

# 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  $1654\text{ cm}^{-1}$  and  $1597\text{ cm}^{-1}$  that resemble the carbonyl stretching vibration and the double bond of dypnone  $C_6H_5COHC=C(CH_3)C_6H_5$ . Additional signals at  $1221\text{ cm}^{-1}$  and a shoulder at  $1284\text{ cm}^{-1}$  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  $\alpha$ -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  $\alpha,\beta$ -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.