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Pyroglutamic acid as a chiral auxiliary in the diastereoselective hydrogenation of disubstituted aromatic rings on Rh(111): a periodic density functional theory approach

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Abstract

In the present work, the role of the pyroglutamic acid as a chiral auxiliary in the hydrogenation of *o*-toluic acid and 2-methylnicotinic acid on the Rh(111) surface has been investigated by using periodical density functional theory. The pyroglutamic acid, indeed, allows the adsorption of the aromatic ring by only one side of the ring plane. This effect is observed for both molecules. In the case of the benzoyl ring, the selectivity should be high on a perfectly flat metallic surface. It is, however, limited in practice by the presence of edges, especially in the case of small catalytic particles. On the other hand, in the case of a nicotinyl ring, the presence of a lone pair of the nitrogen atom has a great influence on the reduction of the diastereomeric excess. The NH group, formed from the partial hydrogenation of the nicotinyl ring, interacts strongly with the surface, preventing the influence of the chiral auxiliary.

Keywords: Chiral auxiliary; Diastereoselective hydrogenation; Rh(111); DFT

1. Introduction

Enantioselective catalysis is of great interest for the pharmaceutical and agrochemical industry. Usually such asymmetric synthesis is attained by soluble metal complexes. This efficient process has, however, a major drawback, which is the difficult separation of the catalyst from the reactant/products in the main stream.

The development of enantioselective heterogeneous catalysts has been receiving a great deal of attention in the past years. Starting from Orito's discovery in 1979 [1], in which for the first time a chiral hydrogenation (of α-ketoesters) has been obtained by the addition of cinchona alkaloids in reaction medium, several different strategies have been employed to develop new heterogeneous catalysts for chiral synthesis.

Some of them follow Orito's original idea, i.e., to modify the catalytic surface by adsorbing chiral modifiers. Cinchonidine derivatives [2–7] or even larger chiral molecules [8–10] have been tested with relative success. The desired enantioselectivity originates from the interaction between modifier and reactant, which allows only one reaction channel that leads to the enantiomer.

In some cases, the chiral molecule has been shown to create chiral domains on the catalytic surface, under specific conditions of temperature and coverage. Examples are bitartaric acid [11–14], alamine [15] on Cu and Ni surfaces, and in the study of adsorption of 2-bromohexadenoic acid on graphite [16]. In these cases each of the different optical isomer of the modifier creates its own chiral assembly, being a mirror image of the other isomer assembly. The enantioselectivity of the reaction is obtained because specific chiral points are formed on the surface, where the reactant adsorbs and reacts, again toward the desired product.

Chiral metal surfaces can be formed without adsorbing chiral molecules. The main idea is to use specific kinked sites of single crystals that are chiral. An example of such a kinked chiral substrate is the {643} surface of a fcc crystal. The decomposition of *R*- and *S*-2-butanol on Ag(643) [17] and the electro-oxidation of D- and L-glucose on Pt(643) [18,19] are just few examples of such an approach.

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The aim of these techniques is to create (in case of kinked surfaces) or induce (adsorbing modifiers) a chiral character on the metallic surface. The mechanisms of the chiral induction and of the reaction in these new chiral sites are, however, under continuous investigation.

In a different approach, chiral induction for heterogeneous catalytic systems may be simplified by modifying the reactant molecule and not the catalytic surface. This strategy consists of coupling a prochiral reactant with chiral auxiliaries (chirons). The advantage of this method is that chirality of the product could be inverted by changing the configuration of the auxiliary without modifying the catalyst [20,22].

One recent application of this idea is the hydrogenation of disubstituted aromatics into the corresponding cyclohexyl derivatives. The reactant (*o*-toluic acid) is coupled with a chiral auxiliary (pyroglutamates). For instance, the hydrogenation of the (*S*)-methyl *N*-(2-methylbenzoyl)pyroglutamate on Rh/C or Rh/Al_2O_3 (achiral catalysts) results in a diastereoselectivity of more than 70% [20].

In the present work this novel strategy has been investigated at a molecular level by applying first principle periodic calculations. For the first time some insights about the interaction of the modified molecules *N*-(2-methylbenzoyl) pyroglutamic acid and (2-methylnicotinyl)pyroglutamic acid with the Rh(111) surface are given and the influence of this interaction on the enantioselectivity of the hydrogenation reaction is discussed.

2. Methods and model systems

In the work reported here all calculations were performed using the Vienna Ab Initio Simulation Package (VASP) [23,24]. This code carries out periodic density functional calculations (DFT) using pseudopotentials and a plane wave basis set. DFT was parameterized in the local-density approximation (LDA), with the exchange-correlation functional proposed by Perdew and Zunger [25] and corrected for nonlocality in the generalized gradient approximations (GGA) using the Perdew–Wang 91 functional [26]. The interaction between the core and electrons is described using the ultrasoft pseudopotentials introduced by Vanderbilt [27] and provided by Kresse and Hafner [28].

In the calculations performed here the Rh(111) surface is modeled by a periodic three-layer slab with the adsorbate placed on one side of the slab. The choice of a limited number of metallic layers in the model is imposed by the large size of the molecule. A test has been performed; the adsorption mode of *N*-(2-methylbenzoyl)pyroglutamic acid that gives the lowest adsorption energy has been calculated using three and five metal layer slabs. The energy difference between these two calculations is only 6 kJ/mol; thus a three-layer slab brings a reasonable convergence in the adsorption energies, especially in the relative energies between different adsorption structures. One slab is separated from its periodic image in the *z* direction by a vacuum space, which is equivalent to 7 metallic layers. All atoms have been maintained free in all optimizations.

In order to reduce the effect of the stress that occurs due to the use of a slab model, an optimal bulk Rh–Rh distance was used [29]. This optimized value of 2.72 Å is in good agreement with the experimental Rh–Rh bulk distance of 2.69 Å [30].

All molecules have been ordered on the surface in the following structure: (4×4) 1/16 ML, which corresponds to 16 metallic atoms per metal layer and one substrate molecule in the unit cell. This large unit cell was used to prevent lateral interactions between the periodic images of the molecule. All calculations have been performed at the Γ point of the Brillouin zone, which is adequate due to the large size of the unit cell.

3. Results and discussion

3.1. *N*-(2-Methylbenzoyl)pyroglutamic acid adsorption

The substrate *N*-(2-methylbenzoyl)pyroglutamic acid (pyro) has four possible conformations in the gas phase. The two most stable conformations are shown in the Figs. 1A and 1B. The main difference between these structures is the

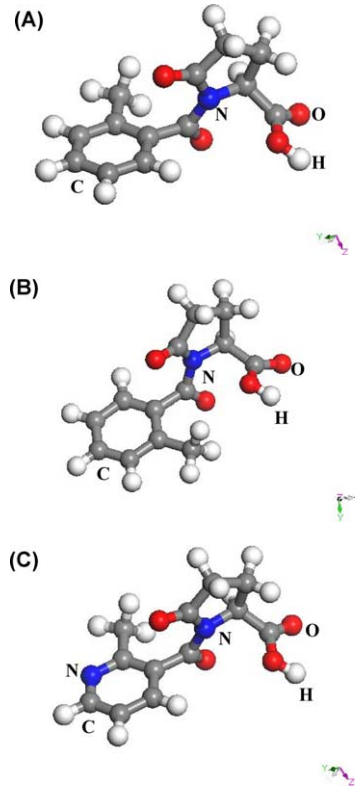

Fig. 1. Different stable conformers of aromatic substrates: (A) conformer 1, (2-methylbenzoyl)pyroglutamic acid; (B) conformer 2, (2-methylbenzoyl)pyroglutamic acid; and (C) conformer 1, (2-methylnicotinyl)pyroglutamic acid.

position of the acid and methyl groups with respect to the pyroglutamic ring plane.

Conformer 1 (Fig. 1A) is the most stable configuration. The energy difference between these two isomers (conformers 1 and 2) is very subtle: 1 kJ/mol. Previously, the same trend has been noted with force-field calculations [20]. The barrier for interconversion between conformers 1 and 2 is very large (more than 1000 kJ/mol) [21], due to the steric hindrance between the methyl group and the oxygen atom. The other two isomers of this molecule can be obtained by rotation of the amide bond (C–N) in both isomers 1 and 2, respectively. This rotation barrier was evaluated to be about 210 kJ/mol [21]. Moreover, X-ray analysis and H NMR spectrum at 278 K of the (*S*)-methyl-*N*-(2-methylbenzoyl)pyroglutamate, which is the methyl ester of pyro, indicated just one structure for this compound that is very close to conformer 1 [21].

With such a structure the molecule presents a different accessibility for adsorption on the two different sides of the benzene ring. In Fig. 1A, the upper side is more hindered than the lower side.

Adsorbing this most stable conformation of the substrate on the Rh(111) surface, three different structures have been revealed by the calculations. In the first one (position A, Fig. 2A) the aromatic ring interacts with the surface from its lower face and has a parallel orientation to the surface plane.

Experimentally it was shown that benzene chemisorbs parallel to the Rh(111) surface occupying a 3-fold site [31]. In the Ni(111) surface the same adsorption geometry has been found by DFT calculations [32]. The aromatic ring of pyro is slightly displaced from the 3-fold position (see Fig. 2A) and the C=C bonds are elongated by 0.05 Å, in average, compared to the gas-phase structure (see Table 1). This elongation is in agreement with the results reported for benzene on Ni(111) [32]. The geometric deviation from the 3-fold position is due to the extra interaction of the C=O of the amide group with the surface (Fig. 2A). The molecule translates along the surface to reach a top position for the oxygen atom. This interaction can be also seen by the change of the C=O bond length in the amide group, elongated by 0.04 Å from the gas-phase value, and by the change of the dihedral angle (D) between both rings, which decreases from 71° (gas phase) to 44°.

In the second position the pyroglutamic ring interacts with the surface via oxygen atoms (position B, Fig. 2B). The strongest interaction for these oxygen atoms is from the C=O of the pyroglutamic acid ring, which lays parallel to the surface and suffers a large elongation (0.14 Å), see in Table 1 the entry for pyroglutamic ring and the oxygen atom O_2 in Fig. 2B. The other strong interaction is from the C=O of the amide group, bond length of which increases by 0.03 Å. The aromatic ring stands up off the surface. There is no activation of the C=C bonds of the ring (see Table 1); therefore, it is clear that this adsorption mode will not lead to the desired hydrogenation reaction. However, this configuration may be the starting point for the hydrolysis reaction of the amide bond, which has been observed to occur experimentally [20].

Table 1
Geometric results for the adsorption positions of the (2-methylbenzoyl)-pyroglutamic acid

Adsorption mode	$\bar{d}$(C=C)	$\bar{d}$(Ar–surf)	$\bar{d}$(C=O)	D
Conformer 1				
Gas phase	1.40	–	1.23	71.4
Position A	1.45	2.2	1.27	71.4
Position B	1.40	–	Amide: 1.26	62.4
		–	Pyroglutamic ring: 1.37	
		–	Acid group: 1.23	
Position C	1.40	4.6	Amide: 1.23	64.8
			Pyroglutamic ring: 1.23	

Values in Å and degrees. $\bar{d}$(Ar–surf) = average distance between the aromatic ring and the surface. D = dihedral angle between the aromatic and pyroglutamic rings.

The last position is similar to position A. The aromatic ring is parallel to the surface plane but facing its other side ("concave" side—the previously noted "upper side" of the molecule) to the surface (position C, Fig. 2C). Because this is the bulky side of the molecule, the interaction with the surface is much different and only the oxygen atom of the C=O group of the pyroglutamic ring interacts with the surface. The C=O bond is not activated, meaning a very weak interaction. This can also be observed by the large distance between the aromatic ring and the Rh(111) surface (about 4 Å) and also the unmodified values for the C=C bonds (see Table 1). The latter results show the influence of the chiral auxiliary (pyroglutamic acid), which favors only one possible adsorption mode for the aromatic ring.

A more precise view of this effect is shown in the Table 2, in which the adsorption energies of the three modes are displayed. For position A this value is about 95 kJ/mol, whereas it is only 13 kJ/mol for position C. Adsorption by the aromatic ring on a specific side is, indeed, clearly favorable, in total agreement with the simple steric argument. The calculations additionally show that adsorption by the auxiliary (position B) is also markedly less stable than adsorption by the aromatic ring.

Table 2
Adsorption energies for all adsorption modes on the Rh(111) surface

Adsorption mode	Adsorption energy (kJ/mol)
(2-Methylbenzoyl)pyroglutamic acid	
Position A	95
Position B	22
Position C	13
Cyclohexenic product—position A	38
(2-Methylnicotinyl)pyroglutamic acid	
Position A	61
Position C	19
Position D	36
Enamine product—position A	28
Enamine product—position D	79

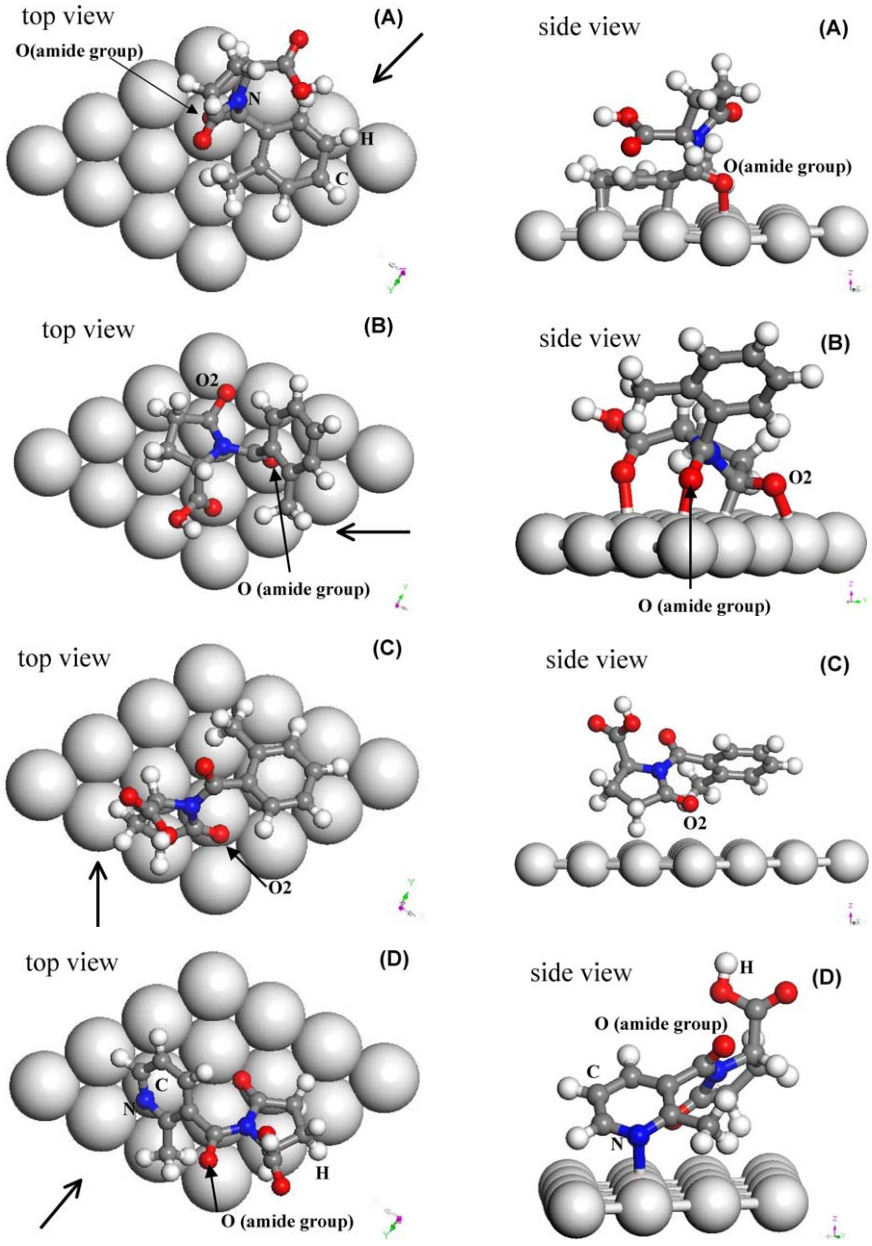

Fig. 2. Different adsorption modes of conformer 1 of (2-methylbenzoyl)pyroglutamic acid. The surface unit cell is shown. (A) Position A—adsorption via aromatic ring (parallel to the surface plane): "convex" side of the molecule. (B) Position B—absorption via pyroglutamic acid. (C) Position C—adsorption via the other side of the aromatic ring plane: "concave" side of the molecule. (D) Position D—adsorption via the lone pair of the nitrogen atom of the nicotinyl ring.

Another interesting point can be observed from the optimized structure of the position C. The acid group of the pyroglutamic acid does not add any steric hindrance for the chiral auxiliary, because this group stands up far from the surface. This explains why the nature of the ester group in the chiral auxiliary has only a small effect on the diastereoselectivity of the asymmetric hydrogenation of (*S*)-alkyl-*N*-(2-methylbenzoyl)pyroglutamates [20]. The acid group can hence be also viewed as a model for ester groups.

In the latter hydrogenation reaction four different cyclohexane diasteroisomers can be formed: two *cis* and two *trans* (see Ref. [20]), being the *cis* product being formed in high probability. The diastereomeric excess (*de*) of the reaction is defined as the normalized concentration difference between these two *cis* isomers.

Although the hydrogenation reaction of the substrate was not explicitly studied here, it is possible to understand the diastereomeric excess found experimentally.

The aromatic hydrogenation on metallic surfaces can be described by two different mechanisms [34]. In the first one a planar π-complex undergoes a step by step hydrogenation via a successive σ-bonded partially hydrogenated intermediaries, while in the other mechanism the aromatic ring is

hydrogenated in one single step. Both mechanisms assume that the molecular hydrogen has been dissociated and hydrogen atoms are present on the surface. The first mechanism is predominant at a low molar ratio of the aromatic ring.

Regardless of the mechanism, position A, which is the most favorable on the (111) surface, would lead to only one *cis* stereoisomer, in agreement with the experiments, and thus a high *de*. Indeed the favored *cis* product corresponds to the one obtained from Fig. 2A by transferring 6 hydrogen atoms from the surface.

Real catalysts are, however, formed of particles with various sizes and shapes. It is clear that the difference between these calculated adsorption energies will be strongly modified if the adsorption site is not on a flat terrace but at an edge or a corner of a particle. Such edges could favor the adsorption of the molecule by the "concave" side, hence stabilize position C. Such argument has been already proposed [20] in order to explain the lower *de* obtained for small particles of Rh on carbon, compared to more flat particles found on an alumina support.

Another interesting point is that the cyclohexenic compound is formed during the hydrogenation of *S*-methyl-*N*-(2-methylbenzoyl)pyroglutamate [20]. This seems to indicate that the step-by-step hydrogenation mechanism dominates the process and that the hydrogenation of substituted carbon atoms is the most difficult one. In order to study the influence of the presence of this by-product, calculations have been done with the cyclohexenic product of pyro. Since only the adsorption mode related to position A leads to the hydrogenation of the remaining double bond, this configuration was the one studied here; see Fig. 3A.

In Table 2, the adsorption energy of the cyclohexenic compound is compared to that of the pyro molecule. The adsorption energy is strongly reduced compared to that of the reactant (pyro). Hence the cyclohexenic molecule will desorb from the surface, by a competitive adsorption of the reactant. This explains its presence in the product stream.

Taking into account that the real catalysts are formed by small particles, their edges can also favor the adsorption of the cyclohexenic molecule by the concave side, similarly to the reactant at position C. This may be the reason that the hydrogenation of the cyclohexenic product decreases the *de* as seen experimentally [20].

3.2. (2-Methylnicotinyl)pyroglutamic acid adsorption

(2-Methylnicotinyl)pyroglutamic acid (pyro(N)) also has four different conformations. Similarly to the pyro substrate, the most stable conformation is the one in which the acid and methyl groups are on opposite sides of the pyroglutamic ring plane (conformer 1); see Fig. 1C. In this case the energy difference between conformers 1 and 2 is about 3 kJ/mol and between conformer 1 and the other two isomers about 30 kJ/mol. The interconversion activation barrier has been evaluated by force-field calculations [33] to be about 120 kJ/mol for the rotation through the amide bond (C–N) and to be more than 1000 kJ/mol to convert configuration 1 to 2. Moreover, H NMR spectra at 278 K have also demonstrated the presence of one isomer of this molecule [33].

The pyro(N) molecule can adsorb on the surface, similarly to the previous molecule, i.e., in positions A, B, and C (not shown here). In addition there is a new configuration (position D, Fig. 2D), in which the molecule interacts with the surface by the lone pair of the nitrogen atom of the aromatic ring. This type of adsorption has also been found for pyridine on Pt(110) [35], Cu(110) [36], and Cu(100) [37]. In this case, the molecule is more or less vertical (see Fig. 2D) and the interaction with the hydrogen atoms on the surface can happen on both sides of the ring with approximately the same probability. This would lead to a nonenantioselective hydrogenation.

For the molecular coverage of 1/16 that was studied here, the adsorption form (the pyridine ring parallel to the surface—position A) is again the most stable structure (Table 2). However, the adsorption energy of this form and the difference in energy of the various adsorption modes of pyro(N) are smaller compared to the previous case (pyro). The new configuration D, by the N atom lone pair, is only 25 kJ/mol less stable. The situation might change at higher coverages, since the adsorption by the lone pair in a more or less vertical structure can lead to a better molecular stacking on the surface. This coverage effect has already been noted for the adsorption of pyridine [35]. Furthermore, it has been shown that there is a local attractive interaction force between a pair of pyridine molecules on Cu(110) at high coverages [36]. Both points indicate that the preference for the form A can be less marked due to the good stability of the nonselective D mode at high coverages, thus reducing the *de*.

A very interesting point is revealed when the adsorption of the partial hydrogenated product (enamine) is studied. There are two different adsorption modes for enamine on the surface. Similarly to the previous cyclohexenic molecule, the enamine molecule can be positioned with its remaining double bond parallel to the surface, facing its less steric side to the surface, see the optimized structures (Figs. 3A and 3B).

In the other position, the lone pair of the nitrogen atom of the saturated ring interacts with the surface. The nitrogen group is a substituted amine, and has a similar adsorption configuration (top position) as reported for ammonia on the same surface [38]. Since the molecule binds to the surface by it N atom, this new position has been also called position D (Fig. 3C).

The adsorption energy of these two different modes of enamine is shown in Table 2. The enamine molecule prefers to bind to the surface as shown in position D. The adsorption energy is about 79 kJ/mol, which is very close to the calculated adsorption energy found for ammonia on Rh(111) at a coverage of 0.11 ML (82 kJ/mol) [38]. This large energy difference between the two positions D (of pyro(N) and of

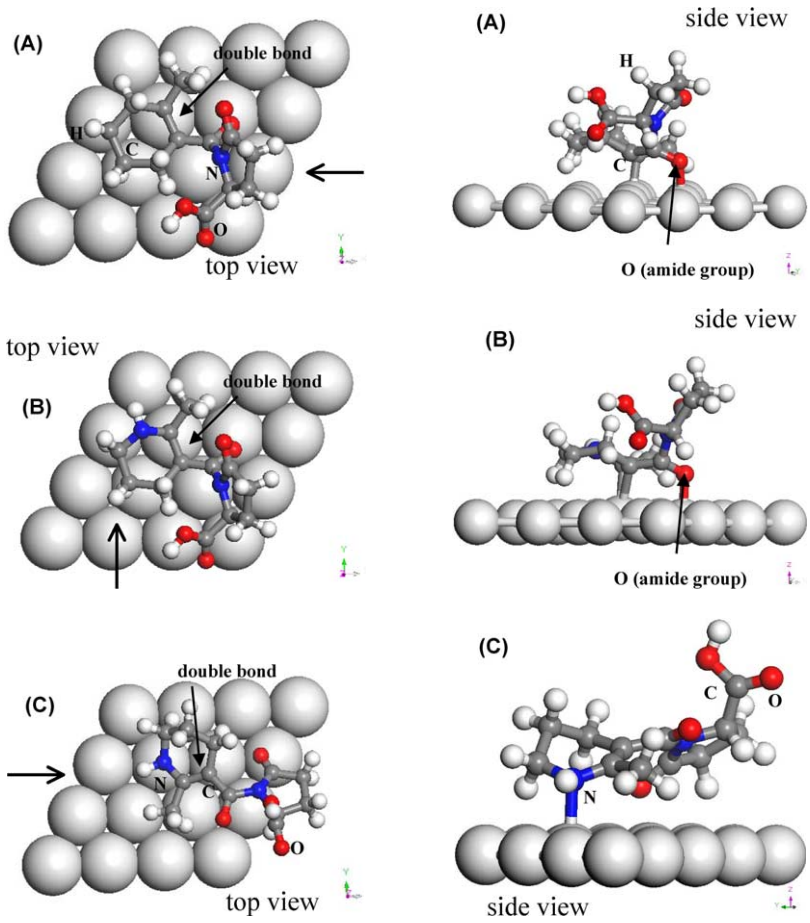

Fig. 3. Different adsorption modes for the hydrogenated products. (A) Position A—methylcyclohexenic from the partial hydrogenation of pyro. (B) Position A—methylenamine from the partial hydrogenation of pyro(N). (C) Position D—methylenamine from the partial hydrogenation of pyro(N).

enamine) is not surprising due to the difference of basicity of pyridine and alkyl-amine. The hybridization of the nitrogen atom in pyridine is sp^2, whereas is sp^3 in enamine. The more *s* character in the sp^n-hybrid atomic orbital, the less the lone pair is available [39].

Comparing Figs. 3B and 3C one may note that the enamine faces the convex side in the first case and the concave side in the latter one. Starting from pyro(N)—position A, the hydrogenation proceeds to the enamine, the configuration, of which is represented by Fig. 3B (convex side). The enamine, however, can follow two different processes: the complete hydrogenation reaction or the desorption of the enamine. If the enamine desorbs, its readsorption is strongly favored by the concave side, due to strong interaction of the lone pair with the Rh surface (see Table 2—Position D). In this case, the hydrogenation reaction leads to the production of the other enantiomer. Thus, the *de* is expected to decrease. This competition between the latter processes explains what has been observed recently in the hydrogenation reaction of (*S*)-methyl-*N*-(2-methynicotinyl)pyroglutamate on supported Rh catalyst [40]: no detection of enamine in the product stream and the *de* reaches a maximum of 28%.

4. Conclusions

In the present work the influence of the pyroglutamic acid, as a chiral auxiliary in the hydrogenation of *o*-toluic acid and 2-methyl nicotinic acid on the Rh(111) surface has been investigated by using periodical density functional theory.

The pyroglutamic acid auxiliary allows the adsorption of the aromatic ring by only one side of the ring plane ("convex" side of the molecule). This effect is observed for both molecules. In the case of the benzoyl ring, the selectivity should be excellent on a perfect flat metallic surface. It is, however, limited in practice by the presence of edges, especially in the case of small catalytic particles.

On the other hand, in the case of a nicotinyl ring, the presence of the lone pair of the nitrogen atom has a great influence in the reduction of the diastereomeric excess. The NH group, formed from the partial hydrogenation of the nicotinyl ring, interacts strongly with the surface, preventing the influence of the chiral auxiliary.

In summary, the use of chiral auxiliaries is shown to be effective for the enantioselective hydrogenation of specific target molecules, viz benzoyl-type rings. The presence of

different functional groups in the target molecule can lead to a reduction of *de* due to a formation of nondiastereoselective strong adsorption modes on the metallic surface.

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