Brazilian Journal of Chemical Engineering

ISSN 0104-6632
Printed in Brazil

Vol. 19, No. 02, pp. 187 - 194, April - June 2002

1,3-BUTADIENE HYDROGENATION ON Pd-SUPPORTED SYSTEMS: GEOMETRIC EFFECTS

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(Received: July 11, 2001 ; Accepted: April 3, 2002)

Abstract - A strong metal support interaction (SMSI) effect was observed on Pd/Nb_2O_5 and Pd/TiO_2 catalysts, and it produces small, exposed Pd ensembles. A decrease in the *trans*/*cis* 2-butene ratio was observed after reduction at 773 K. Selectivity changes were ascribed to the decoration model. Theoretical models were developed based on semi-empirical molecular-orbital calculations for 1,3-butadiene and Pd_n clusters. Experimental results are in agreement with our theoretical model, which proposes a greater stabilization of the *cisoid* intermediate on small Pd ensembles.
Keywords: catalysis, molecular modeling, hydrogenation.

INTRODUCTION

The existence of electronic and geometric effects in metallic and bimetallic catalyst systems which present Strong Metal Support Interaction (SMSI) phenomena has been proposed in the literature since the seventies (Haller and Resasco, 1989). Difficulties in characterizing the ensemble under reaction conditions have led some groups to choose between these effects, but explanations of catalytic results for both effects are also common in the literature (Noronha et al., 1991; Aranda and Schmal, 1997). The main difficulty appears to be the fact that the supported metal ensembles are not known, thus requiring a good model for the metallic clusters.

Studies performed under ultra-high vacuum have shown that different crystal planes in single crystal systems can have a remarkable effect on catalytic properties (Niemantsverdriet and Ribeiro, 2000). For 1,3-butadiene hydrogenation on a Pd surface, (110) open planes showed a higher activity than an arrangement composed of (111) closed planes (Michel et al., 1998; Hermann et al., 1997).

Theoretical models have been applied to Pd and Pd-Ni clusters (Hermann et al., 1996; Borszeky et al., 1996). The bimetallic systems presented fewer delocalized electrons due to the isolation of metallic atoms. Donation of butadiene *p* electrons decreased and back-bonding increased. This behavior produced a decrease in the energy of adsorption, resulting in a higher level of catalytic activity as compared to the Pd system.

Although this model offers an explanation of some bimetallic effects, there are many other effects in real systems which have not as yet been explained. The existence of a large number of sites, the structure of the metal clusters and also the surface dynamics under real conditions cannot be accounted for. In spite of this, the effort to relate experimental and theoretical results can contribute to an

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understanding of surface phenomena.

The hydrogenation of 1,3-butadiene has been experimentally studied over a large range of systems (Porte et al., 1999; Boitiaux et al., 1989). Pd catalysts have high selectivity for butenes and low selectivity for butane formation. This behavior has been attributed to the preferential adsorption of diene in comparison to butene. The *trans*/*cis* ratio is also sensitive to active sites. Upon addition of electron-donating or electron-withdrawing compounds to 1,3-butadiene, it was observed (Boitiaux et al., 1983) that the electron-donating compounds increased the *trans*/*cis* ratio and the electron-withdrawing compounds decreased it. Supported Pd-Cu catalysts showed (Pereira et al., 1993) comparable results. When compared to supported Pd catalysts, no butane was observed and the *trans*/*cis* butene ratio increased. In this study, the size of the palladium ensemble on the surface was on the order of two atoms. These results are in agreement with results obtained with a theoretical model for small Pd clusters (1 - 3 atoms).

However, there are some experimental problems with obtaining a good correlation between the increase in electron density on Pd atoms due to the presence of Cu and a real ensemble. These difficulties are also present in SMSI systems.

The commonly used electronic and geometric effects cannot necessarily be separated. In some cases a direct relationship between electronic properties and the ensemble arrangement, i.e., the structure of the metal clusters, can be proposed.

The main objective of this work is to verify by quantum mechanics calculations the effect of small Pd clusters on the stability of the products of 1,3-butadiene hydrogenation adsorbed on the surface and correlate it with the effect of experimental palladium catalysts.

METHODOLOGY

Theoretical Calculations

The semi-empirical PM3 method (Stewart, 1989) was used for structure optimization and energy calculation for palladium clusters and for the complexes between them and the *cisoid* and *transoid* isomers of 1,3-butadiene. The parameters for those transition metals are based exclusively on experimental information related to their structures. The package used in this part of the work was the PC SPARTAN PLUS commercial package. This software has been successfully used in the simulation of CO adsorption on metallic surfaces as compared to experimental data (Zakharian and Coon, 2001).

The adsorption energies were calculated by the following equation:

$$E_{ADS} = E_{BUT/Pd} - (E_{BUT} + E_{Pd})$$

where E_{ADS} is the adsorption energy, $E_{BUT/Pd}$ is the formation energy of the complex involving the butadiene molecule (*cis* or *trans* arrangement) and the palladium cluster, and E_{BUT} and E_{Pd} are the individual energy of butadiene and the palladium cluster, respectively. As can be easily observed, the negative values for E_{ADS} mean that the corresponding complexes are more stable than the separated species (Sarkany, 1997; Sarkany et al., 1995).

Catalysts

Al_2O_3 (Degussa), Nb_2O_5 and TiO_2 were used as supports. Al_2O_3 was calcined in air at 823K for 16h (BET area = 180 m^2/g). Nb_2O_5 was prepared by calcination of niobic acid (CBMM) as described for alumina.

Pd/Al_2O_3, Pd/Nb_2O_5 and Pd/TiO_2 samples were obtained by incipient-wetness impregnation of Al_2O_3, Nb_2O_5 and TiO_2, respectively, with a hydrochloric solution of $PdCl_2$. Then the samples were dried at 373K for 16h, followed by calcination under air flow at 773K for 2h. The amount of palladium in the catalysts was 1% (w/w).

H_2 Chemisorption

The chemisorption uptakes were measured in an ASAP (Micrometrics) apparatus. Prior to reduction, the catalysts were dehydrated at 423K for 0.5 h. Then the catalysts were reduced at 773K (5K/min.) in flowing H_2 (30 cm^3/min.). Following reduction, the samples were evacuated for 1h at the reduction temperature and cooled to the adsorption temperature under vacuum. Irreversible hydrogen uptakes were determined from dual isotherms measured at 343K.

Catalytic Test

The 1,3-butadiene was hydrogenated in a flow microreactor at atmospheric pressure and 298 K. The catalyst (typically 20-50 mg) was mixed with quartz as the diluent (100 mg) and then dried with flowing hydrogen at 573 or 773 K. The reaction mixture consisted of 1,3-butadiene/hydrogen/nitrogen (10:10:80). Reaction conditions which would keep conversion below 12 % were established so there

were no transport limitations on the rate. The reaction products were analyzed by an on-line gas chromatograph with a 19% picric acid 80/100 Carbopack C/0 column at 313 K.

RESULTS AND DISCUSSION

The starting structures for the complexes between butadiene and palladium clusters were based on the respective complexes of ethylene on palladium clusters (Kragten et al., 1999). In the ethylene complexes there are two types of fundamental interactions, resulting respectively in the π and σ complexes. In the first case, the interaction occurs between the two carbon atoms and one palladium atom. In the second case, the interaction occurs between one carbon atom and one palladium atom. For the ethylene palladium complexes, the electron density between the two palladium atom, reduces as the ethylene molecules approach the metallic cluster. In contrast, the electron density between the carbon atom and the palladium atom increases. This means that as the Pd-Pd bond becomes weaker, the C-Pd bond becomes stronger. As a consequence, the Pd-Pd bond should dissociate completely when the ethylene molecule is near enough to the palladium cluster. Figure 1 shows the potential energy surface for the interaction between one ethylene molecule and the Pd dimer. Figure 2 gives the corresponding structures. This clearly shows the dissociation of the Pd-Pd bond as the ethylene molecule approaches the palladium cluster. The energies of the three stationary points – 1, 2 and 3 – are lower than the energy of the unadsorbed species. However, the 15 kcal/mol energy barrier separating the two complexes should represent a hindrance to their interconversion. Thus, although the breakdown of the Pd-Pd bond would be possible, it does not seem feasible, since the mechanisms involving activation of the C-H bond should have a smaller energy barrier, as observed experimentally (Boitiaux et al., 1983). The most relevant result is that structure 3, with the ethylene molecule bonded to two isolated palladium atoms, is 21 kcal/mol more stable than the complex between ethylene and the palladium dimer (1). Based on these results, one should anticipate similar behavior in the case of the butadiene palladium complexes.

In order to understand the adsorption of butadiene on palladium, we undertake a systematic study of the complexes formed by association of a butadiene molecule with one palladium atom as well as with palladium clusters of two and three atoms. The structures of these complexes are given in figures 3 and 4. Fully optimized geometries and adsorption energies are given in Table 1.

The first point to highlight is the difference in energy between the two butadiene isomers, which is on the order of 1kcal/mol with the PM3 method for the isolated species and becomes larger when the butadiene molecule is associated with the Pd_n system.

The complex between butadiene and one palladium atom is necessarily of the π type, similar to the ethylene palladium complex in a 1:1 ratio (Boitiaux et al., 1983). In this case, the complex with the *trans* isomer is 7 kcal/mol more stable than the complex with the *cis* isomer, both in the singlet state. For the complex between the butadiene and the palladium dimer there are three possible structures, a σ complex involving all the dimer, a π complex involving only one palladium atom and a double bond and finally a π complex involving the two palladium atoms and the two double bonds (structures 5, 6 and 7 in Figure 3). Comparison of the adsorption energies for these three complexes (Table 1) indicates that the third is the most stable. This result agrees with a recent publication relating calculations with the EHT method (Porte et al., 1999). Also, in this case the complex formed by the *trans* isomer is 4 kcal/mol more stable than that formed by the *cis* isomer.

There are several possibilities for complexation between butadiene and the palladium trimer, Pd_3. However, they can be described in a way similar to that used to describe the palladium dimer. Therefore, there are two types of σ complexes and three types of π complexes (Fig. 3). The data in Table 1 show that the π-type complexes involving the two double bonds are always more stable than the σ-type complex involving only one or even the two double bonds. Analysis of the π complexes involving the two double bonds again indicates that the stability of the *trans* isomer is 4 kcal/mol higher than that of the *cis* isomer, which is essentially the same difference in energy as that calculated for the equivalent complex with the Pd_2 dimer.

A clear trend was observed throughout the calculations; the *cis* isomer tends to increase the distance between the palladium atoms, in some cases completely breaking down the Pd-Pd bond. Thus, similarly to the ethylene-palladium complex, this created alternative structures with at least one dissociated Pd-Pd bond. Indeed, due to the high stability of these structures compared to the corresponding ones given in Table 1, it can be

assumed that the *cis* isomer of butadiene would be preferentially adsorbed on clusters with isolated palladium atoms. The Pd-Pd distance calculated in these situations is of about 360 pm. To validate this hypothesis, we analyzed the energies of the 13-*CIS* and 13-*TRANS* structures, given in Figure 4. These species are *cisoid* and *transoid*-butadiene complexed with two palladium atoms formally dissociated. The PM3 energy for these species is lower than the energy for the corresponding complexes with the palladium dimer. The energy of both 13 and 14 however, is reduced in a dissimilar way. While the reduction in the energy of the *trans* isomer is of 39 kcal/mol, the reduction in the energy of the *cis* isomer is of 41kcal/mol. Although this difference is not too large, it seems to indicate that the *cis* isomer acquires a stability nearer to that of the *trans* isomer when butadiene is adsorbed on surfaces with a high degree of dispersion, as is the case for palladium.

The results in Table 2 show the behavior of catalysts under conditions favorable (reduction at 773K) or unfavorable (reduction at 573K) to the formation of SMSI. One can observe that different reduction temperatures could not induce significant changes in the *trans*/*cis* ratio for the Pd/Al_2O_3 catalyst. On the other hand, there is a tendency of decrease the *trans*/*cis* ratio for Pd/Nb_2O_5 and Pd/TiO_2 catalysts reduced at 773 K.

According to the literature, the "decoration model", which proposes the dilution of metallic particles by suboxide species from the support, is the model most commonly used to explain the SMSI phenomena (Haller and Resasco, 1989). In addition, Table 2 shows large decrease in the amount of adsorbed hydrogen after increasing the reduction temperature. If hydrogen adsorption is considered to be stoichiometric on the metallic surface, one can observe a decrease of around two thirds of the active sites after reduction at 773 K. This effect can be ascribed to the migration of suboxide species to the metallic ensembles. As a result, very small metallic clusters are exposed on the surface. In fact, more isolated metallic sites have also been ascribed to explain the large decrease in selectivity for hydrogenolysis of hydrocarbons (Ribeiro et al., 1997). Thus, the cluster calculations performed for 1-3 palladium atoms could be applied as an approximation. Therefore, by using this model, one can explain the lower *trans*/*cis* 2-butene ratios observed on Pd/niobia and Pd/titania after reduction at 773 K using only geometric arguments: the relative increase in the *cisoid* intermediate stability on neighboring isolated palladium atoms (complexes 13 and 14) as produced by the migration of NO_x or NbO_x suboxide species in agreement with the decoration model.

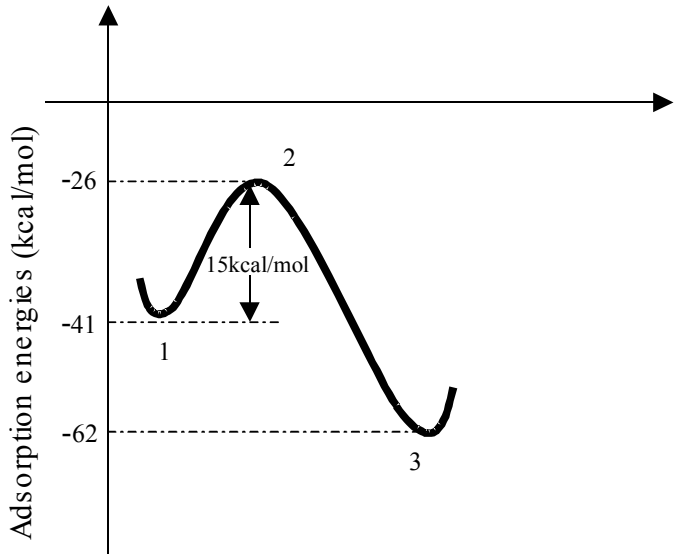

Figure 1: PM3 adsorption energies of 1, 2 and 3 species.

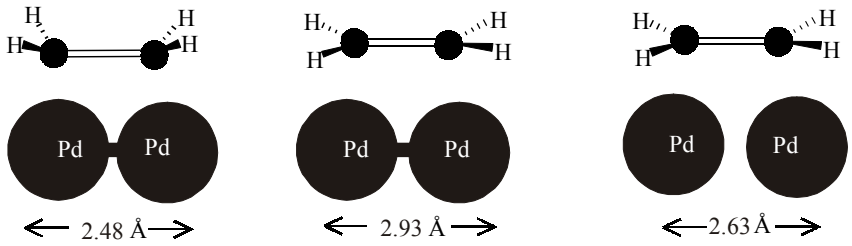

Figure 2: butadiene-Pd_2 π complexes.

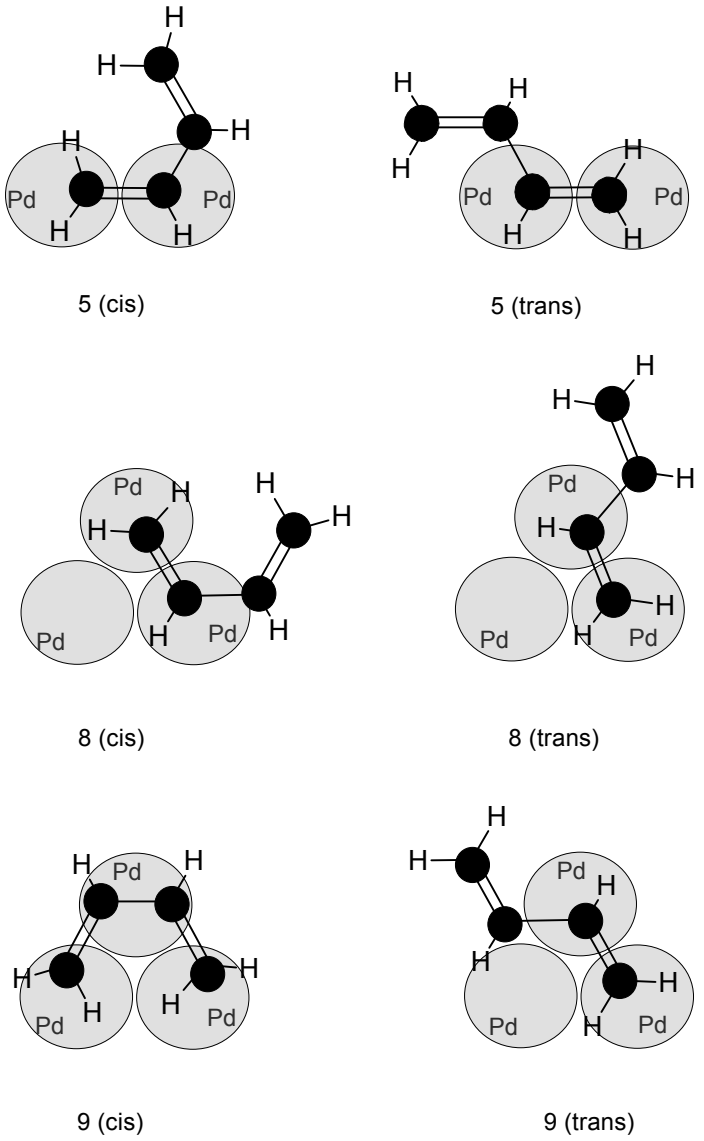

Figure 3: butadiene-Pd_2 and butadiene-Pd_3 σ complexes

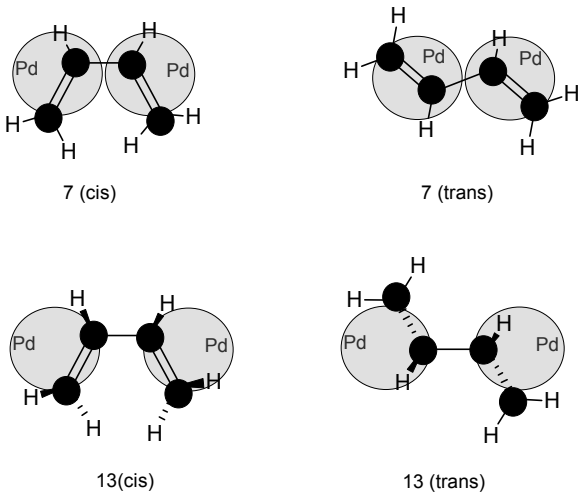

Figure 4: The *cis* and *trans* butadiene isomers adsorbed on Pd_2 dimer (7) and on two isolated Pd atoms (13), respectively.

Table 1: Adsorption energies (kcal/mol) of the butadiene-Pd_n complexes

n	Species	Complex type[1]	*Cis*		*Trans*	
			singlet	triplet	singlet	triplet
1	4	π	-15	-15	-22	-4
2	5	σ	-52	-38	-49	-46
	6	π/1double	-47	-34	-46	-34
	7	π/2double	-57	-50	-61	-44
3	8	σ/1double	-61	-51	-61	-65
	9	σ/2double	-58	-35	-62	-72
	10	π/1double	-54	-35	-52	-----
	11	π/2doubleA	-70	-61	-76	-59
	12	π/2doubleB	-72	-61	"	"

1 Including the number of double bonds involved in formation of the complex.

Table 2: Adsorption, activity and selectivity in 1,3-butadiene hydrogenation.

Catalysts	Chemisorption μmolH_2/gcat	TOF (s^{-1})	T/C(2-butenes)
Pd/niobia reduced at 573K	2.08	5.97	6.6
Pd/niobia reduced at 773K	0.62	0.23	3.5
Pd/titania reduced at 573K	1.82	11.85	5.8
Pd/titania reduced at 773K	0.55	1.17	4.7
Pd/alumina reduced at 573K	2.41	1.47	5.6
Pd/alumina reduced at 773K	2.35	1.64	5.4

CONCLUSIONS

Theoretical calculations have shown that a *cisoid* butadiene intermediate adsorbed on isolated palladium atoms is more stable than that absorbed on metallic dimers or trimers, which is ascribed to the experimentally observed *trans*/*cis* 2-butene ratio.

Pd/TiO_2 and Pd/Nb_2O_5 catalysts reduced at 773 K had a typical SMSI effect, observed as a large decrease in H_2 chemisorption. In addition, a lower *trans*/*cis* ratio was observed on these samples during catalytic tests. Thus, the selectivity on niobia and titania catalysts can be tentatively explained using only the decoration model, which proposes a final configuration of small, isolated, exposed metallic clusters on the catalyst surface.

These results provide a critical view of hydrogenation of 1,3-butadiene as a sensitive reaction to evaluate electronic effects on metallic catalysts since product distribution can be influenced by geometric effects.

ACKNOWLEDGEMENTS

This work was supported by the following Brazilian agencies: PRONEX, PADCT, FNDCT, CNPq, CAPES, ANP, FAPERJ and FUJB. The authors would like to thank NUCAT (COPPE/UFRJ) for the use of its facilities.

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