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Theoretical study of catalytic decomposition of acetic acid on MgO nanosurface



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ABSTRACT

The adsorption and decomposition of acetic acid on the surface of MgO have been investigated using the representative cluster models and at the MP2/6-31G(d,p) level of theory. Adsorption of acetic acid on $(MgO)_n$ clusters for n = 4, 6, 9, and 12 were carried out by fully optimizing the acetic acid while geometry of the MgO fragment was kept frozen at the same level of theory as used for acetic acid. It is revealed that the adsorption energy of acetic acid varies with the cluster size. Strong chemisorption with -197 kJ mol⁻¹ has been observed for acetic acid adsorption on $(MgO)_4$ surface. Decarboxylation path of acetic acid on $(MgO)_4$ surface was investigated by locating the transition state and calculating the Intrinsic Reaction Coordinate. IRC calculation located a physisorbed structure with 325 kJ mol⁻¹ of energy higher than the chemisorbed structure. Detail analysis of adsorbed acetic acid species on $(MgO)_4$ surface and transition state by using Atoms in Molecules (AIM) method and ChelpG method for polarization of electron density in acetic acid upon adsorption revealed that the adsorption of acetic acid is a destructive adsorption preceded by a physisorption. Net energy required for the decarboxylation is found to be about 132 kJ mol⁻¹ on $(MgO)_4$ surface.

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1. Introduction

In recent years it has been paying much attention to investigate the use of nanoparticles in textile industry. Among them, inorganic materials such as metal and metal oxides, especially TiO, ZnO, MgO and CaO, have been attracted much as they are stable under harsh process conditions and generally regarded as safe materials to human beings and animals [1–3]. Recent investigations have revealed that the antimicrobial properties of silver and zinc oxide nanoparticles could be used to stop infectious diseases [4].

Considering the magnesium oxide, it exhibits catalytic activity for variety of reactions [5–9]. This catalytic activity of magnesium oxide is mainly due to a small number of defect sites, such as steps, kinks, corners, with surface ions. Enhancement of the reactivity can be anticipated when the material is scaled down to nanosize due to the increase in surface area, the greater amounts of edge and corner defects sites which are highly reactive [10,11]. 30–40% of the MgO units on the surface results the high surface to volume ratio and its electronic structure involves only s–p electrons. The high surface area and high surface reactivity allows these materials to act as stoichiometric chemical reagents, especially as effective adsorbents. MgO nanoparticles have been successfully used to destroy the toxic materials and hence called the destructive adsorbents which can adsorb and simultaneously break down the substances. For example, nanocrystalline MgO can destroy organophosphorus compounds, organochlorine compounds and also they adsorb large quantities of SO₂, CO₂, HCl, HBr, and other gases [12–14].

Theoretical study carried out by Michalkova et al. [15] on adsorption and decomposition of Sarin, isopropyl methylphosphonofluoridate (C₄H₁₀FO₂P), revealed that Sarin can be physisorbed on MgO nanosurface and hydroxylated small fragments with undestructive adsorption or can be chemisorbed on unhydroxylated small fragments with destructive adsorption. Physisorptions of Sarin on MgO surface is due to the formation of hydrogen bonds and ion-dipole and dipole-dipole interactions between Sarin and the surface while chemisorptions is due to the formation of covalent bond between Sarin molecule and the surface. Similarly worked carried out by Kakkar et al. [16] on adsorption of formaldehyde found that formaldehyde chemisorbed onto the MgO surface producing zwitterionic four-member ring, the adsorption process was highly exothermic and was preferred by lower coordinate sites. These works provide a rationale for the high activity of low-coordination sites than regular metal oxides in the adsorption and dissociation process. Therefore MgO nanoparticle is a very

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effective chemical reagent to be investigated for catalytic decomposition of acetic acid at room temperature.

Kinetic study of gas phase decomposition of acetic acid goes back to 1949 and since then a number of experimental and theoretical studies has been reported. These studies revealed that the gas phase decomposition could occur via two competing processes, decarboxylation (1) and dehydration (2). Bamford et al. [17] derived the first-order rate constants for both process of acetic acid decomposition in a flow system at temperatures of 770-920 °C with the activation energies of -259.4 and -282.4 kJ mol⁻¹ for decarboxylation and dehydration processes, respectively. Blake et al. [18,19] found that in both batch and flow systems carboxylation process is a first-order reaction in the temperature range 530-1950 K whereas the dehydration process is a second-order reaction below 600 K and is first-order above 600 K. Mackie et al. [20] examined the decomposition of acetic acid diluted in argon in a single-pulse shock tube and found that the both processes are first-order reactions over the temperature range 1300-1950 K having nearly equal rates with measured activation energies 271.5-295.0 kJ mol⁻¹ for decarboxylation and 282.4–295.0 kJ mol⁻¹ for dehydration.

$$CH_3COOH \to CH_4 + CO_2 \tag{1}$$

$$CH_3COOH \rightarrow H_2C = C = 0 + H_2O \tag{2}$$

In review of theoretical studies, several attempts of addressing the experimental facts and uncertainties have been reported with conflicting results [21–26]. Nguyen et al. [27] reexamined the acetic acid decomposition channels to address the existing conflicting results using the ab initio MO calculations and quantum version of PRK theory. They concluded that the dehydration of acetic acid via two-step mechanism is much preferred over the direct dehydration, the decarboxylation is a one-step concerted process and the rate constants for both unimolecular decomposition processes are nearly equal at high temperatures. In this study, we have considered only the decarboxylation process and not considered the dehydration pathways, either one-step or two-step processes even though the dehydration reactions may be possible on surfaces.

In recent years, it has been paying much attention to explore the nanosize particles in textile industry to degrade propanoic acid which is a major constituent of sweat responsible for the body smell. Therefore in this article we report the physiochemical process of adsorption and decarboxylation of acetic acid, which has similar structural properties to propionic acid, on MgO nanosurfaces.

2. Computational details

The adsorption and decomposition of acetic acid (AA- adsorbate) on the surface of MgO clusters (adsorbent) was investigated using the representative cluster models. Series of $(MgO)_n$ clusters for n = 4, 6, 9 and 12 were generated and optimized using the hybrid density functional-B3LYP and Pople's split valence doublezeta basis set with polarization functions for Mg, O and C atoms [B3LYP/6-31G(d)] separately following the work reported by de la Puente et al. [28] for the ground state structures of $(MgO)_n$ [29,30]. This group identified and reported the existence of $(MgO)_n$ magic numbers as maxima or pronounced slope changes in the binding energy versus cluster size curve. It is also reported that those magic numbers are n = 4, 6, 9, 12 and in agreement with the experimental results n = 2, 4, 6, 9, 12, 15.

All the other calculations [acetic acid optimization, adsorptions and decompositions of acetic acid on $(MgO)_n$ clusters, transition state optimization and IRC (intrinsic reaction coordinate) search] were carried out at the theory level of Second order Møller– Plesset perturbation (MP2) and Pople's split valence double-zeta basis set with polarization functions for Mg, O, C and H atoms [MP2/6-31G(d,p)] [31–33]. During the calculations, acetic acid, products of decomposition and transition state were fully optimized while geometry of the MgO fragment was kept frozen at same level of theory used for the adsorbate.

The interaction energies calculated were corrected by the basis set superposition error (BSSE). Atomic charge on each atom of the (MgO)₄–AA was calculated by fitting the electrostatic potential using the grid based method (ChelpG) developed by Breneman et al. [34]. "Atoms in Molecules (AIM)" theory developed by Bader [35] was used to examine the topological characteristics of electron density distribution. All calculations have been performed by using the Gaussian 09 program package [36].

3. Results and discussion

3.1. Characterization of acetic acid adsorption on (MgO)₄ surface

At first, we generate the series of $(MgO)_n$ (n = 4, 6, 9 and 12) clusters and then performed the adsorption of acetic acid on each cluster type. Optimized structures of $(MgO)_n$ and adsorbed acetic acid molecule on $(MgO)_4$ surface obtained using at the B3LYP/6-31G(d) level of theory are shown in Fig. 1 and 2, respectively, while adsorption energies are given in Table 1. Structures of adsorbed acetic acid on other $(MgO)_n$ (n = 6, 9, 12) are given in Fig. S1 of the Supporting Information. The adsorption energy (E_{ads}) of the acetic acid on MgO cluster was calculated according to the expression (3)

$$E_{\rm ads} = E_{\rm ace} + E_{\rm MgO} - E_{\rm complex},\tag{3}$$

where E_{ace} is the binding energy of isolated acetic acid in its ground state, E_{MgO} is the total binding energy of the bare $(MgO)_n$ cluster and $E_{complex}$ is the total binding energy of the acetic acid/ $(MgO)_n$ system.

Geometrical orientations, change in bond distance and the electron density redistributions of acetic acid on (MgO)_n have been observed when acetic acid is physisorbed or chemisorbed and a comparison of those for (MgO)₄-AA with isolated acetic acid is given in Table S1 of the Supporting Information. Data shows that there is no significant variation in adsorption energy of acetic acid with the cluster size except n = 6). Strong chemisorptions can be observed for all cases [-194.82, -80.43, -194.61, and -195.40 k] mol⁻¹ for n = 4, 6, 9 and 12, respectively]. Elongation of O–H bond distance from 0.98 to 1.60 Å, shortening of C-O distance from 1.36 to 1.26 Å in hydroxyl group and elongation of C–O double bond from 1.21 to 1.29 in carbonyl group indicate the strong adsorption and a tendency for more favorable catalytic decomposition of acetic acid on (MgO)₄ surface. This is due to the increase in surface area, the greater amounts of highly reactive edge and corner defects sites [10,14].

With these preliminary results, we focused our kinetic study mainly on (MgO)₄ and furthermore to determine an appropriate level of theory, an extensive study was undertaken to determine the relative energy between the reactant (acetic acid) and products of decarboxylation (1). Selection of (MgO)₄ was based on the comparison of the cluster size and adsorption energy of it with other sizes. Increased cluster sizes cause complexity in transition state search and optimization even though they give similar adsorption energy. In addition for comparison, we located the transition sate for decomposition of acetic acid on (MgO)₆, which has very low adsorption energy structures, acetic acid, carbon dioxide and methane were re-optimized using Hartree–Fock, B3LYP, MP2 and CCSD theory and various Pople basis sets, as tabulated in Table S2 of the



Fig. 1. Optimized structures of $(MgO)_n$ Mg atoms in yellow and O atoms in red (a) $(MgO)_4$, (b) $(MgO)_6$, (c) $(MgO)_9$, and (d) $(MgO)_{12}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. Adsorbed acetic acid molecule on (MgO)₄ surface.

Supporting Information. In all cases the geometries were fully converged at the same level of theory as the reported energies. CCSD results for the full range of basis sets considered, show good agreement with the MP2 results, from which we conclude that MP2 is a reliable method for these systems and that both basis sets of 6-31G(d) and 6-31G(d,p) quality are capable to correctly predict the energies of decarboxylation process. However we can consider 6-31G(d,p) as the best basis set which has an extra polarization function on reactive acetic hydrogen for this system.

We re-examined the adsorption and located the transition state on the decomposition path of acetic acid on $(MgO)_4$ surface at the MP2/6-31G(d,p) level of theory. We can see that the position and orientation of acetic acid on $(MgO)_4$ surface is such a way that

Table 1
Adsorption energies of acetic acid molecule (AA) on (MgO) _n surface obtained using a
the B3LYP/6-31G(d) level of theory.

System	(MgO) ₄ -	(MgO) ₆ -	(MgO) ₉ -	(MgO) ₁₂ -
	AA	AA	AA	AA
Adsorption energy (kJ mol ⁻¹)	-194.82	-80.05	-194.61	-195.40

the acidic hydrogen and carbonyl oxygen are pointing toward the O and Mg atoms in the cluster, respectively (Fig. 5a). These interactions were characterized using the "atoms in molecules" AIM theory which provides a rigorous and unambiguous criterion to determine the types of the bonded atoms and nature of the interactions [15,37-41]. The AIM theory has been widely used to characterize the hydrogen bonds; Srivastava et al. [42] calculated and compared the inter-molecular hydrogen bonding interaction energies of hydrogen bonded dimers and complexes of HF, H₂O and NH₃ obtained by Super-molecular and AIM approaches. They concluded that the AIM approach is more reliable. C-H---O contacts of DNA bases [43] and interaction of DNA bases with water were identified by using the AIM theory [44]. In the AIM analysis, the location of the (3, -1) bond critical points on the surface of the total charge density, the analysis of the electron density (ρ) , and the Laplacian of electron density $(\nabla^2 \rho)$ at the bond critical point are included and also it includes an analysis of the distances of formed bonds and changes of electron density on atoms involved in the formation of the bonds.

The values of the electron density (ρ) and the Laplacian ($V^2 \rho$) at the (3, -1) bond critical point and interatomic distances of the lowest energy (MgO)₄–AA complex (Fig. 5a) obtained at the MP2/ 6-31G(d,p) level are tabulated in Table 2. The AIM analysis in the

Table 2

Electron density ρ (a.u), Laplacian of electron density $\overline{\nu}^2 \rho$ (a.u) values and bond distances D (Å) from AIM calculations for the lowest energy (MgO)₄–AA complex (isomer-1) and those for isolated acetic acid in parenthesis at the MP2/6-31G(d,p) level of theory.

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	Bond/ characteristic	Electron density (ρ) (a.u)	Laplacian ($ abla^2 ho$) (a.u)	Distance D (Å)	
	9C—13C 13C—14O 13C—15O 14O—16H 15O—2Mg 16H—8O	0.3 (0.3) 0.4 (0.3) 0.4 (0.4) 0.1 (0.4) 0.0 0.3	-0.8 (-0.8) -0.1 (-0.3) -0.3 (-0.1) 0.2 (-2.3) 0.4 -1.8	1.51 (1.50) 1.26 (1.36) 1.29 (1.22) 1.53 (0.97) 1.98 1.02	

Table 2 reveals the formation of strong chemical bond (covalent) between the acidic hydrogen (16H) of acetic acid and oxygen atom (80) of the MgO surface and ion-dipole interactions between magnesium (2Mg) and the carbonyl oxygen (150) of acetic acid. In the formation of 16H-80 bond, electron density of hydroxyl bond (140-16H) has reduced to 0.1 from 0.4 a.u, the Laplacian of electron density $(\nabla^2 \rho)$ has changed its sign from negative to positive (from -2.3 to 0.2 a.u) and bond length has increased from 0.97 to 1.53 Å while appearing large electron density (0.3), negative $V^2 \rho$ (-1.8) and shorter bond distance (1.02 Å) for the bond between this hydrogen and oxygen in the cluster (16H-8O). Absence of electron density (0.0 a.u), positive $\nabla^2 \rho$ (0.4 a.u) and longer bond distance (1.98 Å) for the bond between carbonyl oxygen and magnesium (2Mg) is due to weak ion-dipole interaction. Furthermore, during the adsorption, electron densities and bond distances of 13C-14O and 13C-15O bonds approach to equal indicating that the adsorption favors the decarboxylation.

Table 3 contains the atomic charges of adsorbed $((MgO)_4-AA)$ and isolated acetic acid (AA) obtained using the ChelpG scheme at the MP2/6-31G(d,p) level of theory. Results show a redistribution of the electron density of acetic acid as a result of an internal polarization due to the adsorption. Charges of atoms involved in the interactions with the surface are increased considerably compared to the others. Atomic charges of 16H and 15O are increased by 0.1 and 0.2, respectively while it is on hydroxyl oxygen (14O) increased by 0.1. The large changes in atomic charges characterizes the astrictive interaction between acetic acid and $(MgO)_4$ surface.

One can conclude that according to these adsorption results, adsorption of acetic acid on $(MgO)_4$ surface is a chemisorptions incurred through formation of a strong bond between oxygen on MgO surface and acidic hydrogen of acetic acid, and ion-dipole interaction between magnesium and the carbonyl oxygen of acetic acid and the adsorption leads to the decomposition of acetic acid and the adsorption energy corrected by the basis set superposition error (BSSE) is -197.66 kJ mol⁻¹ (-47.06 kcal mol⁻¹).

3.2. Decarboxylation of acetic acid on (MgO)₄ surface

Decomposition kinetics of acetic acid through decarboxylation was investigated by searching the transition state and calculating the Intrinsic Reaction Coordinate (IRC) at the MP2/6-31G(d,p) level of theory. We first found the transition state and calculated the activation energy for isolated acetic acid by following the work reported by Nguyen et al. [27] and then followed the reaction path search. Reaction path obtained is shown in Fig. 3. Activation energy calculated for gas phase decomposition of acetic acid is 290 kJ mol⁻¹, which is in an excellent agreement with the range of experimentally observed values [17–20].

The experimental studies of interactions between DMMP and MgO nanoparticles reveal that if adsorption is strong enough, the adsorbate may be decomposed into its fragments [12,45,46]. As we discussed in previous section, acetic acid adsorption results the lowest energy (MgO))₄–AA complex given in the Fig. 5a

Table 3

ChelpG atomic charges of the lowest energy $(MgO)_{4}$ -AA complex (isomer-1) and isolated acetic acid (AA) obtained using the MP2/6-31G(d,p) level of theory.

Atom/characteristic	(MgO) ₄ -AA	AA
9C	-0.4	-0.4
13C	0.8	0.7
10H	0.1	0.2
11H	0.1	0.2
12H	0.1	0.2
140	-0.7	-0.6
150	-0.8	-0.6
16H	0.5	0.4



Fig. 3. Intrinsic reaction coordinate diagram for the gas phase decomposition of acetic acid molecule.

(isomer-1) in which acetic acid is bound to (MgO)₄ through a strong chemical bond between hydrogen of hydroxyl group and oxygen in the (MgO)₄ surface, and the dipole-ion interaction between carbonyl oxygen and magnesium atom. We located a transition state for the decarboxylation process of acetic acid adsorbed on (MgO)₄ and calculated the Intrinsic Reaction Coordinate (IRC). In forward scan from the transition state, it broke down to the carbon dioxide, methane and bare (MgO)₄ but backward scan yielded a different (MgO)₄-AA complex (isomer-2) of what acetic acid is bound to the (MgO)₄ surface only through the weak dipole-ion interaction between carbonyl oxygen and magnesium atom on the surface. This intermediate (isomer-2) lies 325 kJ mol⁻¹ above the lowest energy isomer-1, Fig. 4 shows the reaction path of the decarboxylation of acetic acid starting from the structural orientation given in isomer-2 (Fig. 5b) through the transition state (Fig. 5c). BSSE corrected activation energy calculated for the decomposition process of acetic acid from the high energy intermediate is 330 kJ mol⁻¹.

The values of the electron density (ρ) and the Laplacian ($V^2 \rho$) at the (3, -1) bond critical point and interatomic distances of high energy (MgO)₄–AA complex (isomer-2) are tabulated in Table S3 of the Supporting Information. The AIM analysis in the Table S3 reveals that the high energy intermediate is formed by physisorption only due to the ion–dipole interactions between magnesium (1Mg) and the carbonyl oxygen (14O) of acetic acid in contrast to the lowest energy isomer-1 which has, in addition, a strong



Fig. 4. Intrinsic reaction coordinate diagram for the decomposition of acetic acid molecule adsorbed on $(MgO)_4$ surface: reaction path between isomer-1 and the products of the decarboxylation.



Fig. 5. Equilibrium structures of acetic acid decomposition on $(MgO)_4$ surface at the MP2/6-31G(d,p) level of theory: (a) lowest energy $(MgO)_4$ -AA complex (isomer-1), (b) high energy intermediate $(MgO)_4$ -AA complex (isomer-2), and (c) is the transition state, $[(MgO)_4$ -AA][#], between isomer-2 and the products of the decarboxylation.

chemical bond between hydrogen of hydroxyl group and oxygen in the (MgO)₄ surface (chemisorption). The absence of bond critical point (3, -1) along the 16H-80 line indicates the absence of chemisorptions while about zero electron density (0.0 a.u), positive $\nabla^2 \rho$ (0.2 a.u) and longer bond distance (2.09 Å) for the bond between carbonyl oxygen and magnesium (1Mg) give the evidences for the physisorption. Furthermore, the unchanged bond distance, low electron density (ρ) and increased negative Laplacian ($V^2 \rho$) in hydroxyl bond (150–16H) due to the covalent bond character also indicates the absence of chemisorption through hydroxyl group. Considerable unchanged atomic charge on hydroxyl oxygen (150) of high energy (MgO)₄-AA complex compared to the isolated acetic acid (AA) given in Table S4 of the Supporting Information. Due to lack of internal polarization along the 150-16H further confirms the absence of chemisorption. Therefore we can conclude that the high energy (MgO)₄-AA complex is due to the physisorption and eventually acetic acid would fall into the chemisorbed energy well in the potential energy surface passing the negligible energy barrier created as a results of physisorption.

Decomposition path was characterized by AIM analysis for transition state shown in Figs. 4 and 5c. Electron density (ρ), Laplacian of electron density ($V^2 \rho$) values and bond distances *D* (Å) of

Table 4

Electron density ρ (a.u), Laplacian of electron density $\nabla^2 \rho$ (a.u) values and bond distances D (Å) from AIM calculations for transition state [(MgO)₄–AA][#] complex and those for high energy (MgO)₄–AA complex (isomer-2) in parenthesis at the MP2/6-31G(d,p) level of theory.

Bond/Electron density (ρ) Laplacian $(\overline{V}^2 \rho)$ characteristic(a.u)(a.u)	Distance D (Å)
9C-13C 0.1 (0.3) -0.2 (-0.8) 13C-150 0.4 (0.3) -0.4 (-0.3) 13C-140 0.4 (0.4) 0.0 (0.0) 150-16H No BCP (0.0) - (-2.3) 140-1Mg 0.03 (0.0) 0.3 (0.2) 16H-80 No BCP defined - 16H-9C 0.2 -0.3	1.81 (1.51) 1.25 (1.34) 1.22 (1.23) - (0.97) 2.07 (2.09) - 1.37 ^a

^a Average bond distance of methyl C-H in acetic acid was 1.1 Å (Table 2).



Fig. 6. The transition state on the decomposition path of acetic acid on (MgO)₆ surface at the MP2/6-31G(d,p) level of theory.

transition state $[(MgO)_4 - AA]^{\#}$ compared to those for high energy (MgO)₄-AA complex (isomer-2) are given in Table 4. Noticeable changes in transition state compared to the reactant (isomer-2) are observed in carbon-carbon bond (9C-13C) and the hydroxyl bond (150-16H) while trend in a new bond formation between acidic hydrogen (16H) and methyl carbon (9C) appears. In carbon-carbon bond, electron density has reduced to 0.1 from 0.3 a.u, the Laplacian of electron density ($V^2 \rho$) has changed from -0.8 to -0.2 a.u and bond length has increased from 1.51 to 1.81 Å. These values show the weakening of the carbon-carbon bond at the transition state allowing the decarboxylation. Appearing a bond critical point between acidic hydrogen (16H) and methyl carbon (9C) with 0.2 a.u electron density and negative $\nabla^2 \rho$ (-0.3) parallel to the disappearance of bond critical point in hydroxyl bond (150–16H) is a clear indication for the formation of methane. It should also noticed that at this stage still the distance between 16H and 9C is 1.37 Å which is significantly longer than a C–H bond in a methyl group. These facts with AIM values for the other bonds revel that the transition state formed has a potential tendency toward the decarboxylation as the IRC calculation produced.

In addition for comparison, we located the transition state on the decomposition path of acetic acid on $(MgO)_6$ surface at the MP2/6-31G(d,p) level of theory. The structure of transition state is given in Fig. 6. The transition state located lies about 382 kJ mol⁻¹ above the reactants. Reaction path was not calculated since the activation energy is very high (382 kJ mol⁻¹) and adsorption energy is lower (-80 kJ mol⁻¹) compared to the other sizes. Therefore overall energy required is 300 kJ mol⁻¹, which is very high and not easily available as thermal energy at room temperature.

4. Conclusion

Comparing the strong chemisorptions of acetic acid on $(MgO)_4$ surface, -197.66 kJ mol⁻¹ with the 330 kJ mol⁻¹ decomposition energy for the decarboxylation, one can conclude that the adsorption is a destructive adsorption as the net energy required for the decarboxylation is about 132 kJ mol⁻¹. Initially molecule would reach the surface along the physisorption path and then it may pass into the chemisorptions-well through direct chemisorption process. Strong chemisorption of acetic acid on MgO surface eventually leads to a decarboxylation.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.comptc.2015.04. 011.

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