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Study of CO chemisorption on graphite-supported Ru–Cu and Ni–Cu bimetallic catalysts

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Abstract

The adsorption of CO on graphite-supported monometallic catalysts (Ni and Ru) and bimetallic catalysts (Ru–Cu and Ni–Cu) reduced at different temperatures was studied by microcalorimetry. The calorimetric profiles obtained over these two bimetallic systems provides information about the different types of interaction (bridged, linear or subcarbonyl species) that could exist in the bimetallic system when Cu was introduced in the Ru and Ni monometallic catalysts.

Keywords: Graphite-supported catalysts; Bimetallic catalysts; CO adsorption; Microcalorimetry; Surface alloys

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1. Introduction

Supported bimetallic catalysts have received much attention from both industrial and academic sectors because often these systems exhibit higher activity, selectivity and/or stability making them superior to the monometallic catalysts for a given reaction [1,2]. This type of catalysts is largely employed in processes as different as in the petroleum industry (hydrodesulfurization, hydrocarbon reforming, etc.), fine chemical synthesis (hydrogenation and isomerization reactions), partial oxidations or automobile emission control catalysts.

Bimetallic catalysts are generally defined as a mixture of two metals with alloy formation or with the two metals segregated within a single particle, irrespective of their intimacy of mixing. The surface properties and then the catalytic actions of bimetallic catalysts have been be interpreted in terms of a variation of the electronic density at the surfaces and/or by a change of the surface ensemble structures, with the subsequent modification of the bond order of chemisorbed species [1,2].

On the other hand, the formation and composition of bimetallic clusters are affected by the metal loading and by the nature of the support as the interaction of this latter with the metal precursors apparently determines the mobility of the surface species. The latter fact can be overcome using model (non-oxidic) materials, such as high surface area graphite, where the metal–metal interaction may be favored [1,3]. Metallic dispersion is another important parameter in determining the formation of bimetallic clusters. When the two metals are completely miscible, e.g. Ni and Cu, there is no question that there may be bimetallic particles [1,4]. But, with partially or practically non-miscible metals, e.g. Ru and Cu, a decrease in particle size tends to decrease the miscibility gap allowing bimetallic clusters formation [1,5].

Microcalorimetry of chemisorbed probe molecules is a very suited method to detect and analyze surface states on multicomponent metallic particles. For this, it is necessary to use a molecule whose binding mechanism in chemisorption is sensitive enough to the electronic structure of the adsorbing atoms and to the surface topology, for example,

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carbon monoxide [6]. Such an approach was earlier used by Prinsloo and Gravelle [7] to detect ensemble effects on Ni–Cu/SiO_2 samples. In the same line a lot of work has been performed using O_2 as a probe molecule to study bimetallic systems such as Fe–Rh [8,9] and Fe–Pd [10]. From these studies very valuable information concerning the type of interaction between the two components of the bimetallic catalysts as well as over the support effects were achieved. Also Narayan and King [11] studying hydrogen chemisorption on Ru–Cu/SiO_2 catalysts concluded that electronic effects are not operable in these bimetallic systems. For the same system Ru–Cu Smale and King [12] report that the ethane hydrogenolysis is sensitive to the crystallite surface structure. Moreover, Dumesic and coworkers [13] based on microcalorimetric and infrared measurements of CO adsorption on Ru/Cu/SiO_2 suggest that the addition of Cu to Ru leads to the decoration of the Ru surface by Cu. Our aim in this contribution is to comparatively analyze the microcalorimetry of CO adsorption on Ru–Cu and Ni–Cu samples with different compositions and deposited on an “inert” graphite support.

2. Experimental

2.1. Catalyst preparation

Two bimetallic systems were prepared, Ni–Cu and Ru–Cu system. All catalysts were supported in high surface area graphite (H, $S_{BET} = 195\,m^2/g$, Lonza Ltd.), previously treated under helium at 1173 K in order to fully eliminate the oxygen surface groups. Catalysts were prepared by excess-solution impregnation method, using ethanol as solvent, and as precursors Ru acetyl-acetonate and Cu acetate (Ru–Cu system) and Ni nitrate and Cu nitrate (in the case of Ni–Cu). After impregnation catalysts were dried over night at 383 K.

The composition of bimetallic catalysts was determined by ICP-EAS in a Perkin Elmer 3300 PV after dissolution of the catalysts. Metal loading of monometallic catalysts was estimated by burning away the carbon in air at 1073 K and weighing the residue (thermogravimetric analysis). The prepared catalysts and the chemical compositions are listed in Table 1.

2.2. Microcalorimetry measurements

CO chemisorption heats were measured in a differential heat-flow calorimeter [14], of Tian-Calvet type (Setaram C80 II), operated isothermally at 330 K and connected to a glass vacuum adsorption apparatus. Pulses of approximately 2×10^{17} molecules of the probe were introduced into the system to titrate the surface of metal catalysts. Both the calorimetric and volumetric data were stored and analyzed by microcomputer processing. For experiments, the catalysts were first in situ reduced under hydrogen flow at a given temperature for 2 h, outgassed overnight at the same temperature, and cooled to 330 K. For the Ni–Cu system all catalysts were reduced at 623 K and one of these bimetallic catalysts (4Ni2Cu) was also reduced at 773 K so as to compare results obtained when varying the reduction temperature. In the case of the Ru–Cu system, catalysts were reduced at 673 K and one bimetallic was reduced at 773 K as well.

The metal dispersion was obtained from the total amount of CO uptake at the monolayer. This latter is considered to be covered when the evolved heat falls in the physisorption field (40 kJ/mol) [15] and a stoichiometry of M:CO = 1:1 was assumed [16,6].

3. Results and discussion

Table 1 summarizes some properties of the catalysts such as the metal content, dispersion and particle size, d. The later was calculated from the dispersion values, assuming spherical particles, using the equation $d_{CO}(\text{nm}) = \upsilon/D$, where $\upsilon = 1.32$ and 1.01 for Ru and Ni, respectively [17]. Adsorption of CO on Cu was not considered here since this metal hardly adsorbs CO in its lowest oxidation state [18]. Thus, owing to its complete d orbitals, the σ bond derived from the donation of electrons from the CO molecule to the d orbitals of the metal, becomes difficult. Through combined studies of microcalorimetry and infrared spectroscopy, heats of adsorption of CO in its various valence states have been obtained [19]: 66–43 kJ/mol for CO on Cu(0), 110–66 kJ/mol for Cu(I) and 300 kJ/mol for Cu(II). Since in our case Cu is in its zero valence state, this value of heat of adsorption is very low and adding to its extremely low amount adsorbed, resolvable calorimetric peaks were not observed. In Table 1 it is ob-

Table 1
Main characteristics and chemisorption data of catalysts

Catalysts	Precursors	Metal content (%)	Dispersion (%)	Metal particle size, d (nm)
4Ni	$Ni(NO_3)_2$	4	9	11.0
4Ni1Cu	$Ni(NO_3)_2$, $Cu(NO_3)_2$	3.95, 1.06	6	16.5
4Ni2Cu	$Ni(NO_3)_2$, $Cu(NO_3)_2$	3.91, 2.10	7	14.9
4Ni3Cu	$Ni(NO_3)_2$, $Cu(NO_3)_2$	3.95, 3.14	5	21.9
2Ru	$Ru(C_5H_7O_2)_3$	2	9	14.7
2Ru0.3Cu	$Ru(C_5H_7O_2)_3$, $Cu(COOCCH_3)_2$	1.99, 0.31	10	13.4
2Ru0.6Cu	$Ru(C_5H_7O_2)_3$, $Cu(COOCCH_3)_2$	1.99, 0.62	11	12.5
2Ru0.9Cu	$Ru(C_5H_7O_2)_3$, $Cu(COOCCH_3)_2$	1.98, 0.93	10	13.2

served that the addition of Cu does not appreciably affect the dispersion of Ru in Ru–Cu catalysts while the Ni dispersion becomes lower with the increasing copper loading.

Fig. 1 illustrates the microcalorimetric profiles obtained for the Ni–Cu catalysts previously reduced at 623 K. The monometallic Ni catalyst displays a more heterogeneous profile when compared to the others belonging to this series. It has an initial heat of adsorption of 145 kJ/mol which is similar to that found in the literature [7] (142 kJ/mol). There is a continuous decrease of differential heats throughout the coverage and no plateau is observed. Infrared spectroscopy has proved the existence of different surface chemisorbed CO species on supported Ni [20], as bridged (1960 cm^{-1}), linear (2030–2050 cm^{-1}) and subcarbonyl (2065–2090 cm^{-1}) species could be present at in the same Ni surface. According to this author, CO adsorbs principally as subcarbonyl species, $\mathrm{Ni(CO)}_x$, where $x = 2$, 3, on very small, two-dimensional nickel crystallites while CO adsorbs on large, highly crystalline, three-dimensional nickel crystallites in the bridged or multicentered form. The latter IR results allow the interpretation of the microcalorimetric profile as follows. Differential heats of CO adsorption at the high-value region (145 kJ/mol) can be attributed to the formation of multibonded CO (bridge) species, which results in high strength of CO on Ni. The lower heats of adsorption (120 kJ/mol) can be ascribed to different linear CO species.

When Cu is introduced (4Ni1Cu), a decrease in the initial heat of adsorption (121 kJ/mol) is observed due to the increase in the formation of linear carbonyls at the expense of bridged ones. This is in agreement with other studies carried out on Ni–Cu system [7], where it was observed how the introduction of Cu in the Ni monometallic catalyst gave rise to a decrease in the initial heat of adsorption. At the same time the calorimetric profile of this Ni–Cu bimetallic catalyst is more homogeneous than that of the monometallic Ni catalyst. Increase of Cu content (4Ni2Cu) in the catalysts leads to further decrease in the initial heat of adsorption (109 kJ/mol) as well as increase in the homogeneous calorimetric profile. Beyond this Cu content (4Ni3Cu) it is observed that the amount of Cu necessary for the Ni–Cu alloy formation is over come so there is no further decrease in the initial heat of adsorption. On the contrary this initial heat of adsorption for the bimetallic Ni–Cu catalysts with highest copper loading (4Ni3Cu) is of 115 kJ/mol which is higher than that of 4Ni2Cu of lower copper content.

On observing the adsorption isotherm (Fig. 2) for this Ni–Cu bimetallic series in comparison to the Ni monometallic catalyst, there is a decrease of the amount of CO adsorbed owing to the presence of Cu. This could be due to either a decrease in the metal surface area, or a change of the CO adsorption stoichiometry on the Ni–Cu alloyed phase. This latter is in agreement with the suppression of the CO bridge species over the alloyed phase.

Fig. 3 provides us with the calorimetric profile of a bimetallic Ni–Cu catalyst (4Ni2Cu) reduced at two different temperatures, 623 and 773 K displaying initial heats of

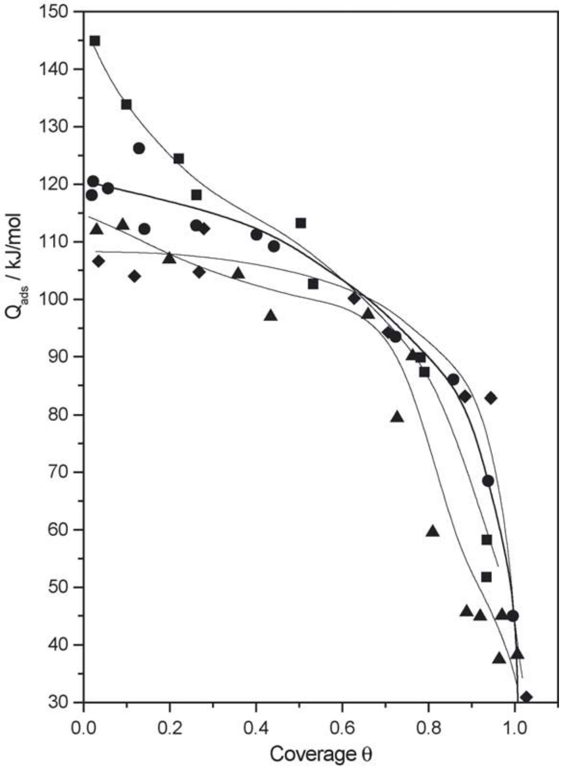

Fig. 1. Heats of adsorption of the Ni–Cu system (reduced at 623 K): (■) 4Ni, (●) 4Ni1Cu, (♦) 4Ni2Cu and (▲) 4Ni3Cu.

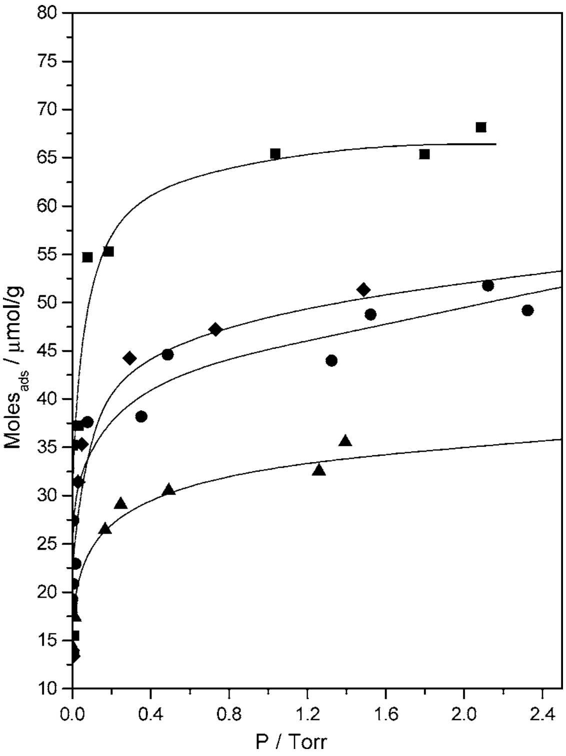

Fig. 2. Adsorption isotherms of the Ni–Cu system (reduced at 623 K): (■) 4Ni, (●) 4Ni1Cu, (♦) 4Ni2Cu and (▲) 4Ni3Cu.

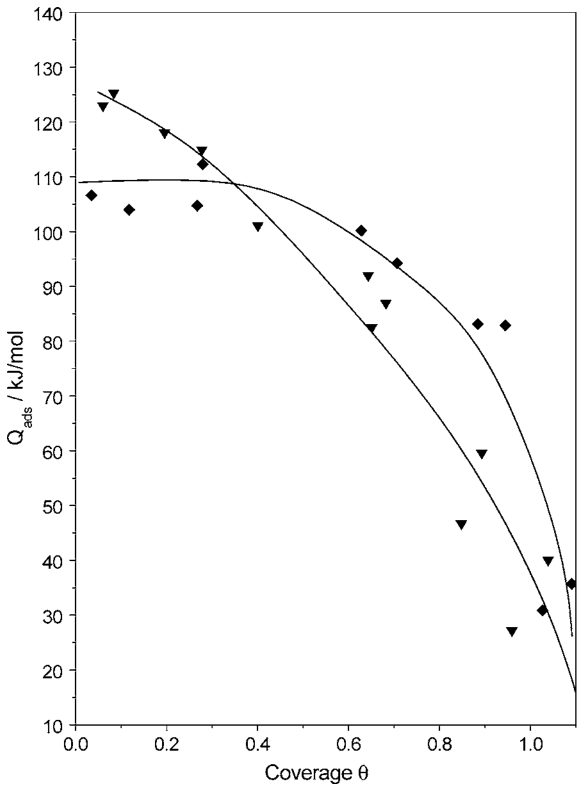

Fig. 3. Heats of adsorption of Ni–Cu system reduced at two different temperatures (623 and 773 K): (▼) 4Ni2Cu-773 and (◆) 4Ni2Cu-623.

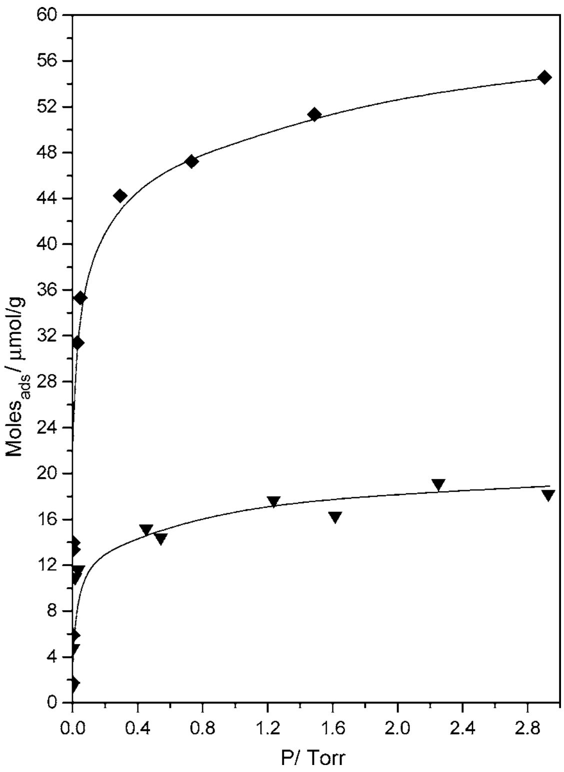

Fig. 4. Adsorption isotherms of the Ni–Cu system reduced at two different temperatures (623 and 773 K): (▼) 4Ni2Cu-773 AND (◆) 4Ni2Cu-623.

adsorption of 109 and 127 kJ/mol, respectively. Higher initial heats are observed at higher reduction temperatures. The latter fact can be explained by assuming that part of the alloyed Cu separates from the Ni when reduced at such high temperatures. This is why we observe a profile similar to that of the Ni monometallic catalyst as we have part of the Ni alloyed with Cu but another acts like monometallic Ni.

From the adsorption isotherm (Fig. 4) of this bimetallic catalyst (4Ni2Cu) reduced at different temperatures we observe that when temperature was increased from 623 to 773 K the amount of CO adsorbed decreased from about 47 to 16 µmol/g. This could be due to the sintering of metal particles which is favoured at higher temperatures.

In a similar manner the Ru–Cu bimetallic system can be evaluated. The monometallic Ru catalyst (Fig. 5) displays an initial heat of adsorption of about 137 kJ/mol. This value is in agreement with other studies carried out with other carbon-supported Ru catalyst (140 kJ/mol [21] and 138 kJ/mol [22,23]). The population sites with high CO adsorption heat is small and this heat decreases in a continuous manner up to values of about 117 kJ/mol at very low coverage of 0.2. There after, a plateau is observed in the coverage range of 0.2–0.6 and later the heat of adsorption decreases once more until complete coverage is achieved. Therefore, we can say that surface site distributions are more homogeneous than that of the Ni catalyst. From IR studies on Ru/Al_2O_3 [24], it has been observed that at 300 K bridged CO species (weak IR band at 1750 cm^{-1}), linear CO species (strong IR

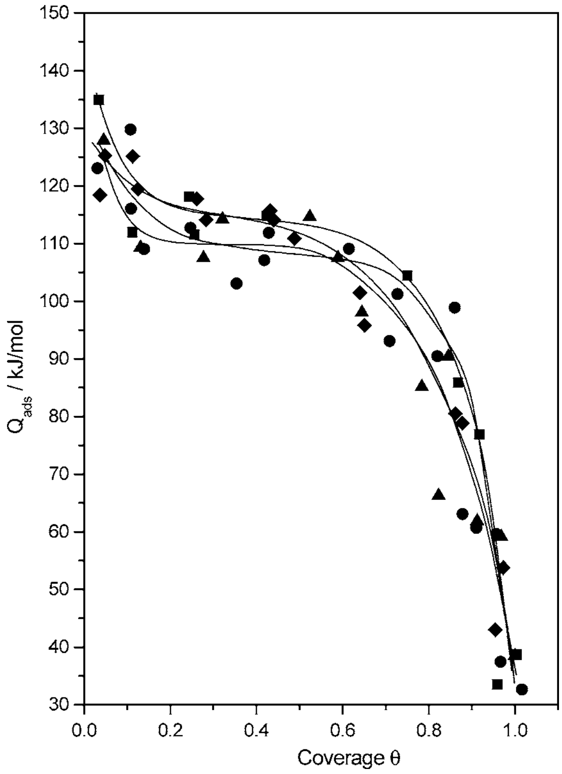

Fig. 5. Heats of adsorption of the Ru–Cu system (reduced at 673 K): (■) 2Ru, (●) 2Ru0.3Cu, (◆) 2Ru0.6Cu and (▲) 2Ru0.9Cu.

band at 2047 cm^{-1}) and gem-dicarbonyl species (weak bands at 2135 and 2080 cm^{-1}) are formed on Ru particles. The two former species can be ascribed to adsorption heat values of 145 and 120 kJ/mol, respectively.

The introduction of Cu (Fig. 5) gives rise to very little change in the initial heat of adsorption. As for the calorimetric profiles, plateau are still observed although not as pronounced as that of the monometallic catalyst. Like wise from adsorption isotherms (Fig. 6) appreciative difference in the amount of CO adsorbed is not observed among the catalysts in the Ru–Cu system. This informs us on the lack of alloy formation between these two metals.

When one of the bimetallic catalysts of this series (2Ru0.6Cu) is reduced at different temperatures, 673 and 773 K (Fig. 7) a decrease in the heat of adsorption is observed at the higher temperature. This fact may be due to the migration of Cu, which hardly adsorbs CO, on the surface of Ru. From the adsorption isotherm (Fig. 8) of this bimetallic catalyst (2Ru0.6Cu) reduced at different temperatures we observe that when temperature was increased from 673 to 773 K the amount of CO adsorbed decreased from about 21 to 12 μmol/g. This could be due to the sintering of metal particles which is favoured at higher temperatures.

Therefore from Figs. 5–7 we can deduce that at these temperatures (673 and 773 K) Ru and Cu are not miscible while Ni and Cu (Figs. 1–3) seem to form an alloyed phase. The current results can be better understood when comparing certain properties of these metals such as the Tamman's

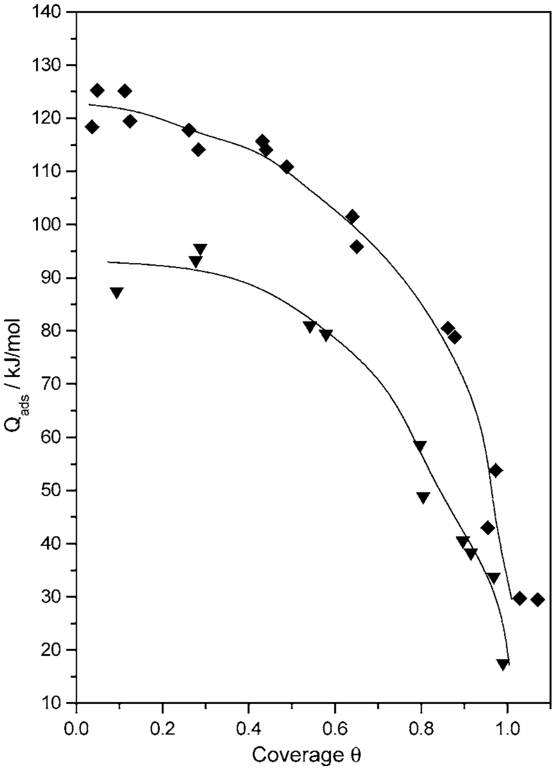

Fig. 7. Heats of adsorption of the Ru–Cu system reduced at two different temperatures (673 and 773 K): (♦) 2Ru0.6Cu-673 and (▼) 2Ru0.6Cu-773.

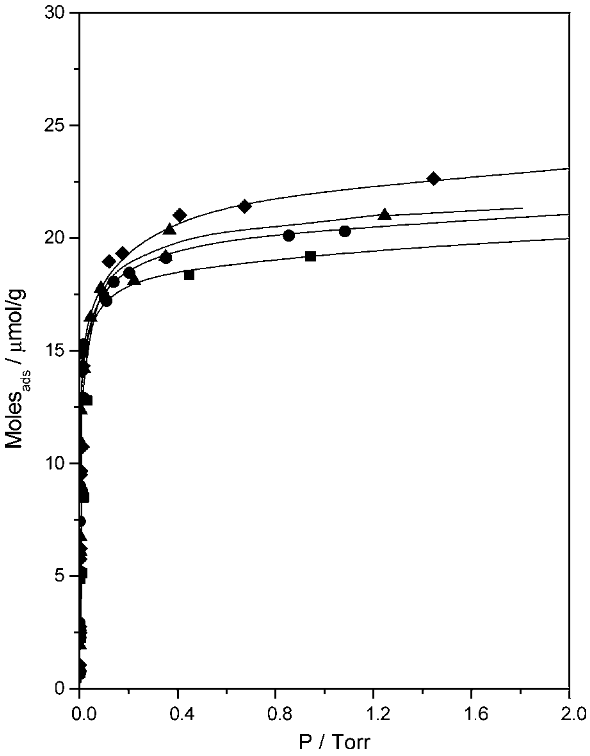

Fig. 6. Adsorption isotherms of the Ru–Cu system (reduced at 673 K): (■) 2Ru, (●) 2Ru0.3Cu, (♦) 2Ru0.6Cu and (▲) 2Ru0.9Cu.

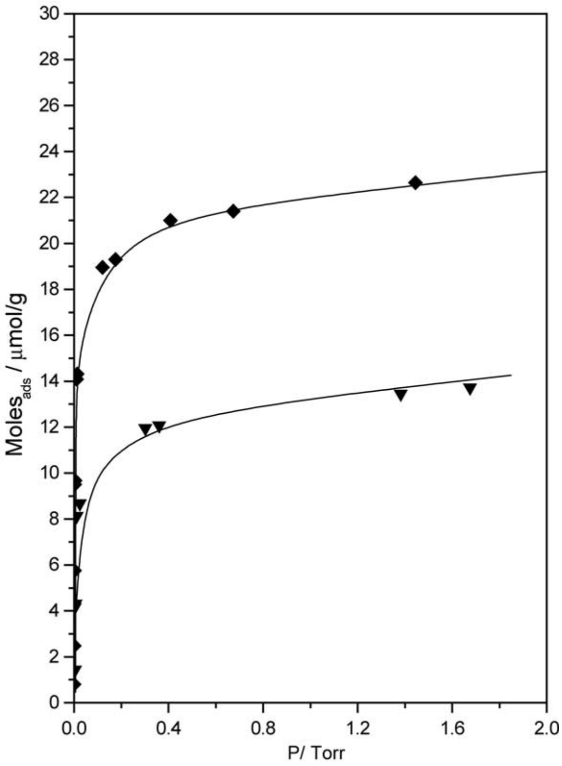

Fig. 8. Adsorption isotherms of the Ru–Cu system reduced at two different temperatures (673 and 773 K): (♦) 2Ru0.6Cu-673 and (▼) 2Ru0.6Cu-773.

Table 2
Physical and thermodynamic properties of metals

	Ni	Cu	Ru
Melting point (K)	1726	1357	2523
Tamman’s temperature (K)	863	679	1262
Atomic radius (Å)	1.62	1.57	1.89
Crystalline structure	fcc	fcc	Hexagonal
Enthalpy of fusion (kJ/mol)	17.2	13.1	25.7
Enthalpy of vaporization (kJ/mol)	378	300	580

temperature, atomic radius and their crystalline structures. Table 2 provides us with this information. As can be observed from this table, Ni and Cu have similar Tamman temperature and atomic radius as well as the same crystalline structure (fcc) which will facilitate the formation of the alloy between these two metals in comparison to the Ru–Cu system where the differences between these properties are greater. Other studies [25] proved that at 627 K miscibility between Ru and Cu is very low. On the other hand, Haller and coworkers [26] gave evidence of the metal–metal interaction between Ru and Cu in Ru–Cu/SiO_2 catalysts although the miscibility of these metals in the bulk state is extremely low. They imagined that the interaction in the Ru–Cu system essentially involved dispersion of Cu on the surface of Ru particles which results in a significant reduction in catalytic activity but had little influence on hydrogen chemisorption.

4. Conclusions

In the case of the Ni–Cu bimetallic system a decrease in the heat of adsorption as well as in the amount of CO adsorbed is originated when Cu is introduced. This is interpreted as a consequence of the modification of the ratio of bridged to linear species formed during CO chemisorption. Therefore, based on our present data (as well as in catalytic behaviour of experiments not published yet) and comparing with the referenced literature there exist alloy formation between Cu and Ni, particularly when the bimetallic catalysts are reduced at 623 K. Moreover, when we reduce a bimetallic sample at 773 K under hydrogen, modifications in the CO adsorption heats appear, that can be assigned to a partial segregation of the metallic particles.

On the other hand, the variations in the CO adsorption heats (and in the adsorbed amounts) when Cu is progressively introduced into a Ru–Cu system are negligible. This suggests that there is no alloy formation between these two metals. Also the fact that Cu can decorate the Ru, but does not adsorb CO itself, should give rise to a reduction in the CO adsorbed amount. Another factor of difficult evaluation, as could be that the presence of Cu modifies the Ru metallic dispersions (i.e. avoiding sintering process) can contribute to the non-appreciable observed variation in the CO adsorbed amounts among the various bimetallic systems.

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