

Metal Catalysed Condensation Reaction

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Abstract

Propanone (acetone) was dimerised to obtain 4-hydroxy-4-methylpentanone-2 (diacetone alcohol) in reasonably good yields in presence of metal catalyst viz aluminium, iron, tin and zinc at different catalytic conditions---pure metal, activated metal and amalgamated metal. Yields of the product was found to decrease exponentially with the increase of proton number of the metal catalyst.

Introduction

Reactions proceeding by a direct union between the carbon atoms of the same or different molecules of the same or different substances to form new compounds are termed as condensation reactions and the products so obtained are termed as condensation products. Of the various types of condensation reactions, one of the very common one is the reactions of aldehydes, ketones, esters, etc of the same or similar molecules with or without the elimination of neutral molecules like water, alcohols, etc. These reactions are generally catalysed by acids, bases (hydroxides, alkoxides, amines, etc), Lewis acids (Ahmed and Ahmed, 1978; Ahmed, *et.al.*, 1982; Ahmed, *et.al.*, 1986; Ahmed, *et.al.*, 1987; Ahmed, *et.al.*, 1988; Ahmed, *et.al.*, 1990; Ahmed, *et.al.*, 1991) likely anhydrous aluminium chloride, ferric chloride, anhydrous zinc chloride, boron trifluoride etherate, etc.

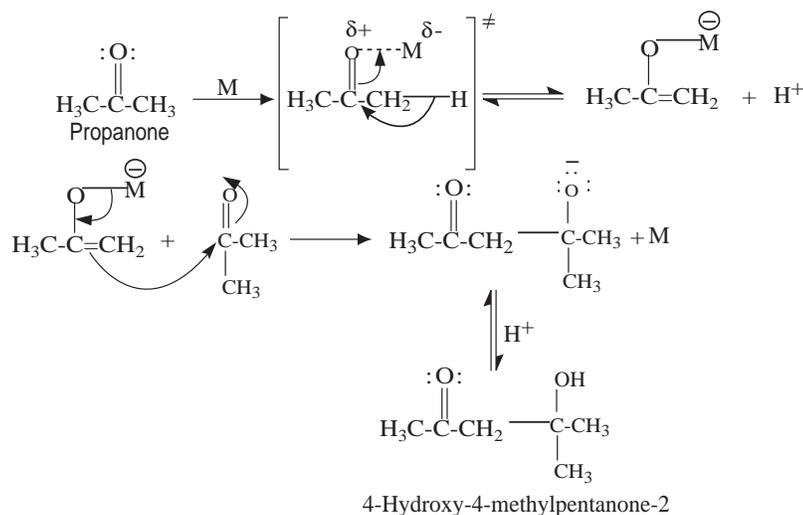
Some of the Lewis acids are also very much known to catalyse the famous Friedel-Crafts alkylation and acylation reactions. Some of

the common Lewis acids include the salts of aluminium, boron, iron, tin, zinc, etc. Some reports (Diughuid, 1941; Azatyan, 1948; Bahar and Akhter, 1988; 2007, Kalam, *et.al.* 2007) are available on the use of these electropositive metals (known to form Lewis acids) in different catalytic conditions as Friedel-Crafts catalyst.

In view of the above reports, our present investigation was directed towards the use of electropositive metals (known to form Lewis acids) like aluminium, iron, tin, and zinc as condensation catalyst.

Materials and Methods

All the recorded temperatures were uncorrected IR spectra were recorded as thin liquid films on a SHIMADZU IR-470 spectrophotometer. The GLC chromatogramme were recorded on a PYE UNICAM PU 4500 Capillary chromatogramme.



Scheme 1 : A possible mechanism for the formation of 4-hydroxy-4-methylpentanone-2 (diacetone alcohol)

Metal Catalyst : Metals like aluminium, iron, tin, and zinc were used as foils, turnings, powder, and granules, etc respectively.

Activated Metal Catalyst (Vogel, 1968) : Metal as foils, turnings, powder, and granules was taken in a flask covered with an aqueous solution of NaOH (10 %). The flask was warmed on a water bath until evolution of gases took place for a few minute. The liquid was then decanted-off; the residue was washed repeatedly with a little warm distilled water till it is free from any alkali. Finally it was washed with a little rectified spirit. Thus obtained exceptionally clean-surfaced metal and was preserved in an air-tight container for use.

Amalgamated Metal Catalyst (Vogel, 1968) : Sufficient amount of aqueous solution of mercuric chloride (2 %) was added to cover the clean-surfaced metal (in foil, turning,

powered, or granular form) (Ca 500 mg) completely in a container and was allowed to react for about two minutes. The aqueous solution was then decanted-off and the metal amalgam was washed with water, rectified spirit and finally with a little moist diethyl ether, which resulted the amalgamated metal (Ca 250 mg).

Condensation of Propanone in presence of Metal Catalyst (Vogel, 1968) : Propanone (1000.0 cm³, 2.54 mole) was taken in a round-bottomed flask fitted with a glass soxhlet containing the catalyst (0.10 mole) and a reflux condenser with a guard tube. Propanone in the flask was then heated to reflux on a heating mantle so that the hot vapour of propanone could pass over the metal catalyst kept inside the soxhlet each time. During reflux, aliquot of the reaction mixture was taken out for GLC study time to time. The reflux was continued for 24 hrs on

an average until no further change was observed in GLC. The mixture was then cooled and set to fractional distillation to obtain (i) unreacted propanone (T_b : 45°C - 50°C), (ii) unreacted propanone-product mixture (T_b : 80°C - 120°C), and (iii) 4-hydroxy-4-methylpentanone-2 (diacetone alcohol) (T_b : 164°C - 168°C) (Vogel).

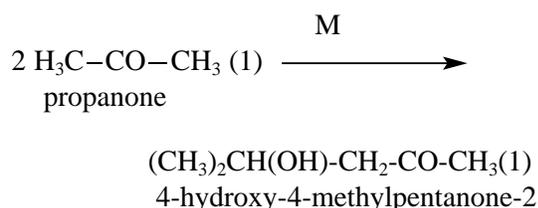
Results and Discussion

Our present investigation includes the use of metals such as aluminium, iron, tin, and zinc as catalyst for the dimerisation of propanone (acetone) to obtain 4-hydroxy-4-methylpentanone-2 (diacetone alcohol). Each of the above mentioned metal was used at different catalytic conditions such as (i) metals as such, (ii) activated metals, and (iii) amalgamated metals. All these reactions were carried out by refluxing propanone in a round-bottomed flask fitted with a glass *soxhlet* and a refluxing condenser with a guard tube so that time fresh and hot vapour of propanone can pass over the catalyst kept in the *soxhlet*. The progress of the reaction was followed by GLC time to time by taking out aliquot of the reaction mixture to observe any further change. During GLC studies, the reaction mixture exhibited the appearance of a new at a retention time corresponding to that of an authentic sample of 4-hydroxy-4-methylpentanone-2 (diacetone alcohol). However, during the GLC studies, the peak for the reactant became weaker and the same for the product appeared intense gradually. This change in GLC spectra was not found to continue after 24 hr progress of the reaction and therefore the reflux was stopped. The reaction mixture was then set to fractional distillation to obtain

unreacted propanone (T_b : 45°C - 56°C) and another liquid (T_b : 164°C - 168°C).

The liquid distilling at 164°C - 168°C exhibited bands in its IR spectrum at 3565, 3510, and 3405 cm^{-1} for O-H stretching of aliphatic system; 1699 cm^{-1} for C=O stretching of acyclic carbonyl compounds; 1414, 1353, and 1221 cm^{-1} for C-H bending of aliphatic system; and 1090 cm^{-1} for C-O bending of C-OH of alcohols. GLC studies of the reaction mixture during the reaction showed the appearance of a new peak (other than propanone-peak) which corresponded to that of authentic 4-hydroxy-4-methylpentanone-2 (diacetone alcohol) by comparing its IR spectrum with that of an authentic sample of 4-hydroxy-4-methylpentanone-2 (diacetone alcohol), the IR spectra of which were completely superposable with other.

On the basis boiling temperature, GLC studies, and superposable IR spectra, the separated product was identified as 4-hydroxy-4-methylpentanone-2 (diacetone alcohol).



Percentage yield of the 4-hydroxy-4-methylpentanone-2 one formed in presence of metal catalyst like aluminium, iron, tin and zinc at different catalytic conditions such as (i) metal itself, (ii) activated metals, and (iii) amalgamated metals is summarised in the following table (Table I).

Table I. Percent-yield of 4-hydroxy-4-methylpentanone-2 at different catalytic condition

Catalyst	Percentage-yield		
	<i>a</i>	<i>b</i>	<i>c</i>
Al [13]	27.0	31.5	35.0
Fe [26]	18.0	21.0	23.5
Zn [30]	15.0	17.0	20.5
Sn [50]	10.0	12.5	15.0

a : Catalyst : pure metal

b : Catalyst : activated metal

c : Catalyst : amalgamated metal

Graphs were plotted with (i) percent-yield of the product Vs catalytic condition (Fig. 1) and (ii) percent-yield of the product Vs proton number of the catalyst (Fig. 2). Yield of the product was found to increase steadily (Fig. 1) for each metal catalyst from pure to activated metals to amalgamated metals. The yield of the product was also decreased

exponentially with the increase of proton number of the metal catalyst (Fig. 2) The above two graphs (Fig. 1 and Fig. 2) can be combined together as a Bar-Diagramme (Fig. 3) which alone shows the exponential decrease of the yield of the product with the increase of the proton number of the metal catalyst and also the steady increase in the yield as activity of the catalyst increases.

A possible mechanism for the formation of 4-hydroxy-4-methylpentanone-2 (diacetone alcohol) due to the dimerisation of propanone in presence of metal catalyst is given below (Scheme 1) :

An increase in the yield of product at catalytic condition from pure metal to activated metal and amalgamated metal may be explained due to the stronger chelation of the metal catalyst with the carbonyl-oxygen making the carbonyl (Scheme 1) (Kalam, *et. al.*, 2007). A decrease (Fig. 2) in the yield of the

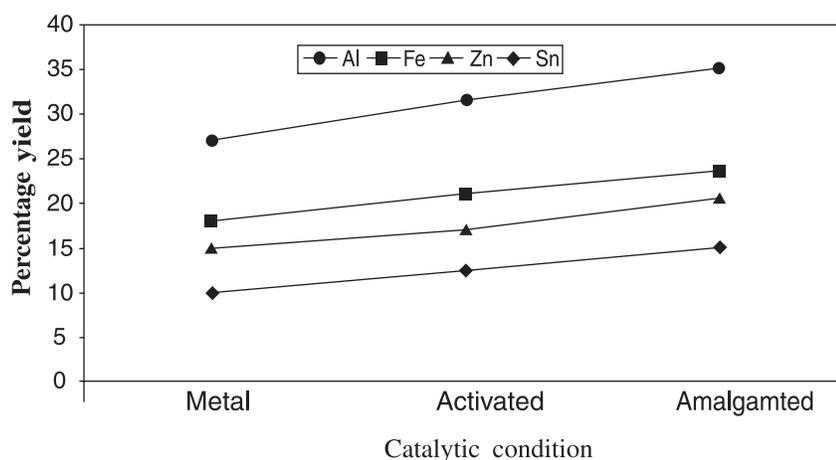


Fig. 1. Graph of percentage yield Vs catalytic condition a -metal; b -activated metal; c - amalgamated metal

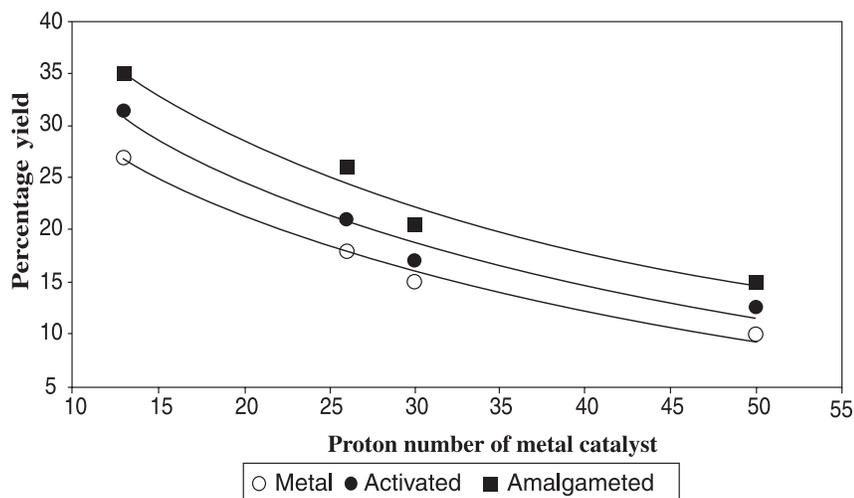


Fig. 2. Graph of percentage yield Vs proton number of metal catalyst

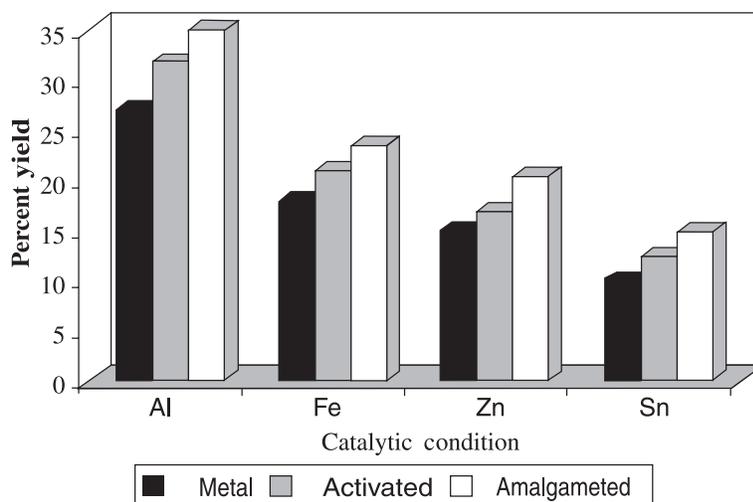


Fig. 3. Bar diagramme showing comparison of yields of alkylated product(s) at different catalytic conditions

product with the increase of proton number of the metal catalyst may be explained as less the proton number of an element, nearer its vacant or partially vacant orbital(s) to the nuclei, making the metal more affinity for

electrons and hence form stronger chelates with carbonyl-oxygen so that the carbonyl carbon becomes more susceptible to attack by nucleophiles.

Conclusion

Metals like aluminium iron, tin and zinc were successfully used as catalysts for the condensation of propanone to 4-hydroxy-4methylpentanone-2. These metals, including some other considerably electropositive metals may be employed for the reactions of Aldol and related condensation reactions.

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Received : October 17, 2006;

Accepted : March 6, 2007