0Rh was located 27 K higher than the one for Rh/SiO_2. The profile of Zr5.0Rh exhibited a second, very broad signal above 800 K. In the RhZr series the peak maxima shifted more with increasing γ than those of the ZrRh series (Fig. 5B). The temperature difference between the TPR peaks of Rh/SiO_2 and RhZr5.0 was 69 K. However, for $\gamma = 0.12$ no shift could be detected. The peaks became broader with increasing γ and the broadening was more pronounced than in the ZrRh series. For RhZr2.0 and RhZr5.0 a broad peak above 800 K was observed, as for the Zr5.0Rh catalyst.

Some experiments were conducted to study the nature of the peak above 800 K. The ZrO_2/SiO_2 sample showed a peak at 861 K (Fig. 6). In two additional calcination–TPR cycles, carried out directly after this TPR, no hydrogen consumption could be measured in this region. The second peak maximum of the Zr5.0Rh catalyst was observed at about 825 K and its intensity was rather low. The second peak of the RhZr5.0 catalyst at 853 K had a greater intensity and therefore this catalyst was chosen for further study. When the RhZr5.0 catalyst was subjected to TPR without *in situ* calcination, the first peak shifted to higher temperature (420 K), but the shape of the second peak above 800 K remained unchanged. After TPR the catalyst was calcined in situ at 773 K with CO_2-free air to avoid the formation of carbonate species during calcination and a second TPR was performed. It exhibited a second peak at 555 K (Fig. 6), almost 300 K below the second maximum in the first TPR of the RhZr5.0 catalyst. In the second TPR the main peak was located at lower temperature as well, and it was narrower than in the first TPR.

The TPR profiles of the Zr55Rh catalyst are plotted in Fig. 7. The signal intensity was lower in these experiments because 5 to 10 times less Rh was present during these experiments than during the other TPR experiments. As a consequence, the uncertainty in the TPR H/Rh values reported in Fig. 7 is about 10%. In all TPR experiments an apparent hydrogen consumption appeared at the beginning of the TPR experiments. The peak is due to unequal flow rates in the reference and detector channels of the TC detector because of gas expansion during the initial temperature increase. It increased the inaccuracy of the H_2 consumption values of the low loaded Zr55Rh samples. In the first TPR of the Zr55Rh catalyst no peak could be observed in the region where the other catalysts showed the first reduction peak, regardless of the fact whether an in situ calcination was performed (Fig. 7, profiles (a) and (b)). It may be that the reduction of Rh^{3+} is hidden under the broad band extending from about 400 to 600 K. The main hydrogen consumption in the first TPR of the Zr55Rh sample took place above 800 K, in the region where a second peak was observed for RhZr5.0 (Fig. 6). The two second TPR profiles were similar, although the intermediate calcination was performed with CO_2-free air in experiment (d). The H/Rh values were lower than in the first TPR runs but still exceeded the stoichiometrically required amount of hydrogen for Rh^{3+} reduction by almost 200%. A peak emerged around 350 K, where the main peak of the RhZr5.0 catalyst was situated. This peak accounted for half the hydrogen consumed during the experiments. The other half produced the broad peaks at about 700 K. This second peak became very flat during a third TPR (after an intermediate calcination at 1023 K with dry air), while the main peak was slightly shifted to higher temperature. The hydrogen consumption could be reduced to H/Rh = 7.

DISCUSSION

Structure of the Catalysts

The H_2 chemisorption, CO hydrogenation, and TPR results of the RhZr catalysts have much in common with those of the RhLa catalysts (12, 14). The chemisorption

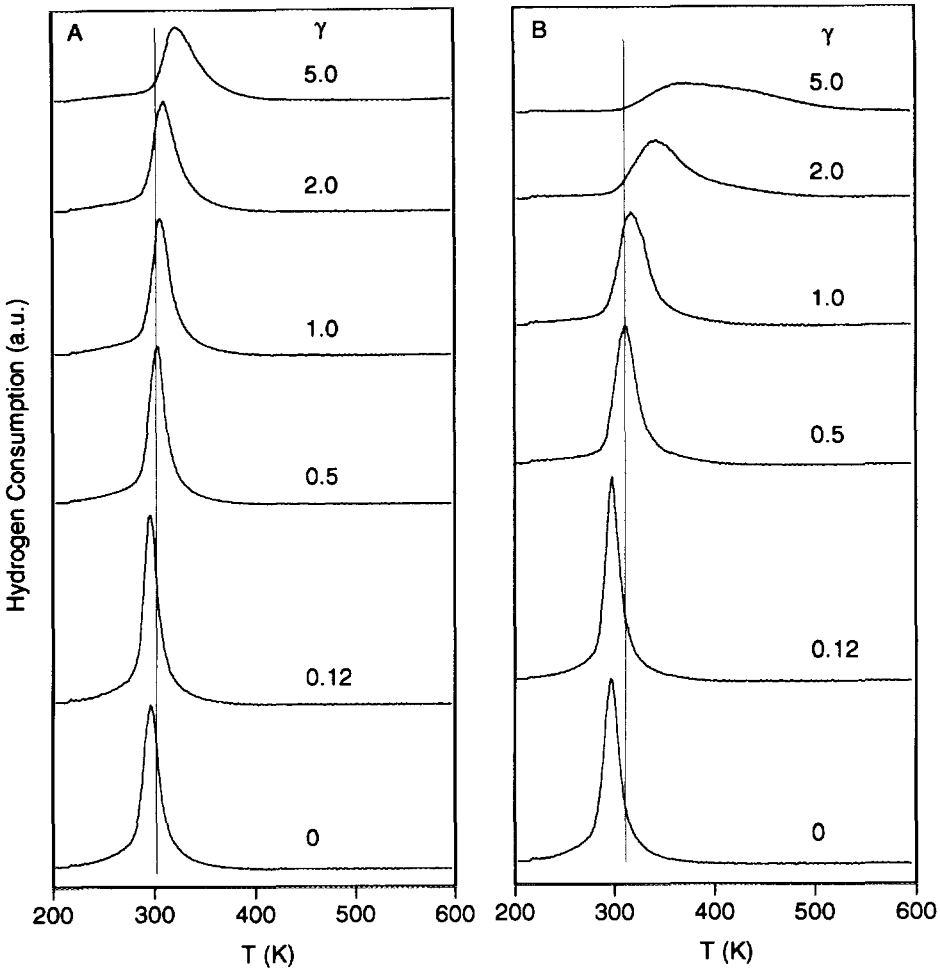

FIG. 5. TPR of ZrO_2-promoted Rh/SiO_2 catalysts. (A) ZrRh series, (B) RhZr series.

decreases, the catalytic activity goes through a maximum and the TPR peak shifts to higher temperature with increasing promoter-to-Rh ratio γ. As in the RhLa series, the results for the RhZr catalysts can be explained by assuming that the promoter oxide covers the Rh particles. During the first impregnation with $Rh(NO_3)_3$, drying, and calcining, Rh_2O_3 particles are formed which are not attacked by the second impregnation solution, since we observed that Rh_2O_3 did not dissolve in a $ZrO(NO_3)_2$ solution. A redispersion of the Rh_2O_3 particles during the second impregnation, drying, and calcination steps can therefore be ruled out and the decreased H_2 chemisorption must be ascribed to covering of the Rh particles in the reduced catalyst by promoter oxide. The CO hydrogenation behavior is also in accordance with this explanation. Initially the activity increases with γ because of an increasing amount of Rh-promoter oxide interface area (10). Several authors have suggested that CO molecules at this interface may bind with their C atoms to Rh atoms and with their O atoms to promoter cations (5–12). In this way the CO bond is weakened and CO dissociation promoted. Indications for such CO simultaneously bound to a Rh atom and a Zr cation were inferred from IR investigations (21, 22). Large amounts of promoter lead to extensive covering of the Rh particles and to a decrease of the Rh-promoter interface. Therefore, at low γ the catalytic activity increases with γ, at high γ it decreases with γ, and at some intermediate value there is an optimum in the catalytic properties. This is indeed the situation observed with the RhZr as well as with the RhLa catalysts.

The behavior of the ZrRh catalysts is different from that of the LaRh catalysts and is much more similar to that of the RhZr and RhLa catalysts. In the LaRh series, the H_2 chemisorption increased with increasing γ and the CO hydrogenation activity did not show a maximum. It increased with γ and the selectivity shifted to methanol (12). The increase of the H_2 chemisorption with γ is due to an improvement of the Rh dispersion by the promoter. Either La_2O_3 particles or La^{3+} ions on the SiO_2 support, formed during the first impregnation, drying, and calcina-

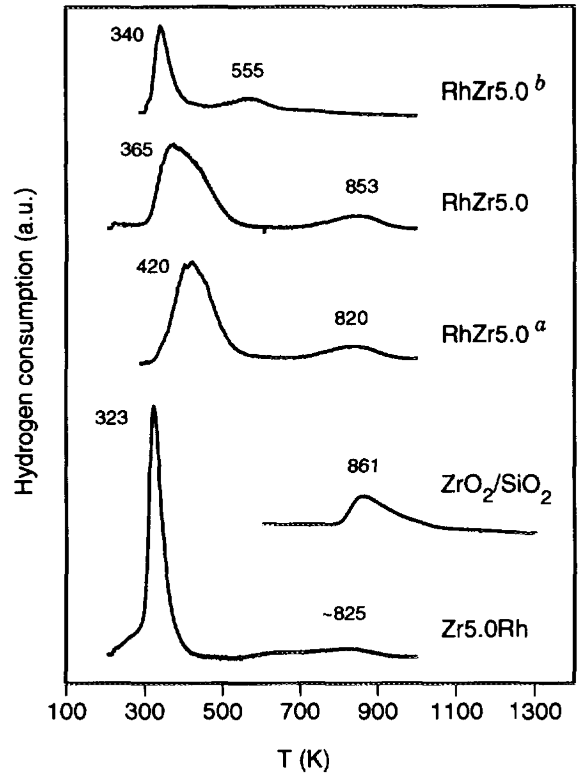

FIG. 6. TPR of catalysts with a high Zr loading. (a) Without *in situ* calcination; (b) second TPR after intermediate calcination with CO_2-free dry air at 773 K.

tion, act as adsorption centers for the Rh^{3+} ions in the second impregnation with $Rh(NO_3)_3$, or they act as stabilizing centers for metallic Rh particles formed during reduction, thus preventing sintering. The very small Rh particles which are present at high La_2O_3 loadings have different catalytic properties as large particles. They efficiently produce methanol, possibly because (although they are not very efficient in the dissociation and hydrogenation of CO) they are still able to efficiently dissociate H_2. H atoms spilled over to the promoter then may hydrogenate formate formed on the basic La_2O_3 by direct reaction with CO. On the other hand, the H_2 chemisorption of the ZrRh catalysts decreases with γ and the CO hydrogenation activity goes through a maximum. ZrO_2 certainly does not improve the dispersion of Rh and the results should be explained either by a decrease in Rh dispersion, by covering of Rh with ZrO_2, or by a combination of both. The maximum in the catalytic activity excludes the possibility that a decrease in Rh dispersion could be the sole explanation. Covering, or covering combined with a decreased Rh dispersion must be the explanation. This immediately raises questions such as how covering came about and why ZrO_2 behaves differently from La_2O_3.

Regarding the first question, it is unlikely that covering of Rh_2O_3 by ZrO_2 will have taken place during impregnation in the ZrRh series of catalysts. In the first impregnation, drying, and calcining, either isolated Zr^{4+} ions or ZrO_2 islands are formed on the SiO_2 support, while during the subsequent impregnation with a $Rh(NO_3)_3$ solution, either separate $Rh(NO_3)_3$ crystals or Rh^{3+} ions adsorbed on ZrO_2 are formed. It was checked that Zr did not redissolve during the second impregnation, because otherwise a coimpregnation-like situation would have occurred and covering of Rh by ZrO_2 in the final catalyst would not have been a surprise. When after the second impregnation and drying Rh^{3+} ions are in contact with ZrO_2 particles or Zr^{4+} ions, it would not be unthinkable that a reorganization of the catalyst structure during the final calcination and reduction might take place, so that part of the ZrO_2 ends up on top of the Rh particles. Zhang *et al.* described

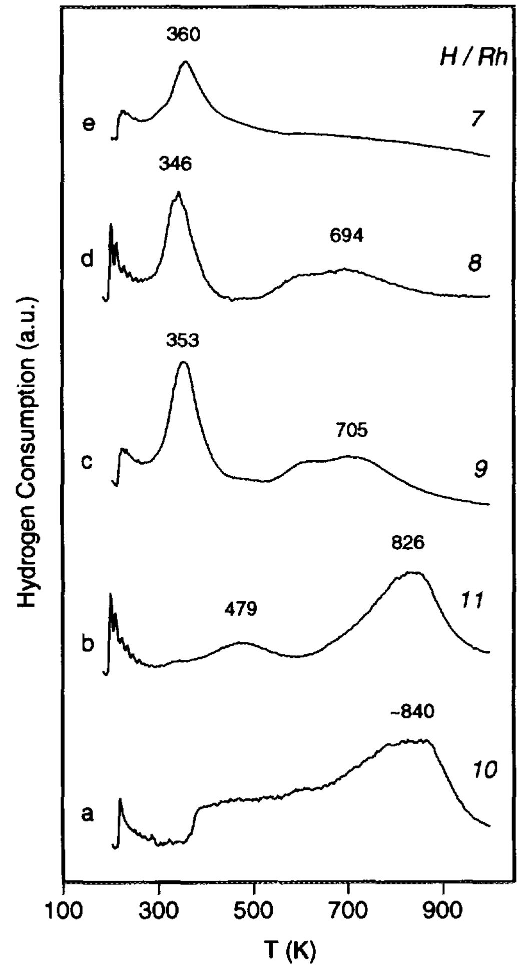

FIG. 7. TPR of the Zr55Rh catalyst after various pretreatments. (a) First TPR without pretreatment; (b) first TPR, after *in situ* calcination with CO_2-free air; (c) second TPR, after intermediate calcination with air; (d) second TPR, after intermediate calcination with CO_2-free air; (e) third TPR, after intermediate calcination with air at 1023 K.

the formation of a solid solution of up to 8% Rh^{3+} in ZrO_2 by a double decomposition of the nitrate salts at 1173 K (23). This Rh^{3+} solubility in ZrO_2 seems low, and the synthesis temperature seems high to explain the formation of a Rh_2O_3–ZrO_2 phase in our ZrRh catalysts. However, the solubility might be higher in small particles, and the formation may be easier. Another possibility could be that during reduction the ZrO_2 is partly reduced and that oxygen vacancies are formed. As a result, the reduced ZrO_2 might become mobile and creep over the Rh particles. Such explanations have been invoked in the past to explain SMSI behavior (24) and in a way, our ZrO_2-promoted Rh/SiO_2 catalysts show behavior reminiscent of SMSI behavior. The H_2 chemisorption decreases with increasing ZrO_2 loading and so does the CO hydrogenation activity. Total suppression of chemisorption and catalytic activity was not observed in our case, apparently because total covering had not taken place. Alekseev *et al.* have, however, observed a sharp decrease of the ethane hydrogenolysis and benzene hydrogenation activities of ZrO_2-promoted Pd/SiO_2 catalysts with increasing reduction temperatures, and have explained their results with the SMSI effect (25). In agreement with the assumption that covering in the ZrRh catalysts takes place during reduction, the TPR peak of the ZrRh catalysts only shifted slightly to higher temperature with increasing γ. In contrast, the temperature shift and peak broadening in the TPR spectra of the RhZr2.0 and RhZr5.0 catalysts was much larger and points to covering of Rh_2O_3 by ZrO_2 already in the oxidic state.

The second question that was raised by the different ZrRh behavior, was why ZrO_2 behaves differently than La_2O_3. Why does La_2O_3 improve the Rh dispersion and not cover the Rh particles and why does ZrO_2 cover the Rh particles, when in both cases Rh was impregnated first and Rh_2O_3 did not dissolve in either second impregnating solution? Although no definite answer can be given to these questions as yet, two possible explanations may be pointed out. It may be that the dispersion of the La^{3+} ions on SiO_2 is much better than that of the Zr^{4+} ions and that La^{3+} ions are rather homogeneously dispersed over the SiO_2 surface, whereas Zr^{4+} ions form ZrO_2 islands. A second explanation could be that La_2O_3 is not reducible, and cannot creep over the Rh particles, whereas ZrO_2 is reducible and ZrO_{2-x} can creep over the Rh particles. The question of the reducibility of ZrO_2 is addressed in the *Reducibility of ZrO_2* section.

Promoter Effect in CO Hydrogenation

A small amount of ZrO_2 was already sufficient to strongly enhance the activity of Rh/SiO_2 for both catalyst series. At higher ZrO_2 loadings the hydrocarbon as well as the oxygenates turnover frequency went through a maximum (Fig. 4). The increase in the turnover frequency at low promoter loadings was much greater for the ZrO_2-promoted than for the La_2O_3-promoted catalysts (12). The turnover frequency of the oxygenates was, in relative terms, enhanced more strongly than that of the hydrocarbons. At high ZrO_2 loadings a large difference in selectivity was observed between the RhZr5.0 and the RhZr5.0* samples. The selectivity pattern of the RhZr5.0 catalyst is very similar to that of Rh/ZrO_2 (26, 27) with its high methane and moderate oxo selectivity, and different from that of the other RhZr catalysts. Figs. 2b, 3b, and 4b indicate that the RhZr5.0* catalyst is a more sensible continuation of the RhZr series after RhZr2.0 than the RhZr5.0 catalyst. The RhZh5.0 catalyst was calcined five times during the $ZrO(NO_3)_3$ impregnation and had more opportunities to build up a strong interaction between the components than the RhZr5.0* catalyst, which was calcined only after the last impregnation–drying cycle with the Zr precursor and after the Rh impregnation. The higher acidity of ZrO_2 in ZrO_2-promoted Rh/SiO_2 than in Rh/ZrO_2, as determined from NH_3 adsorption studies by Ichikawa *et al.* (28), might explain the difference in selectivities between the RhZr5.0 and Rh/ZrO_2 catalysts on the one hand, and the other RhZr catalysts on the other hand.

The selectivity to C_2 oxygenates increased by the presence of ZrO_2. The formation of acetaldehyde was largely suppressed but more than compensated by an enhanced formation of ethanol, ethers, and esters. Like other promoters (6), ZrO_2 stabilizes intermediates for C_2 oxygenates and increases their hydrogenation, resulting in a higher ethanol-to-acetaldehyde ratio and a higher selectivity to C_2 oxygenates. The thermodynamic equilibrium for methanol formation is very strongly dependent on pressure and at ambient pressure and $H_2/CO = 3$ the maximum conversion is below 1% (29). Therefore our yields obtained at 4 MPa are much higher than those of Ichikawa *et al.* (28) and others (30, 31). Our data (Fig. 5) showed that the formation of methanol was enhanced in all cases, especially if, as in Ichikawa's work, Rh was brought on the promoted SiO_2 (ZrRh series). Nevertheless, ZrO_2 is a less efficient promoter in the methanol formation over Rh/SiO_2 than La_2O_3 (12).

The results for the 8.25% ZrO_2/SiO_2 catalyst seem to imply that the intrinsic activity of ZrO_2 at 4 MPa and 530 K can be neglected. However, this conclusion might be premature, because in the Rh–ZrO_2/SiO_2 catalysts Rh metal is present which can furnish adsorbates to the ZrO_2 phase if close contact between Rh and ZrO_2 exists. Our results, including those from TPR discussed below, can hardly be understood without assuming an active interaction between Rh and the promoter. Likewise, Schild *et al.* proposed that the role of ZrO_2 was to stabilize reaction intermediates on Pd/ZrO_2 catalysts (32). The fraction of the catalyst activity due to such a mechanism could be substantial, considering the strong increase in activity that was observed when small amounts of ZrO_2 were added to Rh/SiO_2. Therefore, the increased methanol turnover frequency might at least partly be ascribed to processes on the ZrO_2.

Reducibility of ZrO_2

Partial reduction of ZrO_2 (ZrO_x, $1.5 < x < 2$) is possible by a thermal vacuum or hydrogen treatment, as Zr^{3+} ions were observed by ESR (33). Bulk reduction to a lower valence state does not occur, however, as the XPS binding energy of Zr in a ZrO_2-promoted Rh/SiO_2 catalyst indicated the exclusive presence of Zr^{4+} (34). To study the reducibility of ZrO_2 in our catalysts several ZrO_2/SiO_2 and ZrO_2–Rh/SiO_2 catalysts were studied by TPR. The TPR of ZrO_2/SiO_2 showed a peak at 861 K, as observed before by Dall'Agnol *et al.* (30), and this peak was also present in all other first TPR profiles in Figs. 6 and 7. The peak disappeared in the second TPR (after intermediate calcination), indicating that it is not due to a reversible interaction of hydrogen with ZrO_2 as supposed by Dall'Agnol *et al.* (30), but due to the permanent removal of a species associated with ZrO_2. This may be zirconium carbonate, in analogy to lanthanum carbonate (14). We conclude that ZrO_2 on SiO_2 and bulk ZrO_2 cannot be reduced in this temperature range. Even though ZrO_2 dispersed on SiO_2 was not reduced during TPR, it may be reducible in the presence of Rh. While the peak above 800 K had disappeared in the second TPR of RhZr5.0 (topmost profile in Fig. 6), a new peak emerged at 555 K. This peak, with its long tail up to 900 K, was situated in the range where Zhang *et al.* observed a reduction peak of a Rh_2O_3-ZrO_2 solid solution (23). A similar solid solution phase might have formed on the RhZr5.0 catalyst when it was reduced up to 1000 K and calcined at 773 K in the first TPR. Calcination at 773 K (before the first TPR) was apparently not sufficient to create this phase, in agreement with the fact that Zhang *et al.* prepared their Rh_2O_3–ZrO_2 solid solution by heating at 1173 K.

To increase the chance to detect a possible reduction of ZrO_2, we prepared the Zr55Rh catalyst, which has a large excess of ZrO_2. Both first TPR experiments of the Zr55Rh catalyst had peak maxima above 800 K, like ZrO_2/SiO_2 (Fig. 7, profiles a and b). No peak was present around 350 K, where the other catalysts showed the reduction peak of Rh_2O_3. The hydrogen consumption was very high, but should partly be ascribed to reaction with the carbonate species, as discussed above. In the second TPR of Zr55Rh the usual peak for the reduction of Rh_2O_3 around 350 K was observed and it accounted for the complete reduction of the Rh present on the catalyst. Consequently, the second peak in the second TPR cannot be due to Rh, such as in a solid solution of Rh^{3+} in ZrO_2. The presence of carbonate species can be ruled out as well, because carbonate is successfully removed during the first TPR even in the absence of Rh as shown by ZrO_2/SiO_2. We therefore ascribe the peak around 700 K to a partial reduction of ZrO_2. The long tail of the peak at 555 K of the RhZr5.0 catalyst (Fig. 6) may also be due to the partial reduction of the promoter. The third TPR after high temperature calcination (Fig. 7, upper profile) still showed a high hydrogen consumption due to a peak at 360 K and a long tail up to 900 K. Peaks around 550 and 700 K may be present, but are not clearly discernible. A H/Rh value of 7.5 with the Zr55Rh catalyst represents a stoichiometry of $ZrO_{1.96}$, and means that 8% of the Zr^{4+} ions were reduced to Zr^{3+}.

Thus, although some reduction of ZrO_2 was detected, they occurred only to a minor extent. In this respect, ZrO_2 is intermediate between La_2O_3 and TiO_2, but closer to La_2O_3. In all three metal oxides anion vacancies can be created when the oxides are heated under vacuum or hydrogen. The formation of anion vacancies is accompanied by the removal of oxygen atoms in the form of O_2 and H_2O, and the production of electrons. These electrons either may be trapped on anion vacancies as F-centers, or may reduce metal cations. The existence of F-centers in ionic solids is well documented, but their numbers are extremely small. The creation of reduced metal cations, on the other hand, may be substantial if the reduction potentials of the metal cation are favorable. Thus, it is not surprising that stable phases of low-valent Ti oxides exist, but no other phase than La_2O_3, and that anion vacancies and reduced metal cations occur more readily on TiO_2 than on La_2O_3. The ability of TiO_2 to undergo reduction by a continuous transformation through Magnelli-type Ti_nO_{2n-1} shear structures undoubtedly also plays a role in its SMSI behavior. With its intermediate position, Zr has only one stable oxide, ZrO_2, but ZrO_2 can be slightly reduced to ZrO_{2-x}. The Zr cations may play a role in the promotion of Rh.

CONCLUSIONS

ZrO_2 proved to be a promoter for the CO hydrogenation reaction on 1.5% Rh/SiO_2. The activity was enhanced most effectively at a ZrRh atomic ratio of 0.5, since at higher Zr loadings active sites are blocked. ZrO_2 can enhance the formation of all products and causes higher selectivities to oxygenates, probably by promoting CO dissociation and stabilizing intermediates in the formation of C_2 oxygenates. The impregnation sequence had a minor influence, although the second impregnation solution did not redissolve the already impregnated and calcined component in either impregnation sequence. The final interaction between the components seems to be established only during reduction, because the impregnation sequence was relevant for TPR of the calcined catalysts, but not for CO hydrogenation.

Multiple calcination procedures between the impregnation steps or high temperature reduction, as during TPR (1000 K), can cause the formation of new phases. The formation of a solid solution between Rh_2O_3 and ZrO_2 was assumed upon reduction and recalcination. ZrO_2 in close contact with Rh is partly reducible and forms Zr^{3+} ions to an extent of less than 10%. These ions, which are probably coordinatively unsaturated, may play an important role in the promoter action of ZrO_2. In this way the behavior of ZrO_2 can be compared to the Rh/TiO_2 system, where a strong metal–support interaction (SMSI) is built up upon high temperature reduction, the main feature of which is a strong decrease of the adsorption capacity for hydrogen and CO (35). This is best explained by coverage of the metal by partly reduced TiO_2 species (10, 24) which block adsorption sites. The influence of ZrO_2 can also be described by this model, but the generation of new active sites for CO hydrogenation prevails over their blocking at lower Zr loadings.

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