

# Effect of surface segregation on the catalytic activity of alloys: CO hydrogenation on Pd–Ni(111) surface

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Received 7 January 1997; accepted 16 July 1997

## Abstract

A semi-empirical model has been presented for studying the effect of surface segregation and local environment on the catalytic activity of the PdNi(111) surface for CO hydrogenation. Large Pd segregation to the surface has been found to affect the activation barrier for dissociation of molecules on the surface. It also affects the activation barriers for different reaction steps in the CO hydrogenation process to form methanol on the Pd–Ni surface. It is argued that for the Pd–Ni system, hydrogenation of the adsorbed HCO<sub>s</sub> species is the rate-limiting step. It has then been shown that an addition of even 5 at% of Pd in bulk Ni may increase the activity by as much as four orders of magnitude. So far as the local environmental effect is concerned, it is found that the most active centres for the HCO<sub>s</sub> hydrogenation step are the centre hollow sites having three-fold symmetry with 3 Pd atoms as nearest neighbours followed by centre hollow sites with two Pd atoms and one Ni atom as nearest neighbours. © 1998 Elsevier Science B.V.

**Keywords:** Segregation; Activation energy for dissociation; Carbon monoxide; Methanol

## 1. Introduction

The hydrogenation of CO over transition metals is one of the most important heterogeneous catalytic reactions producing various hydrocarbons and alcohols. Over the last several decades the CO hydrogenation reactions have been extensively studied [1–13]. Since there are several steps involved in the CO hydrogenation process to produce methane and/or methanol, it becomes important to find the most probable reaction path and the rate-limiting step for each metal catalyst. It is known that Pd is a very

good catalyst for hydrogenation and, therefore, it is important to know the activity of Pd for various steps in the CO hydrogenation process. This has been done by many workers in recent years [2,4,5,9,11,12]. Because of the cost factor, however, it is also important to look for Pd-based alloys which could be used in place of pure Pd catalysts. We have selected the Pd–Ni system for this purpose. This is due to the following facts: Ni(111) surface favours CH<sub>4</sub> formation from CO and H<sub>2</sub> compared to methanol formation while Pd can produce methane as well as methanol. Furthermore, Pd atoms segregate largely to the surface of the Pd–Ni alloy. It is interesting, therefore, to study how the use of the segregation properties of the Pd–Ni alloys

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can selectively produce methanol. The plan of the paper is as follows:

In Section 2 we briefly discuss a segregation model developed recently by the authors [14]. The model predicts Pd segregation in Pd–Ni and Pd–Pt systems and segregation of the column 11 metals in case of alloys like Pd–Cu, Pd–Ag and Pd–Au in agreement with the experimental observations. It is then shown how segregation properties affect the activation barrier for dissociation of simple molecules like CO, NO, H<sub>2</sub> and O<sub>2</sub>. In Section 3 we develop the model for calculating the activity of the Pd–Ni (111) surface for methanol formation and present the results. Conclusions are drawn in Section 4.

## 2. Segregation of Pd-based alloys and activation barrier for dissociation of CO, NO, H<sub>2</sub> and O<sub>2</sub>

In order to determine the Pd concentration on the surface we make use of our earlier results obtained from a model calculation. The model described in detail elsewhere [14,15] was based on several modifications of a broken bond model as follows:

(i) The bond enthalpies in the bulk alloy were obtained from the bond enthalpies of pure constituent metal and the heat of mixing.

(ii) Five layers at the top were considered to have a composition different from that in the bulk. The bond enthalpies in the top layers would then be dependent on the local environment. In order to determine the effect of the local environment on the parameters like the bond enthalpies, the interatomic distance and the mixing energy etc. it was assumed that an atom located in the *i*th layer may be considered as embedded in an equivalent medium with concentration  $X_{ic}$  given by

$$X_{ic} = (Z_v/Z) \cdot X_{i-1} + (Z_l/Z) \cdot X_i + (Z_v/Z) \cdot X_{i+1} \quad (1)$$

where  $Z_v$  is the number of vertical bonds between two adjacent layers,  $Z_l$  is the number of

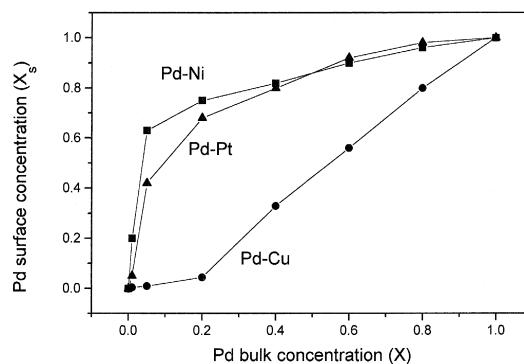


Fig. 1. Segregation behaviour in a few Pd-based alloys as predicted by segregation model [14] ( $T = 800$  K).

lateral bonds in each layer and  $Z$  is the total coordination number. As a consequence of this approximation the pair potentials were allowed to be different from layer to layer in the surface region.

(iii) The bond energies in the surface layer were carefully evaluated taking into consideration the coordination of the surface sites. This was done by modifying the tight binding scheme in the second moment approximation in such a way as to produce the site energy in the bulk, the surface energy, the monovacancy formation energy and the bond energy of metallic dimer. This approach, termed as the modified tight binding (MTB) model gave the relaxation parameter by which the surface–surface and surface–bulk bond enthalpies are modified. The layer compositions were found by minimizing the free energy.

The results for a few Pd-based systems are shown in Fig. 1. It may be noted that the top layer in the case of Pd–Ni and Pd–Pt are strongly enriched in Pd, while in the case of the Pd–Cu alloy the top layer is mildly enriched in Cu. The segregation behaviour shown in Fig. 1 is obtained from calculations done at some arbitrary concentrations and gives only a qualitative picture. Semi-quantitative results and other details may be obtained from Ref. [14]. For the Pd–Ni alloy, for example, the surface composition has been found to be in good agreement with our experimental results obtained from low

energy ion spectroscopy (LEIS) studies [16]. For all the surfaces of the Pd–Ni alloy, strong segregation of Pd to the top surface layer has been found both theoretically as well as experimentally. Segregation to the top layer may be predicted correctly by many other models such as the bond-breaking model and tight-binding models, etc. (see, for example, the articles in Ref. [17]); but with the equivalent medium approximation (EMA) used in the present calculation one can find the concentration profile in the top few layers. This model, for example, predicts for the Pd–Ni system some oscillation in the concentration profile in moving from surface to bulk. This has been experimentally corroborated by the work of Derry et al. [18] where for the (100) surface of a Pd<sub>50</sub>Ni<sub>50</sub> alloy, oscillation in concentration in the top three layers was found. The equivalent medium approximation (EMA) along with the modified tight-binding scheme in the second moment approximation helps one to describe the concentrations in the top few layers as a function of both the local concentration and the changing coordination. This is the advantage of the current model in predicting the surface segregation.

The segregation behaviour discussed above has important effects on the activation barrier for dissociation of molecules,  $E^*$ . In Table 1 the values of activation barrier for dissociation of CO, NO, H<sub>2</sub> and O<sub>2</sub> on the (111) surface of a few transition metals are presented.  $D_{AB}$  in Table 1 is the gas phase dissociation energy of a molecule. These values were obtained from the work of Shustorovich [11]. It may be mentioned here that Shustorovich's method of calculating the activation energies by using the bond-order conservation Morse potential (BOCMP) model

relies on the heat of adsorption of the relevant atomic and molecular species on the surface. In principle, these heats of adsorption depend on the adsorbate coverage. However, since for small coverage (coverage  $\theta \leq 0.25$ ) the heat of adsorption does not change appreciably, one may find almost the same value for the activation energy of dissociation at such coverages.

Now, since all the systems under consideration have an fcc structure, it is assumed that at low coverage the atoms and molecules are chemisorbed at central hollow sites having three-fold symmetry. To find the activation barrier for dissociation in alloys we use a simple assumption that the activation barrier for a reaction on the alloy would be a function of the surface composition of the alloy. For the Pd–Ni alloy, for example, we may write for the activation energy

$$E_{\text{al}}^* = X_{\text{s}}(\text{Pd}) E^*(\text{Pd}) + (1 - X_{\text{s}}(\text{Pd})) E^*(\text{Ni}) \quad (2)$$

where  $X_{\text{s}}(\text{Pd})$  is the Pd concentration on the surface. Eq. (2) considers, in effect, some kind of average effect of the alloy on the activation energy for dissociation. The results for the activation barrier for dissociation of some simple molecules like CO, NO, H<sub>2</sub> and O<sub>2</sub> as a function of bulk palladium concentration  $X$  in Pd–Ni, Pd–Pt and Pd–Cu are shown in Fig. 2. It may be noticed that Pd–Ni alloys offer a lower activation barrier for the dissociation of H<sub>2</sub> and CO. In the case of O<sub>2</sub> and NO dissociation, however, Pd–Ni alloys with a bulk palladium concentration  $< 0.15$  offer a lower activation barrier for dissociation and for  $X > 0.15$  Pd–Cu alloys show a lower barrier. It may be men-

Table 1

Activation barrier (in kJ/mol) for dissociation of CO, NO, H<sub>2</sub> and O<sub>2</sub> on the (111) surfaces of Pd, Ni, Pt and Cu

Molecule	Pd(111)	Ni(111)	Pt(111)	Cu(111)	$D_{\text{AB}}$
CO	210.8	140.3	227	213	1079
NO	38.2	–37.4	52.6	3.5	634
H <sub>2</sub>	9.2	6.4	13	30.7	437
O <sub>2</sub>	–47.5	–130.6	–40.3	–106	500

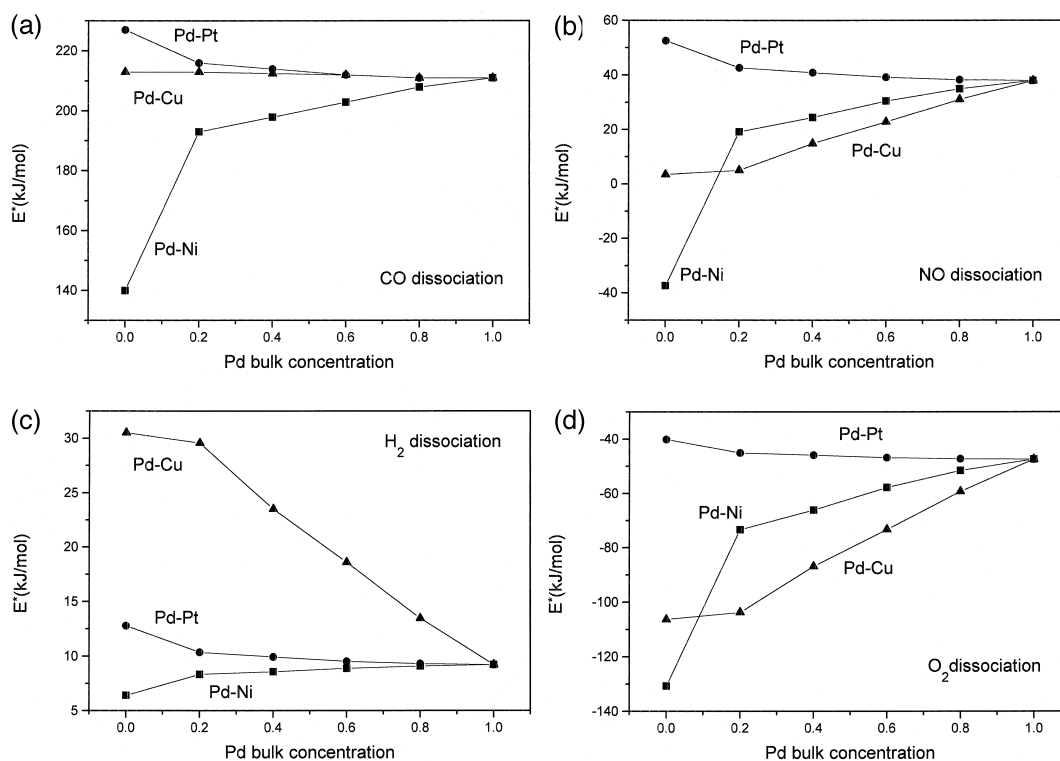


Fig. 2. Activation barrier for dissociation of a few diatomic molecule on Pd–Ni, Pd–Pt and Pd–Cu (111) alloy surfaces: (a) CO, (b) NO, (c) H<sub>2</sub> and (d) O<sub>2</sub> ( $T = 800$  K).

tioned that in the absence of surface segregation phenomena one could find only a linear variation of  $E_{al}^*$  with  $X$  for all the systems. From Fig. 2(a) for example, one can find that for CO on the Pd–Ni system  $E_{al}^*$  for  $X = 0.2$  is higher by almost 37.8 kJ/mol for the segregated alloy compared to the case if there is no segregation. In catalysis work this phenomenon can be gainfully utilized for selectively controlling the reaction paths to obtain desired products.

### 3. Activity of Pd–Ni(111) surface for CO hydrogenation to methanol

We consider here the CO hydrogenation on pure Pd and Ni metals and on a Pd–Ni alloy. The CO hydrogenation on the pure metals has been studied in the framework of the BOCMP model by Shustorovich et al. [9–12]. In the

present work we use their results to study the role of surface segregation on CO hydrogenation on the Pd–Ni (111) surface.

For the activity  $a$  of a Pd–Ni catalyst for CO hydrogenation we may write

$$a = \sum_i A p_i(X_s) \exp(-E_i^*/RT) \quad (3)$$

where  $A$  is a constant depending on the collision frequency of the gas–solid system.  $X_s$  is the Pd concentration at the surface.  $p_i(X_s)$  is a steric factor and is a function of the surface geometry of the system. It denotes the probability of finding a chemisorbed bond with  $i$  Pd and  $(3 - i)$  Ni nearest neighbours.

Usually,  $p_i(X_s)$  is given by the binomial distribution [19–21]

$$p_i(X_s) = \frac{3!}{i!(3-i)!} X_s^i (1 - X_s)^{3-i} \quad (4)$$

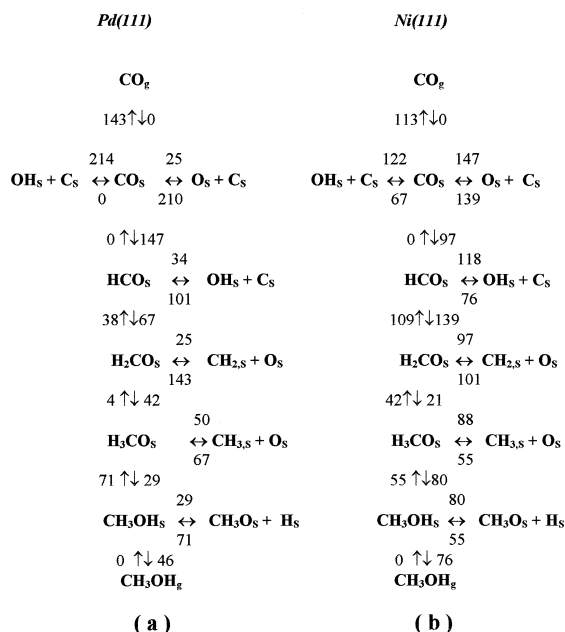


Fig. 3. Schematic reaction paths of CO hydrogenation with activation energies  $E^*$  (in kJ/mol); (a) on Pd(111), (b) on Ni(111) ( $T = 800$  K). The number below the symbol  $\leftrightarrow$  indicates the activation energy for forward reaction and the number above the symbol is the activation energy for backward reaction.

The number 3 comes into the picture since the adatoms are assumed to occupy the centre positions (sites with three-fold symmetry in the (111) surface of fcc lattice).

$E_i^*$  in Eq. (3) is the activation energy for catalytically active sites with  $i$ Pd and  $(3 - i)$ Ni atoms as nearest neighbours. In Eq. (3) the activation energy  $E_i^*$  for the rate-limiting step would be of real importance.  $E_i^*$  for various reaction steps may be calculated for  $i = 0, 1, 2$  and 3. For a reaction step involving chemisorption at a site with  $i$ Pd and  $(3 - i)$ Ni atoms we calculate the local activation barrier as

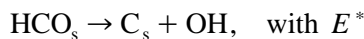
$$E_i^* = [iE_{\text{Pd}}^* + (3 - i)E_{\text{Ni}}^*] / 3 \quad (5)$$

The calculation of activity  $a$  is then straightforward. Now, there are several steps in the hydrogenation of CO to methane or methanol formation. The results are shown in Fig. 3. From Fig. 3 the following features may be noticed:

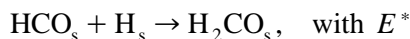
(1) CO is molecularly adsorbed on both Pd and Ni.

(2) Direct dissociation of  $\text{CO}_s$  is less probable on both Pd and Ni, and, rather,  $\text{HCO}_s$  formation is preferred on both the metals. However,  $\text{HCO}_s$  decomposes back to  $\text{H}_s + \text{CO}_s$  with zero activation barrier for both Pd and Ni.

(3) Some of the  $\text{HCO}_s$  undergoes two parallel reactions as



= 100.8 kJ/mol on Pd and 75.6 kJ/mol on Ni.



= 67.2 kJ/mol on Pd and 138.6 kJ/mol on Ni.

From the above values of  $E^*$  it is obvious that  $\text{HCO}_s$  would decompose on Ni but on Pd further hydrogenation of  $\text{HCO}_s$  is preferred.

(4) Since Pd segregates to the surface of the Pd–Ni alloy  $\text{HCO}_s$  hydrogenation becomes the more probable reaction path than the others.

(5) Furthermore, it may be noticed that on Pd the successive hydrogenation reactions to produce methanol requires a lower activation energy than that for the  $\text{HCO}_s$  hydrogenation. From this result we conclude that  $\text{HCO}_s$  hydrogenation is the rate-limiting step in the methanol formation on Pd–Ni(111) surface. We study therefore the activity of Pd–Ni(111) surface for this  $\text{HCO}_s$  hydrogenation reaction. The effect of segregation and local environment on the activity can also be estimated by studying this reaction.

In Fig. 4 we have shown the activity of the Pd–Ni alloys as a function of the bulk Pd

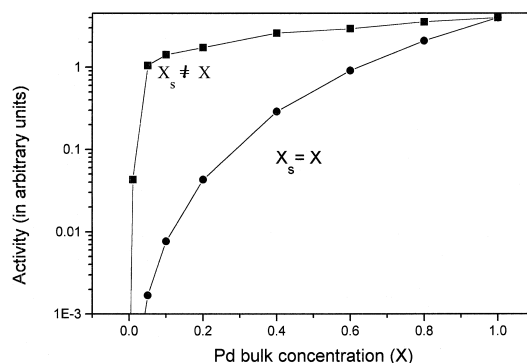


Fig. 4. Activity of Pd–Ni (111) surface for  $\text{HCO}_s$  hydrogenation as a function of Pd concentration in the bulk ( $T = 800$  K) ( $X_s$  is the Pd concentration on the surface).

concentration for the  $\text{HCO}_s$  hydrogenation reaction. We have compared the activity of the segregated alloy with that of the alloy if there is no segregation. It may be noticed that an addition of just 5 at% of Pd in the bulk Ni increases the activity by four orders of magnitude.  $\text{HCO}_s$  hydrogenation being the rate-limiting step in the CO-hydrogenation-to-methanol reaction, this increased activity due to segregation of Pd to the surface is highly significant.

In Fig. 5 we show the contribution of the  $i = 3$  and  $i = 2$  terms to the activity. It may be noticed that  $i = 3$  contributes most to the activity. For a typical concentration, say  $X = 0.1$ , the contribution of  $i = 0, 1, 2$  and  $3$  terms to the activity are  $0.23 \times 10^{-10}$ ,  $0.5 \times 10^{-8}$ ,  $0.49 \times 10^{-6}$  and  $1.37 \times 10^{-5}$ , respectively (in arbitrary unit). It is obvious, therefore, that the total activity curve is very close to the  $i = 3$  curve. This means that the most active centres for  $\text{HCO}_s$  hydrogenation (and hence CO hydrogenation to methanol) are the centre hollow sites having three Pd atoms as the nearest neighbours.

In Fig. 6 we compare the activity for parallel reactions  $\text{HCO}_s$  hydrogenation and  $\text{HCO}_s$  decomposition as a function of bulk Pd concentration. The two curves cross over Pd concentration  $X = 0.05$ . This means that just by adding approximately 5 at% of Pd in Ni would lead to

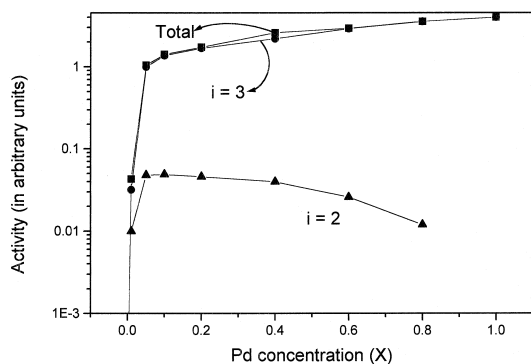


Fig. 5. Contribution of the  $i = 3$  and  $i = 2$  terms to the total activity of the Pd–Ni (111) surface for  $\text{HCO}_s$  hydrogenation, where  $i$  is the number of Pd nearest neighbours of an adsorbed  $\text{HCO}_s$  at the centre hollow site ( $T = 800$  K).

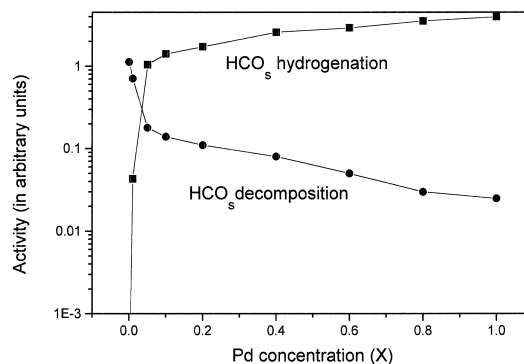


Fig. 6. Comparison of  $\text{HCO}_s$  hydrogenation and  $\text{HCO}_s$  decomposition as a function of bulk Pd concentration in Pd–Ni alloys ( $T = 800$  K).

greater  $\text{HCO}_s$  hydrogenation than  $\text{HCO}_s$  decomposition. In the absence of segregation this crossover point is found to shift to a much higher Pd concentration  $X = 0.55$ . The effect of segregation, therefore, is to enhance the activity of Pd–Ni alloys for CO hydrogenation to methanol at much lower Pd concentration in the bulk.

It is important to mention here that in the calculation of the activity of Pd–Ni alloys the Pd surface concentration of the clean alloys was used. Under realistic catalytic condition, however, it could be more appropriate to use the surface composition of the gas-covered surfaces. This is because of the fact that adsorption may change the segregation behaviour of a bimetallic alloy. However, in the absence of experimental results for coverage-dependent surface composition and the theoretical difficulties in the equivalent medium approximation to take into account the role of adsorbate coverage we have calculated the activities with clean alloy surface segregation. The effect of adsorbate coverage ( $\theta$ ) on the segregation behaviour, however, may be roughly estimated from a semi-empirical formalism where the Pd surface concentration  $X_s$  is expressed as [22]

$$\frac{X_s}{1 - X_s} = \frac{X}{1 - X} \exp\left(\frac{Q_{cs}}{RT}\right) \quad (6)$$

where  $X$  is the bulk Pd concentration and  $Q_{cs}$  is the heat of segregation in the chemisorbed state (i.e. the work involved in exchanging a surface Pd atom with a bulk Ni atom). This  $Q_{cs}$  may be further expressed as  $Q_{cs} = Q_s + \theta(Q_{Pd} - Q_{Ni})$ , where  $Q_s$  is the heat of segregation of Pd in a clean Pd–Ni alloy and  $Q_{Pd}$  and  $Q_{Ni}$  are the heats of adsorption of an adsorbate on Pd and Ni, respectively. Of the reactants important in this work, hydrogen has almost the same heat of adsorption on Pd and on Ni and, therefore, the segregation behaviour does not change (i.e.  $Q_{cs} = Q_s$ ). In the presence of adsorbed CO, however,  $Q_{cs} \neq Q_s$  since  $Q_{Pd} - Q_{Ni} = 25$  kJ/mol [22]. For the low coverage regime with  $\theta = 0.25$  (say) the heat of segregation is 23 kJ/mol compared to the clean alloy value of 16 kJ/mol. Thus, for CO hydrogenation on the Pd–Ni alloy the effect of CO coverage is to lead to more Pd segregation. This, in turn, would make the reactivity curves shown in Figs. 4–6 slightly more surface concentration sensitive. However, qualitatively the results would be similar to those as shown in the Figs. 4–6.

It is also important to mention here that the present calculation attempts to understand the activity of Pd–Ni alloys towards the CO hydrogenation to methanol on the basis of one reaction step, arguably the rate-limiting step. In a realistic situation, however, there may be several reaction steps which together give an apparent or global activation energy for the system. In experiment, it is always this apparent activation energy which is found. Therefore, we have not directly compared the results obtained in the present model calculation with the experimentally observed results.

#### 4. Conclusions

We have used a simple model to study the activation barrier for dissociation of some simple diatomic molecules on Pd-based alloys. We find that the segregation properties of alloys affect the activation barrier for dissociation.

Assuming that  $HCO_s$  hydrogenation is the rate-limiting step in the methanol synthesis on Pd catalyst we find that there exists a critical bulk concentration of Pd in Pd–Ni above which hydrogenation of  $HCO_s$  to  $H_2CO_s$  is favoured and below which  $HCO_s$  decomposition is favoured. In presence of segregation this concentration is  $X = 0.05$ , while in absence of segregation this concentration is  $X = 0.55$ . This indicates segregation behaviour of Pd in Ni will minimise the use of Pd in methanol synthesis. The most active sites for methanol formation are the three-fold hollow sites with three Pd atoms as nearest neighbours of adsorbed  $HCO_s$ .

#### Acknowledgements

The authors gratefully acknowledge partial financial support from the Indo-French Centre for the Promotion of Advanced Research under Project No. 806-2.

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