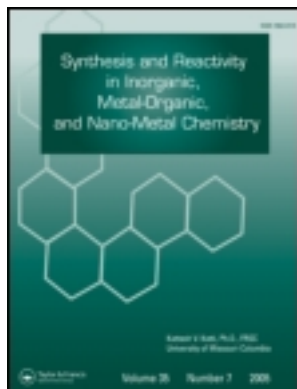


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## Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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# Selective Oxidation of Thiols and Alcohols by Physically Encapsulated Nickel Schiff-Base Complex Prepared Via Sol-Gel Method as Nano-Catalyst

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A heterogeneous catalyst was prepared by direct physical encapsulation of nickel Schiff-base complex into the silicon dioxide matrix via sol-gel method. The compounds were characterized by FT-IR, SEM, TEM, XRD, CHNS, and AAS. The catalytic performance in the alcohols and thiols oxidation was investigated in the presence of H<sub>2</sub>O<sub>2</sub> (10 mmol, 30%) as oxidant. After five recycle runs, the catalyst showed 13% reduction in activity with slightly Ni(II)-complex leached to the solvent. Varieties of primary and secondary alcohols were efficiently oxidized to the corresponding ketones. Thiols were oxidized in coupling reaction to disulfides in excellent yields using nano-catalyst with H<sub>2</sub>O<sub>2</sub>.

**Keywords** aldehyde, disulfides, heterogeneous catalyst, Schiff-base, selective oxidation

## INTRODUCTION

The oxidation of alcohols to the corresponding carbonyl compounds is fundamental and important in organic chemistry. Carbonyl groups are valuable synthetic intermediates; many oxidation methods have been reported for this conversion.<sup>[1]</sup> In addition, the selective oxidation of thiols to the corresponding disulfides is of great interest from biological and chemical point of view.<sup>[2–5]</sup> The development of new oxidation processes continues to attract attention in spite of the availability of numerous oxidizing agents.<sup>[6,7]</sup>

In recent years, the structures of target molecules in organic syntheses are becoming more complicated; hence better structure compatibility and higher selectivity have become synonymous with an efficient oxidation. In this regard, conventional oxidants always satisfy the requirements. As a result, the exploration of new oxidizing agents remains a challenging area of research in organic syntheses.<sup>[8,9]</sup>

Chromium(IV)-based oxidizing reagents such as Jones and Collins reagents are commonly used in organic syntheses. However, toxic chromium residues, formed after the oxidation, cause problem in the workup and also in the disposal. To solve the problems, various catalytic systems have been developed using environmentally benign oxidants such as molecular oxygen, hydrogen peroxide, and organic peroxides under homogeneous as well as heterogeneous conditions during the last two decades.<sup>[10]</sup> Hydrogen peroxide as an oxidant has many advantages compared with other oxidants because water is the only by-product. However, only a limited number of such useful oxidation procedures have been reported.<sup>[11,12]</sup> Also, a variety of different catalytic systems for oxidation of alcohols, using hydrogen peroxide, have been developed.<sup>[13–18]</sup> There is still an ongoing interest in the search for new efficient metal catalysts for this system.<sup>[19–24]</sup>

Use of some homogeneous catalysts such as metal complexes of Ru,<sup>[25–31]</sup> Pd,<sup>[32–34]</sup> Co,<sup>[35,36]</sup> Os,<sup>[37]</sup> and Cu<sup>[38,39]</sup> has given rise to high catalytic activity and selectivity. Schiff-base complexes of nickel, palladium, and platinum have played an extremely important role in the development of homogeneous catalysis.<sup>[40]</sup> In particular, nickel catalysis is of great interest due to high performance and low cost. As the widespread use of traditional organic solvents in many chemical processes is an issue of great environmental concern, the use of ionic liquids as reaction media is a topic of much current interest.<sup>[41]</sup>

The homogeneous catalysts have some difficulties in the catalyst recovery and product separation.<sup>[42–44]</sup> In order to overcome these problems, the heterogeneous catalysts with similar activity to homogeneous catalysts have been used. For this purpose, immobilization of metal Schiff-base complexes on organic and inorganic media has been widely reported.<sup>[45–48]</sup> In this work, we are going to report a very efficient and selective oxidation of alcohols and thiols into corresponding products using hydrogen peroxide as oxidant catalyzed by the encapsulated Ni(II) Schiff-base complex (Scheme 1).

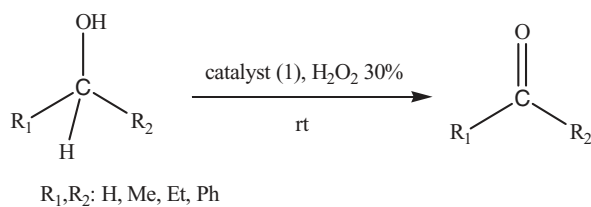
## EXPERIMENTAL

Chemicals were purchased from Kimia Exir (Tehran, Iran). All yields refer to isolated products. The reactions

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SCH. 1. Oxidation of alcohols.

were monitored by thin-layer chromatography (TLC) carried out on silica plates. The products were characterized by comparison of their physical data with those of known samples or by their spectral data. IR spectra were recorded on a Shimadzu-IR 470 spectrophotometer (Ferdowsi University of Mashhad, Iran).  $^1\text{H}$  NMR spectra were recorded on a Bruker 100-MHz spectrometer (Ferdowsi University of Mashhad, Iran) in  $\text{CDCl}_3$  as the solvent and TMS as internal standard.

### Preparation of *S*-ethyl- $\beta$ -N-(benzylidene)dithiocarbazate

Carbon disulfide (6.1 mL, 0.1 mol) was added to a cold mixture of hydrazine hydrate (5 mL, 1 mol) and KOH (5.6 g, 1 mol) in 20 mL of absolute ethanol, making two phases. Then, ethyl bromide (7.8 mL, 0.1 mol) was added slowly to the reaction mixture.

Benzaldehyde (10.6 mL, 0.1 mol) dissolved in absolute ethanol (15 mL) was mixed with the above solution. The mixture was heated on a water bath for approximately 1 h and then left to stand overnight. A yellow product was separated by filtration, washed with ethanol, and dried in a vacuum desiccator over silica gel. The compound was recrystallized from ethanol. Yield: 74%. Anal. Calcd. for  $\text{C}_{10}\text{H}_{12}\text{N}_2\text{S}_2$  (224.35 g/mol): C, 53.54; H, 5.39; N, 12.49; S, 28.59. Found (%): C, 52.86; H, 5.41; N, 12.62; S, 29.11.

### Preparation of bis(*S*-ethyl- $\beta$ -N-(benzylidene)dithiocarbazate)-nickel(II) Complex

Nickel(II) nitrate hexahydrate (0.07 g, 0.22 mmol) in boiling ethanol (15 mL) was added to the ethanolic solution of the ligand (0.1 g, 0.45 mmol). The mixture was heated in a water bath for 30 min and then left to stand overnight. A brown product was filtered off, washed with ethanol, and dried in a vacuum over silica gel. Yield: 48%. m.p. 349°C. Anal. Calcd. (%): C, 47.53; H, 4.39; N, 11.09; S, 25.38. Found (%):  $\text{C}_{22}\text{H}_{22}\text{N}_4\text{NiS}_4$  (505.37 g/mol): C, 47.39; H, 4.27; N, 10.98; S, 26.08.

### Preparation of Physically Encapsulated Ni(II) Schiff-Base Complex

An amount of 0.25 g Ni(II) Schiff-base complex was dissolved in 30 mL of TEOS and 10 mL of methanol at 60°C under stirring. Then 14.5 mL of water was added into the mixture to obtain a homogeneous solution. Then, concentrated hydrochloric acid was introduced to the solution to adjust the pH to 4. The stirring was continued under 60°C until gelation was completed. Then, the catalyst was dried at 80°C until a constant weight was obtained. The gel was washed with water until the pH of the

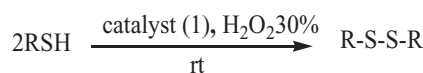
filtrate increased to 7, and then it was extracted by methanol in a Soxhlet extractor (Islamic Azad University, Gorgan Branch, Iran) for 6 h. Then the content of Ni was determined by AAS.

### Typical Procedure for Oxidation of Alcohols

In a 25 mL round-bottomed flask, a solution of alcohol (1 mmol), a solvent (5 mL), catalyst **1** (0.025 g), and hydrogen peroxide (10 mmol, 30%) were added to the previous solution. Then, the reaction mixture stirred vigorously at room temperature.

### Typical Procedure for the Oxidative Coupling of Thiols

In a 25 mL round-bottomed flask, a solution of thiol (1 mmol) in a solvent (2 mL) was prepared. Catalyst **1** (0.02 g) was added to the solution, and the reaction mixture was stirred at room temperature in the presence of hydrogen peroxide as oxidant (Scheme 2).



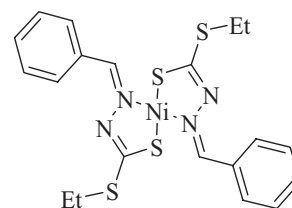
SCH. 2. Oxidation of thiols.

The progress of the reaction was monitored by TLC (eluent: ethyl acetate/ *n*-hexane, 1:4). The unreacted thiol was estimated by titrating against standard alcoholic iodine solution using pyridine as a base. After the completion of the reaction, the reaction mixture was filtered and the solid material was washed with 10 mL of the solvent used during the reaction. Evaporation of solvent, using a rotatory evaporator, to dryness gave the product that was purified by recrystallization. Comparison of the melting points and  $^1\text{H}$  NMR spectra of the purified products with those of the authentic disulfides proved the existence of pure disulfide with 85–98% yields. All reference disulfides were prepared from the corresponding thiols according to the method described in Vogel.<sup>[49]</sup> The analysis of spectral and physical data revealed that only disulfides were formed and no further oxidation occurred.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of the Catalyst

First, the homogeneous catalyst Ni(II) Schiff-base complex with the structure shown in Figure 1 prepared as described previously.

FIG. 1. The structure of bis[S-ethyl- $\beta$ -N-(benzylidene)dithiocarbazato]-nickel(II).

The complex was then encapsulated physically into the  $\text{SiO}_2$  matrices by sol-gel method. This method is simple and straightforward: the complex was added to polymerization mixture of TEOS, which is catalyzed by hydrochloric acid; when the polycondensation was completed, the complex was entangled into the  $\text{SiO}_2$  polymeric network. The encapsulation conditions are milled, to ensure the stability of the complex in the process. The FT-IR spectra of the neat complex and catalyst **1** showed the bands at  $1592\text{ cm}^{-1}$  and  $673\text{ cm}^{-1}$ , which were assigned to CN and phenyl group. The reason for non-appearance of other bands of complex is the masking of these bands by the presence of strong background bands of the  $\text{SiO}_2$  matrix. Furthermore, frequencies of  $1100\text{ cm}^{-1}$  and  $800\text{ cm}^{-1}$  are assigned to stretching vibration of Si-O-Si and Si-OH, respectively.

The atomic adsorption was employed to confirm the entrapping of Schiff-base complex into  $\text{SiO}_2$  matrices. After the catalyst was washed thoroughly with methanol, less amount of impure complex was left the matrices. The washing process continued until the extracted methanol did not show leached nickel complex. Thus, the investigation of the nickel content by AAS revealed that the nickel complex was entrapped in the  $\text{SiO}_2$  matrices.

### TEM, SEM Test Results

SEM and TEM images were used to evaluate the surface morphology and size distribution of the Nickel complex deposited in the silica network. The prepared catalyst **1** was analyzed by SEM (Figure 2). A clear change in the morphology of the catalyst occurred after the addition of nickel complex to the support (Figure 3). SEM showed that the number of pores for the catalyst decreased dramatically. It is deduced that Ni(II) Schiff-base complex was grafted in the silica support. The TEM images of the Si/Ni complex composites showed that they are nonagglomerated, scattered spherical particles of complex at a high

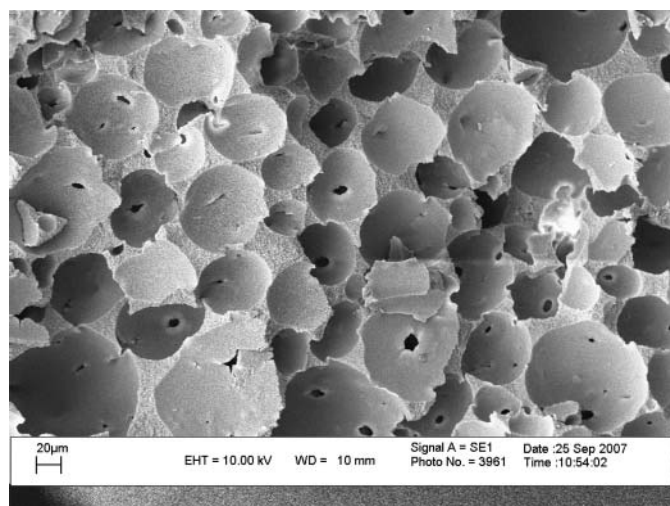


FIG. 2. SEM image of silica prepared via sol-gel method without Schiff-base complex.

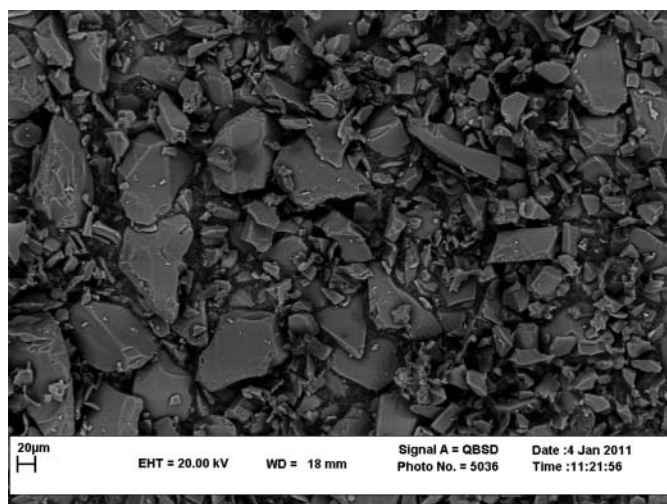


FIG. 3. SEM image of heterogeneous catalyst.

concentration, and TEM image also determined particle size of catalyst **1** to be in the range of 10 nm (Figure 4).

### X-Ray Diffraction

X-ray diffraction (XRD) pattern of calcined catalyst **1** is shown in Figure 5. The peaks at (111) and (200) confirmed cubic structure of calcined catalyst **1**.<sup>[50]</sup> Furthermore, the XRD pattern of silicon dioxide showed that the characteristic of Bragg reflection can be indexed to (100) planes of hexagonal lattice of silicon dioxide.<sup>[51]</sup> The XRD pattern revealed the typical band of the nickel phase, but it did not show the typical band of silicon dioxide phase because the silicon dioxide peak was

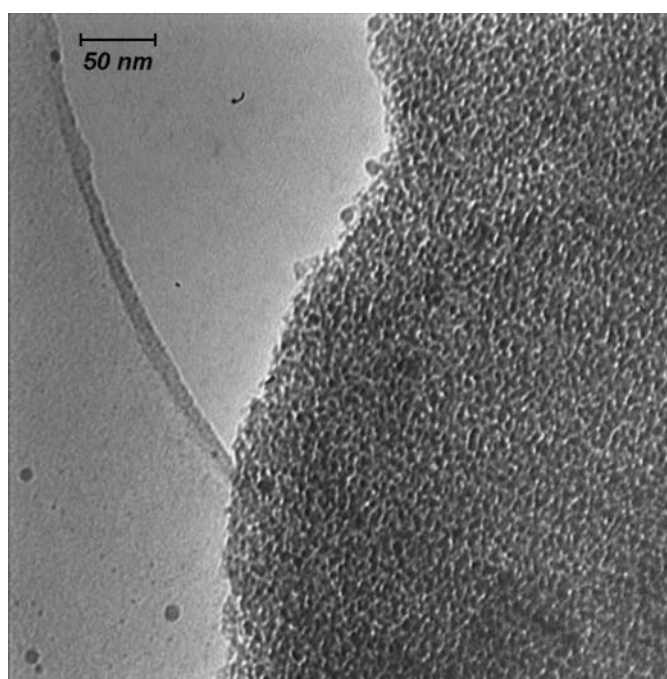


FIG. 4. TEM image of heterogeneous catalyst.

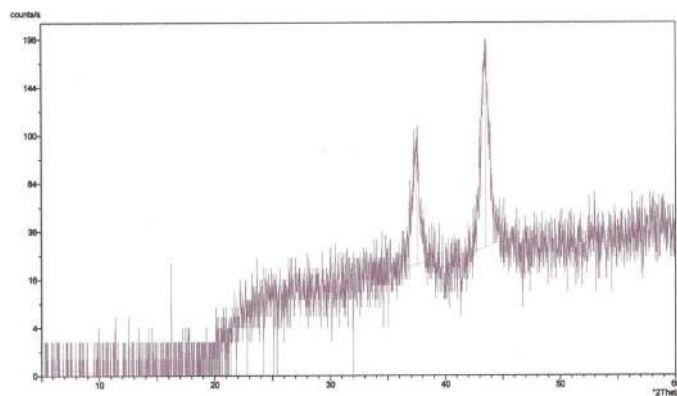


FIG. 5. XRD diagram of heterogeneous catalyst.

broadened by the presence of Ni(II)Schiff-base complex.<sup>[52]</sup> Thus, the XRD pattern of physically entrapped nickel complex revealed that nickel Schiff-base complex was immobilized in the SiO<sub>2</sub> matrices without any change. Also, the XRD demonstrated that the particle size of catalyst is 19.8 nm at  $2\theta = 43.5^\circ$  and 39.4 nm at  $2\theta = 38^\circ$ .

## Catalytic Test

### Optimization reaction of alcohols oxidation

Benzylalcohol (1 mmol), acetonitrile (5 mL), catalyst **1** (0.025 g), and H<sub>2</sub>O<sub>2</sub> (10 mmol, 30%) were taken in a 25 mL round-bottomed flask (Scheme 1). We designed a reaction as a model in order to find the optimum reaction variables such as temperature, solvent, appropriate amount of catalyst, and length of the reaction time. The results are shown in Table 1. Among the various solvents investigated, CH<sub>3</sub>CN showed better results compared with other solvents for oxidation of alcohols under our experimental conditions (Table 1, entry 6), while toluene and ethanol afforded lower conversion and selectivity (Table 1, entries 2 and 3). Moderate conversion and selectivity were obtained when the reactions were carried out in CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>OH (Table 1, entries 1 and 5). Poor results were observed when the reactions were carried out in THF (Table 1, entry 4). The Oxidation took place to afford benzaldehyde in the presence of catalyst and H<sub>2</sub>O<sub>2</sub> (10 mmol, 30%) in 50 min (Table 1, entry 6). Perhaps some of the hydrogen peroxides were decomposed in the presence of catalyst **1**, and O<sub>2</sub> was released in the course of reaction. To determine which of H<sub>2</sub>O<sub>2</sub> or released O<sub>2</sub> plays more essential role in the oxidation reaction in the presence of our catalyst, we examined this reaction

TABLE 1  
Optimization of reaction conditions by oxidation of benzylalcohol in acetonitrile by catalyst **1** at room temperature and in presence of hydrogen peroxide as oxidant<sup>a</sup>

| Entry           | Solvent         | Temperature (°C) | Catalyst (g)     | Reaction Time (min) | Conversion% | Selectivity% |
|-----------------|-----------------|------------------|------------------|---------------------|-------------|--------------|
| 1               | Dichloromethane | 25               | 0.025            | 50                  | 80          | <60          |
| 2               | Toluene         | 25               | 0.025            | 50                  | 30          | Small        |
| 3               | Ethanol         | 25               | 0.025            | 50                  | 60          | Small        |
| 4               | THF             | 25               | 0.025            | 50                  | 45          | Small        |
| 5 <sup>b</sup>  | Methanol        | 25               | 0.025            | 50                  | 100         | <60          |
| 6               | Acetonitrile    | 25               | 0.025            | 50                  | 100         | 100          |
| 7 <sup>c</sup>  | Acetonitrile    | 25               | 0.025            | 180                 | <20         | Small        |
| 8 <sup>d</sup>  | Acetonitrile    | 25               | 0.05             | 45                  | 100         | <70          |
| 9               | Acetonitrile    | 25               | 0.01             | 150                 | 100         | 100          |
| 10 <sup>e</sup> | Acetonitrile    | 25               | Neat complex     | 55                  | 100         | >85          |
| 11              | Acetonitrile    | 50               | 0.025            | 30                  | 100         | <80          |
| 12 <sup>f</sup> | Acetonitrile    | 25               | Without catalyst | 240                 | 100         | <20          |
| 13              | Acetonitrile    | 0                | 0.025            | 180                 | <20         | 100          |
| 14 <sup>g</sup> | Acetonitrile    | 25               | 0.025            | 50                  | 92          | 100          |

<sup>a</sup>General reaction condition: benzylalcohol 1 mmol, room temperature; 0.025 g of catalyst **1**; aqueous 30% H<sub>2</sub>O<sub>2</sub> 10 mmol.

<sup>b</sup>The reaction was performed in methanol and the product obtained is a mixture of benzaldehyde and benzoic acid.

<sup>c</sup>The reaction was performed in the presence of molecular oxygen as oxidant.

<sup>d</sup>The reaction was performed in the presence of 0.05 g of catalyst **1** and the product obtained is a mixture of benzaldehyde and benzoic acid.

<sup>e</sup>The reaction was performed in the presence of 0.01 mmol of neat complex as catalyst and the product obtained is a mixture of benzaldehyde and benzoic acid.

<sup>f</sup>The reaction was performed in the presence of hydrogen peroxide and without catalyst. Yield is very poor and the product obtained is a mixture of benzaldehyde and benzoic acid.

<sup>g</sup>The reaction carried out with the first recycled catalyst **1** and the catalyst used four times more. Yields obtained excellent at all cases and the conversion is decreased after five time recycling by 13%.

by simply bubbling molecular oxygen through reaction mixture under similar conditions, and only a poor yield of product was obtained (Table 1, entry 7). So decomposition played a small role in the oxidation of alcohols. When concentration of catalyst increased in the presence of  $\text{H}_2\text{O}_2$ , the reaction took place in a shorter time but the selectivity decreased (Table 1, entry 8). Furthermore, when the oxidation of benzylalcohol was carried out using less catalyst, the reaction was found to reach completion over much longer time (Table 1, entry 9). Alternatively, the reaction was carried out in the presence of neat complex as homogeneous catalyst using hydrogen peroxide as oxidant. The results revealed that the oxidation was happened similar to catalyst **1** under the same condition. But, the purification of neat complex had some difficulties (Table 1, entry 10). The reaction was carried out at  $50^\circ\text{C}$  under the same conditions in which the oxidation completed after 30 min but the selectivity decreased (Table 1, entry 11). Furthermore, the reaction was carried out in the same condition at  $0^\circ\text{C}$ , and the reaction completed with small conversion after 180 min (Table 1, entry 13). Oxidation of benzylalcohol took place in the absence of catalyst and just in the presence of  $\text{H}_2\text{O}_2$  (10 mmol, 30%). The main product of this reaction was benzoic acid with a few amount of benzaldehyde (Table 1, entry 12). Moreover, in the presence of heterogeneous Schiff-base catalyst, the catalytic performance was effectively improved. The optimal conversion of benzylalcohol reached to almost 100% and benzaldehyde was exclusively obtained over the immobilized catalyst (Table 1, entry 6). The reaction progress was monitored by TLC. After completion of the reaction, the catalyst was removed by filtration. The obtained filtrate was evaporated, and the residual was dissolved in a mixture of ethylacetate/n-hexane (1:4). Then, the solvent was removed and the usual workup gave corresponding products. One of the advantages of heterogenized catalysts is their recyclability. The heterogenized catalyst in this work was used in subsequent catalytic runs, and the results are given in Table 3. It clearly showed that the activity of the encapsulated catalyst decreased by 13%. To prove the advantage of heterogeneous catalyst, the reaction was catalyzed by homogeneous catalyst, which worked only once because the homogeneous catalyst more rapid degradation (Table 1, entry 14). It should be mentioned that the above results confirmed the AAS results of determination of the Ni content. Furthermore, the results showed the content of nickel in fresh catalyst **1** to be 0.25%, and this amount was decreased to 0.21% after the first run of reaction. Just as the test of stability and reusability of catalyst **1**, the reaction was carried out five times, and after these cycles, the nickel content decreased to 0.19%. Therefore, the catalyst was obtained by sol-gel method not only was recyclable, but also showed an appropriate catalytic performance in oxidation of primary and secondary alcohols.

#### *Oxidation of alcohols*

The oxidation of alcohols was carried out to test the catalytic efficiency of the prepared catalyst. To show the generality of

this procedure, various alcohols such as primary, secondary, and aliphatic alcohols were selected, and the results are summarized in Table 2. Efficient oxidation was observed on the benzylic alcohols, but aliphatic alcohols needed extra time (Table 2, entries 15–17). Moreover, the reaction of cyclohexanol (Table 2, entry 17) required an extra 10 mmol% of  $\text{H}_2\text{O}_2$  after 240 min. The primary benzylic alcohols were found to be reactive and afforded selectively their corresponding aldehydes compared to other aliphatic primary alcohols. Secondary benzylic or aliphatic alcohols produced corresponding ketones in high yields. The yields were confirmed after the products were isolated by filtration and purification with ethyl acetate/n-hexane. Although the conversion was observed by TLC, typically, 5–10% of products were lost during the workup procedure. Catalyst **1** affords selectively only aldehyde (Table 2, entries 1–7) instead of the two usual products (aldehyde and carboxylic acid) in oxidation of primary alcohols. In case of the oxidation of secondary alcohols, catalyst **1** afforded selectively only ketone in lieu of two possible products (ketone and carboxylic ester). No pretreatment step was used; however, the recovered catalyst was washed with mixed solvent of ethanol/n-hexane by 1:9 molar ratios to remove traces of the previous reaction mixture and dried before the next cycle.

#### *Oxidation of thiols*

Oxidation of thiols to their expectable products (disulfides and sulfonic acid) occurred in the presence of immobilized nickel Schiff-base complex and the product obtained in excellent yields in the presence of catalyst **1**. 4-methylthiophenol was chosen as a model substrate for optimization reaction. Among the various solvents, methanol had better results compared with the other solvents (Table 3, entries 1–7). Then, the reaction was studied in the same condition and different temperatures; the results showed that the conversion rate of thiols to disulfides decreased at  $0^\circ\text{C}$ . However, at higher temperatures, the rate of conversion increased and the selectivity decreased (Table 3, entries 8–10). Furthermore, the coupling reaction of 4-methylthiophenol was tested using various amounts of catalyst **1**. The results showed that the reaction rate increased in higher amounts of catalyst **1** (0.06 g), and the conversion decreased in lower amount of catalyst **1** (0.01 g), and the conversion was not complete (Table 3, entry 11).

Moreover, two reactions were investigated in the absence of catalyst **1** and only in the presence of silica support as catalyst, respectively. The reaction was studied in the absence of any catalyst and carried out only in presence of hydrogen peroxide. After 360 min, the reaction did not show any conversion (Table 3, entry 12). Also, the reaction was done in presence of silica support as catalyst in the presence of hydrogen peroxide, and it did not show any conversion (Table 3, entry 13). Then, the reaction was studied in presence of catalyst **1** and molecular oxygen bubbling as oxidant. In this situation the conversion happened with excellent yield and without any selectivity (Table 3, entry 14). Also, without hydrogen peroxide and only

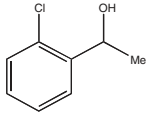
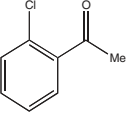
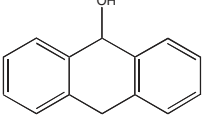
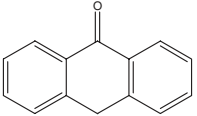
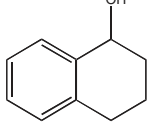
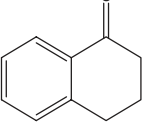
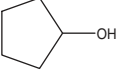
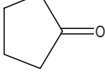
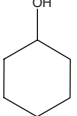
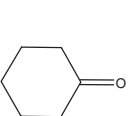
TABLE 2  
Oxidation of alcohols to corresponding carboxylic group by catalyst **1**<sup>a</sup>

| Entry | Substrate | Product | Reaction time (min) | Isolated yields (%) |
|-------|-----------|---------|---------------------|---------------------|
| 1     |           |         | 50                  | 90                  |
| 2     |           |         | 45                  | 99                  |
| 3     |           |         | 35                  | 99                  |
| 4     |           |         | 70                  | 90                  |
| 5     |           |         | 60                  | 98                  |
| 6     |           |         | 60                  | 98                  |
| 7     |           |         | 110                 | 65                  |
| 8     |           |         | 70                  | 95                  |
| 9     |           |         | 75                  | 90                  |
| 10    |           |         | 85                  | 90                  |
| 11    |           |         | 90                  | 95                  |
| 12    |           |         | 75                  | 95                  |

(Continued on next page)



TABLE 2  
Oxidation of alcohols to corresponding carboxylic group by catalyst **1**<sup>a</sup> (Continued)

| Entry | Substrate   | Product   | Reaction time (min) | Isolated yields (%) |
|-------|---|---|---------------------|---------------------|
| 13    |  |  | 105                 | 90                  |
| 14    |  |  | 95                  | 96                  |
| 15    |  |  | 185                 | 95                  |
| 16    |  |  | 225                 | 90                  |
| 17    |  |  | 360                 | 90                  |

<sup>a</sup>The reactions were carried out with 1 mmol of substrate at room temperature, 0.025 g of catalyst **1**, and aqueous 30% H<sub>2</sub>O<sub>2</sub> 10 mmol.

TABLE 3  
Optimization of reaction conditions by oxidation of 4-methylthiophenol in CH<sub>3</sub>OH at room temperature in presence of hydrogen peroxide as oxidant<sup>a</sup>

| Entry           | Solvent         | Catalyst (g) | Temperature | Time (min) | Conversion% | Disulfide selectivity% |
|-----------------|-----------------|--------------|-------------|------------|-------------|------------------------|
| 1               | methanol        | 0.02         | 25          | 30         | 100         | 100                    |
| 2               | dichloromethane | 0.02         | 25          | 150        | 10          | 90                     |
| 3               | ethanol         | 0.02         | 25          | 150        | 60          | 100                    |
| 4               | toluene         | 0.02         | 25          | 150        | 10          | 90                     |
| 5               | tetrahydrofuran | 0.02         | 25          | 150        | 20          | 90                     |
| 6               | acetonitril     | 0.05         | 25          | 150        | 40          | 95                     |
| 7               | DMF             | 0.02         | 25          | 70         | 100         | 100                    |
| 8               | methanol        | 0.02         | 0           | 100        | 20          | 100                    |
| 9               | methanol        | 0.02         | 50          | 20         | 100         | 95                     |
| 10              | methanol        | 0.02         | 75          | 15         | 100         | 90                     |
| 11 <sup>b</sup> | methanol        | 0.01–0.06    | 25          | 55–20      | 100         | 100                    |
| 12              | methanol        | None         | 25          | 360        | 0           | –                      |
| 13              | methanol        | Support      | 25          | 360        | 0           | –                      |
| 14 <sup>c</sup> | methanol        | 0.05         | 25          | 35         | 100         | 0                      |
| 15 <sup>d</sup> | methanol        | 0.02         | 25          | 180        | 0           | 0                      |
| 16 <sup>f</sup> | methanol        | 0.02         | 25          | 30         | 100         | 100                    |

<sup>a</sup>Isolated yield on the basis of the weight of the pure product obtained.

<sup>b</sup>The reaction carried out with various amount of catalyst **1** (0.01–0.06 g). Results show the conversion time is decreased by increasing catalyst amount. Yields obtained excellent at all cases.

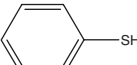

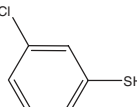

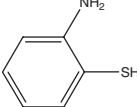
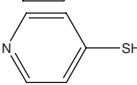
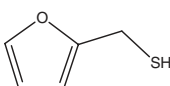
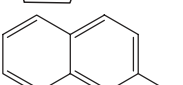
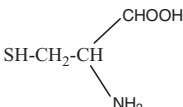
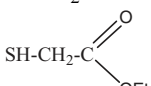
<sup>c</sup>The reaction carried out in the presence of molecular oxygen as oxidant.

<sup>d</sup>The reaction carried out by 0.02 g catalyst in the absence of oxidant.

<sup>f</sup>The reaction carried out with the first recycled catalyst **1** and the catalyst used four times more. Yields obtained excellent at all cases.



TABLE 4  
Oxidative coupling of thiols to disulfides catalyzed by catalyst **1**<sup>a</sup>

| Entry | Substrate   | Time(min) | Isolated yields (%) |
|-------|---|-----------|---------------------|
| 1     |    | 32        | 98                  |
| 2     |    | 27        | 94                  |
| 3     |    | 40        | 95                  |
| 4     |    | 30        | 97                  |
| 5     |    | 25        | 90                  |
| 6     |    | 26        | 85                  |
| 7     |    | 35        | 85                  |
| 8     |   | 34        | 90                  |
| 9     |  | 50        | 80                  |
| 10    | SH-CH <sub>2</sub> -COOH  | 25        | 90                  |
| 11    |  | 45        | 80                  |
| 12    | C <sub>8</sub> H <sub>17</sub> SH   | 40        | 90                  |

<sup>a</sup>The reactions were carried out with 1 mmol of substrate in 2 mL of methanol at room temperature with 0.02 g of catalyst **1** and hydrogen peroxide (10 mmol, 30%) as oxidant.

catalyst **1**, the reaction did not show any conversion (Table 3, entry 15). The stability and recycling possibility of prepared heterogeneous catalyst in oxidation of thiols to disulfides were further investigated. After one time running of the reaction, the catalyst washed with methanol and dried for the next five runs under the same reaction conditions (Table 3, entry 16). It is clear that the obtained thiols conversion was almost the same within the five reaction runs, verifying that catalyst **1** is highly stable and can be reused. In continuation, the oxidation of different types of thiols was happened in the presence of heterogeneous nickel Schiff-base complex as catalyst in methanol and in the

presence of hydrogen peroxide as the oxidant (Table 4). As can be seen from Table 4, a variety of aromatic (entries 1–8) and aliphatic (entries 9–12) thiols were easily converted to corresponding disulfides in appropriate times with excellent yields. From the data of column 2 in Table 4, it is also obvious that aromatic thiols react faster than aliphatic thiols.

## CONCLUSION

In summary, heterogeneous nickel Schiff-base complex as catalyst **1** was prepared by the sol-gel method. A peer study on the structural, morphological and catalytic properties of catalyst **1** was performed by various analytical techniques. XRD and microscopic analysis indicate that the catalyst **1** prepared by the sol-gel precursor has a suitable crystallinity. In addition, the investigations have shown that the prepared catalyst **1** can be a favorable material to selective oxidation of thiols to corresponding disulfide over a wide range of aromatic and aliphatic thiols. The processing parameters such as the amount of catalyst, effect of various solvents, temperature, and different oxidants can all affect the coupling reaction of thiols. The results showed that the prepared heterogeneous catalyst could effectively oxidize thiols to disulfide in a high yield. The percentage of conversion obtained in the 26–45-min of stirring was 80–98%, using 0.02 g/2 mL of catalyst. Moreover, this catalytic oxidation system is clean, safe, and operationally simple and the yields of the products are excellent, so the oxidation method meets the needs of contemporary green chemistry and is suitable for practical syntheses.

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