

Hydrogenation of citral and cinnamaldehyde over bimetallic Ru–Me/Al₂O₃ catalysts

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Abstract

Hydrogenations of citral and cinnamaldehyde have been investigated over Ru–Me/Al₂O₃ (Me = Ge, Sn, Pb). Two series of catalysts have been prepared by using the controlled surface reaction (CSR) technique (RuEC series) and the more conventional co-impregnation method (RuNI series). Addition of Ge increases the catalytic activity on the RuEC series whereas no modifications are found on the samples prepared by co-impregnation. The selectivity to unsaturated alcohols is not influenced by the presence of Ge. Addition of tin increases both the activity and the selectivity regardless of the preparation method. The presence of lead does not modify the selectivity and a slight decrease in the catalytic activity is observed on the sample of the RuNI series. On the basis of the characterization data available on the investigated catalysts, it is suggested that Ru and Ge interacts when the samples are obtained through the CSR technique. Such an interaction increases the catalytic activity likely through a decrease of the strength of adsorption of one of the reaction components. The positive effect of tin on the catalytic activity and selectivity is discussed.

Keywords: Hydrogenation; Unsaturated aldehydes; Aldehydes; Ruthenium; Bimetallic catalysts

1. Introduction

The hydrogenation of α,β -unsaturated aldehydes to the corresponding alcohols is a reaction of relevant importance in the synthesis of various fine chemicals.

Several studies and many efforts have been made in the recent past for developing a suitable catalytic system able to improve the yields of the products of C=O bond hydrogenation. The most investigated catalysts have been the Group VIII metals [1–20]. The reaction selectivity has been found to be influenced by several param-

eters such as metal particle size, precursor, support and presence of promoters. In particular, it has been observed that the addition of suitable elements (Sn, Ge, Fe, Ga) can strongly modify the catalytic properties of the active metal. Electronic and geometric effects have been suggested to explain the improvement in the selectivity to unsaturated alcohols [6,14,15]. However the mechanism by which the promoter improves the reaction selectivity has not been fully elucidated. Questions regarding location and oxidation state of second element, surface composition of the catalyst, electronic and geo-

metric properties of the active site, etc., need to be answered to interpret fully the catalytic results.

In this paper we report a detailed study on the hydrogenation of two unsaturated aldehydes, namely citral and cinnamaldehyde carried out over bimetallic Ru catalysts supported on γ -alumina catalysts. This investigation is part of a broader program carried out within an EC Stimulation Action Programme, the general scope of which is to correlate the structural and catalytic properties of model ruthenium catalysts doped with Sn, Ge, Pb and prepared by the controlled surface reaction (CSR) technique. The results are compared with those obtained on catalytic systems prepared by the classic impregnation method. By the CSR method, starting from the same monometallic 'parent catalyst' different bimetallic formulations were prepared by adding different amount of the second element.

The catalysts used have been extensively characterized in the different laboratories participating to the EC Programme by using several physico-chemical techniques (H_2 and CO chemisorption, TPR, TEM, EXAFS) [21,22]. Their catalytic behaviour has been also tested

by using model hydrogenolysis reactions which are known to be strongly influenced by the geometric properties of the active sites [23].

2. Experimental

2.1. Catalysts preparation

The monometallic catalyst of the series RuEC was prepared by contacting a toluene solution of ruthenium acetylacetonate, $Ru(acac)_3$, with γ - Al_2O_3 (Rhone-Poulenc, S_{BET} 220 $m^2 g^{-1}$).

The Ru catalyst of the RuNI series was prepared by impregnation of the support with an aqueous solution of ruthenium nitrosil nitrate, $Ru(NO)(NO_3)_3$.

Bimetallic catalysts of the RuEC1 series have been obtained by contacting, under a H_2 atmosphere at 353 K, the monometallic RuEC1 sample with the desired amount of an organometallic compound of the second element dissolved in a n-heptane solution. The second metal has been added as $(C_4H_9)_4Sn$, $(C_4H_9)_4Ge$ or $(C_2H_5)_4Pb$.

Bimetallic samples of the RuNI series were

Table 1
Main characteristics of Ru-Me/ Al_2O_3 catalysts

Catalysts	Ru (wt%)	Me (wt%)	Me/Ru	H/Ru	TEM observations
<i>RuEC series</i> ^a					
RuEC1	0.97	—	—	0.88	0.8–1.5 nm narrow distribution
RuEC1/Ge1	0.97	0.15	0.21	0.59	0.8–1.5 nm narrow distribution
RuEC1/Ge2	0.97	0.30	0.42	0.54	0.8–1.5 nm narrow distribution
RuEC1/Ge3	0.97	0.70	1.00	0.41	1.0–2.0 nm narrow distribution
RuEC1/Sn1	0.97	0.26	0.23	0.51	0.8–1.5 nm narrow distribution
RuEC1/Sn2	0.97	0.54	0.47	0.32	0.8–1.5 nm narrow distribution
RuEC1/Pb1	0.97	0.51	0.25	0.66	0.8–1.5 nm narrow distribution
<i>RuNI series</i> ^b					
RuNI	0.92	—	—	0.23	1.0–10 nm bimodal distribution
RuNI1/Ge1	1.12	0.19	0.24	0.59	1.0–1.5 nm narrow distribution
RuNI1/Ge2	1.37	0.36	0.36	0.54	—
RuNI1/Ge3	1.37	0.84	0.85	0.42	—
RuNI1/Sn1	1.43	0.26	0.15	0.38	—
RuNI1/SnSO ₄	1.19	0.23	0.16	0.25	—
RuNI1/Pb	1.20	0.39	0.16	0.36	—

^a Prepared from $Ru(acac)_3$.

^b Prepared from $Ru(NO)(NO_3)_3$.

prepared by co-impregnation of the support with $\text{Ru}(\text{NO})(\text{NO}_3)_3$ and the precursor of second metal. The promoter precursors used were: $\text{Ge}(\text{C}_2\text{H}_5\text{O})_4$, SnCl_2 (for the RuNiSn sample), SnSO_4 (for the RuNiSnSO₄ sample), $\text{Pb}(\text{CH}_3\text{CO}_2)_2$.

All samples, after drying for 2 h, were reduced under H_2 at 623 K. Table 1 reports the chemical composition and the main characteristics of all samples.

2.2. Characterization

Catalysts were characterized by means of H_2 chemisorption, TEM and EXAFS analysis.

Hydrogen chemisorption measurements were carried out using a static volumetric apparatus. The hydrogen adsorption isotherms have been carried out at 373 K in the pressure range 50–400 Torr. The H/Ru ratio was used to measure the Ru dispersion (Ru surface atoms/Ru total atoms).

TEM analyses were performed using a JEOL 100 CX apparatus following the extractive replica technique.

EXAFS (extended X-ray absorption fine structure) measurements were carried out using the beam line at the LURE (Orsay) synchrotron radiation. The samples were reduced in situ by flowing H_2 at 623 K for 1 h. The reference materials were the precursor $\text{Ru}(\text{acac})_3/\text{Al}_2\text{O}_3$ and ruthenium powder. Details on the characterization results and on the experimental procedures used are reported elsewhere [21,22].

2.3. Catalytic experiments

Before catalytic activity measurements the catalysts were reduced for 2 h at 623 K. After cooling at room temperature they were transferred into the reactor. It has been previously demonstrated [21] that, due to the slow oxidation of Ru, catalysts reduced at 623 K can suffer short exposure to air, and can be easily reactivated at low temperature under H_2 .

The hydrogenation of the α,β -unsaturated

aldehydes (citral: Fluka, purity > 97%, 35/65 mixture of the form *Z* and *E*; cinnamaldehyde: Fluka, purity > 98%) has been carried out in a 100 ml four-necked flask fitted with a reflux condenser, a thermocouple, a dropping funnel and a stirred head. The catalyst was added to 25 ml of ethanol and treated at 343 K under flowing H_2 , for 1 h at atmospheric pressure. After this step, the reactor temperature is lowered to 333 K, 0.1 ml of substrate is injected and the progress of the reaction is followed by analyzing a sufficient number of microsamples. Chemical analysis was performed with a gas chromatograph equipped with a flame ionization detector and with a wide-bore capillary column (Supelcowax, 30 m, 0.53 mm i.d.). Quantitative analysis was carried out by calculating the area of the chromatographic peaks using an electronic integrator.

Catalytic activity was measured in terms of initial turnover rate and calculated from the slope of the curves conversion versus time (t) at $t = 0$. Selectivity to unsaturated alcohols was calculated by the expression $S = C_i \Sigma C_p$ where C_i is the concentration of the unsaturated alcohols and ΣC_p the total concentration of the products.

Preliminary tests, with different amounts of catalyst, grain size and stirring rate were carried out in order to ascertain the absence of diffusional limitations.

3. Results

3.1. Catalyst characterization

Two series of bimetallic catalysts (RuEC and RuNI) were investigated. The RuEC series was obtained by using the 'controlled surface reaction' method (CSR) and the RuEC1 sample as a parent catalyst. The RuNI series was obtained by co-impregnation.

An extensive characterization study of these catalysts has been reported elsewhere [21,22] and therefore here we recall only the main conclusions.

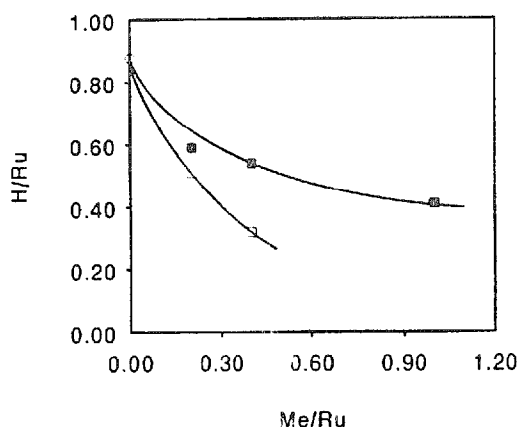


Fig. 1. Influence of the Me/Ru ratio on the dispersion (H/Ru). (■), Me = Ge; (□), Me = Sn.

The H/Ru ratio measured on the investigated samples is reported in Table 1. The characterization results of the samples of the RuEC series shows on the parent RuEC1 monometallic catalyst a high Ru dispersion ($H/Ru = 0.88$). This is in agreement with TEM observations which have shown that on this sample the metal particle size ranges between 0.8–1.5 nm. The addition of tin, germanium and lead decreases the H_2 chemisorption. Despite the reduction of the H/Ru ratio no significant changes in the metal particle size were observed. TEM analysis showed metal particles having a size close to that measured on the parent catalyst (Table 1). Therefore the lower H_2 chemisorption measured on the bimetallic samples can be attributed to the second element which blocks the chemisorption sites.

In Fig. 1 is depicted the H/Ru ratio as a function of the atomic Me/Ru ratio for the bimetallic Ru–Sn and Ru–Ge samples. A larger decrease of the H_2 chemisorption was found with addition of Sn compared to Ge. Sn seems to cover the surface of the RuEC1 catalyst in a better way. The greater coverage observed with tin cannot simply be attributed to the larger size of Sn with respect to Ge. In fact, the Ru–Pb sample (Table 1) having a similar Me/Ru ratio shows a lower effect on the H/Ru ratio notwithstanding the larger size of Pb.

The monometallic sample prepared from the

inorganic precursor (RuNI series) shows a lower dispersion and a broader distribution of the metal particle size. The H/Ru ratio on the RuNI1 sample is 0.23 and the TEM analysis has shown particles in the range 1.0–10 nm and large agglomerates around 50 nm [21]. The co-impregnation with the second component leads to smaller Ru particles. This is shown by the higher H/Ru ratio found on the bimetallic samples and it was confirmed by the TEM analysis of the RuNI1Ge1 sample. On this catalyst, particles in the range 1.0–1.5 nm were in fact observed. These features are in agreement with a detailed EXAFS study [22] which has shown that the addition of a second element to Ru produces different structural effects depending on the preparation method used and the nature of the added component. On the RuEC series, the addition of germanium decreases the coordination number of the Ru–Ru pair from 3.81 on RuEC1 up to 2.05 on RuEC1Ge3, whereas the coordination number of the Ru–O pair increases from 0.31 to 0.61. For the highest Ge loading a number of Ge atoms were found to be incorporated into the Ru particles. The addition of Pb and Sn to RuEC1 does not induce any appreciable variation in the sample local-order structure.

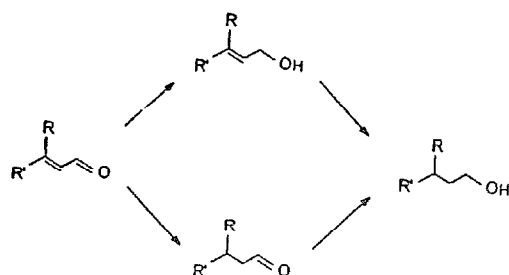
On the RuNI derived samples the addition of Ge decreases the first shell coordination numbers of the Ru–Ru pair from 9.18 on the monometallic sample up to 6.05. A similar decrease was observed on the RuNI1Sn1 sample (prepared from $SnCl_2$). RuNI1SnSO₄ and RuNI1Pb samples did not show any change of the Ru local environment. On these latter samples the presence of the second element does not show any shape modification of the EXAFS spectrum.

3.2. Catalytic activity

The catalytic properties of the Ru–Me/Al₂O₃ catalysts were evaluated in the selective hydrogenation of α,β -unsaturated aldehydes. The re-

actions have been carried out in the liquid phase under mild conditions ($T_r = 333$ K, $P = 1$ atm). Citral and cinnamaldehyde were chosen as test molecules.

Addition of H_2 to the unsaturated aldehydes can be described through the following simplified scheme:



where: $R = H$, $R' = C_6H_5$ for cinnamaldehyde and $R = CH_3$, $R' = C_6H_{11}$ for citral. No evidence was found for the presence of intermediates of the type $R'R-C-C=COH$. A more detailed reaction scheme is reported in Refs. [24,25].

Fig. 2 shows the initial turnover rate, N_H , (expressed as molecules of substrate reacting per ruthenium surface atom per second) measured in the hydrogenation of citral over bimetallic samples of the RuEC series having a Me/Ru ratio of about 0.2. Samples containing Sn or Ge were significantly more active than the parent RuEC1 catalyst, whereas only a slight

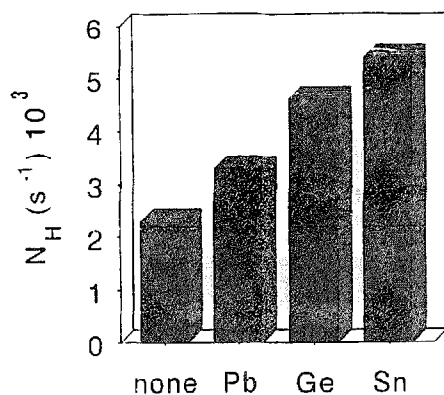


Fig. 2. Turnover rate of citral hydrogenation over Ru-Me/ Al_2O_3 catalysts of the RuEC series. (Me/Ru = 0.2).

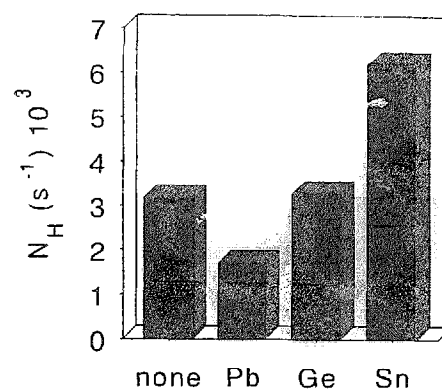


Fig. 3. Turnover rate of citral hydrogenation over Ru-Me/ Al_2O_3 catalysts of the RuNI series. (Me/Ru = 0.2).

increase in the catalytic activity was observed on addition of Pb. Among the catalysts of the RuNI series (prepared by co-impregnation) only the sample containing Sn was found more active (Fig. 3). Germanium did not modify the specific activity whereas the catalyst containing Pb showed a lower activity.

The effect of addition of different amounts of Ge on the catalytic activity is reported in Fig. 4 which shows the turnover rate of citral hydrogenation on the Ru-Ge samples. On the catalysts of the RuEC series, an increase in the catalytic activity was observed with increasing the Ge content. On the RuNI series the turnover rate remained constant regardless of the Ge/Ru ratio. The effect of the presence of Sn on the catalytic activity is reported in Table 2. All the

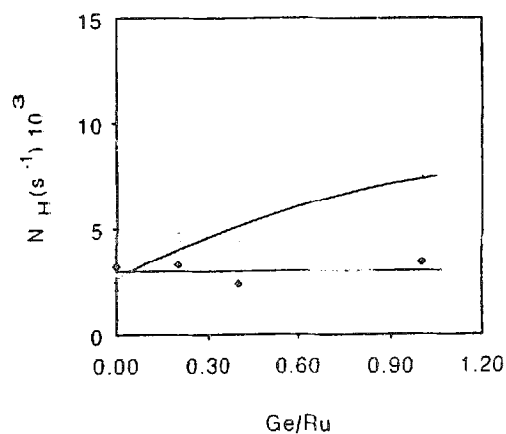


Fig. 4. Influence of the Ge/Ru ratio on the turnover rate of citral hydrogenation. (\blacklozenge), RuNI series; (\circ), RuEC series.

Table 2
Catalytic activity N_H , towards citral hydrogenation over Ru–Sn/ Al_2O_3 catalysts

Catalysts	Sn/Ru	$N_H \times 10^3$
RuEC1	0	2.3
RuEC1/Sn1	0.23	5.4
RuEC1/Sn2	0.47	10.1
RuNI1/Sn1	0.15	6.2
RuNI1/SnSO ₄	0.16	4.5

Sn–Ru samples were more active than the monometallic sample.

The effect of addition of Ge and Sn to Ru on the rate of hydrogenation of cinnamaldehyde was similar to that observed for the hydrogenation of citral. The results obtained on some selected samples are reported in Table 3.

The effect of addition of promoters on the selectivity to unsaturated alcohols was also investigated. Selectivity to unsaturated alcohols were measured at 50% conversion. It should be however noted that the same results are found in a large range of conversion (20–80%). Selectivity to the saturated aldehyde was instead found to decrease with increasing the level of conversion with a corresponding increase in the selectivity to the saturated alcohols. Typical results on the effect of conversion on the product selectivity are reported in Fig. 5.

Among the elements investigated, Sn is the only one which changes drastically the product distribution. Upon the addition of Ge or Pb the selectivity to unsaturated alcohols remains constant, regardless of the Me/Ru ratio and preparation method.

Table 3
Catalytic activity, N_H , towards cinnamaldehyde hydrogenation over Ru–Me/ Al_2O_3 catalysts

Catalysts	Me/Ru	$N_H \times 10^3$
RuEC1	0	2.3
RuEC1/Ge1	0.21	5.8
RuEC1/Sn1	0.23	4.3
RuEC1/Sn2	0.47	8.8
RuNI1	0	3.4
RuNI1/Sn1	0.15	5.8
RuNI1/SnSO ₄	0.16	5.0

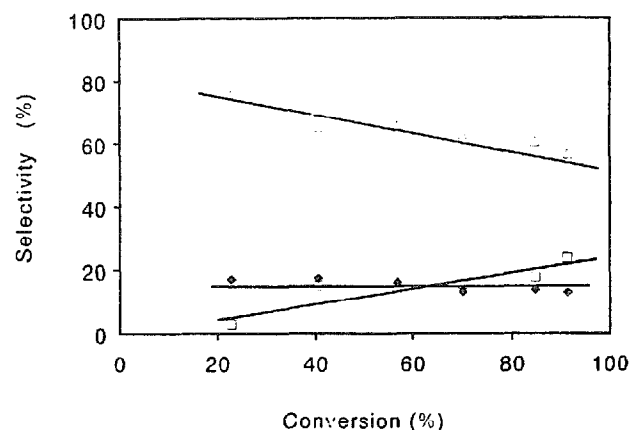


Fig. 5. Hydrogenation of citral: Selectivity to reaction products as a function of conversion. Catalyst: RuEC1/Ge1. (Δ), citronellal; (\diamond), geraniol + nerol; (\square) citronellol.

Fig. 6 shows the selectivity to cinnamyl alcohol, S_{COL} , and geraniol + nerol, S_{GN} , as a function of the Sn/Ru ratio for the catalysts of the series RuEC. Upon the addition of Sn, a large increase in both S_{COL} and S_{GN} is observed. The RuEC1Sn2 sample (Sn/Ru = 0.47) shows a value of S_{COL} of about 53% and a value of S_{GN} of about 75%. A similar increase in the selectivity to unsaturated alcohols was observed on the samples of the RuNI series.

Fig. 7 shows the selectivity to geraniol + nerol as a function of the Ge/Ru ratio, for both series of catalysts. Addition of Ge does not modify the product distribution. No change in the selectivity to cinnamyl alcohol was also

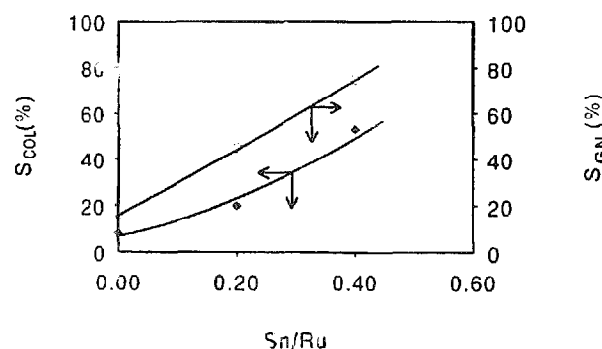


Fig. 6. Influence of the Sn/Ru ratio on the selectivity to unsaturated alcohols over Ru–Sn/ Al_2O_3 catalysts of the RuEC series. (\circ), selectivity to geraniol + nerol; (\diamond), selectivity to cinnamyl alcohol.

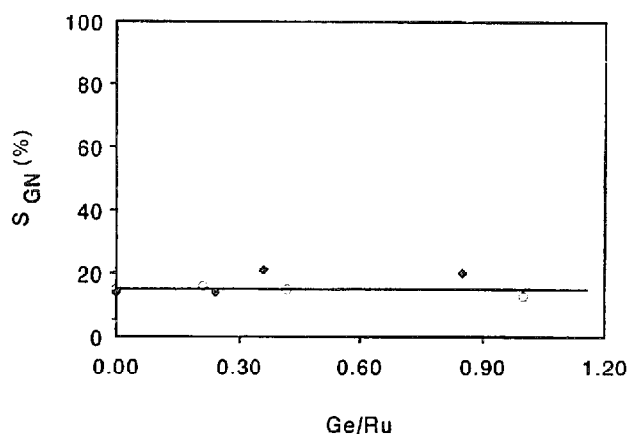


Fig. 7. Influence of the Ge/Ru ratio on the selectivity to geraniol + nerol. (○), RuEC series; (◆) RuNI series.

observed in the hydrogenation of cinnamaldehyde on the Ru–Ge samples.

4. Discussion

A comparison of the catalytic properties of the Ru–Me/Al₂O₃ samples used in the hydrogenation of citral and cinnamaldehyde shows that the effect of the promoter depends on the nature and on the amount of the element used. From the results reported in the previous section it can be observed that the addition of tin increases both the activity and the selectivity to unsaturated alcohols. The addition of germanium increases the catalytic activity on the samples prepared by the CSR method (series RuEC) whereas no modifications are found on the catalysts obtained by co-impregnation. On all Ru–Ge catalysts the selectivity to unsaturated alcohols is not influenced by the presence of Ge. The addition of lead does not modify the selectivity and a slight decrease in the catalytic activity is observed on the samples prepared by co-impregnation. The results summarized above apply to both the unsaturated aldehydes investigated.

The positive effect of the addition of tin on the selective hydrogenation of α,β -unsaturated aldehydes to unsaturated alcohols is well docu-

mented in the literature [2,4,6,18,19]. A much less number of investigations have been instead reported on the effect of Ge and Pb [3,4,7]. To explain the differences observed in the catalytic activity with addition of Ge on the two series of investigated samples (Fig. 4) let us first consider the characterization data available on the Ru–Ge samples. From the chemisorption results (Table 1) it can be concluded that on the samples of the RuEC series, Ru and Ge form mixed particles. In fact, H₂ chemisorption is found to decrease with the addition of Ge whereas the average metal particle size remains constant. The presence of an interaction between Ge and Ru was also confirmed by the EXAFS data [21,22]. Ge addition to the RuEC1 sample produces a decrease of the metallic Ru⁰–Ru⁰ coordination: the higher the Ge content the lower the coordination number. For the sample RuEC1Ge3, with the highest Ge concentration, the best fit of the EXAFS results indicates the presence of the second metal in the first coordination shell of Ru, meaning the incorporation of a certain amount of Ge in the Ru particles. The coordination number of the Ru–Ge bond is 1.8 whereas the bond distance 0.245 nm [22]. For the Ru–Ge samples of the RuNI series, the EXAFS results [22] only show changes of the average coordination number of Ru which is 9.18 on the monometallic RuNI1 sample, 6.10 on RuNI1Ge1, 6.40 on RuNI1Ge2 and 6.05 on RuNI1Ge3. No shape modification of the EXAFS peaks was observed on the RuNI series suggesting that no interaction occurs between Ge and Ru. The lower coordination numbers of Ru observed on addition of Ge on the samples prepared by co-impregnation has been related to the formation of smaller Ru crystallites. This suggests that the presence of Ge limits the growth of the Ru metal particles. The presence of smaller particles on the RuNI₁Ge samples was confirmed by TEM (Table 1).

On the basis of these results it can be suggested that the higher activity observed on the Ru–Ge samples of the RuEC series is related to the presence of an interaction between Ru and

Ge. An increase in the rate of hydrogenation of unsaturated aldehydes has been also reported on Pd–Ge and attributed to a decrease of the strong adsorption of one of the reaction components [7].

The results reported in Fig. 7 show that, regardless of the preparation method used the selectivity to unsaturated alcohols remains unchanged at all Ge/Ru ratios. The role of Ge as promoter for the selective reduction of the carbonyl group is still a matter of controversy. In the liquid phase hydrogenation of cinnamaldehyde Galvagno et al. [3] have reported a selectivity to cinnamyl alcohol over Pt–Ge supported on Nylon greater than 90%. On these catalysts an increase in the catalytic activity was also observed. In a study on the effect of promoters on the gas phase hydrogenation of acrolein over Pt/SiO₂, Marinelli et al. [4] have also reported an increase in the selectivity to allyl alcohol on addition of germanium. Unfortunately in the above mentioned studies no detailed characterization of the bimetallic samples used has been reported.

On Pd/C catalysts, instead, the addition of Ge has been reported [7] to increase the hydrogenation rate of the C=C double bonds conjugated with hydroxyl, carbonyl or phenyl groups. No promotion effect was observed in the reduction of substrates having a C=C double bond in conjugation with carboxyl, nitrile or ester functional group. In the hydrogenation of unsaturated aldehydes the rate of reduction of the carbonyl decreased compared to the rate of C=C double bond saturation.

Even though a definitive conclusion cannot be made it seems that the effect of Ge on the catalytic performance depends strongly on the nature of the active metal. A more detailed investigation is necessary to explain the different nature of interaction between Ge and the noble (Pt, Ru, Pd) metals.

The addition of tin to Ru/Al₂O₃ increases the catalytic activity and the selectivity to unsaturated alcohols for both series of catalysts investigated (Figs. 2, 3 and 6). Similar results are

obtained in the hydrogenation of citral and cinnamaldehyde.

It is interesting to note that the promoting effect of tin has been reported for several noble metals (Ru, Pt, Rh, etc.) and attributed to: (a) preferential occupancy by lower coordination tin sites which are thought to be responsible for C=C hydrogenation; (b) modification of the electronic properties of the noble metal by electron transfer from tin to the active sites which decreases the likelihood of C=C hydrogenation; (c) activation of the substrate by interaction with tin ions.

It has previously been suggested that using the CSR method for the preparation of bimetallic catalysts, the promoters tend to segregate differently on the surface of the noble metal [8,24,25]. In particular it has been concluded that Sn and Pb have a tendency to occupy preferentially the low coordination sites, whereas Ge appears to be randomly distributed at the surface.

These results have been recently confirmed by a kinetic investigation on the hydrogenolysis of 2,2,3,3-tetramethylbutane carried out over the Ru–Me/Al₂O₃ samples used in this paper. The addition of Sn or Pb onto the RuEC1 sample shows only a small effect on the reaction rate but shifts the selectivity pattern towards that of large Ru particles. The selectivity remains unchanged upon Ge addition [23].

A tentative explanation of the present results on the catalytic hydrogenation of unsaturated aldehydes over the Ru–Me/Al₂O₃ catalysts by a different site segregation of the added promoter has been unsuccessful. On the basis of this hypothesis in fact we would expect, as was observed in the hydrogenolysis of tetramethylbutane, that Ru–Sn and Ru–Pb should behave similarly. We have instead found that addition of Sn increases the catalytic activity and selectivity to unsaturated alcohols whereas no promoting effect was observed in the presence of Pb. It should be also noted that a preferential segregation of the promoter is expected mainly when the bimetallic catalysts are prepared by

the CSR method. Our Ru–Sn samples behave similarly regardless of the preparation method used.

The lack of any appreciable influence of a preferential site segregation on the catalytic hydrogenation of unsaturated aldehydes is in agreement with a recent study on the effect of the Ru particle size on the hydrogenation of citral and cinnamaldehyde carried out on monometallic Ru/Al₂O₃ samples prepared by the same procedure used in this work [26]. The latter investigation has shown that the turnover rate is not influenced by a change in the size of the metal particle and therefore by a change in the coordination number of the metal sites. Moreover the selectivity to geraniol (+nerol) was found to be constant in the whole range of dispersion investigated (0.05–0.9) whereas an increase in the selectivity to cinnamyl alcohol was observed only at Ru dispersions lower than 0.2. A higher selectivity to cinnamyl alcohol on the larger metal particles has been previously reported [5,6,27,28]. However, this effect cannot be attributed to a change in the coordination number of the active sites since it occurs in a range of particle sizes (> 10 nm) in which variations in the relative abundance of atoms in the corners, edges and planes are known to be negligible. It has been suggested that on the larger metal particles the aromatic ring of cinnamaldehyde which is not bonded to the surface lies at a distance exceeding 0.3 nm due to the presence of an energy barrier which prevents a closer approach [29,30]. Under these conditions the cinnamaldehyde molecule is tilted and the C=O extremity will be closer to the surface with respect to the C=C bond.

EXAFS experiments [22] carried out after in situ reduction of the examined samples have shown neither the formation of Ru–Sn bonds nor the presence of metallic tin. No appreciable variation in the local Ru local-order structure was observed in the RuECSn series. The best fit of the EXAFS results on the RuNISn series has shown, as on the RuNIGe samples, a decrease

of the Ru coordination number, pointing to an increasing dispersion.

On the basis of these results it seems likely that Sn is present on the investigated samples mainly as tin ions. This has been also confirmed by a preliminary Mössbauer study carried out after in situ reduction at 400°C which has shown the absence of metallic tin.

It can be therefore suggested, in agreement with previous investigations [2,18], that the positive effect of tin is mainly related to the formation of new sites associated with tin ions on which the unsaturated aldehydes are adsorbed through the C=O group. On these sites the carbonyl group is polarized, facilitating the hydrogen transfer from an adjacent Ru–H site.

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