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Research Paper

Synthesis of Nanocomposite Based on Poly Methylene-imidazole as Effective Catalyst in Oxidation of Some Hydrocarbones

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Abstract

The polymers derived from heterocyclic rings like imidazole was prepared and supported to produce catalytic active supported catalyst. This catalyst was characterized using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), H NMR and UV-visible spectroscopy. The catalyst showed high catalytic activity in the oxidation of cyclohexene and cyclopentene under optimized conditions. In this work cyclohexene and cyclopentene were selected as model alkene for determination the capacity of the prepared imidazole polymer catalyst under optimized conditions of temperature and time of reaction. The catalyst could be readily separated from the catalytic system using uploading 3-5 milligrams of Copper(II), Nickel(II) and Cobalte(II) ions with the surface of polymer the conversion them to nano-particle which are identified by x-ray diffraction. For this research, a statistical method called Response Surface Methodology (RSM) has been used to economize the number of experiments and their meaningful interpretation. The effect of metallated polymer with Copper(II), Nickel(II) and Cobalte(II) were taken to increase the efficiency of oxidation. Optimization results for 0.33 mmole cyclohexene and cyclopentene showed that maximum oxidation efficiency 90. % was achieved at the optimum conditions: catalyst amount 350 mg, temperature 70.0, time 3.30 h and oxidant= 5.25 m mole.

Keywords: *Imidazole polymers, nano particles of cobalt(II) , copper(II) and nickel(II) , oxidation of cyclohexene by nanoparticles.*

1. Introduction

The interesting of scientists with the using of hetero polymers in the catalysis of organic reactions has been importance field in the recent years. The pyrrole and imidazole polymers have several advantages as catalysts which make them economically and environmentally attractive [Yuxi Liu Guofeng Zhao etal 2015, Yuanhang Ren etal 2015, Marek CYPRYK etal 2013, Pavel Drabina etal2017, Chen,Wei 2006, James P.Collman 2001]. On the other hand, these polymers with their metal complexes have a wide spectrum, approaching the super acid region due to enhancement of oxidation ability for the cyclic alkenes in good yields [Paul Christopher R.Yeisley 2013, G.Hayes etal 2001]. Simple methods of preparation, the possibility of changing the chemical or physical properties or qualities and the work of eight or three nanomaterials of heterogeneous polymers are considered to be the most important characteristics and characteristics of nano-crystalline membrane polymers. The eight and three nano-molecules of heterogeneous polymers were performed in the main reversible roles to form multiple types of fluid through the vacant orbits scattered in the Lewis (II), Ni (II) and Cobalt (II) [Paul J.Chirik 2015, E.Rezaee Nezhad etal 2015, Vladimir Valentinovich Kozlov 2016, Nicola Cioffi,Luisa Torsi etal 2005, Wun Shim etal 2002, Joseph Govan etal 2014]. Considered operations alkenes antioxidants that stimulate polymers pyrrole base factor in the new industrial chemistry, working to stimulate polymers pyrrole, such as olefins and cycled octane basic compounds are good for the process of oxidative stress is working to assess the quality of the potential stimulus in the oxidation of non-non-saturated homogeneous these compounds. Preparation of poly polymers as different as nanoparticles spread on the surface of bentonite as a catalyst and enhancer for epoxides of unsaturated compounds such as alkene[Hossein Salavatia etal 2017]. The nanocomposite that have investigated in corrosion of carbon electrodes have combined effects in oxidation of alkenes quickly [Ezzat Rafiee etal 2017]. The present work deals with the synthesis of nano particles of cobalt, nickel and Copper(II) derived from hetero polymer of methylene-imidazole and their applications as catalyst in oxidation of cyclohexane.

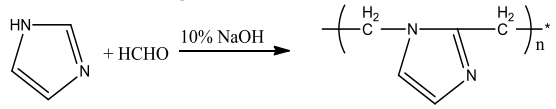
2. Materials and Methods

All Chemicals and Solvents materials were provided Sigma Aldrich and BDH chemical companies.
The samples were ground into a fine powder for characterization by:
FT-IR spectra were obtained as potassium bromide pellets in the range of 400-4000 cm^{-1} with a Shimadzu FT-IR spectrometer instrument at Al-Mustansiryah University/College of Science-Chemistry Department. The electronic spectra of the catalyst and their loaded complexes of Nicklate(II), copper(II) and cobalt(II) were recorded on a 160Shimadzu spectrophotometer at Al-Mustansiryah University/College of Science/Chemistry department-physical chemistry research laboratory.
X-ray diffraction (XRD) patterns were recorded with a Philips X-ray diffractometer (Model PW1840) at Baghdad University /Ibn-Haithum , college of education.

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H^1NMR spectra were recorded on Burker DMX-5000NMR (300-600MHz) spectrophotometer with using $CDCl_3$ as a solvent in Jordan Universities

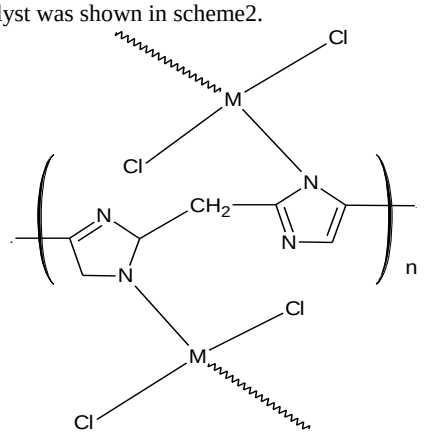
Preparation of poly Methylene-Imidazole: The polymer MI was synthesized by beforehand reported techniques, to describe it briefly: 2 ml of imidazole was dissolved in 10 ml NaOH (10% w/v) after that 3.25 g of sodium sulfate was added to above solution. Then, they the mixture stirred for 3.5 hours. After that, a solution containing 3.08 g of formaldehyde was included into the above solution, keeping the temperature at 25oC for 30min. The mixture was centrifuged and the product was washed three times with water and then dried at 80oC for 3h and 60oC for 2h [Tong Liu etal 2016].



The scheme of MI was shown in scheme 1.

Scheme1. Synthesis of methylene-imidazole polymer

Preparation of supported catalyst : The polymer metal supported on poly imidazole was synthesized through electrostatic interaction between positive charge of poly methyl imidazole and the anionic dichlorido Cobaltite(II), Nickelite(II) or Copprate(II). The synthesis of supported on poly methyl imidazole was carried out by dissolving copolymer (1.5 g) in distilled water (100 ml). This solution was added slowly to a synthesized. The mixture was stirred to obtain catalyst. The catalyst was collected using centrifuged and dried under air for 24hrs at 25oC. The scheme of supported catalyst was shown in scheme2.



Scheme 2): Proposed scheme for supported catalyst.

3. Results and Discussions

Sample characterization: The FT-IR spectra of copolymer showed strong absorptions around 1630,1450 and 2988cm^{-1} which are assigning to bonds of -C=N,-C=C and -C-H of methylene groups res -pectively, Fig.1. All supported catalyst with Co(II),Ni(II) exhibited medium and broad bands at around (1591-1560)cm^{-1} supporting the linkage of metal ions on the structure of copolymer prepared. The broad absorption around 3387cm^{-1} may be assigned to hydrogen bonding in the copolymer chain through -C=N- of imidazole with the molecules of hydra -ted water assisting in increasing the stability of the imidazole-methylene copolymer. The -C-H bending of imidazole ring was shown at 852cm^{-1} as weak band whereas the -CH_2- moiety was observed at 2859 and 711cm^{-1} associated with vibration and rocking motions in IR spectra[Guillermo Mendoza-Díaz 2002, Qingzhong Hu 2008, Yuichi Ikuta2003, Augusto Rivera 2009, Tarun Kumar Misra 1998]. The comparison of IR spectra of imidazole copolymer with IR spectra of its nickel(II) and cobalt(II) catalysts, Figures(2,3)displays new bands in the regions (400-600)cm^{-1} assigning to M-N bonds. As well as the shift in the vibrations of -C=N- and-C=C- functional groups to 1631cm^{-1} confirm the formation of metal catalyst [Lionel E etal 2006, A.Mašlejováa 2006, Yao-Yu etal 1999, R.Carballoa 2004, M.FIskander etal 2000, Ikuko Katsuki etal 2002]. Furthermore the broad band around(3400-3396)cm^{-1} was resulted from the presence of coordinated water molecules in structure of catalysts.

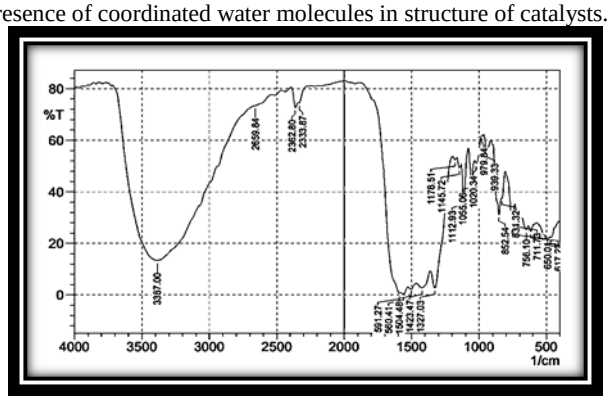


Fig. 1: FT-IR spectra of imidazole-methylene copolymer

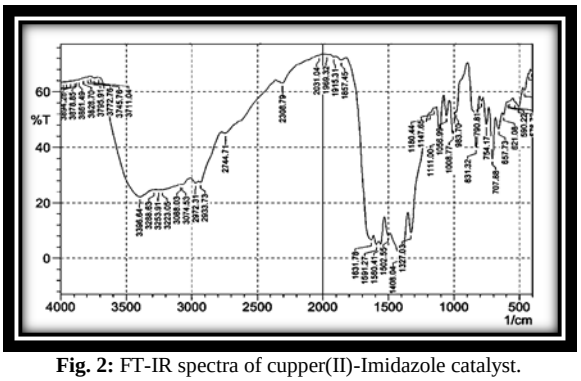


Fig. 2: FT-IR spectra of cupper(II)-Imidazole catalyst.

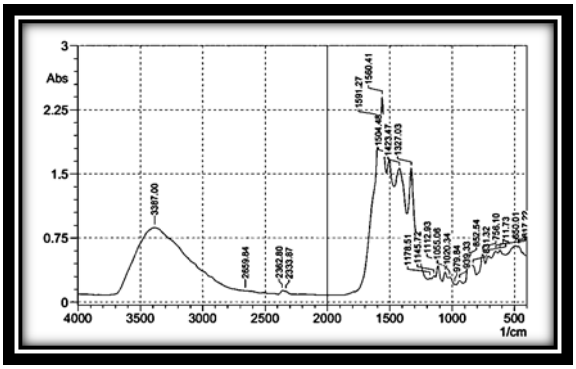


Fig. 3: FT-IR spectra of cobalt(II)-Imidazole catalyst.

NMR characterization: The H^1NMR spectra of imidazole copolymer in CDCl3 showed resonance of aromatic –C-H in the imidazole ring around 7-8ppm. As well as the multiple peaks at 2-4.5ppm may be assigned to aliphatic CH_2- moiety of methylene group as shown at fig.(4). Up on formation the catalyst with Cobalt and Nickel the changes are distinct in H^1NMR of Cobalt(II) and Nickel(II)catalysts. The H^1NMR spectra of cobalt(II) formed with imidazole copolymer,figure(5) exhibits no clear peaks due to the odd electrons in the $3d^7$ configuration causing a little support for the long chain of the metal catalyst[Guoli Huang etal 2011, Umasankar Ray etal 2004, Markus Andersson etal 2010, Giovanni Tabbì etal 1997, Markus Albrecht etal 1999, Scott J.Moore etal 1999, Ying-Ying Liu etal 2007, Ronald Dean But 1958].

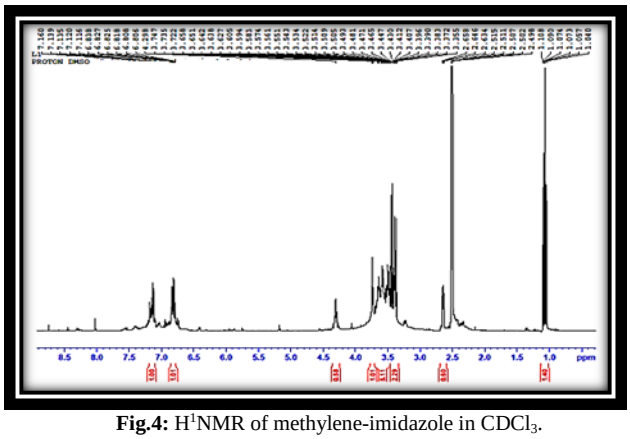


Fig.4: H^1NMR of methylene-imidazole in $CDCl_3$.

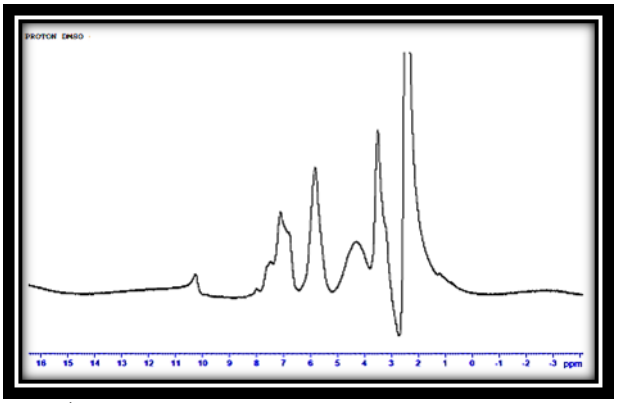


Fig 5: H^1NMR spectra of Cobalt (II)- imidazole-methylene polymer in $CDCl_3$

UV-Visible spectra of the imidazole-methylene copolymer and it's Cobalt(II) , Nickel(II) and Copprate (II) catalysts : The UV-Visible spectra of imidazole copolymer in CH_3CN and CH_2Cl_2 displayed weak intensity bands around (210-245) nm associated to the $\pi \rightarrow \pi^*$ transitions of -C=C- and -C=N- functional groups. As well as the $n \rightarrow \pi^*$ transitions of the chromophores moiety was observed in the range (350)nm [Mahendra Kumar Trivedi etal 2015, Bao Shan Huang etal 1979, Mariel M.Muir etal 1988, S. A. Cotton 2004], Fig.(6) clarified the main bands of imidazole copolymer. The main bands of copolymer metal complexes were shifted to lower or higher vibrations compared to the original spectrum of copolymer. These referred to coordinate of metal to active functional group of imidazole copolymer.

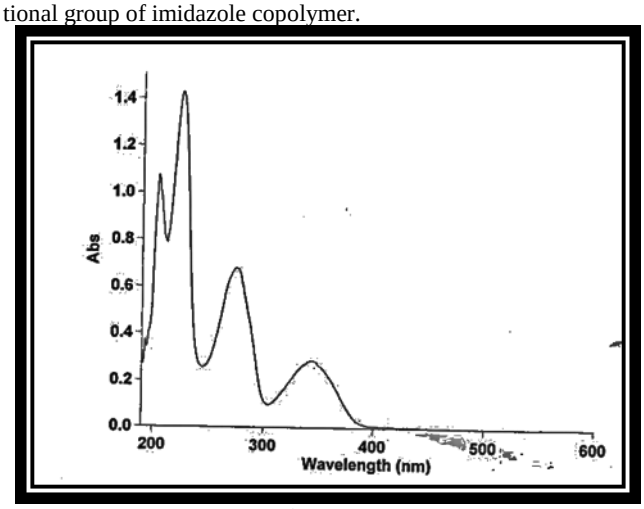


Fig. 6: UV of copolymer imidazole

X-Ray diffraction of Co (II) and Ni (II) catalysts of imidazole copolymers:

XRD patterns of imidazole copolymer indicated that the transition elements under study and derived from their hydrated metal chlorides,i.e,$CoCl_2.6H_2O$ and $NiCl_2.6H_2O$ have remarkably immobilized on the surface position of heterocyclic ring through the aggregation of copolymer chain via nitrogen atom with empty orbitals of Lewis acids of metal ions[41-43]. Moreover the advanced diagnosis of peaks of imidazole-methyl copolymer with Cobalt(II) ion (Fig. 7a) investigated that heterocyclic moiety was strongly prepared in the proposed structure. The powder XRD patterns ($0<\Theta<65$) of poly-imidazole obtained from the samples are shown in Figure (3b) and exhibited amorphous structure of the catalysts. By the same manner the x-ray diffraction curves for Nickel(II) catalysts recorded a range of angle diffraction around $0<\Theta<65$ and $0<\Theta<78$ indicating the amorphous state of the two catalysts[S. Ganeshraja etal 2014, M. Bouchouit etal 2016, G. -H. Cui etal 2012, Norah Barba-Behrensetal 1991, Shui-Sheng Chen etal 2012].

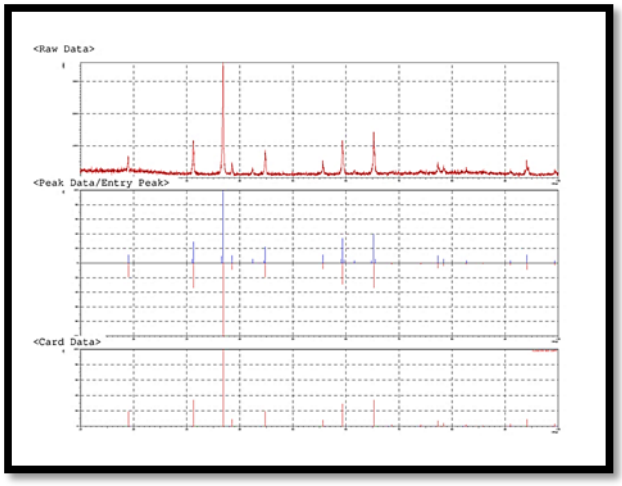


Fig.8: X-Ray diffraction of Cobalt – copolymer

4. Conclusion

From Our study, it was concluded that he efficiency of the catalyst which was prepared by doped of an active catalyst at polymers derived from heterocyclic compound like imidazole ring.
Preparation of catalyst was prepared as nano particles of metals ions which deposited at polymer surface.
Imidazole polymer doped with Co(II) and Ni(II) metals as catalyst complexes used to catalyze the oxidation of unsaturated compounds.
Polymers – imidazole-metals complexes showed good efficiency at oxidation catalyzed of cyclohexanes and cyclopentene.

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