

SURFACE INTERMEDIATE SPECIES OF THE 4-ISOBUTYLACETOPHENONE ADSORPTION-REACTION OVER FOSFOTUNGSTIC WELLS-DAWSON HETEROPOLY ACID

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Abstract— Surface adsorbed species of isobutylbenzene and 4-isobutylacetophenone on bulk fosfotungstic Wells-Dawson acid $H_6P_2W_{18}O_{62} \cdot xH_2O$ (HPA) have been screened in the present investigation. The evolution of chemisorbed species towards products was followed through infrared spectroscopy of systems containing liquid reactants and the solid acid kept at various temperatures.

4-Isobutylacetophenone adsorbs on Brønsted acid sites of the heteropoly acid and further reacts towards a condensation product similarly to the reaction of acetophenone over other acid materials such as, mordenite, niobic acid and sulfated zirconia.

The condensation product possesses well defined infrared signals at 1654 cm^{-1} and 1597 cm^{-1} that resemble the carbonyl stretching vibration and the double bond of dypnone $C_6H_5COHC=C(CH_3)C_6H_5$. Additional signals at 1221 cm^{-1} and a shoulder at 1284 cm^{-1} ascribed to the vibration of the C_6H_5 species in the $C_6H_5COHC=$ group, give more evidences of the formation of a chalcone type compound.

A reaction mechanism of the Aldol condensation of 4-isobutylacetophenone through an enol reactive intermediate is proposed.

Keywords— Aldol condensation, HPA, Wells-Dawson acid, chalcone, 4-isobutylacetophenone.

I. INTRODUCTION

Nowadays, much research is focused on Keggin $[XM_{12}O_{40}]^{3-}$ and Wells-Dawson type $[X_2M_{18}O_{62}]^{6-}$ heteropoly anions due to their promising application as catalytic materials. The free acid form of the heteropoly anions, i.e. Keggin $H_3XM_{12}O_{40}$ and Wells-Dawson $H_8X_2M_{18}O_{62}$ type compounds, are solid super-acids since their acid strength is greater than sulfuric acid. Therefore, many heteropoly acids are more active catalysts than conventional organic and inorganic acids in liquid-phase reactions. Moreover, the insolubility of the heteropoly acids in many liquid organic substances allows the separation and reuse of these catalysts (Valle *et al.*, 2007; Gambaro and Briand, 2004; Briand *et al.*, 2003).

On line with this worldwide trend, our group explores the catalytic activity of fosfotungstic Wells-Dawson heteropoly acid in the Friedel-Crafts acylation of isobutylbenzene with acetic anhydride. Surprisingly, the preliminary results showed that isobutylbenzene was

acylated towards 4-isobutylacetophenone and this substance was further condensed towards a dypnone like compound (data not published). Therefore, the present investigation was conducted in order to establish the nature of the surface adsorbed species of the substituted acetophenone and further understand the deactivation of the heteropoly acid during the acylation.

The compound called dypnone $C_6H_5COC=C(CH_3)C_6H_5$ that is used as plasticizer, perfume base and light-stable coatings is obtained through the Aldol self-condensation of acetophenone $C_6H_5COCH_3$ over acid catalysts. The conventional organic synthesis of dypnone requires a homogeneous solvent base media and is catalyzed through a variety of acid compounds such as, aluminum tert-butoxide, hydrogen halides (bromide, fluoride and chloride) and aluminum chloride (Calloway and Green, 1937; Adkins and Cox, 1938; Simons and Ramler, 1943). This organic synthesis is not environmentally friendly since the acid catalysts are not reusable and the solvents removed out of the product mixture leads to a considerable amount of dangerous liquid wastes.

More recently, greener Aldol condensation processes involving solid acid catalysts in heterogeneous liquid reagents-solid catalyst fashion were reported. The investigations of Garcia *et al.* showed that HY zeolites catalyze the crossed Aldol condensation of acetophenone with benzaldehyde producing cis and trans-chalcones (Garcia *et al.*, 1995).

R. Mestres indicates in a very interesting review on this topic that heterogeneous catalysis for the Aldol reaction offers the possibility of the easy separation of the catalyst from the reaction mixture (Mestres, 2004). The author highlights hydrotalcites and microporous silica as promising catalytic materials for the synthesis of pharmaceuticals and fine chemicals through the Aldol reaction. In fact, a modified hydrotalcite such as, Na-MCM41 has been used to catalyze the condensation of substituted benzaldehydes with α -hydroxyacetophenone with 100% conversion and 90% yield.

Singh *et al.* demonstrated that sulfated metal oxides and acid zeolites catalyze the self condensation of acetophenones towards α,β -unsaturated ketones (Venkatesan and Singh, 2002; Venkatesan, 2004). Sulfated zirconia SO_4^{2-}/ZrO_2 , sulfated titania SO_4^{2-}/TiO_2 and H-beta zeolite selectively catalyze the condensation of acetophenone to dypnone up to 85 % in a solventless reaction media.

Although, the processes based on solid heteropoly acids replacing liquid acid catalysts are an outstanding contribution in the development of environmental benign technologies, the literature does not mention any research related to the use of HPAs in the Aldol condensation processes.

The present investigation focuses on the intermediate adsorbed species of the self condensation of 4-isobutylacetophenone over the solid heteropoly acid. This investigation is a starting point on the potential use of fosfotungstic Wells-Dawson heteropoly acid to catalyze Aldol condensation reactions.

II. EXPERIMENTAL

A. Synthesis of the Fosfotungstic Wells-Dawson Acid

The fosfotungstic Wells-Dawson heteropoly acid $H_6P_2W_{18}O_{62} \cdot xH_2O$ was synthesized through the ion exchange of ammonium fosfo-tungstic salt $(NH_4)_6P_2W_{18}O_{62} \cdot 13H_2O$ with an ion exchange resin. Although the details of the method were published before, the fundamentals of the synthesis are summarized in the following paragraphs.

The ammonium fosfotungstic Wells-Dawson salt was synthesized according to the method reported in the literature (Lyon *et al.*, 1991). Concentrated H_3PO_4 (Merck ACS, 85%) was added to a boiling solution of Na_2WO_4 (J.T. Baker ACS, 100%) in a 4:1 acid: salt molar ratio. The mixture was kept boiling under stirring for 8 hs. Ammonium chloride NH_4Cl (J.T. Baker ACS, 100%) was added in order to precipitate the salt. Then the salt with the mother liquor was kept overnight at 5 °C to improve the yield of the precipitation process. The salt was dissolved in water at room temperature and filtered to remove impurities. Again, ammonium chloride was added to re-precipitate the salt and kept at low temperature overnight. Finally, the salt was filtered, washed with water and dried under vacuum at room temperature.

The starting ammonium salt was dissolved in absolute ethanol (Merck, 99.8 %) and kept in contact (batchwise) with a Dowex HCR-W2 (Sigma-Aldrich) acid resin in a (1:0.9) salt: resin weight ratio. The exchange of the ammonium ions by protons was followed through the infrared analysis of the salt in the liquid media until no signal at 1400 cm^{-1} due to NH_4^+ was observed (Matkovic *et al.*, 2005).

After the completeness of the exchange, the solution was allowed to dry at room temperature leading to the precipitation of the heteropoly acid that was used without further pretreatment.

B. Spectroscopic Investigation of Adsorbed-Reactive Surface Species

The nature of the surface species due to the adsorption and/or reaction of isobutylbenzene (Aldrich, 99%), 4-isobutylacetophenone (Lancaster Synthesis Inc., 97%) and trans-benzylidenacetophenone (trans-chalcone $C_6H_5CH=CHCOC_6H_5$, Aldrich 97%) over fosfotungstic Wells-Dawson heteropoly acid were investigated through infrared spectroscopy under ambient conditions.

The above mentioned substances were allowed to interact with the heteropoly acid (100-200 mg) at room temperature, 323 K, 353 K and 368 K for 30 minutes in a batch reactor under refluxing condition. A sample of the solid was withdrawn at each temperature, placed between KBr crystals (or pressed in a conventional KBr wafer) and further analyzed with a Bruker IFS66 FTIR equipment. The spectra were taken with 100 scans and 2 cm^{-1} resolution.

The experiments performed with 4-isobutylacetophenone possessed isobutylbenzene as co-solvent in a 1:10 reactant:co-solvent volume ratio, in order to avoid the solubility of the acid in the liquid media.

Similarly, dichloromethane (Sintorgan, 99.5 %) was used to dissolve the chalcone (typically a solid chemical) since the heteropoly acid is not soluble in this solvent. This co-solvent was used in a 40:1 mg/ml weight of chalcone per volume of solvent ratio.

III. RESULTS AND DISCUSSION

A. Evidences of the Aldol Condensation of Substituted Acetophenone over the Heteropoly Acid: Surface Adsorbed Species

The interactions between isobutylbenzene (IBB) and 4-isobutylacetophenone (IBA) with bulk fosfotungstic Wells-Dawson acid are discussed in this section.

Figure 1 presents the infrared spectra of the acid after being exposed to IBB at room temperature, 323 K, 353 K and 368 K. The spectra show only the signals belonging to the Wells-Dawson heteropoly acid and there is no evidence of reaction products or surface adsorbed species.

The spectra of the acid possess an intense band at 1086 cm^{-1} assigned to the stretching mode of the P-O species. This band is a fingerprint of the Wells-Dawson heteropoly anion $P_2W_{18}O_{62}^{6-}$ structure. The bands at 966, 916 and 778 cm^{-1} correspond to the W-O species of the cage structure surrounding the central phosphorous species (Briand *et al.*, 2003; Valle *et al.*, 2007).

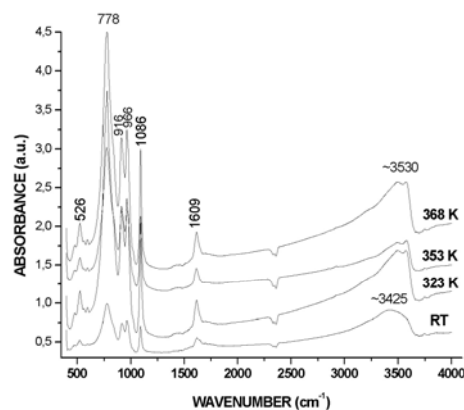


Figure 1. Infrared spectra of isobutylbenzene adsorbed over fosfotungstic Wells-Dawson heteropoly acid at various temperatures.

At difference with IBB, the heteropoly acid is highly soluble in 4-isobutylacetophenone and its infrared features are greatly modified when in contact with this sub-

stance. The infrared spectra of the solid phase after exposure to IBA at various temperatures are presented in Figs. 2A and 2B. The infrared spectrum of liquid IBA was subtracted in order to eliminate the contribution of physisorbed species. Therefore, the signals appearing between 500 cm^{-1} and 4000 cm^{-1} (with the exception of the vibration of water molecules at 1604 cm^{-1}) could be ascribed to chemisorbed species and the characteristic signals of the fosfotungstic heteropoly acid.

The HPA maintains the typical vibrations of the P-O and W-O bonds of the heteropoly anion structure nevertheless, they shifted to higher wavenumbers due to the interaction with IBA (see Figure 2A). The band belonging to the asymmetric stretching of W-O-W corner sharing species splits in three signals at 767 cm^{-1} , 779 cm^{-1} and 820 cm^{-1} . A similar behavior was observed with the $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$ anion dissolved in organic media due to the chemisorption of polar organic substances (Valle *et al.*, 2003).

The tungsten species of the Wells-Dawson structure are associated with terminal OH species that vibrate at $\sim 3400 \text{ cm}^{-1}$ which is clearly observed as a broad and in-

323 K and 353 K and re-appears at 368 K. This observation indicates that IBA chemisorbs on surface Brønsted sites consuming OH species during the process.

In general, the chemisorption of IBA over the heteropoly anion leads to the shifting of the characteristic bands of liquid IBA as can be observed in Table 1. A series of intense and well defined signals of chemisorbed IBA are observed from room temperature to 368 K (see Figs. 2A and 2B). The signals between 2954 cm^{-1} to 2849 cm^{-1} are characteristic of symmetric and asymmetric stretching of methyl and methylene groups of the isobutyl group (see Table 1). The infrared band at 1682 cm^{-1} is attributed to the stretching vibration of carbonyl species and a series of signals of low intensity between 1560 cm^{-1} and 1514 cm^{-1} are assigned to C-C aromatic ring stretching vibrations. The bands at 1460 cm^{-1} , 1416 cm^{-1} and 1359 cm^{-1} correspond to bending modes of the out of plane methyl groups along with the signal at 1267 cm^{-1} that is attributed to the stretching of C-C species. Moreover, the signal at 1183 cm^{-1} is attributed to the C-CO-C bonds bending of the ketone group.

Additional signals are observed at 353 K and 368 K which could be ascribed to the presence of another compound due to the Aldol condensation of two adsorbed IBA species such as a trans-chalcone like product (see highlighted signals in Fig. 2A).

The signal at 1654 cm^{-1} has been attributed to the carbonyl stretching vibration of chalcone $\text{C}_6\text{H}_5\text{COCH}=\text{C}(\text{CH}_3)\text{C}_6\text{H}_5$ that is, the product of condensation of two molecules of acetophenone (see Fig. 2A and Table 1). The presence of the double bond of the chalcone unit $-\text{COCH}=\text{C}-$ is evidenced by a shoulder at 1597 cm^{-1} . More evidences of the presence of adsorbed chalcone type species are obtained through the signals at 1221 cm^{-1} and a shoulder at 1284 cm^{-1} ascribed to the vibration of the C_6H_5 species in the $\text{C}_6\text{H}_5\text{COCH}=\text{C}$ group (Ahmad *et al.*, 1998; Ahmad *et al.*, 1999).

The series of signals observed above 3000 cm^{-1} belong to the stretching vibrations of aromatic and olefinic C-H groups. Specifically, the signal at 3086 cm^{-1} has been attributed to the C-H stretching vibration of the $-\text{CH}=\text{C}-$ group of a branched-alkene structure such as, the one of isoprene (Silverstein *et al.*, 1991).

B. Additional Evidences of the Presence of Surface Trans-Chalcone Species over the Heteropoly Acid

Further insights on the nature of the product of condensation of 4-isobutylacetophenone were obtained through the adsorption of a commercial trans-chalcone over the HPA.

Figure 3 compares the infrared spectra of a solution of trans-benzylidenacetophenone (trans-chalcone) in dichloromethane and the adsorbed species over the fosfotungstic Wells-Dawson acid at 323 K and 353 K.

The signals belonging to the solvent (indicated in the spectrum of chalcone- CH_2Cl_2 in the liquid media) do

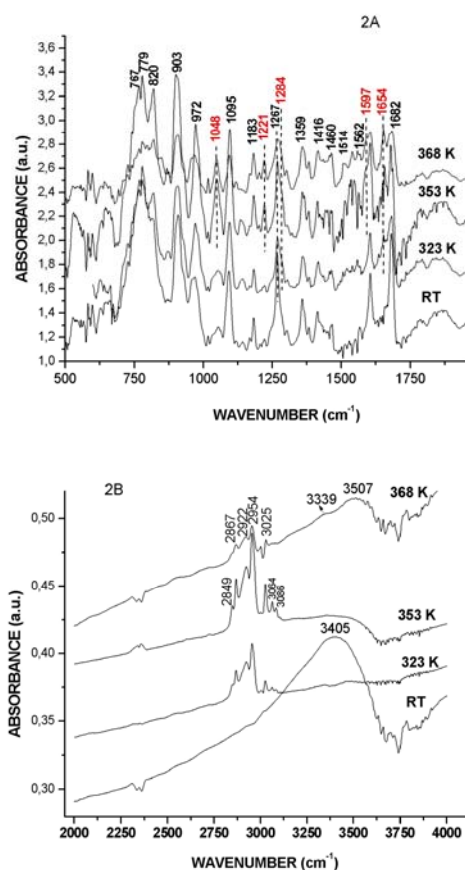


Figure 2. Infrared spectra of 4-isobutylacetophenone adsorbed over fosfotungstic Wells-Dawson heteropoly acid at various temperatures: (2A) 500 cm^{-1} to 1800 cm^{-1} region and (2B) 2000 cm^{-1} to 4000 cm^{-1} region. The signals highlighted correspond to chalcone-type species.

tense signal at room temperature (see Fig. 2B). The signal almost vanishes when the acid interacts with IBA at

Table 1. Infrared vibrations of 4-isobutylacetophenone in the liquid phase and adsorbed over fosfotungstic Wells-Dawson heteropoly acid.

Wavenumbers (cm ⁻¹)		Assignment	reference
liquid	adsorbed		
----	3086 ^a	v(C-H) in the =C-H group	Silverstein <i>et al.</i> , 1991
3085	3065 ^a	v(C-H) aromatic ring	Silverstein <i>et al.</i> , 1991
3034	3025 ^a	v(C-H) aromatic ring	Silverstein <i>et al.</i> , 1991
2959	2954	v _{as} (CH ₃) of isobutyl group	Silverstein <i>et al.</i> , 1991
2924	2922	v _{as} (CH ₂) of isobutyl group	Silverstein <i>et al.</i> , 1991
2867	2867	v _s (CH ₃) of isobutyl group	Silverstein <i>et al.</i> , 1991
----	2849	v _s (CH ₂) of isobutyl group	Silverstein <i>et al.</i> , 1991
1684	1682	v(C=O)	Ahmad <i>et al.</i> , 1997 and 1999
----	1654 ^a	v(C=O) of condensed IBA	Ahmad <i>et al.</i> , 1998 and 1999; Choi <i>et al.</i> , 2001a, b; Patil <i>et al.</i> , 2007.
----	1597(s) ^b	v(C=C) of condensed IBA	Ahmad <i>et al.</i> , 1999; Choi <i>et al.</i> , 2001a, b; Patil <i>et al.</i> , 2007
1568	1562	v(C-C) aromatic ring	Ahmad <i>et al.</i> , 1999 and 1998
----	1514	v(C-C) aromatic ring	Ahmad <i>et al.</i> , 1999
1464	1460	δ _s (CH ₂) of isobutyl group	Silverstein <i>et al.</i> , 1991
1413	1416	δ _a (CH ₃) of isobutyl group	Ahmad <i>et al.</i> , 1999
1356	1359	δ _s (CH ₃)	Ahmad <i>et al.</i> , 1999
----	1284(s) ^a	v(C-C) of condensed IBA	Ahmad <i>et al.</i> , 1999
1266	1267	v(C-C)	Ahmad <i>et al.</i> , 1999
----	1221 ^b	Vibration of C ₆ H ₅ in =CHCOC ₆ H ₅ group	Ahmad <i>et al.</i> , 1999
1184	1183	δ[C-(C=O)-C]	Silverstein <i>et al.</i> , 1991
----	1048 ^b	v(C-O) tertiary alcohol	Silverstein <i>et al.</i> , 1991

(s) shoulder; ^a signals observed at 323 and 353 K.; ^b signal observed at 353 K and 368 K.

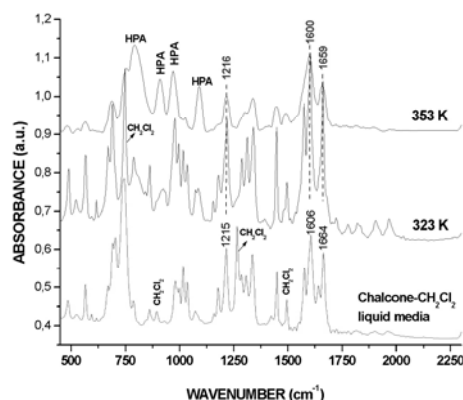


Figure 3. Infrared spectra of trans-chalcone dissolved in dichloromethane and adsorbed over fosfotungstic Wells-Dawson heteropoly acid at 323 K and 353 K. The signals highlighted correspond to chalcone-type species.

not overlap with the characteristic infrared vibrations of the trans-chalcone therefore, the spectra of this solvent was not subtracted. Moreover, the characteristic vibrations of molecular trans-chalcone (in the liquid media) and the surface species adsorbed over the heteropoly acid are highlighted for a straightforward identification of the adsorbed species.

The molecular trans-chalcone possesses three characteristic infrared vibrations at 1215 cm⁻¹, 1606 cm⁻¹ and 1664 cm⁻¹ that correspond to the vibration of the =CHC=O group, C=C stretching and C=O (carbonyl) stretching, respectively (Ahmad *et al.*, 1998; Choi *et al.*, 2001a and 2001b; Patil *et al.*; 2007). These signals were described when 4-isobutylacetophenone reacts over the HPA as discussed previously and are also observed when the trans-chalcone adsorbs over the

HPA at 323 K and 353 K (see Fig. 3). Moreover the shift of the vibration assigned to the carbonyl species towards 1659 cm⁻¹ (5 cm⁻¹ compared with the molecule in the liquid media) might indicate that the trans-chalcone is adsorbed on the heteropoly acid through this species.

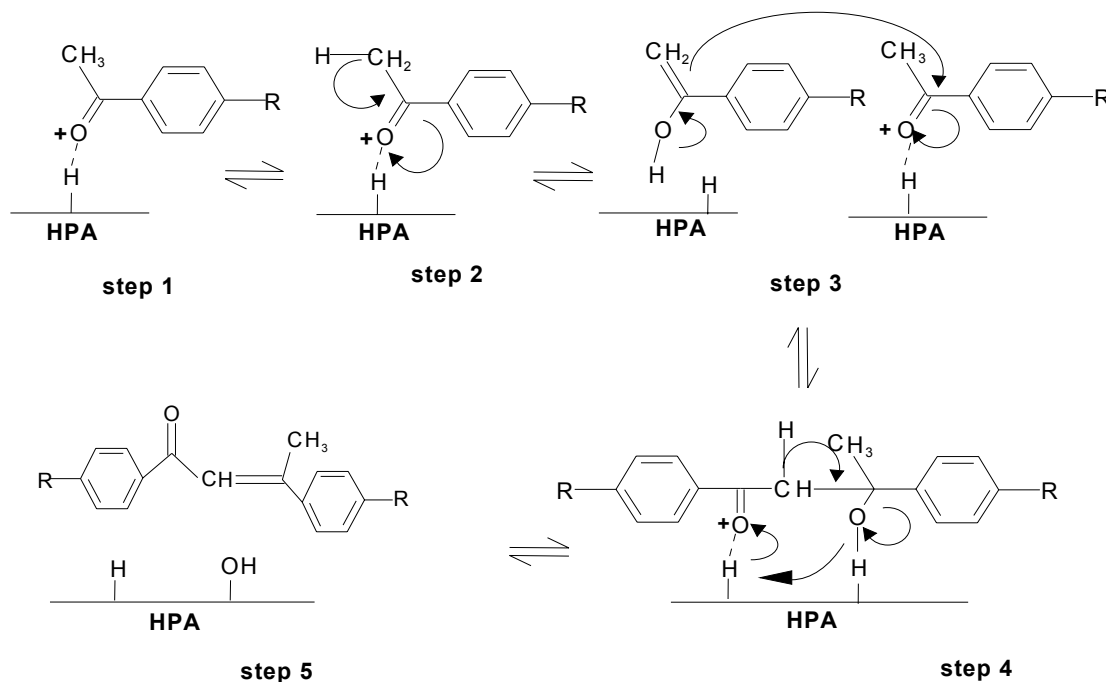
Nevertheless, no vibration at 1048 cm⁻¹ was observed in this experiment, which demonstrates that this signal does not belong to a chalcone type compound.

C. Mechanism of the Aldol Condensation of Substituted Acetophenone over an HPA

The evidences obtained during the adsorption-reaction of 4-isobutylacetophenone and trans-chalcone over the solid acid allow to propose a mechanism for the Aldol condensation of 4-isobutylacetophenone catalyzed by the Brønsted acid sites of the heteropoly anion.

In the first step of the mechanism, a molecule of IBA chemisorbs on a surface Brønsted site through the carbonyl group as shown in Scheme 1. The adsorbed IBA goes through an enolisation process generating an intermediate reactive enol species R-COH=CH₂ (step 2). This species further condensates with another adsorbed IBA molecule (step 3). The condensation turns a methyl -CH₃ into a methylene group per molecule of condensate product (step 4) and generates one water molecule (and/or regenerates the active surface site) per molecule of the 1,3-isobutylphenyl-2-propen-3-methyl-1-one compound formed in this process (step 5).

According to a typical Aldol mechanism the condensation of alkyl phenones involves an enol intermediate species. The mechanism depicted in Scheme 1 suggests the presence of a substituted enol species such as, CH₂=COHC₆H₄R which might explain the infrared signal that can not be assigned to a chalcone type species.



Scheme 1. Mechanism of 4-isobutylacetophenone Aldol condensation over Wells-Dawson HPA

The signal at 1048 cm^{-1} might be an evidence of the enol intermediate since is characteristic of the C-O stretching vibration of a tertiary α -unsaturated alcohol such as the species presented in step 3 of the mechanism (Silverstein *et al*; 1991). Nevertheless, further investigations are necessary in order to identify this signal.

The presence of the signals belonging to the intermediate species of dyppone at 323 K and 353 K coincides with the absence of the bands of the Brønsted acid sites of the HPA. The re-appearance of these active sites at 368 K (see the signal at 3507 cm^{-1}) gives more evidences of the generation of H_{ads} and OH_{ads} species during the last step of the proposed mechanism.

IV. CONCLUSION

4-Isobutylacetophenone strongly chemisorbs over fosfontungstic Wells-Dawson heteropoly acid through the interaction with Brønsted acid sites. These active sites catalyze the enolisation of the adsorbed species that further condensates to a chalcone type compound. The condensation of two adsorbed 4-isobutylacetophenone molecules produces both H_{ads} and OH_{ads} species that regenerate the active acid sites of the heteropoly acid.

These evidences demonstrate that the heteropoly acid is a promising catalyst in the Aldol condensation of 4-isobutylacetophenone. However, the high solubility of the bulk HPA in the reaction medium makes it not suitable for this particular reaction. Further investigation of the activity of the acid dispersed over oxide supports as a catalyst in the Aldol condensation processes must be performed.

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