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# Ethylcyclopentane reactions on alumina supported low loaded platinum-copper catalysts

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## Abstract

This work is focused on the catalytic behaviour of alumina supported low loaded Pt-Cu catalysts. Ethylcyclopentane is the probe molecule. In fact this molecule can lead to several primary reactions as: (i) ring opening, (ii) ring enlargement, (iii) aromatisation, and (iv) hydrocracking. Due to these various pathways we can follow the modifications of the catalytic activities as well as selectivity changes when the surface composition of the catalyst is changed. Various techniques were used to characterise these catalysts: (i) by TPR we showed that an interaction between platinum and copper is present and (ii) by hydrogen chemisorption we found that the platinum dispersion decreased from 100 to 20% when the copper content increased. The ring opening reaction is non-selective for platinum catalysts and for Pt-Cu systems with low copper content and is selective for catalysts with a high copper content. We noted that the apparent activation energy values also changed with the amount of copper which confirms the modifications in the catalytic mechanisms when changing copper concentration. We proposed that the ring enlargement reaction is similar to a bond shift reaction, when ring opening corresponds to hydrocracking reactions. Such comparative relation can help to understand the results obtained.

*Keywords:* Hydrogenolysis; Ethylcyclopentane ring opening; Alloys; Bimetallics; Pt-Cu catalysts

## 1. Introduction

In the past, the focus of research in catalysis science was activity to optimise turn over rates. In the future, selectivity to form the desired product without the formation of by-products will be the major research challenge [1]. Our understanding of the molecular ingredients of selectivity needs to be improved. The importance of selective site blocking, by alloying can alter the reaction selectivity.

The extent to which the properties of metal catalysts can be modified by alloying is a subject which still attracts many scientists working in the field of catalysis [2]. We can note in the literature that copper was used as second metal to improve the catalytic behaviour in the following systems, Ni-Cu, Ru-Cu, Os-Cu, and Rh-Cu [3–10]. With these catalysts the hydrocracking reactions, favoured on the base metals, is strongly inhibited by adding copper.

Because of the important role played by Pt in chemical industry and in electrocatalysis it is not surprising that alloys with this metal are still deeply studied.

Very fundamental works using either carbon-13 labelled hydrocarbons or not labelled ones have already been performed with the Pt-Cu systems [11–13]. At the opposite of what was found above, with Pt-Cu catalysts, hydrocracking reactions were favoured when adding Cu but these bimetallics present lower activities than copper free catalysts. An explanation was that Cu was involved in the C–C bond breaking reaction. The use of 13C hydrocarbons pointed out that the relative contribution of the various mechanisms changed along with the Cu content. The isomerisation mechanisms involving large catalytic sites as bond shift and selective cyclic mechanism [14] evolved to mechanisms involving smaller active sites as non-selective cyclic mechanisms [15]. Furthermore, the previous Pt-Cu catalysts [11] were loaded to 9 wt.% of metals and only pentanes and hexanes were studied when it was observed that with heptanes another reaction may take place: the aromatisation reaction.

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Table 1
Catalyst studied: 0.2%Pt-X%Cu/γ-$Al_2O_3$; calcined and reduced

| Catalysts used: calcined and reduced | Chemical analysis by X-ray fluorescence | |
|---|---|---|
| | Pt (wt.%) | Cu (wt.%) |
| 0.2%Pt/γ-$Al_2O_3$ | 0.23 ± 0.02 | |
| 0.2%Pt-0.06%Cu/γ-$Al_2O_3$ | 0.23 ± 0.02 | 0.069 ± 0.002 |
| 0.2%Pt-0.2%Cu/γ-$Al_2O_3$ | 0.23 ± 0.02 | 0.21 ± 0.01 |
| 0.2%Pt-0.6%Cu/γ-$Al_2O_3$ | 0.23 ± 0.02 | 0.59 ± 0.01 |

The aim of this study is to analyse, versus the Cu concentration, the various reactions occurring with a molecule able to follow several reaction pathways as ethylcyclopentane can do. In fact the hydrogenolysis reaction is a very sensitive reaction for the selectivity as we already observed for methylcyclopentane hydrogenolysis versus the mean metallic particle sizes [14,15]; but we may ask ourselves if ethylcyclopentane has the same behaviour? Moreover, the total platinum loading is constant and low, around 0.2 wt.%; hence the metal–support interaction can be present.

## 2. Experimental

### 2.1. Catalyst preparation

A series of alumina supported Pt-Cu catalysts were prepared. The platinum loading was always 0.2 wt.% and the copper loading varied from 0.06 to 0.2 and 0.6 wt.%. The samples were prepared following a successive impregnation technique [16,17]. After each impregnation step the catalysts were calcined in air at 400 °C for 2 h followed by a reduction at 400 °C for 5 h under hydrogen. The starting salts were $H_2PtCl_6 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 6H_2O$. The support used was a Woelm non-acid γ-alumina. In Table 1 are reported the catalysts prepared, used and characterised.

### 2.2. Characterisation techniques

To determine the metallic loading, chemical analysis were performed by X-ray fluorescence. Specific surface areas were determined by the BET method. To analyse the reducible properties of these systems, TPR were performed on samples calcined in air at 400 °C for 1 h, with a temperature slope of 10 °C/min. These experiments were realised under 1% hydrogen in argon, from room temperature up to 800 °C. Prior to hydrogen chemisorption which was used to determine the metallic dispersion, the samples were reduced at 400 °C for 2 h. To determine the metallic particle size and surface composition TEM and XPS were respectively used.

### 2.3. Catalytic reactions

All experiments were carried out in a differential reactor all-glass flow system already described [18]. Ethylcyclopentane, the hydrocarbon used in this study, maintained in a cold U-tube at constant temperature to get a constant partial pressure, was mixed and pushed by hydrogen and introduced through the catalyst. The gaseous product was analysed by gas chromatography. The cooling product used was benzylic alcohol the melting point of which is −18 °C; the partial hydrocarbon pressure was then 666.5 Pa. Pulses of hydrocarbon (5 μl) were injected through the catalyst bed. The total pressure ($P_{HC} + P_{H_2}$) was equal to atmospheric pressure. The total conversion was always less than 20%. The catalysts obtained from successive impregnation were all calcined and reduced prior to the catalytic reactions performed between 280 and 350 °C.

## 3. Results and discussion

In Table 1 the chemical compositions of these samples obtained by X-ray fluorescence are reported. Similar results are obtained between "expected" and "found" weight compositions.

The average BET surface area for all these catalysts is in the range 139 ± 10 $m^2$/g.

In Table 2 and Fig. 1 the results obtained by hydrogen chemisorption on mono- and bimetallic catalysts are reported. We have also given the metallic particle sizes determined by TEM. We can observe that hydrogen chemisorption is decreasing when copper content is increased. This point can be explained by a surface enrichment in copper as its superficial energy is lower than the platinum one; $\gamma_{Cu} = 1720 \pm 100$ erg/cm$^2$ and $\gamma_{Pt} = 2280 \pm 800$ erg/cm$^2$ [19–21]. This Cu surface segregation is also observed by XPS when measuring the relative atomic ratios; this result is in the right part of Table 2. The surface composition is higher in Cu than in Pt.

Table 2
Mean metallic particle sizes from hydrogen chemisorption and TEM; and XPS results

| Samples on γ-$Al_2O_3$ | Hydrogen comsumption (cm$^3$/g of catalyst) | Dispersion (H/Pt) | Mean metallic particle sizes (Å) | | XPS results | |
|---|---|---|---|---|---|---|
| | | | From $H_2$ chemisorption | From TEM | Cu/Pt × $10^3$ theoretical | Cu/Pt × $10^3$ experimental |
| 0.2%Pt | 0.18 | 1 | 8 | 12 | | |
| 0.2%Pt-0.06%Cu | 0.119 | 0.83 | 12 | 14 | 0.5 | 3 |
| 0.2%Pt-0.2%Cu | 0.045 | 0.32 | 31 | 28 | 1.6 | 5.7 |
| 0.2%Pt-0.6%Cu | 0.028 | 0.20 | 49 | 41 | 5.1 | 13.4 |

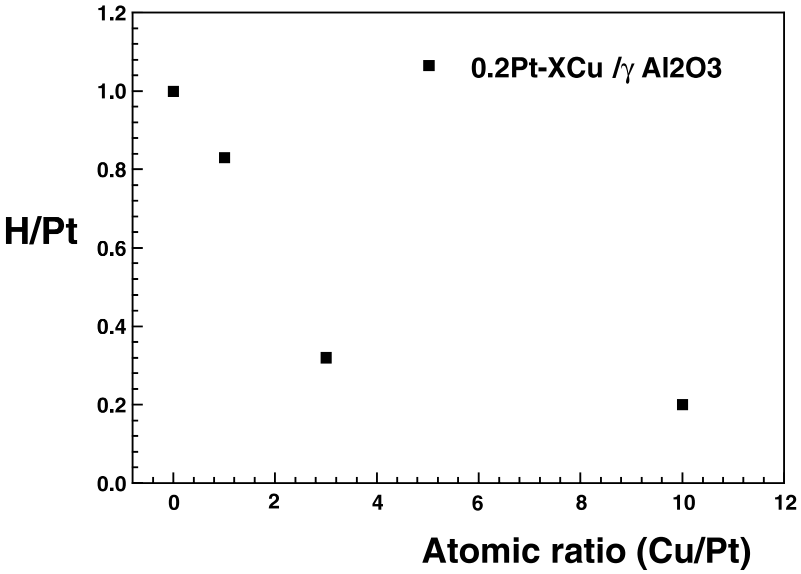


Fig. 1. Influence, at room temperature, of addition of copper on hydrogen chemisorption on Pt and bimetallics Pt-Cu catalysts.

The rates, or turn over frequencies ($s^{-1}$), were determined thanks to the metal dispersion obtained with hydrogen chemisorption. In Table 3 are reported the micromoles of accessible platinum, copper and Pt-Cu reported to 1 g of catalyst. As copper does not chemisorb hydrogen we made an assumption that the moles of accessible copper are proportional to the moles of platinum following their molar ratios.

To determine the presence, or not, of a platinum-copper interaction we studied by TPR the mono and bimetallic samples. The results are in Table 4. Hydrogen consumption is calculated from Eq. (1) and is compared with the experimental results.

$$x\mathrm{Pt}^{4+}\mathrm{O}_2 + y\mathrm{Cu}^{2+}\mathrm{O} \xrightarrow{[2x+y]\mathrm{H}_2} x\mathrm{Pt} + y\mathrm{Cu} + (2x+y)\mathrm{H}_2\mathrm{O} \quad (1)$$

The good agreement between these results shows that $Pt^{4+}$ and $Cu^{2+}$ are completely reduced to metallic state under hydrogen in the temperature range of 100–400 °C.

For these systems, the maximal temperatures obtained are function of Cu content. It shows that Pt and Cu are in contact and it is confirmed by the fact that, for the monometallic sample, the maximal temperature has values different than those obtained on the bimetallics. We can see that platinum is reduced at a lower temperature than all other bimetallics Pt-Cu, but these samples are much easier to reduce than

Table 3
Pt and Cu accessible to the gas phase

| Samples | Pt accessible (μmole/$g_{cat}$) | Cu accessible (μmole/$g_{cat}$) | Pt + Cu accessible (μmole/$g_{cat}$) |
|---|---|---|---|
| 0.2%Pt/γ-$Al_2O_3$ | 12.7 | 0 | 12.7 |
| 0.2%Pt-0.06%Cu/γ-$Al_2O_3$ | 8.5 | 7.8 | 16.3 |
| 0.2%Pt-0.2%Cu/γ-$Al_2O_3$ | 3.2 | 10.0 | 13.2 |
| 0.2%Pt-0.6%Cu/γ-$Al_2O_3$ | 2.0 | 18.8 | 20.8 |

Table 4
Results from TPR

| Samples | Maximum of temperature for the reduction peak (°C) | Experimental consumption of $H_2$ (μmole/$g_{cat}$) | Theoretical consumption of $H_2$ (μmole/$g_{cat}$) | $R = H_{2exp}/H_{2theory}$ |
|---|---|---|---|---|
| 0.2%Pt/γ-$Al_2O_3$ | 253 | 20.4 | 20.4 | 1.0 |
| 0.06%Cu/γ-$Al_2O_3$ | 437 | 10.6 | 9.4 | 1.12 |
| 0.2%Cu/γ-$Al_2O_3$ | 457 | 34.6 | 31.4 | 1.1 |
| 0.6%Cu/γ-$Al_2O_3$ | 397 | 101.5 | 104.6 | 0.97 |
| 0.2 %Pt-0.06%Cu/γ-$Al_2O_3$ | 257 | 27.0 | 29.8 | 0.91 |
| 0.2%Pt-0.2%Cu/γ-$Al_2O_3$ | 281 | 45.2 | 51.8 | 0.87 |
| 0.2%Pt-0.6%Cu/γ-$Al_2O_3$ | 348 | 144.5 | 125 | 1.15 |

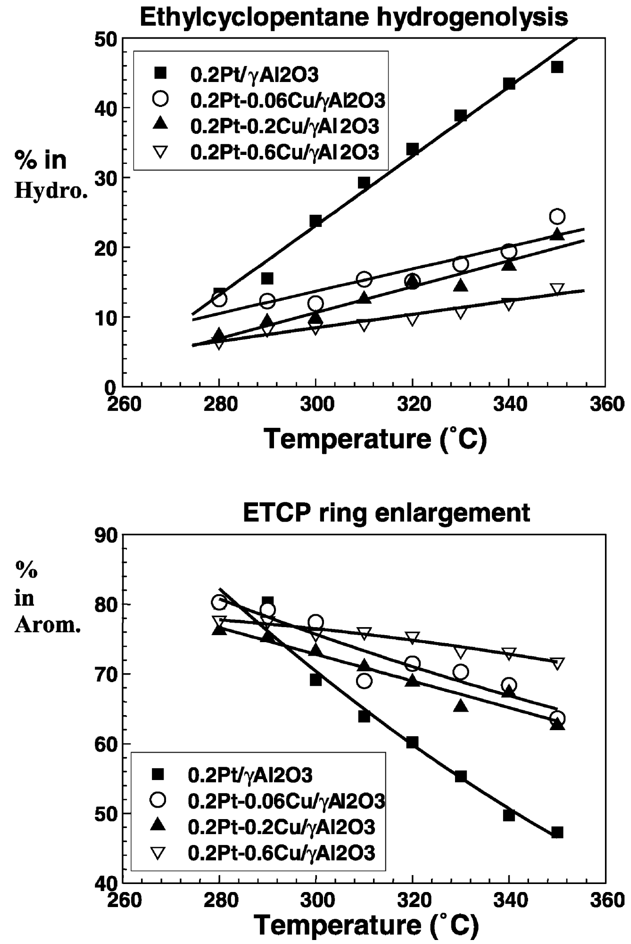


Fig. 2. Temperature influence on hydrogenolysis and ring enlargement reactions between 280 and 350 °C.

Cu alone. Platinum helps copper to be reduced but copper inhibits platinum reduction.

### 3.1. Catalytic activity of ethylcyclopentane

This model molecule has been chosen to characterise these catalysts, and to analyse the copper influence on the catalytic properties of platinum. The contact reactions of such molecule can be classified into two classes corresponding to the primary products obtained and to the secondary ones. Initially we may have: (i) ring opening, also called hydrogenolysis reaction, giving *n*-heptane (*n*-H), 3-methylhexane (3-MH) and ethylpentane (EtP), (ii) ring enlargement giving methylcyclohexane (MCH) and toluene (Tol), aromatisation reaction and (iii) hydrocracking giving cyclopentane and ethane. After, following consecutive reactions we may have hexanes, pentanes, butanes, propane, ethane and methane as well as some isomers.

We shall call, in most cases, ring enlargement the global reaction where are formed toluene plus methylcyclohexane, we must keep in mind that the ratio toluene/methylcyclohexane is around 10.

We shall first analyse the influence of the temperature on these reactions, then we shall follow the effect of copper concentration on the platinum properties.

#### 3.1.1. Influence of the reaction temperature

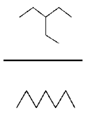
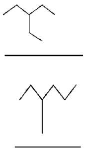
Hydrogenolysis selectivity and aromatisation selectivity from ethylcyclopentane are reported in Fig. 2. These two reactions are irreversible, and hydrogenolysis is more characteristic of the metallic activity when ring enlargement is more related to acidic behaviour. Hydrogenolysis is favoured when reaction temperature is increased and it is the opposite for aromatisation even it is a dehydrogenation reaction. Such a result points out that we have not to focus on the aromatisation reaction but only to look at the ring enlargement reaction and such reaction will be disfavoured when the reaction temperature is increased. In consequence the apparent activation energy values will be higher for hydrogenolysis than for ring enlargement.

#### 3.1.2. Copper influence on the catalytic properties of platinum

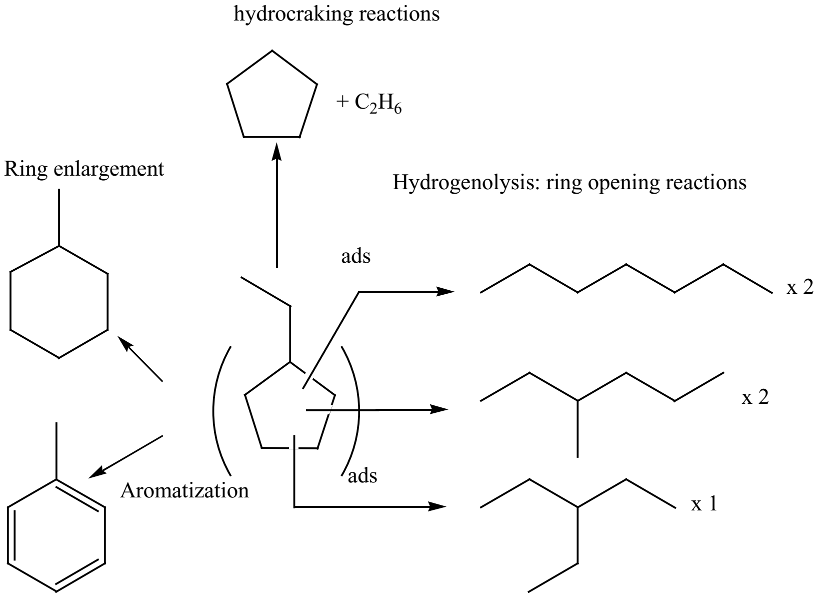
When, at a constant temperature of 350 °C, the amount of Cu is increased, the catalytic activity is decreased as well as the relative contribution of the hydrogenolysis reaction. At the opposite the percentage of the ring enlargement reaction is increased. In Table 5 are the results.

The activity is expressed in μmole/g s. The hydrogenolysis ratios ethylpentane/*n*-heptane and ethylpentane/3-methylhexane correspond respectively to the following

Table 5
Results obtained from the contact reaction of ethylcylopentane at 350 °C

| Catalysts | Activities (μmole/g s) | Selectivity in hydrogenolysis (%) | Selectivity in ring enlargement (%) |  |  |
|---|---|---|---|---|---|
| 0.2Pt | 107 | 41.5 | 49.2 | 0.6 | 0.7 |
| 0.2Pt-0.06Cu | 9.5 | 23.0 | 59.7 | 0.2 | 0.2 |
| 0.2Pt-0.2Cu | 6.2 | 20.0 | 64.5 | 0.6 | 0.8 |
| 0.2Pt-0.6Cu | 4.2 | 14.3 | 72.0 | 1.4 | 1.4 |

Initial selectivities and hydrogenolysis ratio.



Scheme 1. General reactions taking place with ethylcylopentane as reactant.

carbon–carbon bonds breaking: $C_{II}$–$C_{II}$/$C_{II}$–$C_{III}$ and $C_{II}$–$C_{II}$/$C_{II}$–$C_{II}$. The values of the first ratio will characterise the selectivity in carbon–carbon bond breaking between only secondary carbon atoms and secondary–tertiary carbon atoms. The former ratio may give information about the selectivity in ring opening reaction.

The reactions are shown in Scheme 1.About the ring enlargement reaction we have two products: toluene and methylcyclohexane. We can noticed that initially, when the Cu content increases, the selectivity in aromatisation increases and in hydrogenolysis decreases.

Furthermore, if the value of the hydrogenolysis ratio (EtP/*n*-H) is not too far from the statistic value (~0.5) the hydrogenolysis is non-selective, for other values, it is a selective hydrogenolysis. These results can give information on the mean metallic particle sizes if we follow what we noticed with the methylcyclopentane reaction [14,15]. On 0.2% Pt/γ-$Al_2O_3$, 0.2% Pt-0.06%Cu/γ-$Al_2O_3$, 0.2%Pt-0.2%Cu/γ-$Al_2O_3$ catalysts, the results obtained pointed out values near the statistical one, moreover the particles are small (Table 2). Moreover, at high temperature non-selective hydrogenolysis is favoured versus the selective one. At the opposite for the catalyst 0.2%Pt-0.6%Cu/γ-$Al_2O_3$ the reaction mechanism is selective.

About activity and selectivity in hydrogenolysis and ring enlargement, in Fig. 3, we can see that an increase of copper deactivates the catalysts (Fig. 3c), decreases the relative contribution of hydrogenolysis reaction (Fig. 3a) and increases the aromatisation process (Fig. 3b).

We are now going to analyse the results obtained from the apparent activation energy values, then we will be able to discuss about the reactivity of such systems.

### 3.2. Kinetic data

As the rate determining step takes place in the adsorbed phase we are measuring apparent activation energies $E_a$:

$$E_a = E^0 + \Delta H_{ads}$$

The real activation energy $E^0$ is reduced by the enthalpy of adsorption $\Delta H_{ads}$ which is negative. One problem is that $\Delta H_{ads}$ is unknown for the contact reactions with ethylcyclopentane which may involve several dehydrogenation steps. We noticed that $E_a$ decreases when the amount of

Table 6
Apparent activation energy values (kJ/mole), turn over frequency ($s^{-1}$) and logarithm of the pre-exponential factor (ln *A*) for hydrogenolysis and ring enlargement reactions

| Catalysts on γ-$Al_2O_3$ | Hydrogenolysis | | | Ring enlargement (RE) | | | *a* and *b* (kJ/mole) for hydrogenolysis | *a* and *b* (kJ/mole) for RE |
|---|---|---|---|---|---|---|---|---|
| | TOF ($s^{-1}$) | $E_a$ (kJ/mole) | ln *A* | TOF ($s^{-1}$) | $E_a$ (kJ/mole) | ln *A* | | |
| 0.2%Pt | 0.33 | 164.7 | 19.4 | 0.34 | 87.8 | 4.6 | $a$ =76.97, $b$ = 4.51 | $a$ = 65.96, $b$ = 4.62 |
| 0.2%Pt-0.06%Cu | 0.13 | 118.7 | 9.6 | 0.31 | 82.8 | 3.8 | | |
| 0.2%Pt-0.2%Cu | 0.10 | 122.9 | 10.0 | 0.27 | 73.6 | 1.6 | | |
| 0.2%Pt-0.6%Cu | 0.05 | 98.2 | 4.6 | 0.06 | 66.9 | 0.2 | | |

In the last two columns: the compensation effect obtained on these catalysts for hydrogenolysis and ring enlargement reactions from: $E_a = a + b \ln A$.

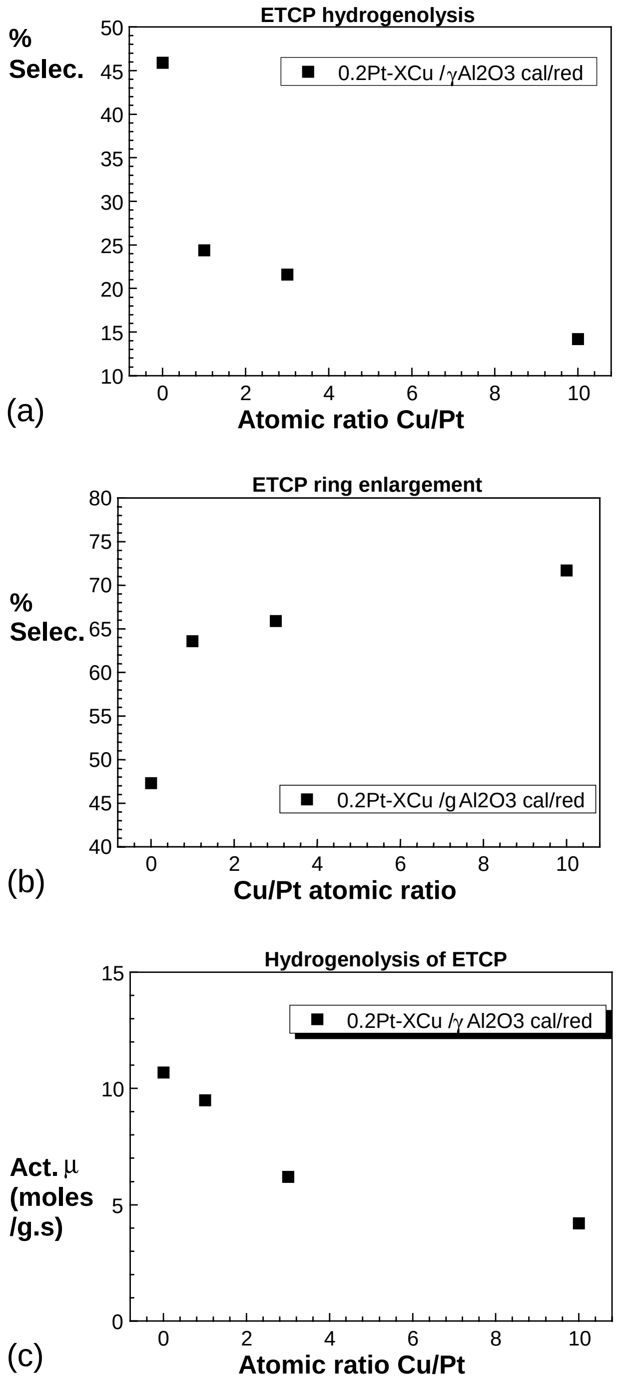


Fig. 3. Copper influence on catalytic selectivities in hydrogenolysis, ring enlargement and on hydrogenolysis activity for a reaction at 350 °C.

copper increases, which can mean that more dehydrogenation steps are involved. We obtained, for the ring opening reaction, three classes of $E_a$ values: 165 ± 5 kJ/mole on Pt catalyst, 120 ± 5 kJ/mole on 0.2%Pt-0.06%Cu and 0.2%Pt-0.2%Cu, and 98±4 kJ/mole on 0.2%Pt-0.6%Cu. We have to keep in mind that the higher value will correspond to the non-selective ring opening reaction [14,15,22]. On the other hand, the $E_a$ value for ring enlargement reaction is around 77.5 ± 10 kJ/mole. This process is less activated (Table 6).

### 3.2.1. Reaction rates

About the initial rates $N(\mathrm{s}^{-1})$ in ring enlargement and in hydrogenolysis we noted, as a general tendency, that the turn over is higher in ring enlargement than in hydrogenolysis. This is in good agreement with the apparent activation energy values.

We noticed that $N(\mathrm{s}^{-1})$ decreases when the amount in copper increases. To establish a correlation between the activity and the energy we have determined the pre-exponential factor A. We obtained a linear relation between $\ln A$ and $E_a$ (Table 6), $E_a = a + b \ln A$. This relation was first observed by Constable [23]. A compensation effect takes place for these reactions, i.e. hydrogenolysis and ring opening, occurring on these different catalysts.

This compensation effect has not a straightforward explanation. More than a dozen explanations have been proposed. They can be divided into (i) fact-oriented explanations, which are based on the experimental results showing this phenomenon and (ii) theory-oriented or speculative concepts [24]. The explanations for compensation phenomena can be linked to: (i) active site distribution and inhomogeneous surfaces, (ii) kinetic conditions, apparent and true Arrhenius parameters, (iii) enthalpy–entropy relation, (iv) isokinetic temperature and (v) heat bath concept [24].

Following the conventional transition state theory, the experimental rate constant $k_{\mathrm{exp}}$ for a bimolecular reaction is equal to $k_{\mathrm{exp}} = (k_B T/h)K^\#$, where $K^\#$ is the equilibrium constant between the activated species and the reactants [25]. Following the Patterson–Rooney approach we have, with a catalyst, the following reactions:

$$\text{reactant} + \text{catalyst} \overset{K_{\mathrm{ads}}}{\leftrightarrow} \text{reactant–catalyst} \overset{K^\#}{\leftrightarrow} \text{transition state}$$

In that case

$$k_{\mathrm{exp}} = \frac{k_B T}{h} K^\# K_{\mathrm{ads}}$$

and

$$\Delta G^\circ_{\mathrm{ads}} = -RT \ln K_{\mathrm{ads}} \quad \text{and} \quad \Delta G^\# = -RT \ln K^\#$$

Then

$$k_{\mathrm{exp}} = \frac{k_B T}{h} \mathrm{e}^{(\Delta S^\circ_{\mathrm{ads}} + \Delta S^\#)(1/R_e) - (\Delta H^\circ_{\mathrm{ads}} + \Delta H^\#)(1/RT)}$$

We can write

$$k_{\mathrm{exp}} = A\ \mathrm{e}^{-E_a/RT}$$

$\Delta H^\circ_{\mathrm{ads}} + \Delta H^\#$ corresponds to the experimental values of the apparent activation energy $E_a$. When the strength of adsorption increases, then $E_a$ decreases and by consequence $\Delta S^\circ_{\mathrm{ads}} + \Delta S^\#$ decreases as well as the value of $A$. This can explain the compensation effect between $E_a$ and $A$.

Table 7
Activation enthalpy and entropy values for hydrogenolysis and ring enlargement

| Catalysts | Hydrogenolysis | | | Ring enlargement | | |
|---|---|---|---|---|---|---|
| | $\Delta S^\#$ (J/K mole) | $\Delta H^\#$ (kJ/mole) | $E_a - \Delta H^\# = nRT$[a] | $\Delta S^\#$ (J/K mole) | $\Delta H^\#$ (kJ/mole) | $E_a - \Delta H^\# = nRT$ |
| 0.2%Pt/γ-$Al_2O_3$ | 17.6 | 160.1 | 1.1 | −106.2 | 83.2 | 1.1 |
| 0.2%Pt-0.06%Cu/γ-$Al_2O_3$ | −63.9 | 114.1 | 1.1 | −113.3 | 77.7 | 1.2 |
| 0.2%Pt-0.2%Cu/γ-$Al_2O_3$ | −61.4 | 117.9 | 1.2 | −130.8 | 68.6 | 1.2 |
| 0.2%Pt-0.6%Cu/γ-$Al_2O_3$ | −106.6 | 93.6 | 1.1 | −143.4 | 61.9 | 1.2 |

[a] $RT = 5.208$ kJ/mole.

From the Eyring equation, we can determine $\Delta S^\#$ and $\Delta H^\#$:

$$\ln\left(\frac{k_{\mathrm{exp}}}{T}\right) = \ln\left(\frac{K}{h}\right) + \left(\frac{\Delta S^\#}{R}\right) + \left(-\frac{\Delta H^\#}{RT}\right).$$

All the results are reported in Table 7.

When making a comparison with 0.2%Pt/γ-$Al_2O_3$, the addition of Cu provokes a decrease of the activation entropy. This point can be explained by the fact that more Cu is present more dehydrogenation steps are involved.

## 4. Conclusion

In this work we used ethylcyclopentane as the probe molecule which may give information about surface structure modifications via its two reactions: ring opening and ring enlargement reactions. We already saw, with methylcyclopentane (MCP), that the former reaction is a very structure sensitive reaction with platinum catalysts [14,15]. We may ask ourselves if ethylcyclopentane is as performing as MCP.

From kinetic data, three classes of apparent activation energy values were obtained. The higher value is related to the non-selective ring opening reaction, and it takes place on the platinum catalyst. When copper is added, this reaction shifts to more selective one. To explain such results we have to take in account that an ensemble Pt + Cu is responsible for the ring opening reaction. Moreover, from TPR experiments, we noticed that platinum is in interaction with copper; and from XPS analysis, a copper surface segregation takes place. Then a Pt+Cu ensemble should be present at the surface.

Furthermore, when the atomic ratio Cu-Pt increases, ring opening selectivity decreases, ring enlargement selectivity increases and the total activity decreases. These two reactions can be considered as hydrocracking and isomerisation reaction, respectively. Hence, we can understand such an evolution. We have to underline that with branched heptane hydrocarbons as reactants, the cyclic mechanism predominates whatever the platinum dispersion is [14,26,27]; then the only case where bond shift takes place is for ring enlargement reaction, which reaction is favoured by increasing the copper amount.

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