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Hydrogenation of Carbon Monoxide: Evidence of a Strong Metal–Support Interaction in Rh/ZrO$_2$ Catalysts

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Temperature-programmed desorption (TPD) studies are reported on a series of Rh catalysts dispersed on ZrO$_2$ and γ-Al$_2$O$_3$ and activated under H$_2$ flow at 250, 400, and 600°C. While the high temperature of activation did not show any significant difference in the Rh/γ-Al$_2$O$_3$ samples, in the case or Rh/ZrO$_2$ a pronounced effect is quite evident. The experimental observations have been associated to a modification of the metal–support interface, for which a possible model is suggested. Parallel experiments in the hydrogenation of carbon monoxide at 220°C and $P = 1$ atm have shown a sharp decrease in the overall activity while the selectivity was virtually unaffected by the temperature of reduction. © 1985 Academic Press, Inc.

INTRODUCTION

The interest in the hydrogenation of carbon monoxide has been renovated in recent years, since the possibility of obtaining appreciable amounts of ethanol has been reported (*1*, *2*) by using Rh catalysts dispersed on a variety of oxides such as La$_2$O$_3$, CeO$_2$, TiO$_2$, ZrO$_2$, ThO$_2$. The production of oxygenated compounds has been associated by Somorjai and co-workers with the presence of an oxidized state on Rh by studies on model systems (*3*), however, the nature of the interaction between Rh and the support in dispersed catalysts is still a problem under discussion.

The synthesis and reactivity in the CO + H$_2$ reaction has been recently reported for a series of Co and Rh catalysts dispersed on ZrO$_2$ (*4*) which have yielded up to 46% selectivity in the formation of EtOH. These catalysts have been characterized by H$_2$ and O$_2$ chemisorption, ESR techniques and their behavior has been compared with similarly prepared samples on γ-Al$_2$O$_3$ (*5*, *6*).

The Rh/ZrO$_2$ catalysts when reduced with H$_2$ at high temperature have shown a dramatic drop in the H$_2$ chemisorption properties while retaining their ability to chemisorb O$_2$, which is a characteristic feature of metals in the Strong Metal–Support Interaction (SMSI) state (*7–9*). This effect has been widely studied when titania or other readily reducible oxides are used as the support. Conversely, for ZrO$_2$, only a few examples of such effect have been observed in the case of Ni/ZrO$_2$ (*10*, *11*) for which no interpretation has been suggested.

We now wish to report some Temperature-Programmed Desorption (TPD) studies on Rh/ZrO$_2$ and Rh/γ-Al$_2$O$_3$ catalysts with the aim of shedding more light on the factors which affect the metal–support interaction after high-temperature reduction. Moreover, since the catalytic behavior may be significantly altered by the nature of the interaction, we also carried out some parallel experiments in the hydrogenation of carbon monoxide.

EXPERIMENTAL

The same catalysts discussed in Ref. (*5*) have been used. They were prepared via impregnation of ZrO$_2$ (Strem, 70 m^2/g) and

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γ-Al_2O_3 (Akzo-Kemie CK 300, 200 m^2/g) with two different metal precursors $Rh_4(CO)_{12}$ (*12*) and $RhCl_3 \cdot 3H_2O$ (Engelhard). Full details on the preparation procedure are given in Ref. (*5*). Analytical data are reported in Table 1.

Temperature-Programmed Reduction (TPR) measurements of the supported Rh precursors were performed in a standard apparatus by the same technique as described by Hurst *et al.* (*13*). The reducing gas mixture (5% H_2 in Ar) was purified over an Oxy-trap (Alltech) and dried in a molecular sieve trap cooled at −78°C. The gas flow [40 ml (STP)/min] was regulated by a Matheson Model 8240 mass flow controller. The reactor had a diameter of 4 mm and was heated at a linear rate of 5°C/min from room temperature to 550°C. An appropriate trap for water or other undesired products was placed between the reactor and the thermal conductivity detector.

Temperature-programmed desorption of H_2 studies were performed in the same apparatus used for TPR experiments with some minor modifications. The catalysts were activated in flowing hydrogen by heating (5°C/min) to the chosen temperature (250, 400, 600°C) and holding at that temperature for 2 h. Samples were then cooled from the reduction temperature down to 25°C in flowing hydrogen. The H_2 flow was stopped and a stream of carrier gas (Ar, 40 ml/min) was started. When the base line of the recorder connected to the thermal conductivity detector became steady, the tubular furnace was linearly heated (10°C/min) to 600°C. Catalysts were then kept at that temperature for 30 min. Calibration of the TPD apparatus enabled a quantitative detection of the H_2 evolution.

TABLE 1

Analytical Data of the Catalysts

Catalyst	Precurosr	Rh (%)
Rh_C/γ-Al_2O_3	$Rh_4(CO)_{12}$	1.6
Rh_T/γ-Al_2O_3	$RhCl_3 \cdot 3H_2O$	1.0
Rh_C/ZrO_2	$Rh_4(CO)_{12}$	1.3
Rh_T/ZrO_2	$RhCl_3 \cdot 3H_2O$	1.0

Catalytic investigations were conducted in a flow microreactor made from an 8-mm-i.d. Pyrex glass tube immersed in a fluidized sand bath heated by an external oven. A small glass tube containing a Fe–Ko thermocouple was placed in the middle of the catalyst bed. The catalyst was diluted at a 1 : 8 ratio with carborundum (60–100 mesh) to minimize temperature gradients. No increase in the catalyst temperature was observed during the reaction. The system was operated at the following conditions: reaction temperature 220°C, total pressure 1 atm; $H_2 : CO = 3 : 1$, space velocity 2000 h^{-1}. The samples were activated *in situ* in flowing hydrogen for 2 h at the same three different temperatures (250, 400, 600°C) chosen for the TPD experiments. All reactant and product gas concentrations were measured chromatographically using thermal conductivity and flame ionization detectors. Complete separation of the products was performed with a 5-m-long 0.25-in.-diameter column packed with Porapak QS. Calibration curves of the individual components of the reaction mixture were used for quantitative analysis. Carbon balances generally accounted for 99% of the input carbon.

RESULTS AND DISCUSSION

Four different catalysts have been employed in the present study starting from two different Rh precursors, $RhCl_3$ and $Rh_4(CO)_{12}$, and dispersed on two different supports, γ-Al_2O_3 and ZrO_2.

Preliminary TPR experiments have been carried out in order to determine both the optimum temperature for the reduction of the precursors and acquire some informations concerning the possibility of producing different metal phases (*13*). The results are shown in Fig. 1 where TPR profiles relative to the supports alone are also reported for comparison. As it appears, both catalysts prepared from $Rh_4(CO)_{12}$, after an ini-

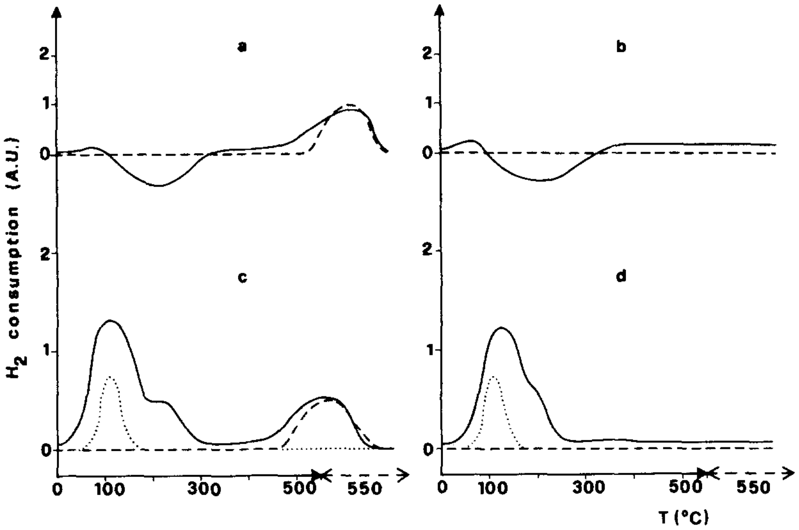

FIG. 1. TPR profiles of the catalysts (—), supports (---) and unsupported precursors (··········). (a) Rh_C/ZrO_2; (b) $Rh_C/\gamma\text{-}Al_2O_3$; (c) Rh_T/ZrO_2; (d) $Rh_T/\gamma\text{-}Al_2O_3$.

tial small uptake, show a broad, low-intensity negative band, due to CO evolution which is consistent with the fact that the "reduction" procedure is indeed a simple decarbonylation process. As for the two catalysts derived from $RhCl_3$ an intense band centered at about 110°C along with a shoulder in the range 200–300°C are present. These suggest the presence of the precursor on the support in two different states: physisorbed and chemisorbed for which slightly different reduction temperatures would apply. This view is consistent with the observation that TPR of unsupported $RhCl_3$ shows (dotted line) a single band centered at about 110°C and that the position of the shoulder is somehow dependent on the support used. An additional band starting above 500°C is also evident in the case of the catalysts supported on ZrO_2. However, as it is clear from Figs. 1a and c this H_2 consumption is to be ascribed to the support rather than indicative of a further reduction step of the metal. Since all the catalysts were prepared by reduction under H_2 flow for 2 h at the minimum temperature of 250°C, the above TPR experiments suggest that only one type of metal species is produced. This view is further supported by the observation that, after O_2 treatment all metal surfaces show only one reduction step centered at about 85°C.

TPD experiments have been performed on these catalysts after pretreatment in H_2 flow at three different temperatures (250, 400, 600°C). These temperatures have been chosen identical to those used for the chemisorption measurements in order to find a possible explanation for the dramatic drop in H_2 chemisorption after high-temperature reduction (HTR), which was observed for the ZrO_2-supported catalysts (Table 2).

TPD technique offers some advantages with respect to chemisorption. In fact it allows to span a temperature range which is normally not accesible to chemisorption and to gain several informations concerning the nature of the interaction between adsorbate and catalytic surface, namely: (i) the number of adsorbed species and their relative amounts; (ii) the bond energy between adsorbate and metal surface; (iii) the possible chemical form of the adsorbed species (*14*).

Initially a $Rh_C/\gamma\text{-}Al_2O_3$ sample, for which a regular chemisorption behavior was observed has been studied after activation under H_2 at the three different temperatures

TABLE 2

Quantitative H_2 Chemisorption and TPD Data

Catalyst	Temperature reduction (°C)	Chemisorption (ml (STP)/g Rh)	TPD (ml (STP)/g Rh)	
			α	β
Rh$_C$/γ-Al$_2$O$_3$	250	92.6	83.7	—
	400	83.1	75.2	—
	600	72.4	71.6	—
Rh$_T$/γ-Al$_2$O$_3$	250	51.0		
	400	49.8		
	600	47.5		
Rh$_C$/ZrO$_2$	250	89.0	82.9	—
	400	42.7	36.5	—
	600	5.9	5.2	50.8
	After O_2, 500°C, 1 h			
	250	81.9	81.0	—
Rh$_T$/ZrO$_2$	250	41.5	40.8	—
	400	16.6	16.5	—
	600	1.2	1.1	27.6
	After O_2, 500°C, 1 h			
	250	36.8	39.2	—

250, 400, 600°C. The corresponding desorption spectra are reported in Fig. 2. As shown the spectrum consists, in all the three cases, of two largely overlapping peaks centered at about 100 and 200°C (α band). An analogous experiment carried out on γ-Al$_2$O$_3$ alone did not show any desorption. HTR pretreatment on this catalyst has no particular effect unless a slight decrease in the total amount of H_2 desorbed. These results are in good agreement with the corresponding H_2 chemisorption data at 25°C (Table 2) and similarly suggest the occurrence of a slight sintering effect.

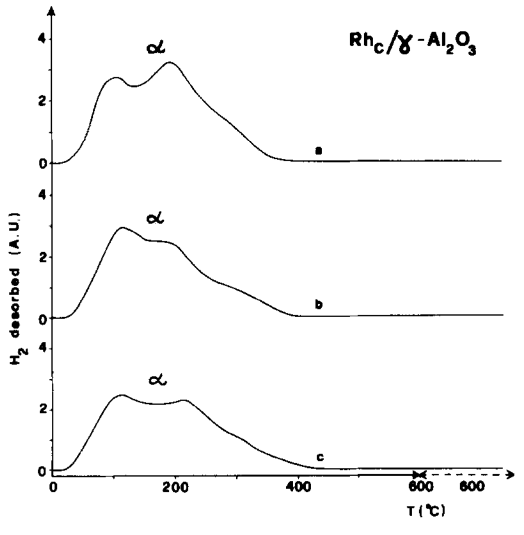

FIG. 2. TPD profiles of Rh$_C$/γ-Al$_2$O$_3$ after activation in H_2 flow at 250°C (a), 400°C (b), 600°C (c).

The effect of HTR is quite different in the case of the catalysts supported on ZrO$_2$ (Figs. 3, 4). The support itself shows a large desorption band centered around 600°C (β band). As for the catalysts, after activation at 250°C the behavior of Rh$_C$/ZrO$_2$ (Fig. 3a) is similar to that above described for Rh$_C$/γ-Al$_2$O$_3$, while Rh$_T$/ZrO$_2$ (Fig. 4a) shows a slightly different desorption spectrum which probably reflects a different physical state of the metal. After activation at 400°C TPD spectra of both catalysts become very similar (Figs. 3b, 4b) and the amount of H_2 desorbed is reduced to less than one half in agreement with the chemisorption data (Table 2). Finally, after HTR at 600°C, the α band almost disappears, while the occur-

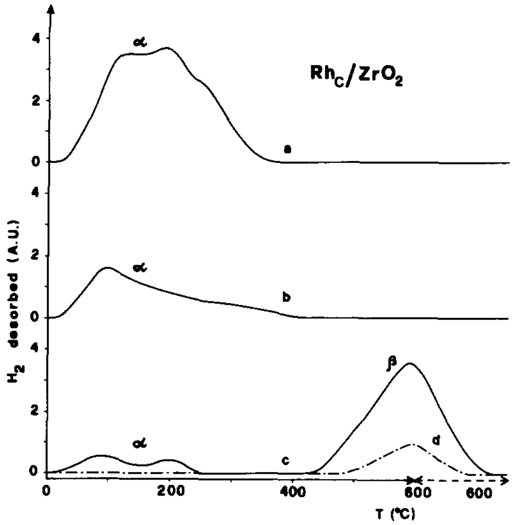

FIG. 3. TPD profiles of Rh$_C$/ZrO$_2$ after activation in H_2 flow at 250°C (a), 400°C (b), 600°C (c). Profile d (—·—·) refers to ZrO_2 alone.

rence of a new desorption centered at 590°C (β band) can be noticed independently of the precursor used (Figs. 3c, 4c). Again the amount of H_2 desorbed in the α band is in agreement with the chemisorption data (Table 2).

As already pointed out (*5*), samples reduced at high temperature recover their H_2 chemisorption properties when contacted with O_2 for 1 h at 500°C. Analogously a sample of Rh$_C$/ZrO$_2$, for which the TPD spectrum reported in Fig. 3c was observed, when treated with O_2 for 1 h at 500°C and reactivated at 250°C in H_2, showed a TPD spectrum like that reported in Fig. 3a. This proves the reversibility of the phenomena related to HTR and the absence of any permanent structural changes during this activation procedure.

In Fig. 3c the occurrence of desorptions at two very different temperatures suggests the existence of superficial sites capable of binding hydrogen with very different bond energies. While the more weakly bound hydrogen (α band) can be ascribed to the chemisorbed Rh–H species, the β band is indicative of the existence of a cooperative effect between the metal and the support surfaces, as the same band is present with a lower intensity also in ZrO_2 alone. The decrease of H_2 chemisorption with the temperature treatment is widely known in the literature for Rh/TiO$_2$ catalysts and has been associated to the general phenomenon known a SMSI (*15*). In the case of TiO_2 as the support, the suppression of H_2 chemisorption capacity after HTR has been generally associated to the bulk reducibility of the Ti^{4+} centers. The case of ZrO_2 is more intriguing since the material itself is considered as a refractory (*16*). On the other hand, when used as a catalyst support, HTR induced H_2 chemisorption suppression has been already noticed at least for Ni and Ir catalysts, for which no possible explanation for this kind of behavior was suggested (*10, 11*).

In an attempt to provide for a reasonable interpretation of the data here reported, one must take into account the following considerations:

(a) At the metal–support interface, HTR treatment generates an interaction which must be sufficiently strong to suppress the metal capacity for H_2 chemisorption, but can be removed by treatment with O_2 at 500°C.

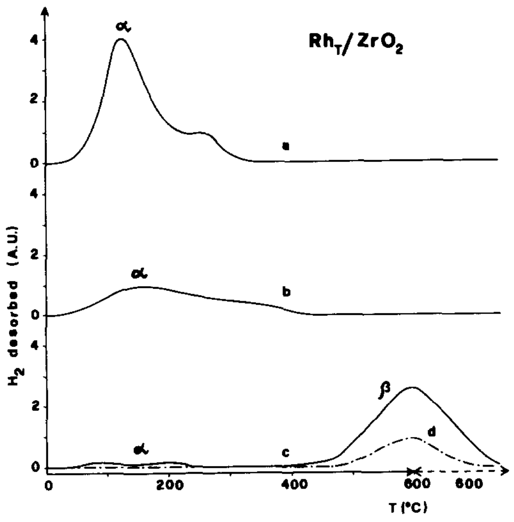

FIG. 4. TPD profiles of Rh$_T$/ZrO$_2$ after activation in H_2 flow at 250°C (a), 400°C (b), 600°C (c). Profile d (—·—·) refers to ZrO_2 alone.

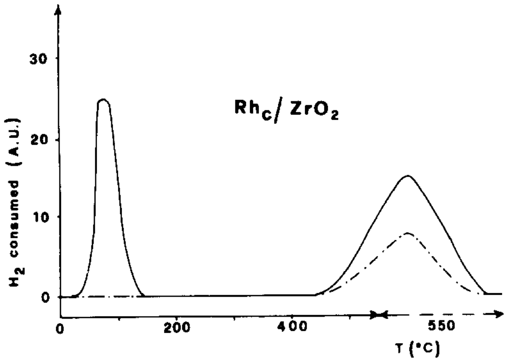

FIG. 5. TPR profiles of Rh_C/ZrO_2 (—) and ZrO_2 alone (-·-·) after heating in O_2 for 1 h at 500°C.

(b) The shape of the TPR spectrum shown in Fig. 5 clearly indicates that the total H_2 consumption on ZrO_2 supported catalysts takes place in two distinct steps.

(c) Although usually considered as a non-reducible oxide, ZrO_2 proves to be able to interact with H_2 reversibly as already found by other authors (*17, 18*).

(d) The bond energy associated to the β band in the TPD spectra appears to be the same for ZrO_2 alone and the Rh/ZrO_2 catalysts. This implies that the H_2 desorbed comes from the same type of binding sites in both cases.

Points c and d are consistent with an increase of the concentration of surface –OH groups (terminal and/or bridging), due to Zr–O–Zr bond breakage, which is induced by the treatment with H_2 at high temperature. This H_2 adsorbed is reversibly released during TPD procedure (β band). The formation of surface –OH groups when treating ZrO_2 with H_2 under similar experimental conditions has been already suggested by He and Ekerdt (*17*). The extent of the process is increased in the catalysts by the presence of Rh which transfers hydrogen on the support giving rise to the same band (β) in the TPD spectrum although more intense. However a comparison of the TPR (Fig. 5) vs TPD (Fig. 3) spectra for Rh_C/ZrO_2 indicates that the amount of H_2 consumed is much wider than the H_2 desorbed. Since a negligible water production was experimentally detected in connection with the 550°C TPR band, the hydrogen difference can be justified by assuming that part of the hydrogen adsorbed is spilled from the metal into the support during the HTR procedure.

The overall process here envisaged determines a deep modification of the support surface both geometrically and electronically which results in a new metal–support interaction at the interface. We infer that Zr–O–Rh entities may be formed to such an extent that the metal particle is partly covered by the support and its average oxidation state is increased so that the capacity of the metal to dissociate and chemisorb hydrogen at low temperature is drastically reduced.

A simplified model which summarizes the modifications at the metal–support interface induced by HTR is depicted in Fig. 6.

This provides also a chemical pathway to account for the possibility of a support "migration" to cover the metal particle as has been already pointed out by several authors (*19–23*) for a variety of group VIII metals dispersed on TiO_2.

It has to be pointed out that in the case of catalysts dispersed on TiO_2, the phenomena induced after HTR treatment have been interpreted on the basis of a redox-type mechanism involving the Ti^{3+}/Ti^{4+} couple (*7–9*). This assumption in the case of ZrO_2 is not straightforward because of the well known lack of bulk reducibility of this material (*16*). However we cannot exclude the possibility of a partial reduction of the surface layers of the support as has already been suggested by other authors for "unre-

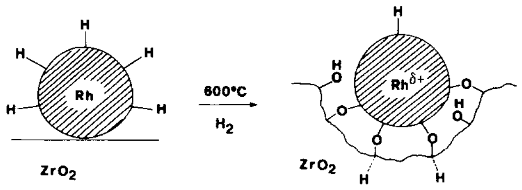

FIG. 6. Schematic model for the interfacial metal–support interaction induced by high-temperature treatment in Rh/ZrO_2 catalysts.

ducible'' oxides such as La_2O_3 (*24*) and Al_2O_3 (*25, 26*). This process, which is implicit in Fig. 6, may be written as

$$\text{Zr–O–Zr} + H_2 \xrightarrow[600^\circ\text{C}]{\text{Rh–H}} \text{Zr–OH} + \text{Zr} \ldots \text{H}$$

$$\text{Zr–O–Zr} + \text{Rh–H} \xrightarrow[600^\circ\text{C}]{} \text{Zr–O–Rh} + \text{Zr} \ldots \text{H}$$

where the Zr . . . H species may formally be viewed either as a Zr^{4+} hydride or a Zr^{3+} interacting with the atomic hydrogen spilled into the support. Indeed ESR measurements carried out on these catalysts under similar experimental conditions have revealed the existence of paramagnetic signals which might be attributed to Zr^{3+} species (*27*).

Restoration of the original properties of these catalysts requires heating in O_2 at 500°C. We suggest that this process may be associated with the removal of the hydrogen spilled into the surface layers of the support thereby providing the necessary driving force capable of breaking the O–Rh bonds leading to a surface reconstruction.

Since the HTR treatment induces deep modifications in the general chemical behavior of the Rh/ZrO_2 catalysts, we thought of interest to test the reactivity of these materials in the hydrogenation of carbon monoxide. For this purpose experiments were carried out on Rh_C/ZrO_2 activated at 250, 400, 600°C and the results were compared to those obtained with analogously treated $Rh_C/\gamma\text{-}Al_2O_3$. The CO conversion and the product distribution for these catalysts are reported in Table 3. As a general trend the ZrO_2-supported samples show a higher activity and a significantly different selectivity in the formation of ethanol. This latter effect has been already noticed by other authors (*28*) in the case of Rh dispersed on oxide supports capable of promoting SMSI behavior. Moreover a rather different behavior is observed as the temperature of activation increases. In fact, while for $Rh_C/\gamma\text{-}Al_2O_3$ both the conversion and the product distribution are only slightly affected, in the case of Rh_C/ZrO_2 the conversion is drastically decreased, while some variations are evident only in the C_2 fraction composition. The CO conversion as a function of the activation temperature parallels, in both catalysts, the behavior already observed in the chemisorption of H_2 (*5*) and the results obtained in the TPD spectra (α band). Moreover, even in this case, the Rh_C/ZrO_2 sample reduced at 600°C can recover completely its original activity and selectivity after O_2 treatment for 1 h at 500°C. These observations suggest that we may calculate the turnover numbers (*N*) for these catalysts by computing only those centers which can be titrated with H_2 at 25°C, although this assumption in the case of Rh_C/ZrO_2 may not be correct since some

TABLE 3

Product Distribution in CO–H_2 Reaction as a Function of the Activation Temperature

Catalyst	Temperature activ. (°C)	CO conv. (%)	Product distribution in carbon efficiency (%)[a]										
			CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	C_4H_{10}	MeOH	EtOH	HCHO	CH_3CHO
$Rh_C/\gamma\text{-}Al_2O_3$	250	1.6	64.6	0.4	20.9	2.7	4.3	2.8	—	2.5	—	1.8	—
	400	1.2	64.3	0.4	18.8	3.2	5.3	3.0	—	2.1	1.1	1.8	—
	600	1.1	63.4	0.5	17.8	4.2	4.6	3.7	2.1	1.5	1.0	1.2	—
Rh_C/ZrO_2	250	4.8	59.7	0.1	3.4	4.8	4.1	5.1	2.3	1.6	18.1	—	0.8
	400	1.9	58.2	0.6	5.8	4.8	3.5	5.3	2.2	3.2	16.4	—	—
	600	0.3	58.1	2.7	5.7	4.9	3.5	6.1		3.2	15.8	—	—
			After O_2, 500°C, 1 h										
	250	4.8	59.3	0.1	3.1	5.4	4.1	5.6	2.6	0.9	18.2	—	0.7

Note. Reaction conditions: $T = 220°C$; $CO : H_2 = 1 : 3$; $P_{tot} = 1$ atm.

[a] Carbon efficiency = $(n_iA_i/\Sigma n_iA_i) \times 100$, where n_i = carbon number of the product; A_i = moles of product i.

TABLE 4

Turnover Numbers in CO–H$_2$ Reaction as a Function of the Activation Temperature

Catalyst	Temperature activ. (°C)	N $\left(\frac{\text{mol CO}}{\text{s} \times \text{g} \cdot \text{atom Rh}}\right)$
Rh$_C$/γ-Al$_2$O$_3$	250	5.0×10^{-4}
	400	4.2×10^{-4}
	600	4.4×10^{-4}
Rh$_C$/ZrO$_2$	250	1.4×10^{-3}
	400	1.1×10^{-3}
	600	1.3×10^{-3}

Note. Reaction conditions: T = 220°C; CO:H$_2$ = 1:3; P_{tot} = 1 atm.

activity at 220°C from the new centers arising after HTR treatment cannot, in principle, be discounted. The data are reported in Table 4. As it appears the turnover number in the ZrO$_2$ dispersed samples is practically unaffected by the HTR treatment. This implies that, following activation at 600°C, only the centers which do not interact strongly with the support remain active in the hydrogenation of carbon monoxide according to the model proposed (Fig. 6). This view is further supported by the observation that also the selectivity is only slightly modified by the increase in the activation temperature, the effect of which is simply a redistribution within the C$_2$ fraction. The fact that after HTR at 600°C the yield of ethylene and ethane is increased at the expenses of ethanol, can be explained on the basis of an increase of the acidity (*29*) of the ZrO$_2$ surface in agreement with the model proposed.

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