EXAFS investigations of lanthana-promoted Rh/SiO_2 catalysts

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EXAFS investigations at the Rh K edge of lanthana-promoted Rh/SiO_2 catalysts showed that the local environment of the Rh ions in the oxidic catalyst precursor state did not depend on the La_2O_3 content and resembled that of Rh_2O_3. No $LaRhO_3$ formation could be detected. In the reduced state, EXAFS as well as H_2 and CO chemisorption demonstrated that La_2O_3 increased the Rh dispersion. Covering of the Rh metal particles by La_2O_3 was minor, because during catalyst preparation, La was impregnated prior to Rh.

Keywords: Lanthana-promoted Rh/SiO_2 catalyst; EXAFS; H_2 chemisorption; CO chemisorption

1. Introduction

Rh catalysts in combination with transition metal oxide supports or promoters show extraordinary catalytic properties in the hydrogenation of CO. High selectivities to oxygenates, chiefly methanol, have been observed when La_2O_3 was used as a support [1–5]. The Rh surface was found to be partially covered by LaO_x moieties [5–9] and the special catalytic properties were ascribed to the Rh–LaO_x interface. Also when La_2O_3 was added to a catalyst consisting of Rh supported on SiO_2, the selectivity to oxygenated products was increased by the presence of La_2O_3 [8–11]. New absorption bands during CO adsorption were observed by IR spectroscopy and attributed to CO bound at the Rh–La_2O_3 interface [7,12].

Transition metal oxide promoters like V_2O_5 [13] and Nb_2O_5 [14,15] form mixed $MRhO_4$ oxides on Rh/SiO_2 after impregnation and calcination, and influence the properties of the catalysts in the metallic state. It has been suggested that the formation of the mixed oxide is influential in the formation of a reduced promoter oxide on top of the Rh metal particles after reduction of the catalyst. Analogously, the formation of $LaRhO_3$, a compound with perovskite structure, has been proposed to explain the role of La_2O_3 in Rh

Table 1
Composition and pretreatment of La_2O_3-promoted catalysts

Catalyst	La:Rh atomic ratio	Rh content (wt%)	Pretreatment
A	1.0	1.44	sequential impregnation calcined 773 K reduced 723 K
B	5.0	1.32	sequential impregnation calcined 773 K reduced 673 K
C	11.1	1.08	sequential impregnation calcined 773 K reduced 723 K
D	1.0	1.44	coimpregnation calcined 1023 K reduced 723 K

catalysts [5]. In order to better understand the La–Rh interaction, we have undertaken an EXAFS study of La_2O_3-promoted Rh/SiO_2. By performing measurements at the Rh K edge we have been able to determine the local structure of the Rh centers. Supporting H_2 and CO chemisorption measurements are also reported.

2. Experimental

Four catalysts (A, B, C, D) with increasing La/Rh ratio and almost the same Rh content were prepared by the pore volume impregnation method. The pretreatment and the composition of the calcined precursors and of the reduced forms of the catalysts are shown in table 1. The silica support was obtained from CF Uetikon, Switzerland. It was washed three times in 2 M HNO_3 (360 K, 1 h) and twice in H_2O (360 K, 1 h), followed by calcination at 773 K. The support was impregnated to incipient wetness with aqueous solutions of $La(NO_3)_3 \cdot H_2O$ (Fluka puriss. p.a.) and $Rh(NO_3)_3$ (Johnson Matthey, 5% solution in 1.7 M HNO_3). Starting with the lanthanum solution, the impregnation was performed in two steps with an intermediate and final calcination in air at 773 K (3 h). Catalyst D was prepared in one step using a solution of both $Rh(NO_3)_3$ and $La(NO_3)_3$ and a calcination temperature of 1023 K (6 h).

For the preparation of $LaRhO_3$ a precipitation method described by Crespin and Hall [16] was used. A two-fold excess of 40% $(C_2H_5)_4NOH$ (Fluka, purum) was added rapidly to a stirred equimolar solution of $La(NO_3)_3 \cdot 6H_2O$ and $Rh(NO_3)_3$. The spongy precipitate was separated by centrifugation and washed several times with water to bring the pH of the supernatant solution close to 7.

This perovskite precursor was calcined in a platinum crucible at 1350 K for 6 h. The purity of the product was controlled by an XRD measurement. No La_2O_3 or Rh_2O_3 impurity could be detected. The resulting XRD spectrum is in perfect agreement with the one published by Gysling et al. [17], who prepared the perovskite by heating a mixture of $La_2(C_2O_4)_3$ and Rh_2O_3. As the crystallinity of the sample was low no refinement of the atomic positions could be done. Longer calcination treatments with repeated grinding of the sample led only to slight sharpening of the XRD peaks. For comparison with catalyst D an additional La_2O_3 sample was prepared using a calcination temperature of 1023 K.

The CO and H_2 chemisorption measurements were carried out in a volumetric adsorption apparatus equipped with an Edwards 590 Barocel pressure sensor. The catalysts were reduced in situ at 723 K for 1 h and evacuated at 673 K for 30 min. They were subsequently cooled to room temperature and the total adsorbate uptake between 10 and 40 kPa was determined by extrapolating the linear part of the isotherm to zero pressure.

The X-ray absorption spectra were measured at stations 9.2 and 9.3 at the Synchrotron Radiation Source at Daresbury (UK), with the synchrotron ring operating at an electron energy of 2 GeV, a wiggler at 5 T and a current of 100–250 mA. The samples as well as the reference compounds were pressed to self-supporting wafers and mounted in a transmission EXAFS cell [18]. The calcined catalysts and the reference compounds were measured in a dry helium atmosphere. All catalyst samples were measured in the reduced state as well. The reduction was performed by H_2 at a flow rate of 60 cm^3 min^{-1} through the EXAFS cell while raising the temperature from 293 K to the final value at a rate of 10 K/min. After a holding time of 1 h at the final reduction temperature the samples were cooled rapidly while continuing the H_2 flow. In all experiments the monochromator was detuned to 50% of the maximum intensity to minimize higher harmonic radiation. All samples were measured at liquid nitrogen temperature.

3. Results and discussion

The data were analyzed with the aid of the program NEX V1.0.32 [19]. The background was removed by using a cubic spline routine and the normalization was performed by division by the apparent edge height which is obtained by back extrapolation of the EXAFS region. Reference compounds were used in order to obtain phases and backscattering amplitudes for the fitting routines: Rh foil [20] for Rh–Rh atom pairs and a low temperature form of Rh_2O_3 [21] for Rh–O atom pairs. The crystallographic data of the reference compounds are listed in table 2. The data of the reference compounds were treated in the same way as those of the catalyst samples.

Table 2
Crystallographic data and Fourier transform ranges for the reference compounds

Compound [ref.]	Coordination	N [a]	R [b] (Å)	Transformation range in k ($Å^{-1}$)	Backtransformation range in R (Å)
Rh foil [20]	Rh–Rh	12	2.687	2.59–24.77	1.82–2.7
Rh_2O_3 [21]	Rh–O	3	2.032	2.67–24.66	0.74–2.08
	Rh–O	3	2.049		
	Rh–Rh	1	2.715		
	Rh–Rh	4	2.988		

[a] Coordination number.
[b] Atomic distance.

The Fourier transform of the k^3 weighted EXAFS of $LaRhO_3$ is presented in fig. 1A. This compound was measured to check the formation of $LaRhO_3$ on the Rh–La_2O_3/SiO_2 catalysts. Although the heights of the peaks were smaller because of a lower crystallinity, the perovskite-type oxide ($LaRhO_3$) was still formed when the synthesis temperature was reduced from 1350 to 1023 K, since both Fourier transforms showed the same distances. However, neither the coimpregnated catalyst sample calcined at 1023 K (D_C), nor the calcined catalyst precursors with high La_2O_3 contents (B_C, C_C), which were calcined at 773 K, showed any sign of perovskite formation. In fig. 1B the Fourier transform of B_C is compared with that of $LaRhO_3$ and Rh_2O_3. The distances in the Fourier transform of the B_C catalyst sample are very well resolved because the X-ray absorption spectrum could be measured up to $k = 19.82$ $Å^{-1}$. The Rh–Rh distances of B_C do not match those of the perovskite but are close to those in Rh_2O_3 (2.715 and 2.988 Å). The results of the fitting procedures applied to the EXAFS of the calcined forms of the catalysts are collected in table 3. As the resolution for the samples C_C and D_C was lower than that for sample B_C, only two, respectively one, Rh–Rh neighbour distances are reported. The calcined catalysts consist of very small Rh_2O_3 particles, which have almost the same structure. This can be seen very well from the k^1 and k^3 weighted Fourier transforms presented in fig. 2, which show that the second and third shell Rh peaks are very small.

In contrast to the calcined forms, the reduced forms of the catalysts show a strong dependence on the La/Rh ratio. When this ratio is increased to 5 the Rh–Rh coordination number decreases, while the corresponding disorder is about doubled as can be seen from the Debye–Waller factors (table 4). Furthermore, hardly any shells can be detected at higher distances. In fig. 3 the k^1 weighted Fourier transforms of the reduced catalysts are shown. Although the reduction temperature was as high as 673 K for B_R and 723 K for C_R, no Rh–La interaction could be detected. The increase in dispersion at higher La_2O_3 loadings is in accordance with the H/Rh and the CO/Rh values (table

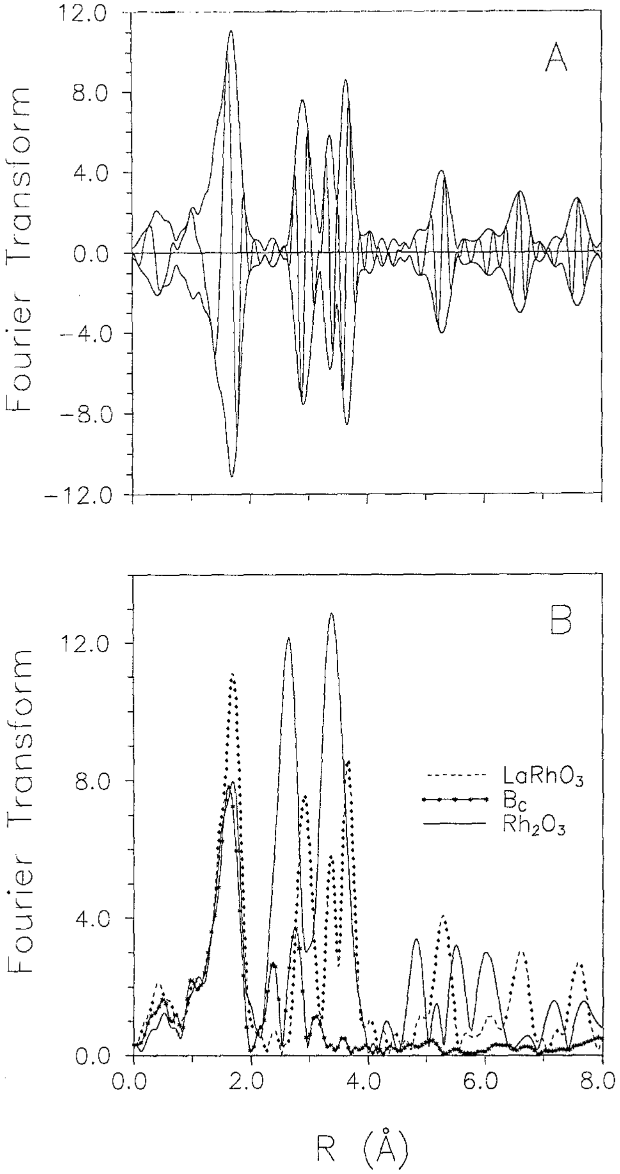

Fig. 1. (A) k^3 weighted Fourier transform of $LaRhO_3$ prepared at 1350 K. Transformation range in k: 2.68–19.59 Å^{-1}. (B) Magnitudes of the k^3 weighted Fourier transforms of $LaRhO_3$ (dashed line) prepared at 1350 K, Rh_2O_3 [21] (straight line) and the calcined catalyst B_C (line with symbols). Transformation range in k: $\approx$ 2.7–19.6 Å^{-1}.

4) determined by chemisorption. For the samples B_R and C_R, with La/Rh = 5 and 11.1, respectively, the chemisorption values are higher than for the sample A_R with La/Rh = 1.0. In the reduced form, the spectra for catalysts A_R and D_R are very similar. There is no indication for a SMSI effect, which would give

Table 3
Structural parameters for the calcined catalysts. The coordination numbers have been corrected for the photoelectron mean free path ($\lambda = 5$ Å) dependency. The accuracies are: N, ±0.1; R, ±0.02 Å; $\Delta\sigma^2$, $\pm 5 \times 10^{-4}$ Å^2; ΔE, ±1 eV

Sample	Coordination	N	R (Å)	$\Delta\sigma^2$ (10^{-4} Å^2)	ΔE (eV)
B_C	O	6.1	2.03	11	−3.1
	Rh	0.3	2.69	1	1.7
	Rh	0.8	3.04	−1	−2.3
	Rh	0.3	3.38	0	4.1
C_C	O	5.9	2.04	0	−2.8
	Rh	0.2	2.64	0	10.8
	Rh	0.7	3.08	0	−11.6
D_C	O	5.9	2.03	25	−2.2
	Rh	2.2	3.03	38	4.3

evidence for special Rh promoter interactions. The results of the fits for the EXAFS of the reduced catalysts are given in table 4. The contribution of the oxygen neighbours to the first shell was estimated by applying the difference method. Alter isolation of the first shell via backtransformation, the k^3 weighted EXAFS was fitted with a Rh reference. The difference EXAFS spectrum was then used to calculate the structural parameters for the first shell oxygen neighbours. These parameters were used as input in the final fitting of the total EXAFS spectrum. In analogy to previous results for Rh/Al_2O_3 catalysts [22–24], we assign the Rh–O distance of 2.6–2.8 Å to the direct contact at the Rh-support or Rh-promoter interface between Rh atoms in the Rh particles and oxygen anions in the SiO_2 support or La_2O_3 promoter, respectively. Such distances are only observed for very small metal particles, with a relatively large metal–support (or metal–promoter) interface. Former studies indicated that the Rh–Rh coordination numbers should be smaller than 7 to observe the Rh–O contribution [22].

Our findings are quite different from those reported by other authors for Rh/La_2O_3 [8] and Rh-La_2O_3/SiO_2 [7] systems. These differences are most probably due to the way in which the catalysts were prepared. The catalysts of Underwood and Bell [7], which were prepared by impregnating a passivated 4 wt% Rh/SiO_2 catalyst with a $La(NO_3)_3$ solution, showed a decrease in CO adsorption with increasing La content, while the H_2 adsorption remained almost constant. A decrease of CO adsorption relative to H_2 adsorption has also been reported by Gallaher et al. [8] for Rh supported on La_2O_3. This was explained by a partial coverage of the Rh particles resulting from the dissolution of La_2O_3 when impregnating $Rh(NO_3)_3$. The fact that the H/Rh values were higher than the CO/Rh values was explained by spillover of H atoms to the La_2O_3 and to

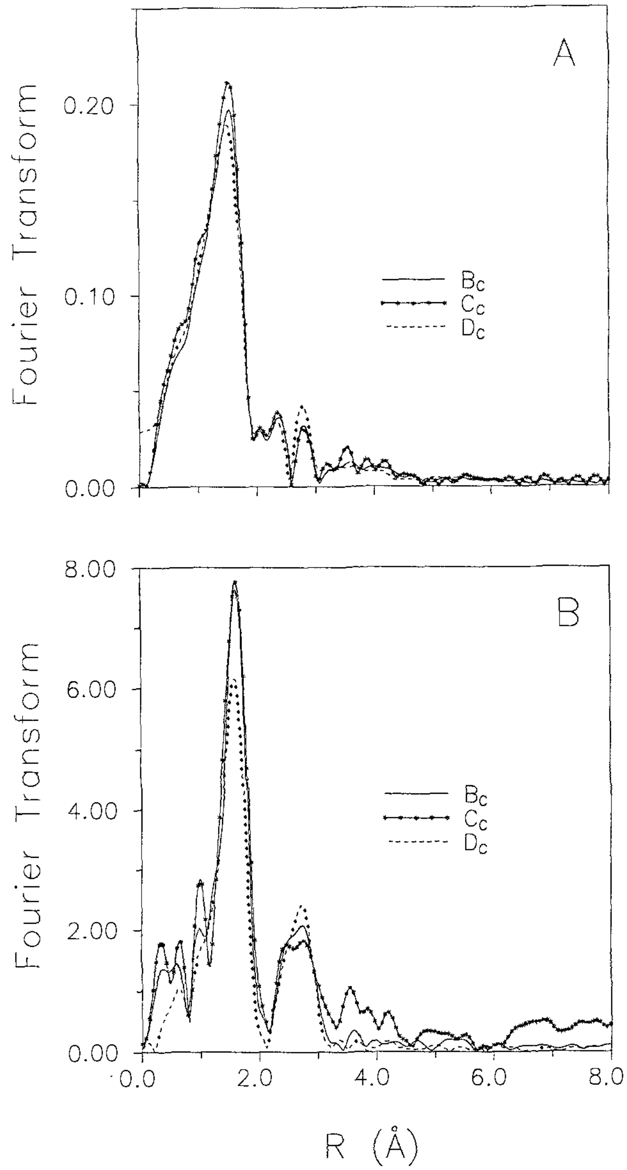

Fig. 2. Fourier transforms of the calcined samples B_C, C_C and D_C. (A) weighted by k^1, (B) weighted by k^3. Transformation range in k: ≈ 2.7–14.5 Å^{-1}.

reduction of the promoter oxide to LaO_x ($x < 1.5$). None of those effects were found in our catalysts, in which calcined La_2O_3/SiO_2 catalysts were impregnated with a $Rh(NO_3)_3$ solution. We do not observe spillover of hydrogen to the promoter or to the support, since our H/Rh and CO/Rh chemisorption data are almost equal. Furthermore, the increase in H/Rh and CO/Rh with increasing La/Rh ratio indicates the absence of covering of the Rh crystallites by LaO_x moieties in the reduced state of the catalyst.

Table 4
Structural parameters for the reduced catalysts. The coordination numbers have been corrected for the photoelectron mean free path ($\lambda = 5$ Å) dependency. The accuracies are: N, ±10.1; R, ±0.02 Å; $\Delta\sigma^2$, ±20%; ΔE, ±1 eV

Sample	Coordination	N	R (Å)	$\Delta\sigma^2$ (10^{-4} Å^2)	ΔE (eV)	H/Rh	CO/Rh
A_R	Rh	7.0	2.69	22	−3.3	0.81	0.81
	O	3.1	2.62	200	−1.3		
B_R	Rh	5.0	2.69	49	−3.0	1.17	1.06
	O	2.4	2.62	200	4.2		
C_R	Rh	4.2	2.67	47	4.3	1.04	1.18
	O	3.9	2.80	180	−8.2		
D_R	Rh	6.4	2.69	20	−1.3	0.59	
	O	2.3	2.78	200	−6.0		

Although our EXAFS experiments give no indication for Rh–La interactions it cannot be excluded that small amounts of mixed oxides are formed. A pronounced promoter effect due to the presence of La has been observed in all

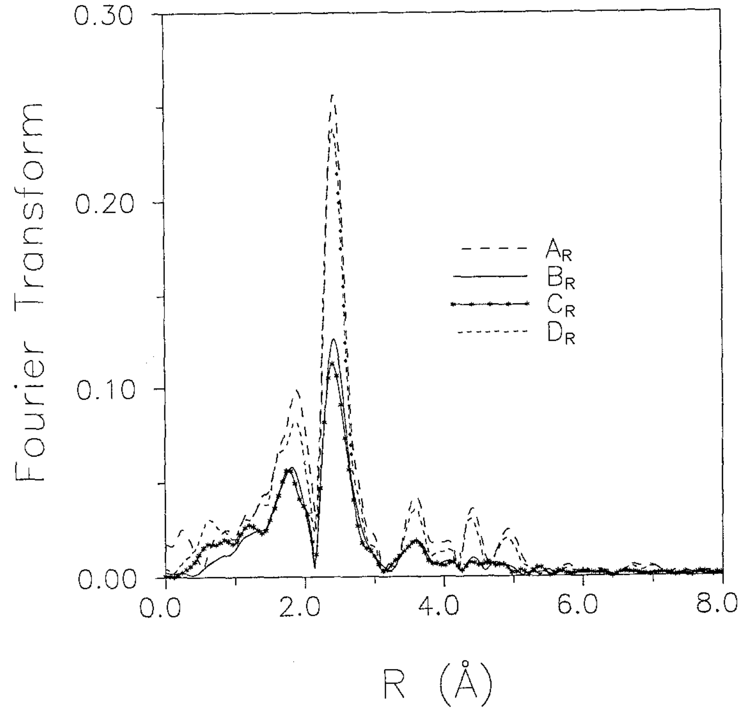

Fig. 3. k^1 weighted Fourier transforms of the reduced samples A_R to D_R. Transformation range in k: ≈2.7–16.5 Å^{-1}.

samples in the CO hydrogenation reaction [25]. Even though the redissolution of La_2O_3, which takes place during $Rh(NO_3)_3$ impregnation [25,26], could lead to an intense mixing of the Rh and La precursors and subsequent partial coverage of Rh, the high chemisorption values, except for catalyst D_R, make decoration of the Rh crystallites in the reduced state of our catalysts very improbable. It is more likely that the interaction between the Rh metal and the La_2O_3 promoter in catalysts A, B, and C, which is clearly shown by the higher dispersion at increasing La_2O_3 content, develops in the course of the reduction process. The higher the La/Rh ratio, the smaller the Rh particles become during reduction. The main role of the promoter in our catalysts might therefore be the prevention of sintering of the Rh crystallites, rather than their decoration.

As evidenced by the chemisorption data, catalyst D must be different from catalyst A, although the EXAFS spectra are similar in the reduced state. So even if the particle sizes are the same, much less Rh is exposed in catalyst D. We believe that the different calcination temperatures are the reason for this behaviour, because the redissolution of La during the second impregnation of sample A with $Rh(NO_3)_3$ [25] should lead almost to the same result as the coimpregnation of sample D. The high temperature during the calcination of sample D leads to a structural rearrangement including partial covering of Rh, which cannot be reversed during reduction. The reason for this could either be the complete dehydration and decarboxylation of lanthana already during calcination in the case of catalyst D, and not only during reduction as in catalysts A, B and C, or an involvement of transformations of the SiO_2 support, which might cover part of the Rh_2O_3 in an irreversible way.

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