Preparation of Perovskite Catalyst for Oxidative Reactions

A Thesis

"Submitted for the degree of the Philosophy As a partial Fulfillment for the requirements of the Philosophy Degree"

Student name:

Delvin Dosouky Mohammed Ibrahim

Supervisors:

Prof. Dr. Suzy A. Selim

Prof. Dr. Sara Mikhail Soliman

Prof. Dr. Tamer Zaki Sharara

Ain Shams University
Faculty of Science
Chemistry Department

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A Thesis Submitted by

Delvin Dosouky Mohammed Ibrahim
(M.Sc.,Chemistry,2008)

For "Ph.D." Degree in Chemistry

Supervised By

Prof. Dr. Suzy A. Selim
Chemistry Department
Faculty of Science
Ain Shams University

Prof. Dr. Sara Mikhail Soliman
Refining Department
Egyptian Petroleum Research Institute

Prof. Dr. Tamer Zaki Sharara
Refining Department
Egyptian Petroleum Research Institute

Chemistry Department
Faculty of Science
Ain Shams University
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Faculty of Science
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Dissertation Submitted

By

Delvin Dosouky Mohammed Ibrahim
(M.Sc.,Chemistry,2008)

Researcher Assistant -Egyptian Petroleum Research Institute

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Faculty of Science
Ain Shams University
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Title of the thesis:

Preparation of Perovskite Catalyst for Oxidative Reactions

Submitted by:

Delvin Dosouky Mohammed Ibrahim

Supervisors:

Signature

Prof. Dr. Suzy A. Selim

Prof. Dr. Sara Mikhail Soliman

Prof . Dr. Tamer Zaki Sharara

Prof. Dr. Hesham Ahmad Ali Madani

Head of Chemistry Department
Faculty of Science
Ain Shams University

Qualification

Name: Delvin Desouky Mohammed Ibrahim

Scientific Degree: Ph.D.

Department: Chemistry

College: Faculty of Science

University: Al-Azher University

M.Sc.: 2008

B.Sc.: 2003

Job: Researcher Assistant - Refining Department -Egyptian Petroleum Research Institute

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Dedication

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The Aim Of The Present Work

Oxidation reactions including oxidative dehydrogenation of cyclohexane and oxidative coupling of methane are options to generate more useful products for petrochemical industries.

The catalytic oxidative dehydrogenation (ODH) of cyclohexane is one of the most attractive routes for converting cyclohexane into more valuable products as benzene. On the other hand the conversion of methane into valuable added products is of high interest for the chemical industry. Methane is the major constituent of natural gas, whose reserves is expected to be much higher than those of crude oil. As methane is the most stable coumpound (among the light alkanes), and difficult to activate therefore oxidative coupling of methane reaction is performed at high temperatures ***(Arndt et al., 2009)***.

So, it is necessary to find a catalyst that could activate the C–H bond and provide moderately active oxygen atoms to avoid the nonselective oxidation to CO and CO_2 during the OCM reaction ***(Jin et al., 2009)***.

Perovskite metal oxides have many catalytic applications. Perovskite materials are mostly composed of complex mixed metallic oxides (oxides of rare earth elements and d transition metals). The ideal perovskite oxide has a stoichiometry formula of ABO_3 and belongs to the cubic structure, with the six-fold coordination B (smaller cation) and the twelve-fold coordination A (larger cation) attached to the oxygens.

The catalytic activity of such compounds is primarily attributed to the transition metal cation at the B-site, whereas the thermal endurance of the catalyst is largely derived from the rare earth ion at the A-site ***(Aman et al., 2011)***. Moreover, partial substitution at A and B sites can strongly affect catalytic activity due to stabilization of unusual oxidation states of the B component and to the simultaneous formation of structural defects, which are responsible not only for part of the catalytic activity, but also for oxygen mobility within the crystal lattice ***(Moradi and Rahmanzadeh, 2012)***.

Depending on that, this study is interested in:

“Preparation of Perovskite Catalyst for Oxidative Reactions”

Part of this investigation is directed to a deeper understanding of structural and textural changes that may be undergone by the prepare perovskite oxide material under the various experimental conditions. This is achieved through X-ray diffraction analysis ***(XRD)***, Nitrogen adsorption-desorption isotherm ***(BET)***, Differential thermal analyses ***(DTA/TG)***, Transmission electron microscope ***(TEM)*** and Inductively coupled plasma-optical emission spectroscopy ***(ICP-OES)***.

The *first chapter* of this thesis presents a comprehensive literature review of the subject, thereby, giving a background about the problem under investigation.

The *second chapter* exhibits the various experimental techniques used throughout the present investigation.

In the *third chapter* the experimental results of the physicochemical characteristics and the catalytic activity (Oxidative dehydrogenation of cyclohexane) of the prepared catalysts are represented, correlated together and thoroughly discussed. The mathematical modeling equations for oxidative coupling of methane are also investigated.

The conclusions that may be drawn from the present investigation are briefly summarized at the end of the thesis.

ABSTRACT

Perovskite-type oxides of the general formula ABO_3 is a promising material as catalyst for the oxidative dehydrogenation of cyclohexane and oxidative coupling of methane to produce benzene and C_2 (ethane and ethene) respectively.

Perovskite $LaNiO_3$, substituted La-perovskites ($La_{1-x}Sr_xNiO_3$ and $La_{1-x}Li_xNiO_3$) and doubled layered perovskite La_2NiO_4 samples were prepared by single and/or reverse microemulsions.

Characterizations of the prepared perovskite samples have been studied by different teqnices; *XRD*, *N_2 adsorption-desorption*, *DTA/ TGA*, *TEM* and *ICP-OES*. The observed results indicated that all prepared samples are well crystalline, high surface area SB|Et, nanaparticles of 9-38 nm in size and their particle sizes are almost uniform.

The results of the catalytic activity showed that the prepared nano structured perovskite $LaNiO_3$ and $La_{0.6}Sr_{0.4}NiO_3$ samples are the most selective catalysts towards the oxidative dehydrogenation of cyclohexane (i.e. towards benzene formation) reached to 91 , 95% respectively.

From the application of the polymath program to analyze the mathematical modeling equations for oxidative coupling of methane on using the most active perovskite $La_{0.6}Sr_{0.4}NiO_3$ catalyst (towards oxidative dehydrogenation of cyclohexane), the

calculated data confirmed that the prepared $La_{0.6}Sr_{0.4}NiO_3$ sample will be selective catalyst for the production of C_{2+} hydrocarbons at reaction temperature $\geq$ 925ºC, under methane partial pressure of 0.3 and an oxygen partial pressure of 0.1.

Keywords: *Perovskite, oxidative, dehydrogenation, coupling, cyclohexane, methane, $LaNiO_3$, $La_{1-x}Sr_xNiO_3$, $La_{1-x}Li_xNiO_3$, La_2NiO_4, microemulsion.*