

EXAFS study of monometallic and bimetallic ruthenium based catalysts: Ge K-edge environment in RuGe/Al₂O₃ and structural effects of CO adsorption

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Abstract

We report on the study of the structural modifications induced in Ru/Al₂O₃ catalysts by Ge addition and on the changes in the Ru environment upon CO adsorption in monometallic (Ru/Al₂O₃) and bimetallic (RuMe/Al₂O₃, Me = Ge, Sn, Pb) samples. Extended X-ray absorption fine structure measurements were performed at the Ge and Ru K-edges. Samples prepared by the controlled surface reaction (CSR) technique and by the classical impregnation method with different Ru loadings and different Ru/Me weight ratios were studied. The results show that germanium is present as oxide even after reduction at high temperatures. Germanium modifies the catalysts in two ways, (i) inducing a greater dispersion of the catalysts and (ii) covering the surface of the ruthenium particles as germanium oxide. The interplay of these two effects can explain the differences in the catalytic properties. The EXAFS study of the catalyst after CO adsorption shows that the Ru^{δ+} oxide species disappear from the surface of the metallic ruthenium particles explaining why CO adsorption is higher than H₂ adsorption.

Keywords: Monometallic catalysts; Ruthenium; Bimetallic catalysts; Structural properties

1. Introduction

This paper forms part of a series presenting an extensive and detailed study on Ru-based bimetallic and monometallic catalysts supported on Al₂O₃. The general objectives to be covered, as well as the preparation techniques were reported in the first previous paper [1]. Monometallic formulations were prepared by

means of the controlled surface reaction (CSR) technique [2] and those prepared from inorganic precursors by the classical impregnation method. Bimetallic catalysts were obtained by adding or incorporating as a compound an element of Group IV (Ge, Sn or Pb).

The effects of the dispersion on the reaction rates and selectivity on hydrogenolysis of alkanes have already been reported elsewhere together with the modifications on product selectivity due to the H₂ pressure and pretreatment used [3–6]. The analysis of the products of

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hydrogenolysis of 2,2,3,3-tetramethylbutane is extremely sensitive to the coordination on the metal surface and has been used as model reaction for identifying subtle changes in the surface morphology of small metal particles. It suggests that the germanium atoms are randomly distributed on the surface of Ru particles while the larger Sn and Pb atoms prefer Ru low coordination sites (corners and edges), and in the latter case, the resulting catalytic behaviour is equivalent to the case of large particles [7]. The modifiers induce a lower activity for structure-sensitive reactions and changes related to the chemisorption mechanism of alkane molecules. The validity of these models has been studied by quantum chemical calculations [8]. Changes of the catalytic activity have been also observed for the hydrogenation of polyfunctional molecules [9–11].

A structural study of this family of catalysts, and the effects of thermal pretreatment, by means of XRD and EXAFS at the Ru K-edge were already presented [12,13]. We showed that the main parameter controlling catalyst morphology was the method of preparation, the metal loading and pretreatment. The CSR method (RuEC series) produces catalysts with higher dispersion degree than those prepared by the coimpregnation method (RuNI series). Moreover, the dispersion decreases with the metal loading. Three important results were obtained: (i) in the case of the highest dispersed catalysts (sample RUEC1) the particles were formed by no more than twelve atoms and some ruthenium atoms were oxidized; (ii) bimetallic particles were not obtained, i.e. no Ru–Me bond was detected; (iii) germanium addition mainly induces a larger dispersion of the catalysts.

It is evident that there is an apparent contradiction between these results and the well known results on the modification of the catalytic activity upon addition of a second metal. The belief that the modification of the catalytic properties is due to the formation of bimetallic particles with topological segregation [7,14] cannot be supported by the present results and, as a conse-

quence, a different and more realistic model should be proposed.

We show that the dispersion degree, measured by the ruthenium coordination number, correlates with the CO adsorption but not with the hydrogen adsorption. We can also note that the addition of a second metal gives rise to opposite effects on the H₂ and CO adsorption indicating that in some way the second metal interacts or modifies the morphology of the parent monometallic catalysts.

In order to obtain direct structural information about the complicated microscopic structure of this system and to check the structural models proposed to explain their catalytic behaviour we completed the previous study by: (i) determining the local structure around the germanium atom by means of EXAFS at the germanium K-edge and (ii) studying the modification of the morphology of the catalysts after CO adsorption by means of EXAFS at the Ru K-edge. We were also interested in the study of the local structure around Sn and Pb, but due to the low absorption at the correspondent edges, it was impossible to obtain good spectra.

In this paper we give details on the experiments and on the analysis of the data, the structural results, and in Section 4 we compare our new results with the previous data of the Ru K-edge [12]. A model about the origin of the effects of the modifiers in the catalytic activity of Ru bimetallic catalyst is proposed.

2. Experimental

2.1. Materials

Two kinds of catalysts exchanged on Al₂O₃ were studied: catalysts from organic precursors (RuEC series) prepared at the Montpellier University by the CSR method and catalysts prepared from inorganic precursor prepared at the Messina University (RuNI series). The preparation and physical characterization of the catalysts prepared specifically for this program have

already been described [1], but for convenience the composition and H₂ and CO adsorption are reproduced in Table 1. We briefly recap that the RuEC series was prepared using Ru(acac)₃, and Ge, Sn or Pb elements were added by reaction of a tetra-alkyl compound with the reduced Ru/Al₂O₃. RuNI series was obtained from ruthenium nitrosyl nitrate and the modified catalysts by co-impregnation with this salt and a salt of the modifier.

2.2. EXAFS

X-ray absorption spectra at the Ge and Ru K-edges were performed at the beam line XAS IV of the storage ring DCI of LURE (Laboratoire pour l'Utilisation de la Radiation Electromagnetique) at Orsay. A double crystal Si(111) (Ge K-edge) and Ge(400) (Ru K-edge) monochromators were used, harmonic rejection was performed by a small misalignment of the two crystals. The storage ring operated at 1.8 GeV with an average current of 150 mA.

The experiments were carried out at room temperature in the transmission mode and the samples were mounted in a special chamber to be reduced 'in situ'. As in the experiments at the Ru K-edge [12] the catalysts were measured before and after reduction by flowing hydrogen at 480°C for one hour. The sample RuEC1Ge3 was also measured after reduction at 600°C. CO adsorption was performed at room temperature after reduction with hydrogen and flowing helium up to room temperature. CO adsorption was performed by flowing CO/He 1% for 5 min, and the measurement was then performed under helium flux.

Transmission electron microscopy measurements of catalyst RuEC3Ge1 were carried out in a JEOL JSM-6400 with an electron beam at 20 keV. Elemental analysis was performed by energy dispersive X-ray analysis (EDX) of Link Analytical, using a Si(Li) detector.

The experimental EXAFS signal has been extracted from the raw spectra following standard methods [15]. Background removal and the

Table 1
Composition and chemi-adsorption characteristics of the Ru catalysts

Sample	Ge,Sn,Pb ^a (wt.%)	Ru (wt.%)	(H/Ru) _{tot} ^b	(H/Ru) _{irr} ^c	CO ^d
RuEC1		0.97	0.88	0.71	1.31
RuEC2		2.5	0.44	0.38	0.64
RuEC3		4.0	0.25	0.19	0.27
RuEC1Ge1	0.15	0.97	0.59	0.43	1.18
RuEC1Ge2	0.30	0.97	0.54	0.38	1.21
RuEC1Ge3	0.7	0.97	0.41	0.27	1.17
RuEC1Sn1	0.2	0.97	0.51	0.37	0.86
RuEC1Pb1	0.2	0.97	0.66	0.53	1.30
RuEC3Ge1	0.41	4.0	0.12	—	—
RuNI1		1.0	0.23	0.17	0.37
RuNI2		2.0	0.23	0.19	0.31
RuNI4		4.0	0.26	0.20	0.30
RuNIGe1	0.14	1.0	0.59	0.45	1.07
RuNIGe2	0.20	1.0	0.54	0.40	1.03
RuNIGe3	0.72	1.0	0.42	0.28	1.04
RuNI1Sn1	0.23	1.0	0.38	0.26	0.98
RuNI1SnSO4	0.23	1.0	0.25	0.18	0.79
RuNI1Pb1	0.41	1.0	0.36	0.27	0.83

^a Ge, Sn, Pb and Ru weight percentages (wt.%).

^b Total H₂ chemi-adsorption as ratio between H₂ and Ru content.

^c Irreversible H₂ chemi-adsorption.

^d Ratio between CO chemi-adsorbed and Ru content.

atomic absorption coefficient was determined by a low order polynomial fit of the spectra. The Fourier transform of the Ru K-edge $k^2\chi(k)$ spectra was calculated using a Gaussian window in the range 3.4 to 14 \AA^{-1} . The FT of the Ge K-edge spectra, $k\chi(k)$ was calculated to lie between 2.7 to 10.5 \AA^{-1} also using a gaussian window. The structural parameters were obtained by least square fitting of the Fourier-filtered EXAFS signal between 1.2 and 3. \AA to the EXAFS formula [12]. Backscattering amplitudes and phase shifts were obtained from the EXAFS of metallic ruthenium and $\text{Ru}(\text{acac})_3$ for the Ru–Ru and Ru–O contributions. For the Ru–Ge contribution, theoretical phases and amplitudes, generated from the FEFF3.11 code [16] were used, because of the lack of suitable reference samples.

3. Results

3.1. Bimetallic Ru, Ge/ Al_2O_3 . EXAFS at the Ge K-edge

X-ray absorption experiments were performed in catalysts RuEC1Ge2 , RuEC1Ge3 , RuNIGe2 and RuNIGe3 . The catalysts RuEC1Ge1 and RuNIGe1 were not measured because of their Ge content was too low.

The EXAFS spectra and the FT at the Ge K-edge of RuEC1Ge3 and RuEC1Ge2 after activation at 480°C are compared with the EXAFS spectra of GeO_2 and metallic Ge in Fig. 1. The oscillatory signal of the catalysts is characterized by only one frequency component which corresponds to the main frequency of the GeO_2 spectra. The FT shows a main peak at 1.3 \AA at the same distance of the Ge–O first shell contribution of GeO_2 , a small contribution is observed, at least for the higher Ge loading (RuEC1Ge3), also at 2.7 \AA . It appears at the same distance of the Ge–O–Ge in GeO_2 indicating the existence of some weak ordering of the germanium oxide, what is clearly related to the weak structuring of the EXAFS signal that

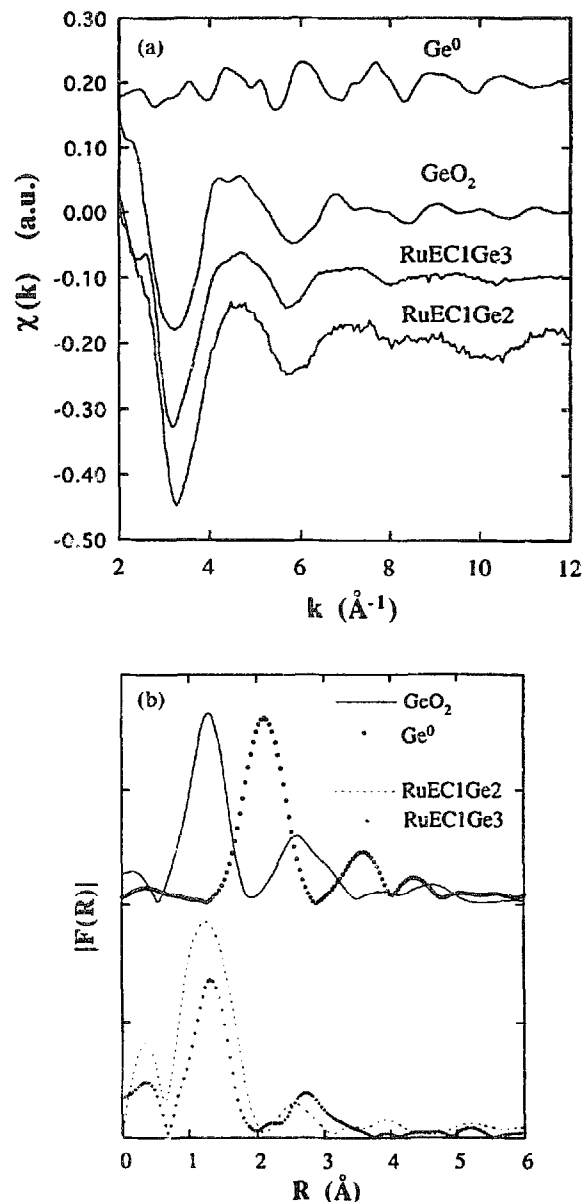


Fig. 1. Ge K-edge EXAFS spectra (a) and its Fourier transform (b) of RuEC1Ge2 and RuEC1Ge3 catalysts compared with the spectra of GeO_2 and metallic germanium. The FT shows a large peak at 1.35 \AA characteristic of Ge–O scattering.

is still visible in the spectrum of RuEC1Ge3 . This small peak (second shell contribution) cannot be attributed to any Ge–Ru coordination because of the long distance at which it appears [17], and it is more typical of the Ge–O–Ge coordination in germanium oxide. This result clearly shows that after normal activation conditions, germanium remains as an amorphous oxide and Ru–Ge bimetallic particles are not formed.

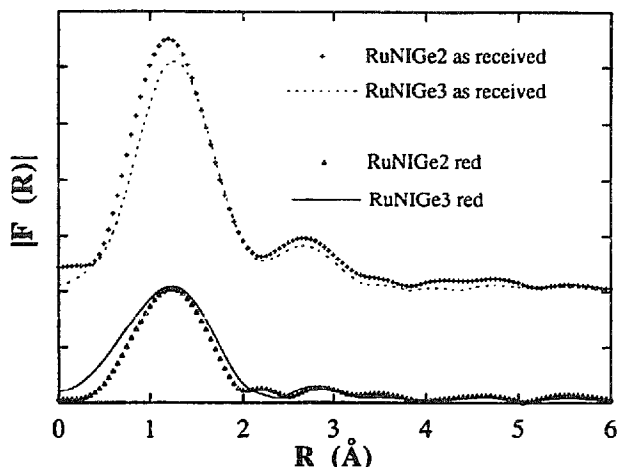


Fig. 2. Comparison of the FT of the Ge K-edge EXAFS spectra of catalysts RuNiGe2 and RuNiGe3. Upper curves: air exposed samples. Lower curves: After reduction in H₂ flow at 480°C.

Similar results were obtained for the RuNi1Ge series. Fig. 2 compares the FT of RuNiGe2 and RuNiGe3 EXAFS spectra of 'as received samples' and after reduction at 480°C. Only one peak at a distance of 1.3 Å corresponding to the Ge–O bond is observed. The difference between the air-exposed sample and that after reduction is shown in the intensity of this peak, it decreases upon H₂ reduction. This means that oxygen coordination is greater before reduction, indicating that reduction induces a partial loss of oxygen.

In order to check if Ru–Ge particles could be formed after more drastic reduction conditions, we kept sample RuEC1Ge3 under hydrogen flux at 600°C. The Ge K-edge EXAFS spectra do not show any important change, except for a lowering of the EXAFS amplitude. The FT of the RuEC1Ge3 EXAFS reduced at 480°C and 600°C are shown in Fig. 3 compared with GeO₂. It can be deduced that reduction at 600°C produces non-stoichiometric germanium oxide but it is not sufficient to reduce germanium to the metallic form. The ruthenium K-edge spectrum was also recorded. The FT at the Ru K-edge is shown in Fig. 4 and compared with the FT of the same sample reduced at 480°C. We observe a large increase of the Ru–Ru peak intensity indicating that after reduction at high tempera-

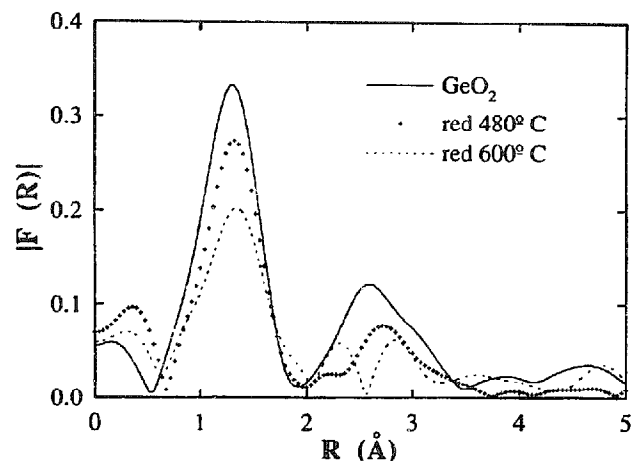


Fig. 3. FT of the Ge K-edge EXAFS spectra of RuEC1Ge3 catalysts after reduction at 480°C and 600°C compared with the FT of germanium oxide.

ture the ruthenium particles grow up. The analysis of the spectra, performed in the same way as in Ref. [12] leads to a Ru–Ru coordination number of 9.2 which is larger than the value of about 3.5 found for the catalyst activated at 480°C. It is clear that this treatment induces a migration of Ru atoms to form larger particles.

From these experiments the main outcome is that Ru–Ge particles are not formed. In order to confirm this conclusion, we have performed transmission electron microscopy experiments on sample RuEC3Ge1 with EDX analysis. This sample was chosen for being less dispersed and

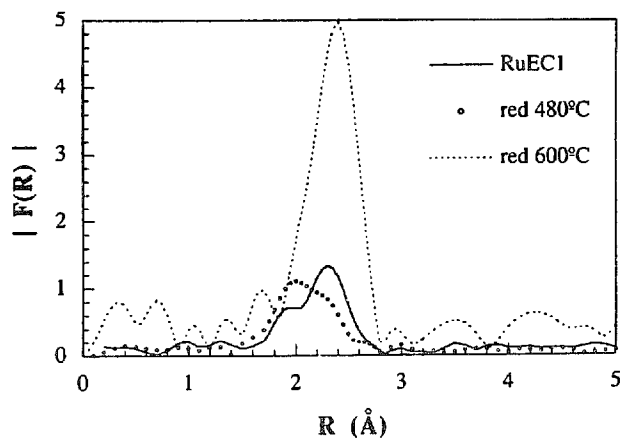


Fig. 4. Modulus of the FT of Ru K-edge spectra of RuEC1Ge3 sample after activation at 480°C and 600°C compared with the parent catalysts RuEC1 activated at 480°C.

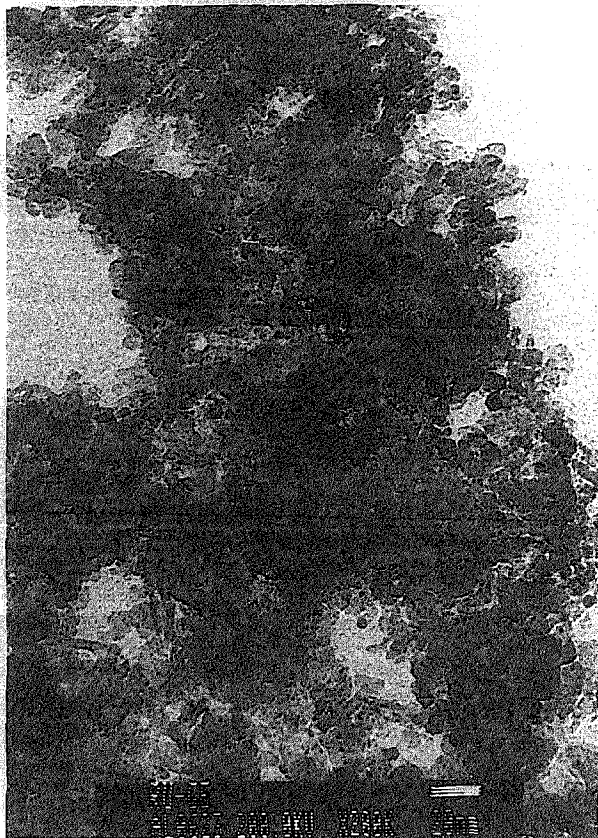


Fig. 5. Transmission electron microscopy image of RuEC3Ge1 catalyst.

after air exposure only partial oxidation of the surface of the ruthenium particles occurs.

A TEM image of RuEC3Ge1 catalyst showing well defined metallic ruthenium particles is reported in Fig. 5. The mean size is approximately 6.5 nm. We made an elemental analysis by EDX in two situations: first, the electron beam was defocussed on a large area, to get an average composition of the catalysts. Second, the electron beam was focused on a single particle (several particles were sampled in order to get an average composition). The fluorescence spectra from the large area show a large aluminium contribution, as expected from the support, together with ruthenium and copper (the latter coming from the sample holder). It is also observed a small peak from germanium $K\alpha$ emission. The fluorescence spectrum collected from the individual particles shows also a small contribution from aluminium, but the most

intense peak correspond to the Ru K and L emission. No signal from germanium was observed in this case. Quantitative analysis of the fluorescence peaks of Ge and Ru gives a composition ratio 93 Ru/7 Ge in the case of large area sampling while analysis on individual particles gives a germanium/ruthenium ratio of less than 1/100, a value which is at the detection limit of the technique.

These results confirm the previous conclusions derived from EXAFS that no bimetallic particles have been formed.

3.2. CO adsorption. EXAFS at the Ru K-edge

We carried out EXAFS experiments at the Ru K-edge of the catalysts after CO adsorption. The EXAFS spectra of catalysts with high Ru content and low dispersion do not show appreciable modifications after CO adsorption with respect to the untreated material. The comparison of the EXAFS spectra of catalysts RuEC3 and RuEC3 + CO is shown in Fig. 6. The lack of sensitivity of EXAFS to the CO adsorption is due to the large particle size. CO is adsorbed only at the surface and the contribution of the surface atoms to the EXAFS signal is negligible if compared with the contribution from the bulk.

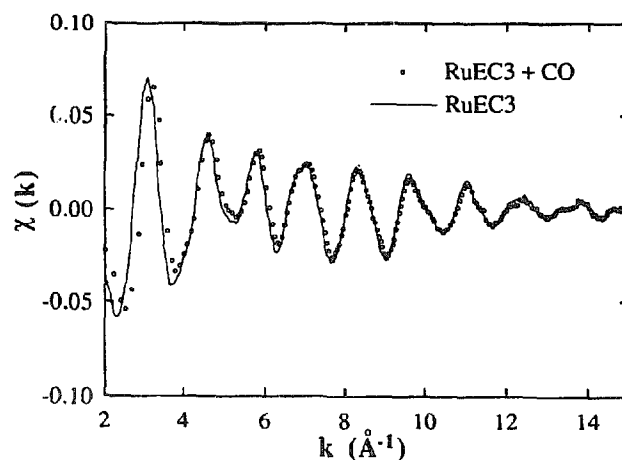


Fig. 6. Ge K-edge EXAFS spectra of RuEC3 catalyst before and after CO adsorption. The effects of CO adsorption on the EXAFS spectra in low-dispersed catalysts is negligible because of the large contribution of the bulk atoms. A small difference is observed at low k values.

On the other hand, the absence of appreciable changes in the EXAFS spectra clearly indicates that Ru particles maintain their size and shape after CO adsorption, and consequently, no disintegration of these particles is produced under these CO adsorption conditions.

The effect of CO adsorption in the EXAFS spectra of highly dispersed catalysts is instead quite evident. The FT spectra of RuEC1 selected samples after and before CO adsorption are shown in Fig. 7. It is evident that the main Ru–Ru peak is split after CO adsorption showing an extra contribution at lower interatomic

distances which indicates the presence of Ru–CO coordination. We have performed a first shell analysis by Fourier filtering the EXAFS signal between 1.5 and 2.9 Å. As a model contribution we use the signal from metallic ruthenium and Ru–acetylacetonate while for the Ru–C contribution we used the theoretical signal obtained from the FEFF3.11 program [16]. The best fit data are given in Table 2 and are consistent with the data from Ref. [12]. The only change refers to RuEC1Ge3 where the presence of some germanium in the ruthenium environment was erroneously considered. The

Table 2
Best fit parameters obtained from the first shell contribution of Ru, Me/Al₂O₃ catalysts^a

Sample	Treatment		<i>N</i> (±0.2)	<i>R</i> (Å) (±0.01)	$\Delta\sigma^2$ (Å ²) (±0.001)
RuEC1	HTR	Ru ⁰	3.8	2.6	0.003
		Ru ^{δ+}	0.5	1.99	0.002
		O	0.3	2.02	0.002
	CO	Ru ⁰	3.01	2.64	0.006
		C	1.6	2.2	0.004
		O	2.3	2.72	0.007
RuEC2	HTR	Ru ⁰	7.4	2.67	0.001
	CO	No appreciable changes after CO adsorption.			
RuEC3	HTR	Ru ⁰	9.9	2.67	0.002
	CO	No appreciable changes after CO adsorption.			
RuEC1Sn1	HTR	Ru ⁰	4.6	2.63	0.003
		Ru ^{δ+}	0.9	1.99	0.002
		O	0.3	2.02	0.002
	CO	Ru ⁰	4.2	2.62	0.006
		C	2.3	2.16	0.003
		O	2.5	2.73	0.007
RuEC1Ge3	HTR	Ru ⁰	2.4	2.62	0.005
		Ru ^{δ+}	1.9	2.33	0.002
		O	0.1	1.97	0.002
	CO	Ru ⁰	1.9	2.62	0.008
		C	4.0	2.13	0.004
		O	3.6	2.73	0.009
RuN11	HTR	Ru ⁰	9.2	2.67	0.001
	CO	No appreciable changes after CO adsorption.			
RuN1Sn1	HTR	Ru ⁰	6.	2.66	0.01
	CO	Ru	4.6	2.66	0.010
		C	1.68	2.17	0.009
RuN1Ge2	HTR	Ru ⁰	6.4	2.65	0.001
	CO	very small changes after CO adsorption.			

^a After reduction in hydrogen flow at 480°C (HTR) and after room temperature CO adsorption. *N* coordination number, *R* distance from the Ru adsorber, $\Delta\sigma^2$ Debye–Waller factor difference between catalysts and model.

EXAFS study at the Ge K-edge of this work clearly shows the absence of Ru–Ge coordination due to the easy identification of Ge as oxide. The origin of the preceding confusion is related to the dominant Ru–Ru contribution that makes the detection of the Ru–Ge pairs contribution at the Ru K-edge, quite difficult and unclear. The effects observed are that CO adsorption produces a slight decrease of the Ru–Ru coordination, the disappearance of the $\text{Ru}^{\delta+}$ contribution and the replacement of oxygen by CO in the first coordination shell. The oxygen of the second shell, i.e. at a distance $R(\text{Ru}-\text{O}) = 2.72 \text{ \AA}$, belongs to the CO molecule and the difference in coordination is within the precision in coordination numbers given by EXAFS.

The FT spectra of selected samples of the RuNI series after and before CO adsorption are given in Fig. 8. RuNI1 monometallic catalysts do not show any significant change after CO adsorption. This is due, as pointed out before, to the low catalyst dispersion which makes the contribution of the surface atoms negligible with

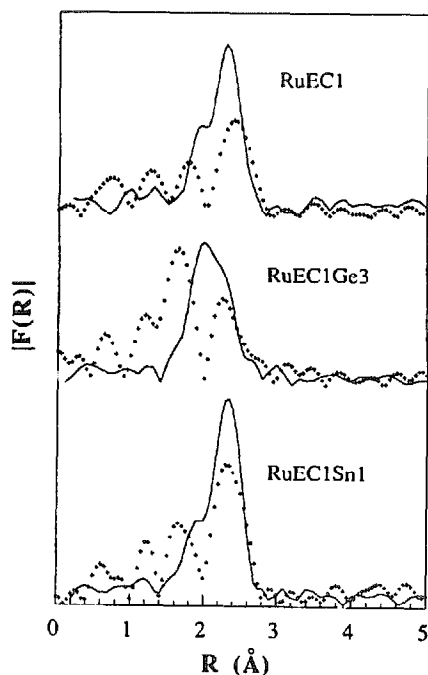


Fig. 7. FT of RuEC1, RuEC1Ge3 and RuEC1Sn1 spectra activated at 480°C (continuous line) and after CO adsorption (+ + +). In high dispersed catalyst the effect of CO adsorption is clearly evidenced.

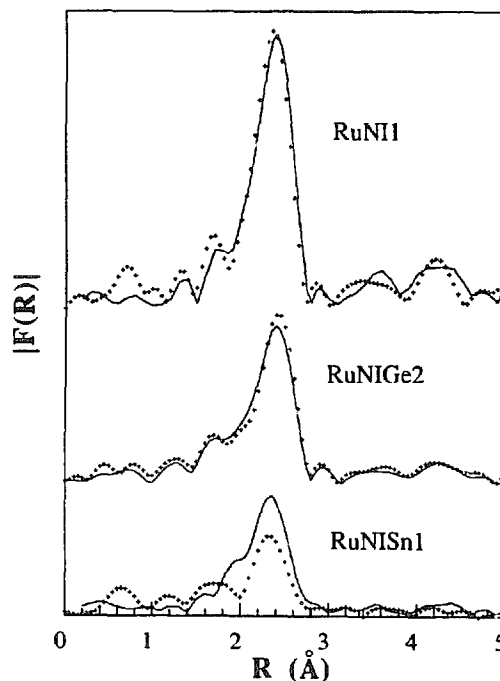


Fig. 8. Fourier transform of the EXAFS spectra of RuNI1, RuNIGe2 and RuNISn1 before (continuous line) and after CO adsorption (+ + +). Also for these series the effect is clearly observable for the most dispersed catalyst.

respect to the contribution of the bulk atoms. The same occurs with the RuNIGe2 sample for which the spectra are very similar except for very low k values. This indicates the presence of some effects related to the CO adsorption, but it is impossible to extract quantitative information. For sample RuNISn1, the most dispersed catalysts, the effect of CO adsorption is to increase the dispersion. The Ru–Ru coordination number indeed decreases from 6 to 4.6 upon CO adsorption, being probably related to a strongly non-homogeneous distribution of particle sizes.

4. Discussion

This work supplements the results already obtained in previous EXAFS works [12,13] allowing us to obtain a clearer picture of the structure of these catalysts and a better understanding of their catalytic properties.

4.1. Monometallic catalysts

Our previous study at the Ru K-edge of monometallic catalysts showed the following important conclusions [12]: (i) the dispersion of the catalyst depends on the preparation method, i.e. the CSR method yield to larger dispersion than those prepared from inorganic precursors. (ii) Dispersion decreases with the Ru loading, the RuEC1 sample being the most dispersed. (iii) The most dispersed RuEC1 sample is formed by cluster of no more than 12 atoms. Moreover surface oxidation is also observed.

Further information was obtained in this work by studying the effect of CO adsorption. As we can see in Table 2, CO adsorption removes the oxidized ruthenium. This result is found for all the highly dispersed catalysts of the series, which also show residual oxidation after reduction at 480°C. In all these cases CO adsorption is higher than H₂ adsorption. This effect is related to the incomplete reduction at the normal activation temperature and to the strong capability of CO to bond to the Ru surface atoms. In this sense CO adsorption would measure the total surface of the catalysts while H₂ depends on the equilibrium of oxidation/reduction at the surface. The isotherms performed at different H₂ pressures give different adsorption rates supporting this explanation.

4.2. Bimetallic catalysts

Bimetallic formulation of the catalysts induces changes in their catalytic activity, which were initially ascribed to the formation of bimetallic particles with the modifier atoms occupying specific sites in the Ru particles. Our results show instead that bimetallic particles are not formed and the main effect, when germanium or tin are added, is a lowering of the Ru coordination number.

The results at the Ge K-edge provide a clearer picture. We find that germanium remains in the oxide form after normal activation conditions and, as already suggested in previous work [12],

that it does not form bimetallic particles, as also confirmed by the TEM study on the RuEC3Ge sample. The effect of germanium addition is a lowering of the particle size that manifests itself as a decrease of the Ru coordination number.

These results can be explained in terms of a strong interaction between germanium oxide and the unreduced Ru^{δ+} on the Ru particles surface, probably before activation. This interaction, or bonding, prevents the clustering of larger particles of ruthenium provoking a higher dispersion. On the other hand, and as a consequence of this hypothesis, germanium oxide probably remains at the surface of the ruthenium particles giving rise to a partial poisoning of the catalyst. The different behaviour of the bimetallic catalysts in the hydrogen adsorption versus CO adsorption can be easily understood considering that H₂ is unable to remove the germanium oxide from the ruthenium surface, while CO, as it has been demonstrated by the EXAFS results, removes the oxygen of the surface showing adsorption similar to that of monometallic samples. In other words, H₂ adsorption gives a measurement of the active surface of the catalysts while CO adsorption depends on the total surface including the regions covered by oxide.

The effect of the addition of a second metal is therefore twofold: (i) it induces a higher dispersion of the catalyst, in principle, an increase of the active surface, and (ii) the particles are partially covered by the second metal oxide producing a decrease of the active surface. The overall effect on the catalytic properties of the sample depends on the dominating effect.

For the RuEC1 series, due to the high dispersion of the material, the main effect is the coverage of the surface resulting in a lowering of H₂ adsorption when Ge is incorporated. A certain reduction of the particle size, related to a lowering of the EXAFS coordination number is also observed. The same kind of mechanism takes place due to the coverage of lead oxide when lead is added. Also in this case the H₂ adsorption decreases upon lead addition and the CO adsorption remains unaltered. In contrast,

the addition of Sn seems to produce the opposite effect. The particle size, deduced from the EXAFS coordination number values, increases and a corresponding decrease of the CO adsorption rate is observed.

In the case of the RuNi series, characterized by a lower degree of dispersion, the main effect of the addition of the second metal is to increase the dispersion and raise H₂ and CO adsorption due to the increased amount of active ruthenium surface. This is very clear for the RuNiGe1 and RuNiGe2 (low Ge content) samples, since an clear increase in both H₂ and CO adsorption is observed together with the corresponding decrease of the coordination numbers (*N*) obtained for the latter samples. On the other hand, for the highest Ge content the effect of surface covering is dominant, the adsorption of CO does not change appreciably but the H₂ adsorption undergoes a strong reduction. The addition of tin or lead seems to produce the same kind of effects but the lack of EXAFS measurements at the lead or tin K-edges renders the interpretation more speculative.

The catalytic activity of the catalysts has been studied in the hydrogenolysis reaction with 2,2,3,3-tetramethylbutane. The values of the fragmentation factor (depth hydrogenolysis), turnover frequency (TOF) and selectivity are reported in Ref. [6]. Our structural study clearly shows that the main differences in catalytic activity can be related essentially to the dispersion degree. So that, samples RuEC3 and RuNi1 that have a similar coordination number show high TOF values, high conversion and depth hydrogenolysis as expected for a catalyst composed by large particles if compared with the higher dispersed RuEC1 sample. The addition of a second metal can be understood in light of the two effects previously mentioned. Addition of germanium to the RuEC1 catalysts induces a lowering of the conversion and TOF, the depth hydrogenolysis being similar owing to similar particle size. On the other hand in the series RuNi, where the main effect upon addition of the second metal is to increase the dispersion,

the conversion, TOF and the depth hydrogenolysis decrease with the Ge content.

As a conclusion from the structural study of bimetallic catalysts RuMe/Al₂O₃, we can say that two main parameters control the catalytic behaviour: dispersion and coverage of the particle surface by metallic oxides. The equilibrium of these two factors upon addition of the second metal governs the catalytic properties of the material.

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