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A theoretical-experimental study of Wells-Dawson phospho-tungstic heteropolyacid: an explanation of the pseudoliquid or surface-type behaviour.

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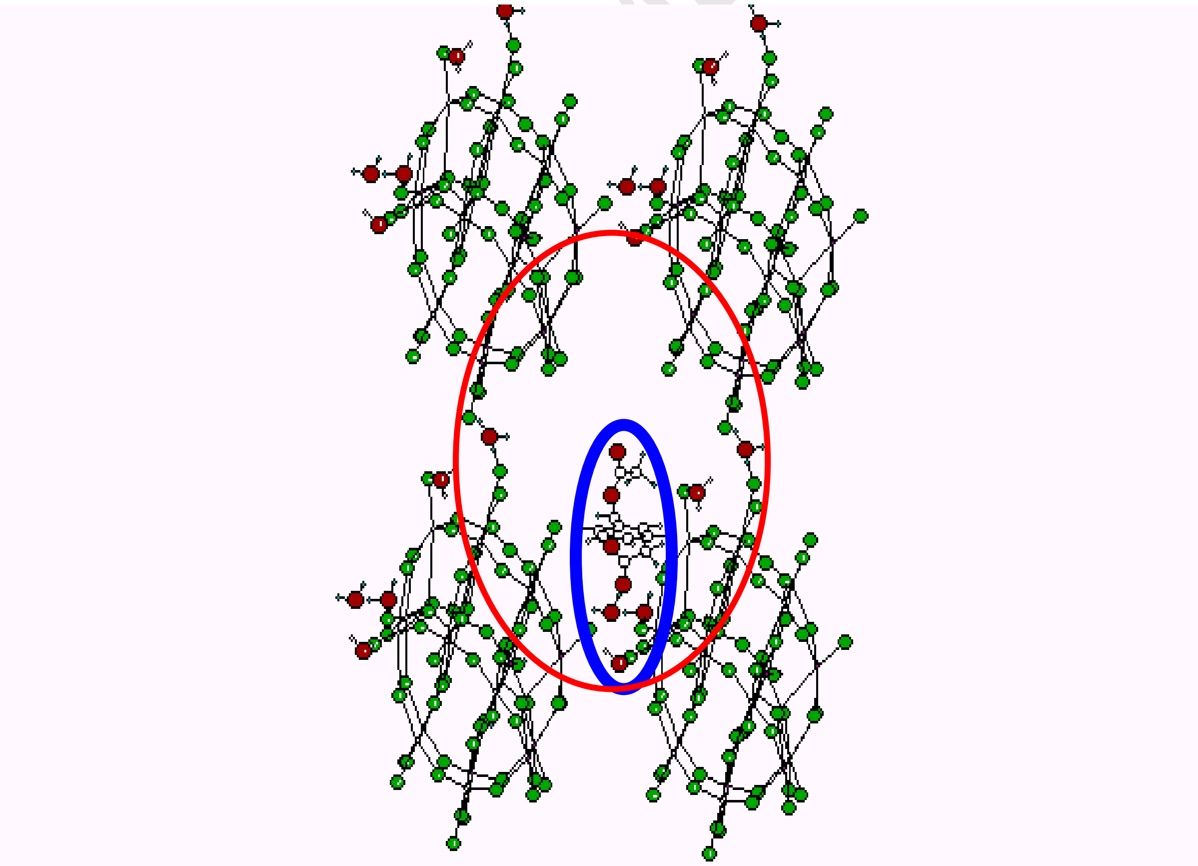

A theoretical-experimental study of Wells-Dawson phospho-tungstic heteropolyacid: an explanation of the pseudoliquid or surface-type behaviour.

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ABSTRACT

The aim of the present work is to predict theoretically the nature of the mechanism of catalytic behaviour, pseudoliquid or surface-type, of Wells-Dawson solid acid (WDA). For this purpose, we took into account the dipolar moment of the substrates and the presence of $H_5O_2^+$ species in their structure, considering both theoretical and experimental results.

In the present paper we studied experimentally the deprotection reaction of aldehydes from 1,1 diacetates. These theoretical and experimental results together with our previous works indicate that the catalytic behaviour of WDA is a function of the dipolar moment of organic molecules and the presence of $H_5O_2^+$ species. The pseudoliquid or surface-type behaviour depends on the physicochemical properties of the organic structure and its possibility of interaction with $H_5O_2^+$.

KEYWORDS: Wells-Dawson Acid, Heteropoly Compounds, Extended Huckel Method, Pseudoliquid Phase, Surface-type activity.

INTRODUCTION

The environmental problems, associated with both handling and disposal of conventional inorganic acids, and the potential hazards have raised the interest in the development of alternative clean processes and technologies involving the use of solid acid catalysts. Nowadays, catalysis by heteropolyacids is a well-established area [1]. In particular, the application of phospho-tungstic acid with Wells-Dawson structure ($H_6P_2W_{18}O_{62}$. $24H_2O$) as catalyst, both in liquid and gas phase, is a field of growing importance in sustainable acid catalysis. [2-4].

The phospho-tungstic Wells-Dawson heteropolyanion posseses the formula $[(X^{n+})_2M_{18}O_{62}]$ where each X^{n+} is a central atom, phosphorus (V) in this case, surrounded by a cage of M addenda atoms such as tungsten (VI), each of them composing MO_6 octahedral units. [5]. This solid acid posseses pure Brönsted acidity and its protons play a role in catalytic active sites. The acidity of these bulk compounds is higher than that of mineral acids and it depends on their hydration state, the strength of acid sites and the accessibility of protons. [6]. Besides, the catalytic behaviour of these materials is strongly influenced by the structural modifications that may occur in their secondary and tertiary structures [7–9].

Another relevant aspect for understanding the catalytic behaviour of heteropolyoxoanions is to determine the type of catalysis involved in the catalytic process. For gas phase reactions, Misono et al [10] have demonstrated that there are three catalysis prototypes for solid heteropoly compounds: surface-type, bulk-type (I) (pseudoliquid), and bulk-type (II). In the case of liquid phase reactions, reaction fields change by the polarities of solvents and substrates as Koyano et al [11] reported. These authors reported that the recognition of these reaction fields is necessary for adequate catalyst design and understanding catalyst behaviour. Recently, Ilnicka has described [12] the role of water in the catalytic behaviour of HPA. In this paper she has shown that water can participate in different reactions either as a substrate or as product.

In a previous work, [6] we reported a pseudoliquid behaviour of Wells-Dawson acid for methyl tetra-butyl ether (MTBE) synthesis and methanol dehydration to dimethyl ether in gas phase at 100 °C. Thus, we reported [6, 9] that the catalytic activity of Wells-Dawson acid, for the above mentioned reactions, was directly related to the presence of water molecules in its secondary structure. We concluded by TGA, DRIFTS, H MAS-NMR and also by theoretical studies that the loss of catalytic activity of Wells-Dawson acid with the increase of pre-treatment temperature was due to the loss of the last two water molecules. EHMO calculations show that $H_5O_2^+$ species bonded two Wells-Dawson secondary structures.

On the other hand, we reported that isobutene alkylation with C_4 olefins was a "surface-type" reaction and the catalyst activity could be related directly to the number of surface acid sites accessible to reactants [13].

In this sense, the aim of the present work is to predict theoretically the nature of the catalytic behaviour mechanism (pseudoliquid or surface-type behaviour) of Wells-Dawson solid acid (WDA). For this purpose, we analysed the catalytic behaviour of WDA in different reactions: MTBE synthesis, methanol dehydration to dimethyl ether and isobutene alkylation with C_4 olefins and deprotection reaction of aldehydes from 1,1 diacetates. The results were correlated with the theoretical studies, which were performed by Extended Huckel Method. It must be noted that the catalytic results of the first three mentioned reactions were reported in our previous works [6, 13], meanwhile the deprotection reaction of aldehydes from phenylmethanediol diacetate using both supported on silica and bulk WDA as catalysts is described in this work.

EXPERIMENTAL

Catalyst synthesis and Characterization

Wells-Dawson acid ($H_6P_2W_{18}O_{62}$.aq.) was synthesized according to that described in detail in a previous work [6]. WDA was obtained from an aqueous solution of α/β

$K_6P_2W_{18}O_{62}.10H_2O$, which was treated with ether and concentrated HCl (37%) solution. The acid so released formed an additional compound with the ether, which allowedit to be separated from the solution. The remaining solution was placed in a vacuum-desiccator until crystallization.

Silica-supported WDA containing 20 wt% (20WD/SiO_2) was prepared by wet impregnation of Grace Davison silica (Grade 59, specific area= 250 m^2/g) with an aqueous solution of the synthesized WDA. After impregnation, the sample was dried at room temperature in a vacuum-desiccator for 8 h.

WDA fresh samples were analyzed by infrared spectroscopy with a FTIR Bruker IFS 66 equipment. ^{31}P MAS-NMR spectra were recorded in a Bruker MSL-300 equipment operating at frequencies of 121.496 MHz.

Catalytic tests

Deprotection of aldehyde reaction

General procedure for the deprotection of aldehydes from phenylmethanediol diacetate (Figure 1) was carried out according to the following sequence: A mixture of a phenylmethanediol diacetate (0.5 mmol), toluene (1 ml) and Wells-Dawson bulk or supported catalyst (1% mmol) was stirred at a temperature range of 298-373 K from 5 to 360 minutes. Then, the solid was removed by filtration and washed twice with toluene (0.5 ml each). The organic solution was washed twice with water (3 ml each) and then it was dried over anhydrous Na_2SO_4. Bare support was tested with the same catalytic procedure. It must be noted that both, bulk and supported WDA are insoluble in toluene [14]. In order to verify the possible catalyst solubilization, additional tests were performed. The 0.2WDSiO_2 sample (60 mg) was refluxed in toluene (3 ml) for 5 h, filtered and dried in vacuum until constant weight. Loss of mass was not detected. The refluxed toluene was used as solvent for the reaction without adding the catalyst. After 20 h, reaction was not detected, and the starting material was quantitatively recovered. In this respect, Romanelli et al. [13] have reported the re-use of this catalyst for three reaction-cycles without loss of weight or activity.

The aldehyde was identified by comparison (TLC, GLC and physical constants) with authentic samples. The yield was calculated as % molar from isolated product. Evaporation of the solvent under reduced pressure and flash column chromatography of the residue on silica gel allows resolving the reaction mixtures.

Theoretical studies

These studies were carried out using Hückel extended method according to that developed by Hofmann [15] and improved by Andersson (ASED-OM) [16] and Calzaferri (ICONC) [17], respectively. The Wells-Dawson structure, which was used in the present work, had been reported in a previous paper [9]. For the analysis of the CH_3OH, acylal (aldehyde 1,1-diacetate) and butene adsorption, we used the "secondary structure" of WDA described in [9], i.e. the hydrated structure of $H_6P_2W_{24}O_{62}$ acid. For methanol molecule we used angles and average distances in gas phase reported by Sambeth et al [18]. The butene molecule was built according to that reported in the bibliography [19]. The acylal was built by taking angles and average distances of the different molecular structures which formed the structure (benzene, methyl group, acetate group). These structures were joined and analyzed until a minimum of energy was obtained.

The adsorption of the organic group over WDA secondary structure was carried out by analyzing the interactions of each molecule with different protonic species of the structure (W-OH, H_3O^+ y $H_5O_2^+$) as it can be observed in Figure 2.

The interaction of organic molecule-WDA for each different interaction indicated in Figure 1 was calculated considering the total energy of the system ($E_{\mathbf{ti}}$) by using the following equation that includes terms for both repulsion and binding energies.

$$E_{\mathbf{ti}} = E_{\mathbf{OMWDA}} - (E_{\mathbf{WDA}} + E_{\mathrm{OM}})$$

Where $E_{\mathbf{OMWDA}}$ is the interaction energy of the organic molecule with WDA, $E_{\mathbf{WDA}}$ is the WDA energy at infinite distance of the molecule, whose energy is represented by $E_{\mathbf{OM}}$ (Organic Molecule). The values corresponding to ionization potentials and Slater coefficients used for calculus are indicated in Table 1

RESULTS AND DISCUSSION

Catalyst Characterization

The characterization by FTIR, ^{31}P MAS-NMR and XRD was reported in detail in a previous work [13]. The results have indicated that the WDA keeps its heteropolyanion structure after impregnation and drying steps, when it is supported on SiO_2 and it is well dispersed on the support.

Catalytic results

In Figure 3, it can be observed the aldehyde yield for deprotection of phenylmethanediol diacetate at 298, 313 and 373 K as a function of reaction time for both bulk and silica supported samples of WDA. Both solids were tested as deprotection catalysts, carrying out the cleavage reaction (according to Figure 1) using toluene as solvent. As mentioned before, the WDA is insoluble in toluene. In all runs no secondary products were observed, assuming then that selectivity was always 100%.

Results indicated that both samples showed a similar catalytic behaviour at the lowest temperature (298 K). A very low activity for bulk acid was observed for the first twenty minutes, and then the conversion began to rise up to 100% after 350 minutes. For supported catalyst this “induction time” was not observed, and the conversion grew continuously up to complete reaction at 250 min.

Nevertheless, the differences on conversion between both catalysts were never higher than 100% at the beginning, being close to 25-30% values at the end of the runs. This fact is an unexpected result taking into account that particle sizes of bulk catalyst were in the range of 20-40 μm and the supported catalyst was highly dispersed on the silica (250 m^2/g) as it was thoroughly discussed [13].

At 313 K, the behaviour of both systems were similar to that shown at low temperature but the difference between absolute conversions curves was lower than that shown at the mentioned temperature, meanwhile at 373 K they were overlapped.

When analyzing the difference between conversion curves at 298 K it was possible to observe that it was not so high as expected considering that the amount of catalyst was always the same but one of them as well disperse phase on support and as small crystallites of several microns in size, so the only possibility for the high activity for bulk catalyst could be that they showed a pseudoliquid behaviour and the difference with supported ones can be explained in terms of diffusion of reactives and products inside and outside crystallites.

As diffusion depends linearly on temperature, it can be expected that at higher temperature, the difference between conversions of both catalysts could diminish, as actually occured.

The pseudoliquid behaviour

Sambeth et al. [9] have demonstrated that the tertiary structure of WDA is formed due to the interaction between W-OH and water molecules. In order to analyse molecular diffusion, molecular size and the solid behaviour we assumed that the secondary structure of Wells–Dawson acid was a parallelepiped (Fig. 4a, parallelepiped called A), whose dimensions were 9.0, 5.0 and 13.5 Å. The parallelepiped A represented the secondary structure of WDA and the volume of each secondary structure was 625.5 $Å^3$. In the same sense, the unit cell of WDA could also be associated to a parallelepiped, which was called B (Fig. 4a). In this parallelepiped B, one secondary structure was placed in each corner. The calculated distances between each corner were 12.1 Å (d_1), 15.5 Å (d_2) and 21.5 Å (d_3) and as it can be seen (figures 4a and 4b), one structure belonged to the unit cell. The volume of the unit cell reached 4032 A^3. The difference between the unit cell volume and the total volume of one secondary structure WDA effective volume (EV) was 3406.5 Å^3.

On the other hand, Okuhara et al [10] have explained the pseudoliquid behaviour as follows: "the reactant molecules are adsorbed between the polyanions in the ionic crystal and the reaction occurs there. The polyanion structure itself is usually intact". This relevant fact allows us to say that the diffusion into WDA and the pseudoliquid behaviour are linked to the presence of $H_5O_2^+$ and the reaction rate is a function of the volume of the polyoxoanion. Sambeth et al [9] have demonstrated theoretically and experimentally the interaction between the protons and the water molecules in the Wells-Dawson acid. These authors showed: (i) the presence of three different water: molecules of crystallization H_2O, H_3O^+ and $H_5O_2^+$; (ii) $H_5O_2^+$ is the most stable species and; (iii) the presence of $H_5O_2^+$ is fundamental in MTBE synthesis and CH_3OH dehydratation. Okuhara et al. [10] have postulated that the adsorption rate and the amount of adsorbed molecules on heteropolyoxoanions are a function of the molecular size and the dipolar moment, respectively. For example, polar molecules such as alcohol, ether, amines are adsorbed on the surface but also in the bulk of solid, while benzene, ethene (non polar molecules) are adsorbed only on the surface. In the first case Misono has called this "pseudoliquid phase" behaviour. As it can be seen in Table 2 the dipolar moment (μ) of CH_3OH is higher than μ of butane. Therefore, the behaviour of the acylal must be pseudoliquid since its molecular structure allows us to suppose that this acylal has a dipolar moment higher than butene as consequence of diacetate groups.

The complex structure of acylal was associated to different geometrical figures: (a) pyramid with a square base, (b) pyramid with a trigonal base and (c) cone. The calculations of the volumes were 120, 55 and 303 Å^3, respectively. The geometrical figures were 3.5, 1.6 and 8.9 % of the EV, this means that acylal group could interact with active sites inside the unit cell.

The theoretical results of the respective interactions of CH_3OH, butene and acylal with the different groups of the WDA are shown in Table 3. The study has demonstrated that acylal structure (See Figure 5) and CH_3OH interact with $H_5O_2^+$.

In both cases the minimum relative energy is produced when the O of the organic molecule interacts with one proton of the dioxonium species. In the case of butene, the minimum energy of the system occurs when C_1 interacts with one proton, which is associated to terminal oxygen (W=O).

The polyoxoanion behaviour is a function of the physicochemical properties of organic molecules; this implies that if the reaction is produced by polar molecule the Wells- Dawson acid behaviour will be "pseudoliquid". Earlier works about CH_3OH dehydratation and MTBE synthesis, and our theoretical results enable us to say that: (a), the catalytic activity of Wells–Dawson acid is directly related to the presence of $H_5O_2^+$ species and (b) the pseudoliquid behaviour depends of the physicochemical properties of organic structure and its possibility to interact with $H_5O_2^+$ species. These results are fully in agreement with the results reported by Gambaro and Briand [20], which have shown that the hydrated WDA has a higher amount of active sites than the dehydrated acid.

CONCLUSIONS

The pseudoliquid or surface-type behaviour of Wells-Dawson acid on organic reactions in liquid phase was analysed theoretically and experimentally. As previously shown [9], $H_5O_2^+$ species, bridged to secondary structures, built the tertiary heteropolyanion structure and then a cage type structure was obtained. This three-dimensional framework was connected with all its neighbours, so all its acid active sites inside the cage could take part in catalysis by diffusion of reactives from the solution.

In the present work, we have shown through those theoretical calculations and experimental results that there is a direct relationship between polarity of organic molecules and the ability to diffuse inside the catalyst cage or framework. A non polar molecule does not diffuse inside and only interacts with surface acidic, but a polar molecule can move into the cage and then all internal acidic sites are available. When diffusion occurs, the number of active sites grows sharply. In this way, the higher the diffusion is the closer the behaviour of bulk catalyst is to a supported one.

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TABLE 1

Ionization Potencials and Slater coeficients

Atom	**s**		**p**		**d**				
	H*ii*	**Exp**	**H*ii***	**Exp**	**H*ii***	**Exp$_1$**	**Coef$_1$**	**Exp$_2$**	**Coef$_2$**
H	-13.6	1.300							
C	-15.1	1.554	-9.8	1.457					
O	-32.3	2.275	-14.8	2.275					
P	-18.6	1.750	-14.0	1.30					
W	-8.3 2	0.341	-5.17	2.309	-10.4	4.982	0.694	2.068	0.563

TABLE 2
Dipolar moment (μ) of metanol and butene molecules

Molecule	Dipolar Moment (μ)
CH_3OH	1.71
Butene	0.34

TABLE 3
Results of the interaction of methanol, butene and acylal molecules with WDA

Molecule	**Adsorption site**		
	W - OH	**W=O - - H_3O^+**	**W=O - - $H_5O_2^+$**
Butene	**-1.8 eV**	**-1.4 eV**	**-1.3 eV**
CH_3OH	**-1.7 eV**	**-2.2.eV**	**-2.4 eV**
Acylal	**-1.0 eV**	**-1.3 eV**	**-2.2 ev**

CAPTION TO FIGURES

Figure 1. Scheme of the deprotection of aldehydes from phenylmethanediol diacetate.

Figure 2. Scheme of Wells-Dawson acid (Secundary Structure).

Figure 3: Aldehyde yield for deprotection of phenylmethanediol diacetate (a) 298 K, (b) 313 K, (c) 373 K as a function of reaction time (■ Bulk WDA; □ WDA/SiO_2)

Figure 4: (a) Dimensions of secondary structure of WDA (called parallelepiped A) and unit cell Wells Dawson acid (called parallelepiped B); (b) Representative scheme of the cell unit of the WDA

Figure 5: Scheme of interaction acylal structure (blue ring) and WDA (red ring, cage of WDA)

FIGURE 1

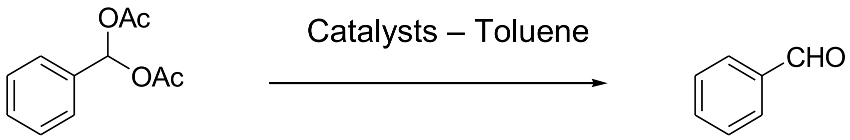

FIGURE 2

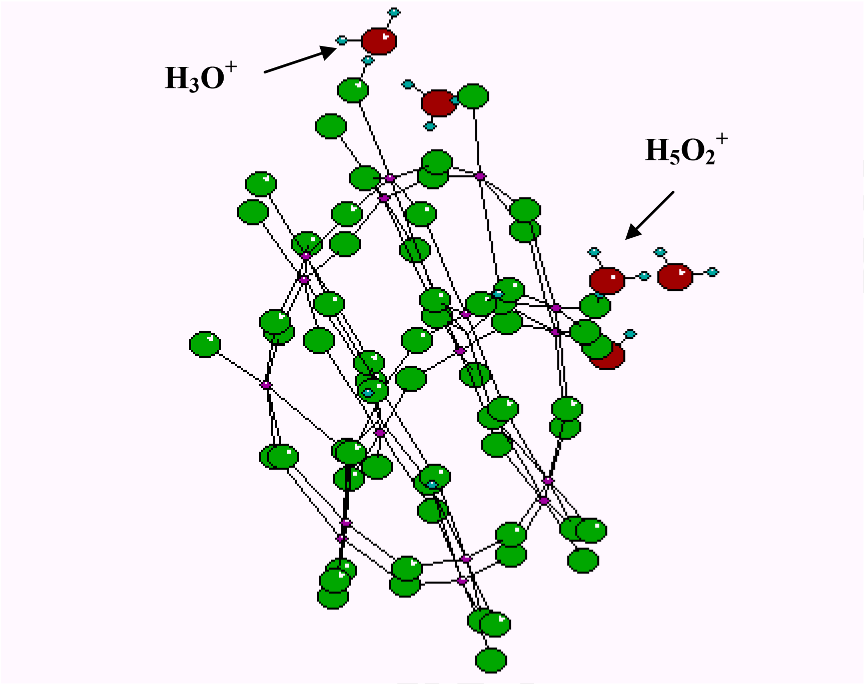

FIGURE 3

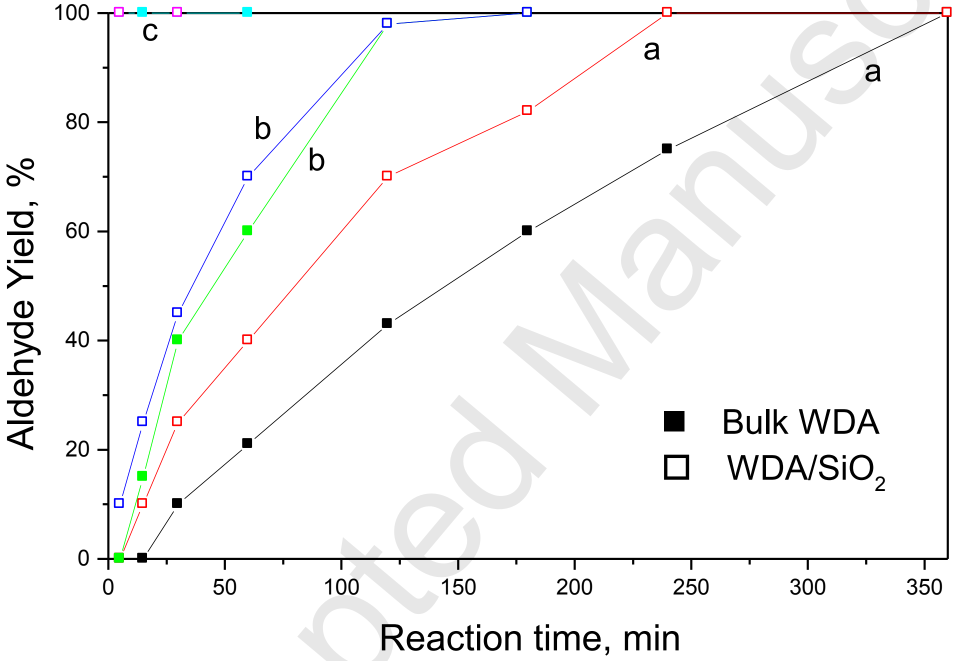
Aldehyde Yield, %
0
20
40
60
80
100
0
50
100
150
200
250
300
350
Reaction time, min
a
a
b
b
c
■ Bulk WDA
□ WDA/SiO$_2$

FIGURE 4 (a)

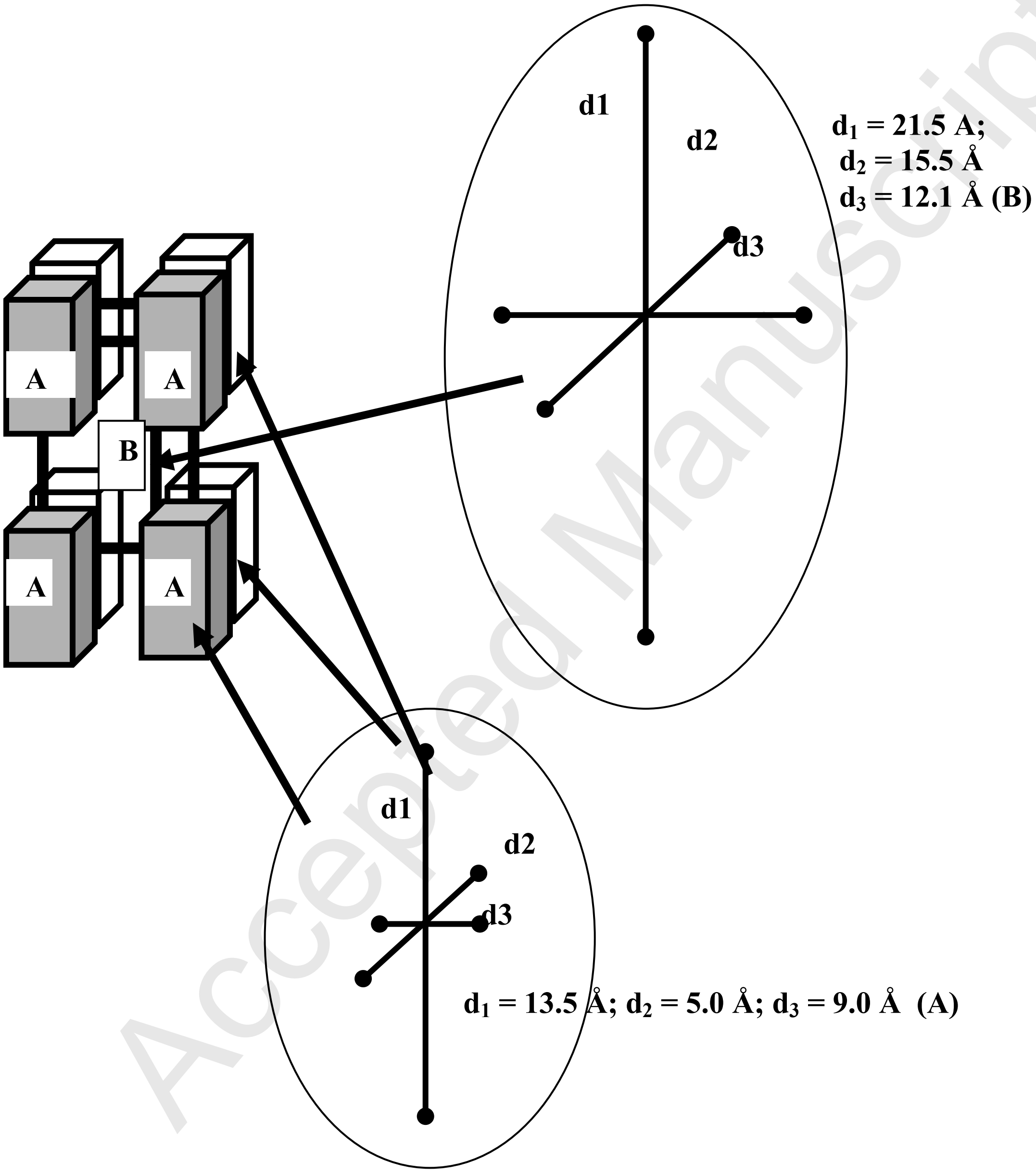
d1
d2
d_1 = 21.5 A;
d_2 = 15.5 Å
d_3 = 12.1 Å (B)
d3
A
A
B
A
A
d1
d2
d3
d_1 = 13.5 Å; d_2 = 5.0 Å; d_3 = 9.0 Å (A)

FIGURE 4 (b)

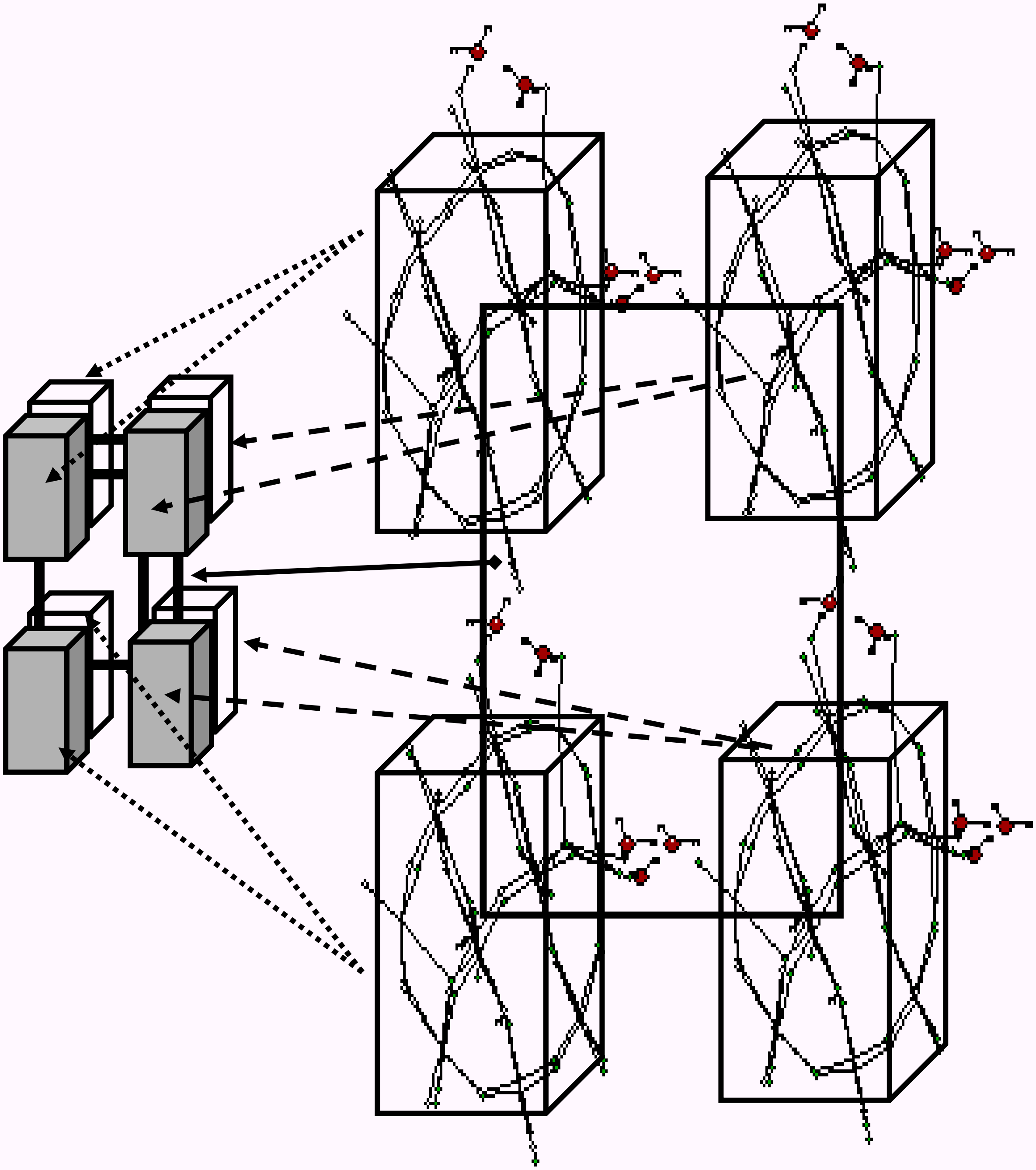

FIGURE 5