A STUDY OF ESTERIFICATION USING LOCAL NATURAL ALUMINOSILICATES AS CATALYSTS

PRESENTED BY

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FOR

THE DEGREE OF MASTER OF SCIENCE

THESIS

SUBMITTED TO CHEMISTRY DEPARTMENT

University College for Women

Ain Shams University

CAIRO, 1987

NOTE

Beside the work carried out in this thesis, the candidate attended post graduate courses for one year including the following topics:

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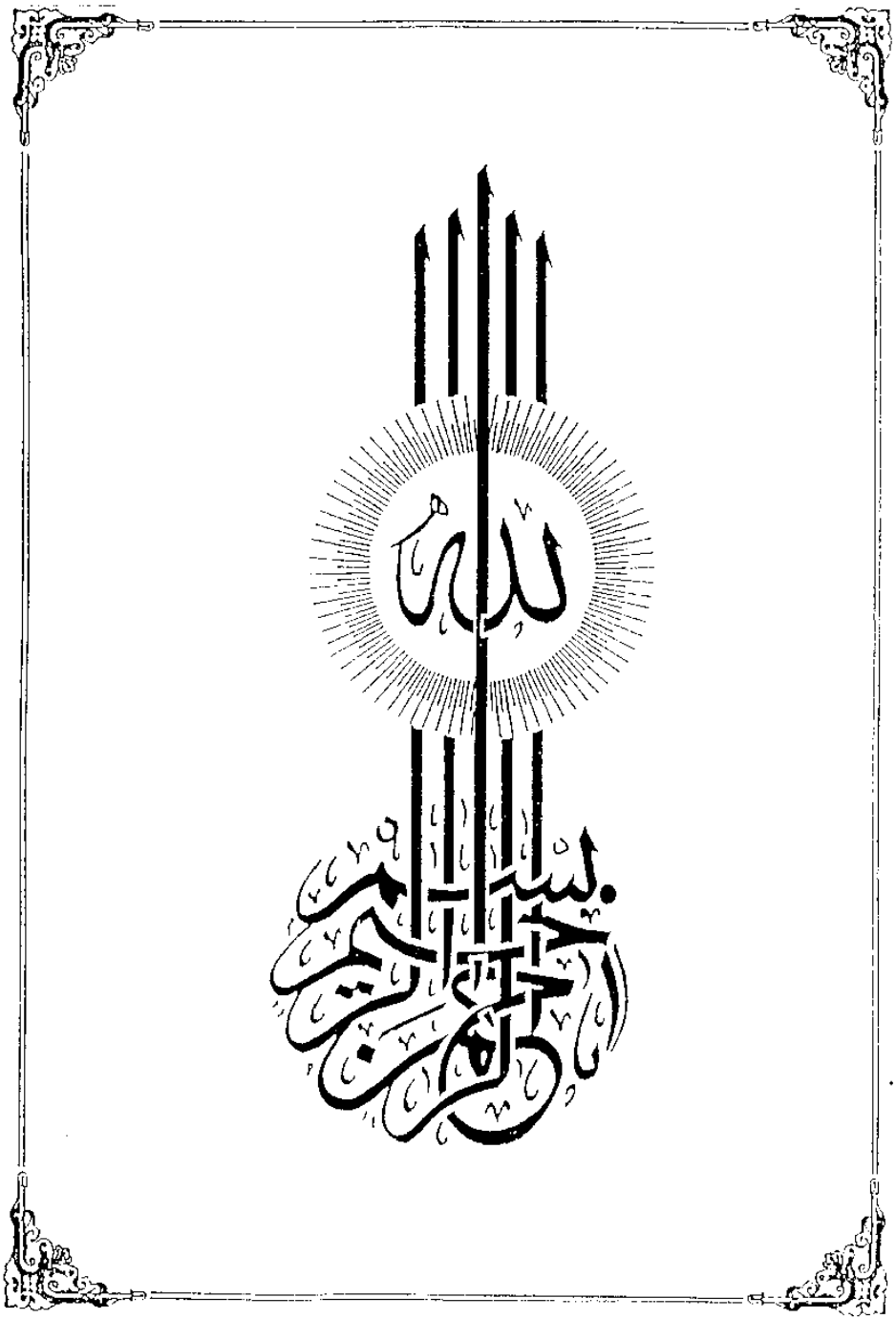

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ACKNOWLEDGEMENT

I would like to express my sincere thanks and gratitude to prof. Dr. Samiha Abdel Wahab for her careful supervision, helpful guidnace and for revising the thesis.

I am deeply grateful to Prof. Dr. Bahey El-Deen Mostafa Hassan for suggesting the point of research, supervising and following the progress of the work with great interest.

Sincere thanks are due to Assist Professor Dr. Fathia Mohamed Tawfik for guidance, advise and valuable help.

CONTENTS

I SUMMARY

A catalyst was prepared from Egyptian natural alumino-silicates, of the kaolinite type, and zinc chloride.
It was tested in esterification runs which were done as liquid-phase batch processes or as vapour-phase continuous processes.

In the liquid-phase batch runs, acetic acid, its anhydride as well as a mixture of both, were esterified by ethyl alcohol. n-Butyl alcohol was used to esterify acetic acid and phthalic acid; the latter being esterified to its diester.

In the vapour-phase continuous runs, ethyl acetate, butyl acetate and ethyl butyrate were prepared from the corresponding acids and alcohols.

Generally, the yield increased with rise of the reaction temperature and contact time or-in the batch processes duration of the experiment. In some cases, rise of temperature decreased the esterification yield due to the acceleration of a side reaction; namely, the dehydration of the alcohol to the corresponding olefin.

In continuous vapour-phase runs, equimolecular mixtures of the acid and alcohol gave the highest yield. Rise of the initial molar ratio of any of the reactants which is on the expence of the other, resulted in a lowering of the yield indicating a second order reaction depending on the concentrations of both the acid and alcohol.

In liquid-phase batch runs, the acid anhydrides gave higher yields than the acids themselves, the aromatic acid which is used in this investigation, reacted slower than the aliphatic acid used.

With respect to the mechanism of the reaction, the rate determining step, which involves the addition of an alcohol molecule to the protonated acid molecule, is deduced to be enhanced by rise of temperature rather than by increase in the concentration of the alcohol. Rise of temperature is also deduced to enhance the following step, in which a molecule of water is eliminated from a transitional compound.

Runs which were carried out, both as batch liquid-phase and as continuous vapour-phase, proved the remarkable efficiency of the catalyst prepared; fulfilling, thus, the aim of the work done in this thesis.

II AIM OF THE WORK

It is known that synthetic aluminosilicates which are widely used in chemical processes especially in esterification are very expensive. The aim of the work done in this thesis is to find out a cheap catalyst from the local natural aluminosilicates of the kaolinite type and to study its efficiency in esterification processes. This kaolinite is used in combination with zinc chloride which is also very cheap.

III INTRODUCTION

Esterification is the process of formation of esters. An ester is a salt in which the basic radical is organic, the acidic radical being organic or inorganic.

In petrochemical fields both the acidic and basic radicals of the most important esters are organic, e.g. ethyl and butyl acetats which are used as organic solvents; several acrylates which polymerise to produce plastics, the famous diethylene terephthalate synthetic fibres...etc.

Esterification may be catalytic or non-catalytic as will be discussed later.

1- Non catalytic esterification

Although esterification is usually carried out, in presence of a catalyst, yet some are not catalytic as in the following cases:

A- Esterification of acetic acid with ethyl alcohol at 60-85°C[1].

The reaction rate, as well as the activation energy were determined; using gas chromatography.

The reaction was shown to be of 2nd order and the reaction rate constant is 7.50×10^{-7} mol^{-1} sec^{-1}. at 60°C. The activation energy was 14.300 cal./mole.

B- Preparation of acetates by the use of acetic anhydride instead of acetic acid, then distilling off the formed acetic acid[2]. By this method pentyl, hexyl, cyclohexyl, phenyl and benzyl acetates were prepared in yields amounting to 74-96%.

The acid anhydride is used, to overcome tne inhibiting effect of water resulting from the reaction of the alcohol with the carboxylic acid. This problem was solved by many ways as will be mentioned later.

In the esterification of phthalic anhydride with butyl alcohol to produce dibutyl phthalate, a thermal process was applied[3]. However, in a later stage of the esterification a synthetic resin, Wolfatit KPS which is a cation exchanger, was used. During this esterification, water resulting from the reaction was continuously removed. Thus a 96-99% yield was obtained after 8 hours in this batch process.

2- Catalytic Esterfication

Catalysts used in esterification processes are of different natures and categories. The most commonly used catalysts are:

a- Sulphuric acid

Sulphuric acid is a well known catalyst used in esterification processes since a long time. Besides being a catalyst, it eliminates water resulting from the reaction; thus helping the process of esterification, to be completed e.g. the esterfication of acetic acid with ethyl alcohol[4] and of acetic acid with cyclic alcohols e.g. cyclohexanol[5]. These and other such processes most of which are patented in different foreign countries are widely applied in industry involving other alcohols (sometimes olefins) and acids as will be explained later.[6,7,8,9]

Sulphuric acid is also used to catalyse other processes of the continuous type e.g. the esterification of phthalic anhydride with 2-ethyl hexanol[10] and of acrylic acid with ethylene at 127°C under pressure[11].

Pavlov et al[12] prepared tertiary butyl esters from isobutylene and the respective acids.

b- Sulphonic acids and Sulphonates

The most important sulphonic acid used as catalyst in esterification processes is p-toluene sulphonic acid. This catalyst is used in the esterification of phthalic anhydride with 2-ethyl hexanol to obtain the dibutyl phthalate, in the preparation of the diacetyl and diisoamyl phthalates, bis (2-ethyl hexyl) adipate and tris (2-ethyl hexyl) trimellitate. These processes are done according to Japanese patents.[13,14]

Wolfgang Langenbeck and Richard Mahrwald[15] used metal salts of benzene sulphonic acid to catalyse esterification of acetic acid with methyl alcohol. Comparing these catalysts with each other and with copper salts of other acids as well, it is found that the activity of the catalyst decreases as the strength of the acid decreases.

Chlorosulphonic acid is used as catalyst in the esterification of butyric acid with ethyl alcohol in a discontinuous process[16], and of some organic acid anhydrides with phenol.[17,18] It was found that the best proportion of the catalyst was 0.01 mole catalyst/mole phenol, even at room temperature, appreciable reaction was stated.

c- Phosphoric acids

According to a Check patent, phosphoric acids are used as esterification catalysts. Thus, orthophosphoric acid is used in presence of solid silica to catalyse the esterification of phthalic anhydride with 2-ethyl hexanol[19]; this process is batch. Terephthalic acid is esterified with ethylene glycol in presence of sodium acetate, phosphoric acid is also used in presence of solid antimony oxide[20].

Other phosphoric acids are reported in some esterification Hasegawa, Ryoichii and Asano Hiroshige[14] used H_3PO_3 and H_3PO_2 and their salts in esterification of organic acids or their anhydrides with alcohols e.g. adipic acid or phthalic anhydride with 2-ethyl Hexanol.