Synthesis and characterization of novel transition metal complexes with L-Proline and their catalytic activity evaluation towards cyclohexane oxidation

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Abstract
Some of first row transition metals [M = Mn(II), Fe(II) and Co(II)] complexed with L-proline amino acid were synthesized by thermal heating and characterized by FT-IR, UV–visible spectroscopy, XRD, SEM and TEM. The characterization data showed that the metal ions were bonded through N- and O-donor atoms of the amino acid. The metals-L-proline complexes exist in mixed particle sizes of amorphous and agglomerated nature. The prepared complexes were investigated to catalyze the liquid phase oxidation of cyclohexane in the presence of TBHP as an oxidant. Iron-proline complex was found to be an excellent catalyst with high selectivity towards K/A oil under the optimized reaction conditions.

1. Introduction

The selective oxidation of alkanes has been one of the most significant challenging task in modern catalysis due to the stability of sp\(^3\) C–H bond in saturated hydrocarbons [1], it is well known that direct functionalization of these readily available and less expensive hydrocarbons into more value-added stable products [2]. The activation of C–H bond in hydrocarbons are really tough due to the chemical inertness [3]. The oxidative conversions of functional groups are fundamental reaction in organic chemistry, the oxidation reaction widely used in the laboratory for the synthesis of fine chemicals and large number of petrochemical derivatives [4, 5].

The selective oxidation of cyclohexane to cyclohexanol and cyclohexanone is one of the important industrial application. The mixture of cyclohexanol and cyclohexanone also known as KA oil, these two oxidized products from cyclohexane are known to be main precursors for the preparation of adipic acid, caprolactam [6, 7], which are the intermediates for the synthesis of nylon-6 and nylon-6,6 polymers [8, 9].

Number of methods have been reported in the literature for the oxidation of cyclohexane using various types of oxidants such as molecular oxygen [10, 11], tert-butyl hydroperoxide (TBHP) [12, 13] hydrogen peroxide (H\(_2\)O\(_2\)) [14]. In spite of broad interest in developing new methods for the oxidation of cyclohexane, there is still scope for improvement of simple, efficient, inexpensive, widely applicable and environmentally friendly catalysts. amino acids are classified as promising biomolecules that can be complexed with metals to form stable and active catalysts [15]. Therefore; Amino acid-metal complexes and their derivatives have attracted many researchers in the fields of pharmaceuticals and petrochemical industries [16, 17].

In the present study, selected transition metal (e.g. Mn(II), Fe(II) or Co(II)) are prepared through complexing these metals with the amino acid, L-proline and characterized. The prepared complexes were applied as catalysts for the cyclohexane oxidation with tert-butyl hydroperoxide (TBHP) under reflux condition. The optimization was carried out for the best performed complex in terms of reaction temperature, the concentration of catalyst and solvent.
2. Experimental study

2.1. Complexes preparation

The catalysts were prepared in a stochiometric amounts of Mn (II) chloride (MnCl₂.4H₂O, LABACHEIE, 97.5%), Fe (II) acetate (Fe(ac)₂, AVONCHEM, 95%), or Co (II) chloride (CoCl₂.6H₂O, Riedel-deHaen, 97%) were complexed with L-proline with a molar ratio of 1:2 metal:ligand. In a real procedure, 2 mmol (1.15 g) of L-proline ligand was added to hot ethanol solution with continuous stirring (Solution A). In another beaker, 1 mmol of metal salt was dissolved in 50 ml hot ethanol (solution B). Solution B was added to solution A dropwise, followed by the addition of few drops of 0.01 M Na₂CO₃ solution to neutralize the pH. The resulting mixture was continuously stirred under reflux at 353 K for 3 h. After completion of the reaction, the mixture was cooled to room temperature; the solid precipitated product was separated by filtration, washed with cold ethanol. The obtained crude product was further recrystallized by using a mixture of acetone, n-hexane and diethyl ether in the ratio 2:1:1 under heating with continuous stirring. The obtained crystalline material was allowed to cool, and then dried under vacuum.

2.2. Characterizations

UV-Vis spectrophotometer of type Shimadzu Pc-1601 was used for exploring the complex formation, samples were scanned in the range of 200 to 800 nm with a step of 1 nm. Infrared (IR) spectroscopy Shimadzu 8101 IR spectrometer, was used to identify the various functional groups of the prepared complexes. The spectra was collected between 400 cm⁻¹ to 4000 cm⁻¹ by using KBr pellets. X-ray powder diffraction (XRD) type Schimadzu 6000 DX instrument was applied to measure the crystallinity degree of the prepared complexes. Scanning Electron Microscopy (SEM) type JEOL (JSM 6390 LV) was used to study the morphology of the prepared complexes. Transmission electron microscopy (TEM) type EM-Jeol model 6360 LVSEM-USA, was used to provide further support. The morphology and particle size were investigated by using different magnification in the range between 5–100 nm.

2.3. Catalytic activity study

The catalytic oxidation of cyclohexane reaction has been performed in a 100 ml stainless steel reactor equipped with a Teflon beaker, a magnetic stirrer, an internal thermocouple and cooling coils for regulating reaction temperature. In a typical experiment, the cyclohexane (15 ml; 139 mmol) was mixed with 22 mg (0.075 mmol) of the catalyst sample in acetonitrile (20 ml), moreover, 10 ml of tert-butyl hydroperoxide [TBHP] was used as an oxidant. The reaction mixture was heated up to 353 K with continuous stirring. During the reaction, the autogenous pressure was developed in the autoclave and reached 6 to 7 bar. The progress of the oxidation reaction was monitored by Gas chromatographic analyzer (GC), which was performed on Shimadzu 2014 GC system equipped with silica column chromosorb 60/80 using FID detector.

3. Results and discussion

3.1. Characterization data

The results of the UV-visible and IR spectra suggest that the metals in all three different metal-L-proline complexes prepared are bounded with two molecules of amino acids to form an amino acid-metal complex (figure 1(A)), where (metal = Fe, Co, or Mn) with 1:2 molar ratios. This result agrees with the work on Cu²⁺ ions proposed by Mascaros et al [18].

The UV-visible spectra of L-proline and the metal-L-proline complexes were collected at ambient conditions and presented in figure 1(B). An absorption peak of the proline ligand was observed at ~λmax 220 nm, this is attributed to the electronic movements within the L-proline ligand and such an absorption band has not been changed when proline is complexed with metals. However, new absorption maxima, in adjacent vicinities or interfering with the original peak of the ligand has been exhibited as well as new peaks appeared for the complexes of M-proline [M = Mn (II), Fe (II) and Co (II)] at ~λmax 335 nm, figure 1(C), which indicates the successful complexation between proline and metals.

It is known that metal ions act as Lewis acid and coordinates to the potential proton-binding sites of the ligands. The coordination results in increasing the bond strength of the ligand, which in turn changes the vibrational energy of the ligand. The infrared spectral comparison of free ligand and metal complexes are shown in figure 1(D). The IR spectra showed that the absorption bands are shifted to higher frequency and appears at 1646 cm⁻¹ corresponding to asymmetric stretching vibrations of carboxylate group COO⁻ and the peak at 1465 cm⁻¹ caused by asymmetric stretching vibrations of carboxylate group of L-proline, which clearly indicates the coordination of the carboxyligic group to the central metal ion. The C–O bond belongs to the O-atom linked to coordination sphere while the other one, involving the O-atom occupies the apical position. The strong band
of C–N stretching for the imine spectrum of free proline ligand displayed at 1473 cm$^{-1}$ was shifted to lower frequency and appeared for all studied transition metal complexes at the range between 1417 and 1454 cm$^{-1}$ suggesting the co-ordination of the L-proline ligand through the nitrogen atom at the imine group. The bands showed in the range of 430–560 cm$^{-1}$, are tentatively due to the M–N and M–O, co-ordination vibrations of complexes. Therefore, it can be concluded that the shifts in M–NH bands in metal complexes as well as the widening of the bands clearly reveal that the complexations are successful.

To confirm the existing of the complexes formed, the XRD analysis was performed on metal-L-proline complexes (figure 2). The database for the pure proline suggests that it possesses an orthorhombic phase structure. While, the x-ray powder diffraction pattern for Fe-proline complex, as an example, revealed that the complex is found to be characteristic of semi-amorphous in nature. This morphology is observed in the other

Figure 1. (A) General structure of metal-L-proline complex [ML$_2$]. (B) and (C) UV-Visible spectra of proline with various metal-L-proline complexes, (D) IR spectrum of proline with different metal-L-proline complexes.

Figure 2. XRD spectra of L-proline (left panel) and Fe-L-proline (right panel).
metal-L-proline complexes too. The x-ray result has not shown relative measure of average particle size due to line broadening associated with these amorphous materials.

Furthermore; The SEM images of the metal-L-proline complexes suggested also the morphology of the complexes. The macroscopic inter spaces clearly reveals that the complexes molecules are well dispersed with presence of aggregated small amorphous particles spread on the surface. The SEM images of Fe-L-proline and Co-L-proline, figures 3 and 4, respectively. The morphology of the Fe-L-proline complex showed that It is possessing a smooth crystallite layered structure with aggregation of the complex. This is manifested on the micrograph figures 3(c) and (d) by the small distance separated these species. In the meantime; The morphology of Co-L-proline complex, figure 4 showed the spherical-like shape with crinkly, layered structure and soft macroscopic separations. Hence the particle size of such materials is relatively small, which is in agreement with the XRD result.

To provide further support to the morphology and the particle size of the synthesized complexes, the TEM analysis was carried out on the Fe-L-proline complex. The representative micrograph images are exhibited in figure 5. The micrograph consisting of a mixture of particles; Amorphous particles of small dimensions with superimposed dark spots, and larger particles who are marked more solid, which seem to be severely agglomerated as exhibited in figures 5(c) and (d). This Evidence is illustrated clearly in the Fe-L-proline complex as it maintains a high percentage of an amorphous form, which might be recognized by the presence of transparent color in the TEM images. The particle size was estimated from TEM analysis to be in the range of 20–50 nm.

3.2. Catalytic activity data
The cyclohexane conversion, selectivity percentage of the products, yield and the TOF for the three individual reactions performed over the prepared complexes are listed in table 1. The obtained results show that all the catalysts are active in the reaction with selectivity over 90% for the three applied complexes. It is also noticeable that a change of the metal atom could influence the yields of cyclohexanol and cyclohexanone. The Fe-proline complex has shown the maximum catalytic activity for the oxidation of cyclohexane, moreover, the activity can be placed according to the following order Fe-L-proline > Co-L-proline > Mn-L-proline.
The effect of solvent was also investigated by using various organic solvents. The oxidation reaction of cyclohexane was catalyzed by Fe-proline complex using TBHP, in a typical experiment, the reaction was performed in 20 ml solvent at 353 K. It was observed, when solvents were used in the cyclohexane oxidation reaction, the conversion of cyclohexane declines in the following order: acetonitrile \( > \) acetone \( > \) dichloromethane \( > \) tetrahydrofuran \( > \) dimethylformamide \( > \) solvent free (table 2). This behavior indicates that the solvent system plays a vital role to enhance the oxidation of cyclohexane with TBHP oxidant. The above result reveals that acetonitrile as solvent is favorable for the oxidation of cyclohexane with TBHP and a maximum conversion of cyclohexane was obtained.

Table 1. Effect of different metal-proline complexes on cyclohexane oxidation reaction.\(^a\)

| Complex   | Conversion (%) | CyOH (%) | Cyone (%) | Others (%) | K-A oil selectivity (%) | TOF (h\(^{-1}\)) |
|-----------|----------------|----------|-----------|------------|------------------------|-----------------|
| Mn-Proline| 12.82          | 48.8     | 43.7      | 7.5        | 92.5                   | 11.29           |
| Fe-Proline| 20.47          | 32.8     | 62.4      | 4.8        | 95.2                   | 18.09           |
| Co-Proline| 16.84          | 39.4     | 54.2      | 6.4        | 93.6                   | 15.05           |

\(^a\) Reaction conditions: Catalyst 0.075 g, acetonitrile 20 ml, cyclohexane 15 ml, cyclohexane : TBHP mole ratio = 1:4, reaction temperature 353 K, reaction time 6 h.

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Having investigated the effect of reaction temperature ranging between 353 K to 373 K on the oxidation of cyclohexane, while keeping the other parameters constant (table 3). The total conversion percentage of cyclohexane was found to decrease with increasing the reaction temperature, due to the fast decomposition of TBHP. In the meantime; the selectivity was decreased sharply with increasing temperature, due to the over-oxidation reaction of the K-A oil.
Table 2. Effect of solvent on the activity of Fe-L-proline complex on cyclohexane oxidation reaction. 

| Solvent          | Conversion (%) | CyOH (%) | Cyone (%) | Others (%) | K-A oil selectivity (%) | TOF (h⁻¹) |
|------------------|----------------|----------|-----------|------------|--------------------------|-----------|
| Acetone          | 15.86          | 44.3     | 24.6      | 31.1       | 68.9                     | 14.02     |
| Dichloromethane  | 13.42          | 36.7     | 22.8      | 40.5       | 59.5                     | 11.86     |
| Dimethylformamide| 9.45           | 41.6     | 23.5      | 34.9       | 65.1                     | 8.35      |
| Tetrahydrofuran  | 11.74          | 43.9     | 27.4      | 28.7       | 71.3                     | 10.37     |
| Acetonitrile     | 20.47          | 32.8     | 62.4      | 4.8        | 95.2                     | 18.09     |
| Solvent free     | 7.64           | 42.8     | 23.1      | 34.1       | 65.9                     | 6.75 h⁻¹  |

* Reaction conditions: Catalyst 0.075 g of Fe-L-proline complex, cyclohexane 15 ml, cyclohexane : TBHP mole ratio = 1:4, reaction temperature 353 K, reaction time 6 h.

Table 3. Effect of applied temperature on the activity of Fe-L-proline complex on cyclohexane oxidation reaction. 

| Temp. (K) | Conversion (%) | CyOH (%) | Cyone (%) | Others (%) | K-A oil selectivity (%) | TOF (h⁻¹) |
|-----------|----------------|----------|-----------|------------|--------------------------|-----------|
| 353       | 20.47          | 32.8     | 62.4      | 4.8        | 95.2                     | 18.09     |
| 363       | 17.3           | 33.5     | 18.2      | 48.3       | 51.7                     | 15.28     |
| 373       | 12.5           | 28.7     | 23.8      | 47.5       | 52.5                     | 11.04     |

* Reaction conditions: Catalyst 0.075 g of Fe-L-proline complex, cyclohexane 15 ml, cyclohexane : TBHP mole ratio = 1:4, reaction time 6 h.
Several Fe complexes were reported to catalyze the cyclohexane oxidation under various reaction conditions [19–21]. A comparison between the results obtained in the current study and the previously reported data is shown in Table 4.

The comparison showed that the obtained results in the current study are very comparable with the reported results. L-proline complex even exhibited higher conversion and selectivity than the reported data, which makes the current Fe-L-proline complex very promising in the field of catalysis.

4. Conclusion

In the current study, the synthesis of three complexes of (Mn, Fe or Co) with L-proline amino acid was performed successfully in one-step synthesis method. The catalytic activity of the three complexes was evaluated for the oxidation of cyclohexane using TBHP. It was verified that Fe-L-Proline exhibited the maximum activity, while acetonitrile was chosen as the best solvent used at 353 K.

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Table 4. Effect of applied temperature on the activity of Fe-L-proline complex on cyclohexane oxidation reaction.

| Complexes         | K     | Time(min) | Conversion | K-A oil selectivity | References         |
|-------------------|-------|-----------|------------|---------------------|--------------------|
| L-proline         | 353   | 360       | 20.5       | 95.5                | Current            |
| FeSldiAP          | 343   | 360       | 31.0       | 96                  | [19]               |
| Fe (α-ZrP-Msalicylaldiamine) | 353   | 360       | 6.3        | 98                  | [20]               |
| Fe(Ka-dpa)−1      | 298   | 24        | 22         | 100                 | [21]               |

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