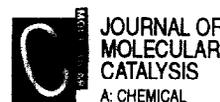




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Hydrogenation of carbon oxides by Ru/activated carbon catalysts obtained from $\text{Ru}_3(\text{CO})_{12}$: effect of pretreatment on their dispersion, composition and activity

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Abstract

Supported Ru catalysts on activated carbons were obtained from $\text{Ru}_3(\text{CO})_{12}$. Two activated carbons with different surface area and porosity obtained by carbonization and CO_2 activation of olive stones were used as catalyst supports. The supported catalysts, once prepared, were heat treated at 673 K for 12 h in a He or H_2 flow or under high vacuum, and subsequently characterized by H_2 and CO chemisorption, transmission electron microscopy and X-ray photoelectron spectroscopy. Results showed that the highest dispersion was obtained after He treatment and that Ru was present as ruthenium carbide, whereas after H_2 treatment metallic Ru was found with a lower dispersion. When the He treatment was carried out at 423 K instead of at 673 K, there was a large increase in both the total and irreversible H_2 uptake. The CO chemisorption stoichiometry was also affected by the atmosphere of the previous treatment. Thus, after He treatment CO was linearly chemisorbed, whereas after H_2 treatment multiple CO chemisorption predominated. Finally, the behaviour of the catalysts in the hydrogenation reactions of CO_2 and CO was also influenced by the treatment atmosphere. Thus, for the H_2/CO_2 reaction, the methane production rate, r_{CH_4} , decreased with reaction time after He treatment, whereas it remained constant after the H_2 treatment. However, in the case of the H_2/CO reaction, r_{CH_4} remained practically unchanged with reaction time after He treatment, whereas it underwent a large increase after the H_2 treatment.

Keywords: Activated carbon; Carbon oxides; Hydrogenation; Ruthenium; Supported catalysts

1. Introduction

Hydrogenation of CO and CO_2 to methane and higher molecular weight hydrocarbons is important in the purification of ammonia feed, methanation of coal-derived gases and Fischer–Tropsch synthesis. The reactions are also of interest in the production of process heat from recyclable waste streams containing dilute carbon oxides [1]. Supported Ru catalysts are some of the most active

catalysts for both CO and CO_2 hydrogenation [1–4]. Their catalysis is also affected by the dispersion of Ru as well as the nature of the supports and the promoters [5–10]. Nowadays, activated carbons are of great interest as supports for metal catalysts due to the fact that these materials can be prepared with a high surface area and a well developed porosity which permits them to stabilize small highly dispersed metal particles [11–30]. The properties and size of these supported metal particles depend on a series of factors, such as: the method of catalyst preparation, precursor

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salt used and the pre-treatment given to the supported catalysts to obtain the metal in its zero valent state.

In this work, supported Ru catalyst were prepared from $\text{Ru}_3(\text{CO})_{12}$. Metal carbonyl clusters provide a new class of supported metal catalysts with well defined structures and high metal dispersions as well as the fundamental aspect of catalysis. Most of the work published in the literature about supported Ru catalysts prepared from metal carbonyl clusters has been carried out using inorganic oxides as supports [31,32]. However, there are very few studies using carbon materials as supports. The main differences of these materials compared with the inorganic oxides is that the latter have a smaller surface area and porosity and a different surface chemical nature which can influence the metal. Thus, different Ru structures on inorganic oxides [32] have been found depending on their surface acidity and/or basicity, which affects the activity and selectivity of the supported catalysts.

On the other hand, it has been found [33] that in Ru/SiO₂ catalysts prepared from $\text{Ru}_3(\text{CO})_{12}$ the pretreatment atmosphere influence catalyst dispersion and activity. Also, with Ru/carbon catalysts prepared from the same precursor [11], the treatment atmosphere influences the decomposition pathway of the ruthenium carbonyl cluster. However, the authors did not report any difference either in catalyst dispersion or activity.

The objective of this work is therefore to study the influence of the pretreatment of Ru catalysts supported on activated carbons on their dispersion, chemical composition and activity in the hydrogenation of carbon oxides in order to determine whether there are differences or not with the behaviour of the previously reported Ru/SiO₂ catalysts.

2. Experimental

Two activated carbons were used in the present study as supports for Ru catalysts. Activated carbons were obtained in the laboratory from olive

Table 1
Characteristics of the supports

Support	%Ash	S_{N_2} (m ² /g)	S_{CO_2} (m ² /g)	V_1 (cm ³ /g)	V_2 (cm ³ /g)	V_3 (cm ³ /g)
H14	0.04	725	974	0.43	0.15	0.05
H35	0.10	1190	1220	0.56	0.25	0.07

V_1 $\varnothing < 3.6$ nm; V_2 $3.6 < \varnothing < 50$ nm; V_3 $\varnothing > 50$ nm.

stones. The procedure followed has been described in preceding papers [34,35]. The raw material was ground and sifted to a particle size between 1.4 and 2 mm, and was carbonized in a N₂ flow at 1273 K for 30 minutes and subsequently activated in CO₂ at 1263 K for two time periods. Samples obtained are referred to in the text as H14 and H35 (the figure denotes the percentage burn-off of the sample during activation).

Activated carbons were characterized by N₂ and CO₂ adsorption at 77 and 298 K, respectively. Surface areas were obtained from the BET equation applied to the N₂ adsorption data and from the Dubinin–Astakhov (DA) equation applied to the CO₂ adsorption data, following the method described elsewhere [34,36]. Cross sectional areas of N₂ and CO₂ molecules were taken as 0.162 nm² and 0.195 nm² respectively [37]. Pore size distribution was obtained by mercury porosimetry up to 4200 kg/cm², using a Quantachrome Autoscan 60 porosimeter. From these experiments, the volume of pores with a diameter smaller than 3.6 nm (V_1), between 3.6 and 50 nm (V_2) and with a diameter greater than 50 nm (V_3) were obtained. Ash content (%) of the activated carbons was obtained by burning a known quantity at 1073 K and weighing the residue. All these data are compiled in Table 1.

Supported Ru catalysts were prepared from $\text{Ru}_3(\text{CO})_{12}$ following a sublimation technique described elsewhere [38]. For this purpose, the powdered carbonyl was mixed with the appropriate amount of support (to yield about 2% metal loading) in a glass tubing which was sealed under vacuum (10^{-3} Torr). This closed reactor was mechanically rotated for about 4 hours at a temperature close to 343 K to encourage the carbonyl

to sublime evenly onto the support. After cooling to room temperature, the supported catalysts were sieved in order to remove the finest particles produced during the preparation procedure. All catalysts were kept in a desiccator with P_2O_5 until their use.

The metal content of the supported catalysts was determined by burning a known quantity of the sample at 973 K in a Mettler TA 3000 thermobalance. These experiments were repeated at least five times in order to obtain a mean value for the metal loading. The catalysts are referred to in the text with the name of the support followed by the percentage of Ru.

The supported catalysts were characterized by H_2 and CO chemisorption at 298 K and, in some cases, at higher temperatures. Prior to the chemisorption runs, catalysts were treated at 673 K with a heating rate of 2 K min^{-1} for 12 h in either He or H_2 flow or under high vacuum (around 10^{-6} Torr) in order to decompose the carbonyl cluster. After He or H_2 treatments, the catalysts were outgassed at high vacuum and at 50 K below the reduction temperature for 1 h and then cooled down to the chemisorption temperature.

Two H_2 chemisorption isotherms were obtained between 50 and 250 Torr [39]. After the first, the catalyst was outgassed (10^{-6} Torr) at the chemisorption temperature for 1 h (this time was arbitrarily chosen), and the second chemisorption isotherm was obtained in the same conditions as the first. The method proposed by Benson and Boudart [40] and Wilson and Hall [41] was followed to determine H_2 uptake. H_2 uptake obtained in the first isotherm, Q_T , gives the total amount of H_2 chemisorbed. It is assumed that the uptake obtained in the second isotherm represents the H_2 chemisorbed more weakly on the surface metal atoms. This quantity, Q_R , is referred to in the text as a percentage of the total H_2 uptake, Q_T . Blank H_2 chemisorption runs were carried out on the supports and they did not exhibit any H_2 uptake.

For the CO chemisorption, the dual technique of Yates and Sinfelt [42] was used. This consists of determining the CO isotherm in the 50–200 Torr range, evacuating for 15 min at the chemi-

sorption temperature and at high vacuum, and measuring a second isotherm. Subtraction of the two isotherms at 100 Torr gave the amount of CO chemisorbed on the metal.

Dispersion, D , and average particle size, \bar{d} , of the catalysts were obtained from the $H_2 Q_T$ value, assuming that one H atom is chemisorbed by one surface Ru atom and that \bar{d} (nm) = $0.91/D$ (20).

After the chemisorption runs, some selected samples were further characterized by transmission electron microscopy (TEM), using a Zeiss EM10C microscope at a magnification of $125,000\times$. Samples were ground and ultrasonically dispersed in toluene. Micrographs were analyzed by a SUN IPC image processor station using Visilog software, the number of particles counted being not less than 3,000. By this procedure, the equivalent circle diameter of the Ru particles was obtained as a length number or arithmetic mean.

X-ray photoelectron spectroscopy (XPS), was carried out in Escalab 200R equipment, that used $MgK\alpha$ ($h\nu = 1253.6\text{ eV}$) as a radiation source, working at 12 kV and 10 mA. Samples were pretreated in He or H_2 at 673 K, and subsequently evacuated at 10^{-5} Torr and transferred to the analysis chamber without exposure to air. The internal standard peak taken to determine the binding energies was that of the carbon C1s (284.9 eV). The precision of the binding energy values was around 0.2 eV.

The H_2/CO_2 and H_2/CO reactions were studied in a plug-flow microreactor. About 0.5 g of catalyst was introduced into the reactor and the reactant gases flowed upwards through it. Catalysts were pretreated in either He or H_2 flow as in the chemisorption runs. Carbon dioxide hydrogenation was studied between 478 and 573 K with a H_2/CO_2 ratio of 4/1 and carbon monoxide hydrogenation between 508 and 583 K with a H_2/CO ratio of 3/1 or 2/1. In all cases the conversions were kept low in order to work under differential conditions. Gases were analyzed by gas chromatography using a HWD following the method described elsewhere [43,44]. All gases used in this work were of high purity and were further

purified with a Deoxo unit and a 5 Å molecular sieve trap.

3. Results and discussion

3.1. Characteristics of the catalysts

The total, Q_T , and the percentage of reversible, Q_R , H_2 uptake at 298 and 373 K (on selected catalysts), obtained after treating the catalysts in different atmospheres at 673 K are listed in Table 2. The uptakes are mean values (up to 3 trials using different samples of the same catalyst) with a precision of better than 10%.

At first, it should be pointed out that although all catalysts were prepared in such a manner to yield a 2% metal loading, the final amount of Ru deposited on the supports following the method described before, was not equal in all cases and depended on the porosity of the support. Thus, support H35 with a higher surface area and a more developed meso- and macroporous network than support H14 was capable of admitting a greater amount of Ru, closer to the initial 2%.

Several trends are evident from Table 2: (i) Q_T values depend on the treatment atmosphere, thus the highest value was obtained after He treatment and the lowest after the H_2 treatment; the high-vacuum treatment (HV) gives a Q_T value closer to that obtained after the He treatment. (ii) H_2 uptake at 373 K is quite similar to that obtained at 298 K, which means that the H_2 chemisorption on these catalysts is a non-activated process. This is

Table 2
 H_2 uptake at 298 K on the catalysts heat treated at 673 K for 12 h

Catalyst	Treatment	Q_T ($\mu\text{mol/g cat}$)	Q_R (%)
H14–0.84%Ru	He	25.2 (21.3) ^b	42.0 (49.7)
	H_2	18.9	38.9
H35–1.47%Ru	He	69.8 (62.3)	43.5 (55.2)
	H_2	39.6	33.2
	HV ^a	57.7 (60.6)	33.7 (44.7)

^a High vacuum.

^b Values in parentheses were obtained at 373 K.

Table 3
 H_2 uptake at 298 K on catalysts heat treated at 673 K for 12 h

Catalyst	Treatment	$Q_T \times 10^{-2}$ ($\mu\text{mol/g Ru}$)	Q_R (%)
H35–1.47%Ru	673 K-He	47.5	43.5
	673 K- H_2	26.9	33.2
	673 K-He- H_2 ^a	30.2	35.1
H35–4.30%Ru	673 K-He	32.1	36.1
	673 K- H_2	16.9	30.6
	673 K-He- H_2 ^a	17.1	29.6
H35–5.66%Ru	673 K-He	32.3	34.3
	673 K- H_2	18.7	29.2
	673 K-He- H_2 ^a	20.5	28.5

^a 1 h in He and 11 h in H_2 .

in agreement with the results reported by Tatarchuk et al [45,46] with Ru/ Al_2O_3 catalysts prepared from $Ru_3(CO)_{12}$. (iii) Q_R values at 298 K are quite similar, ranging between 30 and 40% of Q_R , and are independent of the reduction treatment. As expected, Q_R values obtained at 373 K are higher than those at 298 K.

In order to know the effect of the metal content on the dispersion, two more catalysts were prepared with the support H35. The results of H_2 chemisorption are compiled in Table 3, and indicate that there is a decrease in Q_T when the metal content increases up to 4.30%. A later increase up to 5.66% does not affect the Q_T value. The He treatment again yields catalysts with the greatest capacity to chemisorb H_2 . It is noteworthy that the He- H_2 treatment (the catalysts were treated for 1 h at 673 K in He and subsequently for 11 h in H_2) gives similar results than the H_2 treatment. These results, together with those of Table 2, clearly show that the presence of H_2 during the catalyst treatment at 673 K decreases their H_2 chemisorption capacity either at 298 or 373 K. This could be due to the fact that both treatments produce catalysts with different particle size and/or with a different chemical composition.

Guczi et al [33] also found that decomposition in a He atmosphere of $Ru_3(CO)_{12}$ supported on silica, gives a catalyst with a higher dispersion (measured from CO adsorption) and higher catalytic activity for CO/ H_2 and C_4H_{10}/H_2 reactions

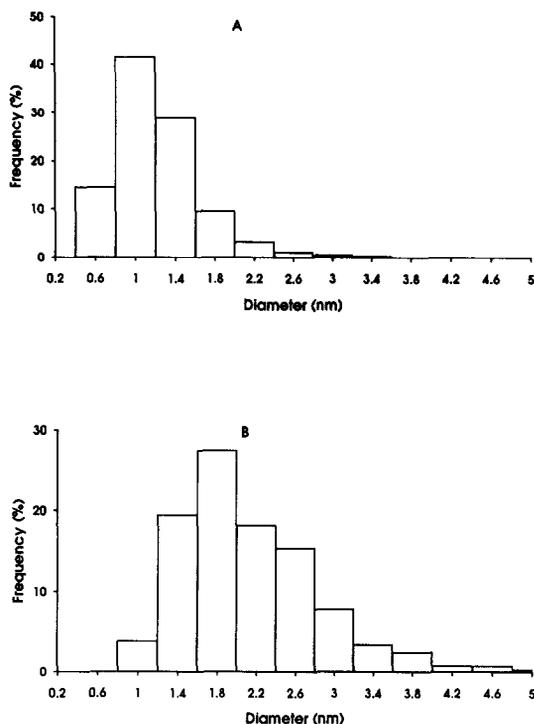


Fig. 1. Particle size distribution obtained from TEM micrographs. H35–1.47%Ru treated at 673 K for 12 h. (A) He flow and (B) H₂ flow.

than catalysts obtained by decomposition in H₂. They suggested that during He treatment, disproportionation of CO occurs producing very highly dispersed carbon which can either prevent the agglomeration of the individual metallic particles or even form to some extent metal carbides more

Table 4

Dispersion and mean particle size obtained from chemisorption of H₂ at 298 K and TEM

Catalyst	Treatment	<i>D</i> (%)	\bar{d} (nm)
H14–0.84%Ru	673 K-He	60.5	1.5
	673 K-H ₂	45.5	2.0
H35–1.47%Ru	673 K-He	96.0	0.9
	673 K-H ₂	54.4	1.7
H35–4.30%Ru	673 K-He	64.9	1.4
	673 K-H ₂	34.2	2.7
H35–5.66%Ru	673 K-He	65.4	1.4 (1.2) ^a
	673 K-H ₂	37.8	2.4 (2.1)

^a Values in parentheses were obtained by TEM.

active than the metallic species. The latter explanation being consistent with several of Fischer–Tropsch synthesis studies [47–50].

On the other hand, Vannice et al [11] studied by DRIFTS the thermal decomposition of Ru₃(CO)₁₂ supported on an amorphous carbon black and they found that the decomposition pathway of the carbonyl cluster depends on the treatment atmosphere. Thus, the decomposition in He appeared to proceed via decarbonylation of Ru₃(CO)₁₂ followed by fragmentation of the metallic cluster, whereas the rapid formation of H₄Ru₄(CO)₁₂ and its subsequent decomposition was observed under H₂. Complete decarbonylation in either gas produced zerovalent Ru with a high dispersion, but not as high as that reported in this study, probably because they used catalysts with a higher metal loading (8.3%). The increase in nuclearity of the original Ru cluster during the initial stages of H₂ treatment could lead to a greater Ru particle size. However, these authors do not report any difference in the CO chemisorption at 673 K under either He or H₂ as reported by Guzzi et al [33].

In order to know whether both treatments produce Ru catalysts of different particle size, the sample H35–5.66%Ru was studied by TEM after treating it in He or H₂ at 673 K for 12 h. Particle size distributions (PSD) obtained are given in Fig. 1 and average particle sizes, \bar{d} , are compiled in Table 4. From Fig. 1, the H₂ treatment gives a wider PSD than the He treatment together with a shift of the maximum to a greater size. Thus, the \bar{d} value found for the H₂ treatment was 2.1 nm, whereas for the He treatment it was 1.2 nm. These results therefore indicate that the H₂ treatment produces a catalyst with a greater average particle size.

It is well known [51,52] that the \bar{d} value, as well as the dispersion (*D*), can be obtained from H₂ chemisorption measurements taking a chemisorption stoichiometry of H/Ru_s = 1/1. In this study, the total amount of H₂ chemisorbed, *Q_T*, was used to obtain both *D* and \bar{d} values. The results are given in Table 4 and they show that \bar{d} values obtained by either H₂ chemisorption or TEM are

Table 5
Binding energies (eV) for catalyst H35–1.47%Ru measured by XPS

Treatment	C1s	Ru 3p _{3/2}	$I_{\text{Ru}}/I_{\text{C}}$
None	284.9	464.2	$9.2 \cdot 10^{-4}$
	286.5		
	290.0		
673 K-He	284.9	464.1	$7.8 \cdot 10^{-4}$
	286.5		
	289.8		
673 K-H ₂	284.9	460.9	$5.7 \cdot 10^{-4}$
	286.5		
	289.8		
Ru ₃ (CO) ₁₂	284.9		
commercial	286.6	460.7	–

in good agreement indicating that the stoichiometry of one H atom per surface Ru atom is a good assumption in this case, as is the calculation of \bar{d} from the total amount, Q_{T} , of H₂ chemisorbed. On the other hand, it is worth noting the high dispersion of all catalysts after He treatment, especially that of H35–1.47%Ru that can be considered as atomic dispersion. Results clearly indicate that He treatment gives a catalyst with a lower metallic particle size than H₂ treatment; but both treatments could produce catalysts with different chemical compositions. For this reason, XPS was applied to the catalyst H35–1.47%Ru after treating it (in situ) in both He or H₂ atmospheres at 673 K for 2 h. After deconvolution of the C1s and Ru3p_{3/2} curves, the corresponding binding energies (eV) were obtained. These values are compiled in Table 5 and they indicate that: (i) both in the fresh catalyst and in that heat treated in He, there is a peak at 464.1 eV which corresponds to Ru(IV); (ii) the catalyst heat treated in H₂ presents a peak at 460.9 eV equal to that for Ru₃(CO)₁₂, which corresponds to metallic ruthenium, and (iii) from $I_{\text{Ru}}/I_{\text{C}}$ values it is shown qualitatively, because Ru is supported on a highly porous solid, that the He treatment produces a slight sintering with regard to the fresh catalyst, that is higher after H₂ treatment.

Therefore, from the H₂ chemisorption, TEM and XPS measurements it can be deduced that the

He treatment at 673 K gives a ruthenium catalyst with a higher dispersion and with a different chemical composition than the same treatment in H₂.

Because Ru(IV) was found in both the fresh catalyst and the one heat treated in He at 673 K, it is reasonable to expect that He treatment at a lower temperature would also yield a catalyst with an active phase capable of chemisorbing H₂. Thus, the catalysts were heat treated in He at 423 K for 12 h and after that the H₂ chemisorption isotherms at 298 K were measured. The Q_{T} and Q_{R} values obtained are shown in Table 6. These results are quite surprising because a treatment as mild as He at 423 K yielded a catalyst with a very large H₂ chemisorption capacity which can be seen more directly from the $Q_{\text{T}}(423 \text{ K})/Q_{\text{T}}(673 \text{ K})$ ratio. To our knowledge, a Ru catalyst has not yet been described with these characteristics. The high H₂ chemisorption capacity of these catalysts could be due to one or more of the following points: (i) a chemisorption stoichiometry, H/Ru_s, higher than unity; (ii) spillover of H₂ from the Ru particles to the support, and (iii) occlusion of H₂ into the metallic network of the active phase. However, point ii probably does not occur because these catalysts usually have quite a low Q_{R} (lower than the same catalysts treated at 673 K); and, point iii is also improbable because the same catalyst treated in He at 673 K has already atomic dispersion (see Table 4), therefore when it is treated at lower temperature (423 K) it would not have the three-dimensional network necessary to occlude H₂. All these considerations lead us to believe that the H₂ chemisorption stoichiometry in these catalysts should be higher than unity, which would be supported by the low electron density of

Table 6
H₂ uptake at 298 K on the catalysts heat treated in He at 423 K for 12 h

Catalyst	Q_{T} ($\mu\text{mol/g cat}$)	Q_{R} (%)	$Q_{\text{T}}(423 \text{ K})/$ $Q_{\text{T}}(673 \text{ K})$
H14–0.84%Ru	141.0	19.8	5.6
H35–1.47%Ru	207.0	20.0	3.0
HW44–1.62%Ru	273.7	18.8	4.3

Table 7
CO uptake on the catalysts heat treated at 673 K for 12 h

Catalyst	Treatment	Chemisorption T (K)	CO uptake ($\mu\text{mol/g cat}$)	CO/H	\bar{d} H ₂ (nm)
H35–1.47%Ru	He	298	146.0	1.04	0.9
	H ₂	298	140.5	1.77	1.7
H35–4.30%Ru	He	298	263.4	0.95	1.4
	H ₂	298	262.1	1.81	2.7
	He	373	258.6	–	–
	H ₂	373	236.7	–	–
	He	448	164.5	–	–
	H ₂	448	180.0	–	–
H35–5.66%Ru	He	298	330.7	0.90	1.2
	H ₂	298	353.2	1.67	2.4

Ru(IV), since it has been shown [53,54] that a lowering of the electron density of the ruthenium particles makes the CO chemisorption weaker and increases the amount of hydride species adsorbed in the hydrogenation of carbon monoxide.

On the other hand, the Q_R value of these catalysts (Table 6) is smaller than that obtained when the catalysts were previously treated in He at 673 K (Table 2). Sayari et al [55] studied the weak H₂ chemisorption on several supported Ru catalysts with a particle size between 0.9 and 12.4 nm and found that Q_R was around 10% for a particle size of 0.9 nm, reached a maximum of 32% for a particle size of 1.5 nm and took a value of zero for a particle size higher than 2.5 nm. The authors related the weak adsorption with special sites, invoking in particular the B₅ sites. It is well known [52,56] that the concentration of these sites on the crystallites is highly dependent on their shape. Therefore, the variation in Q_R with the heat treatment temperature could be due to a change in the shape of the crystallites of the active phase. This change also leads to some degree of sintering of the active phase particles (deduced from XPS measurements) which, brings about a decrease in H₂ chemisorption stoichiometry.

All these results, together with the fact that after He treatment the active phase is as Ru(IV), suggest that this should be a ruthenium carbide (RuC), because, as experimentally tested, RuO₂ has no capacity to chemisorb H₂. This RuC would be formed during the preparation of the catalysts by decarbonylation of the Ru₃(CO)₁₂ and CO dis-

proportionation, since by XPS both the fresh catalyst and the one heat treated in He contained Ru(IV). The H₂ treatment of the catalysts would therefore gasify the carbon atoms of the RuC yielding methane and cause the Ru particles to sinter.

Some of the above catalysts were characterized by CO chemisorption at different temperatures. The results obtained are compiled in Table 7 and show that CO uptake is independent of the treatment atmosphere (He or H₂) and that it decreases when the temperature increases, from 373 to 458 K, indicating that it is not an activated process. These results are different to those previously found [30] with Ru catalysts supported on Saran carbons that reported an increase in CO uptake with temperature. This behaviour was due to the fact that these catalysts were prepared from RuCl₃ · H₂O and it is known [45,46] that after H₂ treatment at 673 K, small amounts of chlorine can remain on the catalysts which deactivates the metal particles, making the CO chemisorption an activated process.

On the other hand, the results in Table 7 indicate that after He treatment the CO/H ratio is close to 1, whereas this ratio is between 1.5 and 2 after the H₂ treatment. It is well known [57–59] that in Ru catalysts the CO/H and therefore the CO/Ru_s ratio depends on the nature of the support and the Ru crystallite size. Thus, the CO/H ratio is lower than unity for large crystallites of Ru revealing that CO is mainly chemisorbed in the bridge form, whereas at a smaller Ru crystallites size the CO/

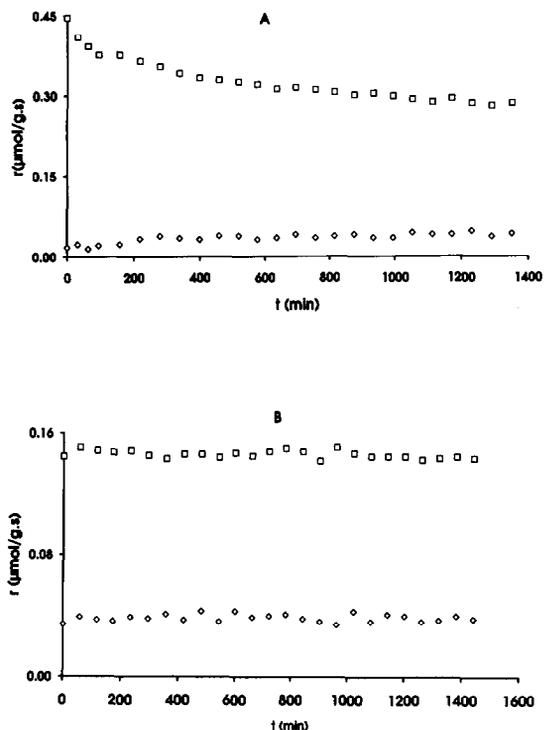


Fig. 2. Variation in activity of catalyst H14–0.84%Ru in the H_2/CO_2 reaction at 493 K against time. (A) Pretreated in He flow at 673 K. (B) Pretreated in H_2 flow at 673 K. (\square) r_{CH_4} , (\diamond) r_{CO} .

H ratio is greater than unity, indicating the formation of surface carbonyl species such as $\text{Ru}(\text{CO})_2$, $\text{Ru}(\text{CO})_3$, $\text{Ru}(\text{CO})_5$ and $\text{Ru}_3(\text{CO})_{12}$. Results from this study (Table 7), show that after heat treatment in He the CO is essentially chemisorbed in a linear form. However, when the samples were treated in H_2 there was multiple CO

chemisorption due to the CO/H ratio being greater than the unity. This is due, in the first case (He treatment), to the fact that the active phase is composed of Ru(IV) which does not have an electronic density high enough to give back-donation bonds with more than one CO molecule per Ru surface atom. However, after H_2 treatment the active phase is metallic Ru, with a higher electronic density and therefore, a higher capacity to give back-donation bonds, with more than one CO molecule per surface Ru atom if the crystallite sizes are small enough.

On the other hand, if heat treatment in He for 12 h is carried out at 423 K instead of at 673 K, there is also an increase in CO uptake. Thus, for catalyst H35–1.47%Ru this is 243.1 $\mu\text{mol/g}$ cat (treatment at 423 K) and 146.0 $\mu\text{mol/g}$ cat (treatment at 673 K). However, the CO/H ratio is now equal to 0.59 and not close to the unity which, as mentioned previously, is due to the multiple H chemisorption after the treatment at 423 K.

3.2. Activity and selectivity of the catalysts in the hydrogenation of carbon oxides

In the case of the H_2/CO_2 reaction, CH_4 and CO were the only products detected. Fig. 2 shows, as an example, the variation in catalyst activity after its treatment either in He or H_2 and in Table 8 the results obtained for all catalysts at 523 K, are compared. From Fig. 2, after He treatment the

Table 8
Activity and selectivity of the catalysts in the H_2/CO_2 reaction at 523 K

Catalyst	Treatment	r_{CH_4} $\mu\text{mol/g cat}\cdot\text{s}$	r_{CO}	$\frac{r_{\text{CH}_4}}{r_{\text{CO}}}$	E_{CH_4} kJ/mol	$\ln A_{\text{CH}_4}$	E_{CO} kJ/mol	$\ln A_{\text{CO}}$
Temperature range = 478–573 K								
H14–0.84%Ru	673 K-He	1.24	0.14	8.9	94.9 ± 2.9	22.6 ± 0.1	95.4 ± 3.6	20.9 ± 0.1
	673 K- H_2	0.84	0.19	4.4	89.8 ± 1.3	20.5 ± 0.1	94.8 ± 3.2	20.1 ± 0.1
H35–1.47%Ru	673 K-He	0.52	0.39	1.3	87.2 ± 2.8	19.3 ± 0.1	82.9 ± 0.1	18.2 ± 0.1
	673 K- H_2	0.40	0.46	0.9	92.3 ± 1.4	20.3 ± 0.1	85.4 ± 1.8	18.8 ± 0.1
H35–4.30%Ru	673 K-He	1.94	0.34	5.7	82.4 ± 2.5	19.6 ± 0.1	92.8 ± 3.9	22.3 ± 0.1
	673 K- H_2	1.11	0.31	3.6	93.4 ± 1.3	21.6 ± 0.1	89.7 ± 1.2	19.5 ± 0.1
H35–5.66%Ru	673 K-He	4.47	0.25	17.9	92.3 ± 2.7	22.7 ± 0.1	97.2 ± 0.9	21.8 ± 0.1
	673 K- H_2	4.30	0.29	14.8	97.8 ± 2.3	24.0 ± 0.1	98.1 ± 4.2	21.1 ± 0.1

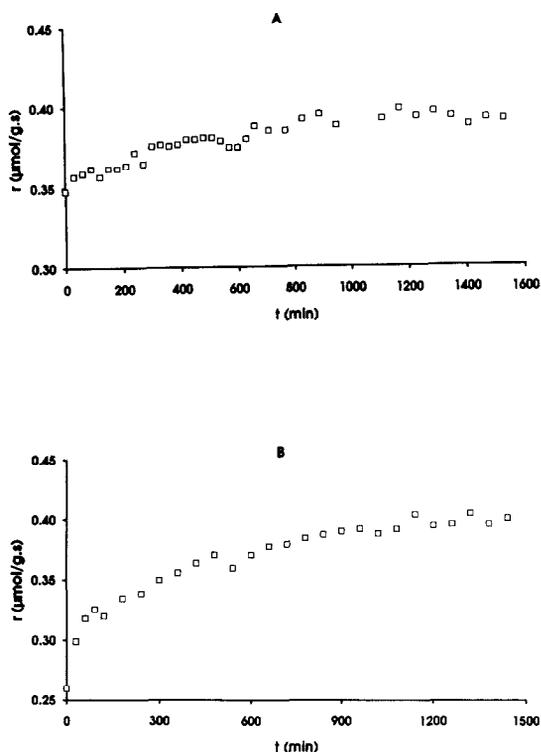


Fig. 3. Variation in activity, r_{CH_4} , of catalyst H35-1.47%Ru in the H_2/CO reaction at 538 K against time. H_2/CO flow ratio 3/1. (A) Pretreated in He flow at 673 K. (B) Pretreated in H_2 flow at 673 K.

activity for the CH_4 formation, r_{CH_4} , decreases with reaction time, and the activity for CO formation, r_{CO} , remains almost constant with time. However, neither r_{CH_4} nor r_{CO} change with time if the catalysts are previously treated in H_2 . The variation of r_{CH_4} with time after He treatment is due to the hydrogenation of the carbon contained in the ruthenium carbide (active phase after the He treatment) under the reaction conditions, which affects the initial catalyst composition and dispersion.

Several trends are deduced from the data in Table 8. All data referring to catalysts heat treated in He were taken after six hours reaction. Firstly, the r_{CH_4} value for a given catalyst is higher after the He treatment than after the H_2 one. However, r_{CO} is practically independent of treatment atmosphere. Secondly, after both treatments, He or H_2 , r_{CH_4} increases and r_{CO} decreases when the average particle size of the catalyst increases. The same

behaviour is observed when the metal loading of the catalyst increases because this increases the average particle size of the metal catalyst. This behaviour is in agreement with that previously observed [6,7,10,32,60]. Finally, apparent activation energy values for CH_4 and CO formation, E_{CH_4} and E_{CO} , respectively, are quite similar and independent of the previous treatment and catalyst. The value is around 90 kJ/mol, which is higher than that reported for Ru/ Al_2O_3 catalysts [61], 70.3 kJ/mol, and Ru/ SiO_2 catalysts, 72 kJ/mol [1] and 67 kJ/mol [3].

It is known [3], that the H_2/CO_2 reaction mechanism on Ru catalysts involves, firstly, the CO_2 dissociation to CO and subsequently, this reaction would proceed with the H_2/CO mechanism. Thus, the CO formed would be dissociated giving a highly active surface species, C_s , which would be rapidly hydrogenated to methane. It has been shown [3] that the concentration of surface species (CO)_s and C_s on the Ru particles is much lower during the H_2/CO_2 reaction than during the H_2/CO one. Therefore, the surface species C_s formed in the first reaction would be rapidly hydrogenated in an excess of H_2 , and as a result of the very low concentration of C_s species, the carbon atoms contained in the ruthenium carbide (active phase after the He treatment) would be gasified which would bring about a decrease in r_{CH_4} during reaction conditions.

When the catalyst H35-1.47%Ru was heat treated in He at 423 K instead of at 673 K, the r_{CH_4} and r_{CO} values, 0.45 and 0.24 $\mu\text{mol/g}\cdot\text{cat}\cdot\text{s}$, respectively, were lower than in the last treatment (see Table 8); and r_{CH_4} also decreased with the reaction time.

The H_2/CO reaction was studied with the catalyst H35-1.47%Ru after its treatment at 673 K for 12 h either in He or H_2 and with a H_2/CO flow ratio of 3/1 and 2/1. The only products detected in this reaction were methane and carbon dioxide which is in agreement with results found previously [30,62]. The presence of CO_2 can be due to both CO disproportionation and the water-gas shift reactions.

Table 9

Activity and selectivity of the catalyst H35–1.47%Ru in the H₂/CO reaction at 523 K

Treatment	H ₂ /CO ratio	%S μmol/g cat s	r _{CH₄} kJ/mol	E _{CH₄}	ln A _{CH₄}
673 K-He	3/1	85	0.17	109.5 ± 5.5	23.4 ± 1.2
	2/1	65	0.14	115.5 ± 1.2	24.6 ± 0.1
673 K-H ₂	3/1	78	0.17	115.6 ± 4.3	24.8 ± 0.9
	2/1	57	0.14	111.9 ± 1.0	23.9 ± 0.1

Variation of r_{CH_4} and r_{CO} with reaction time is given in Fig. 3, as an example, and results obtained at 523 K are compiled in Table 9. From Fig. 3, the behaviour of these catalysts depends on the treatment atmosphere. Thus, after He treatment there is a very slight increase in r_{CH_4} with time, whereas after H₂ treatment r_{CH_4} markedly increases during the first few hours. The behaviour is different to that observed previously with Ru catalysts supported on V3G or Saran carbon [30,62] prepared from RuCl₃ · H₂O and heat treated in H₂, in which r_{CH_4} decreased or remained constant with time. This could possibly be due to the different precursor used in this latter study. Moreover, this behaviour is also different to that found in the H₂/CO₂ reaction, and a possible explanation might be as follows: after He treatment the active phase of the catalysts is RuC that would not be gasified under the reaction conditions because in the H₂/CO reaction the surface concentration of C_s species is much higher than in the H₂/CO₂ reaction. Therefore, all of these surface species are not hydrogenated at the same time and are transformed by aging to another surface species C_s' less reactive. The presence of a higher concentration of C_s would thus prevent gasification of the ruthenium carbide, or if it is partially gasified it would be regenerated again by the C_s species that are not hydrogenated. This argument explains the fact that after the He treatment, r_{CH_4} changes very little with time, and also its large increase during the first hours of the reaction after the H₂ treatment, since now Ru is the active phase and it would be transformed to ruthenium carbide by the excess of C_s species not hydrogenated during the

reaction. Therefore after several hours in the reaction the value of r_{CH_4} is the same (see Table 9) regardless of the previous treatment, with He or H₂.

On the other hand, r_{CH_4} for the H₂/CO₂ reaction is around three times higher than r_{CH_4} for the H/CO reaction, which is also explained by the different surface concentration in (CO)_s and C_s species of both reactions. Thus, the much lower surface concentration of these species in the H₂/CO₂ reaction makes them more easily hydrogenable per unit of time in a richer H₂ atmosphere. The selectivity to produce methane, S, is higher for catalysts previously heat treated in He and for a H₂/CO flow ratio of 3/1.

Finally, the values of E_{CH_4} and ln A_{CH₄} are independent of the previous treatment, and of the H₂/CO flow ratio. The E_{CH_4} value was around 110 kJ/mol, close to the value of 101 kJ/mol [3] for Ru/Al₂O₃ and Ru/SiO₂ catalysts. However, this value is higher than that of the H₂/CO₂ reaction (90 kJ/mol); this behaviour has been observed previously [3] and attributed to the different surface concentration of the C_s species. Thus, as previously suggested, the higher C_s concentration in the H₂/CO reaction prevents all these species from being hydrogenated and they are transformed by aging to another surface species, C_s', less reactive with a slower hydrogenation and a higher activation energy.

In conclusion, this work clearly shows that in the case of Ru/activated carbon catalysts prepared from Ru₃(CO)₁₂, the atmosphere of the previous heat treatment influences both catalyst dispersion and the chemical nature of the active phase. Thus, by heat treating in He at 673 K, the highest dispersion is obtained and Ru is in oxidation state (IV), suggesting that it is present as ruthenium carbide. Treatment in He at 423 K causes an increase in both total and irreversible H₂ uptake, due to multiple H₂ chemisorption. When the catalysts were heat treated in H₂ at 673 K the lowest dispersion was obtained and the catalysts were composed of metallic Ru. The nature of the treatment atmosphere also influences the CO chemi-

sorption stoichiometry as well as catalyst behaviour in H₂/CO₂ and H/CO reactions.

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