Application of Metal Organic Frameworks M(bdc)(ted)0.5 (M = Co, Zn, Ni, Cu) in oxidation of benzyl alcohol

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The selective oxidation of benzyl alcohol to benzaldehyde is an important process in heterogeneous catalysis and green organic chemistry. Herein, we investigated the effect of different metal ions in metal organic framework M(bdc)(ted)$_{0.5}$ (M = Co, Zn, Ni, Cu, bdc = 1,4-benzenedicarboxylate, ted = triethylenediamine) on the catalytic activity of benzyl alcohol oxidation. The catalytic results demonstrated that Co(bdc)(ted)$_{0.5}$ performed good benzyl alcohol conversion (81.8%) and benzaldehyde selectivity (> 99%) by using O_2 as the oxidant. The catalysts could be reused several times without ~~a~~ significant degradation in activity.

1. Introduction

Metal-organic frameworks (MOFs) are porous materials, comprised of metal ions or clusters or organic linkers[1 2]. Usually, the synthesis of MOFs is straightforward, using well soluble salts as the source for the metal ions, typically metal acetates, sulfates or nitrates. The organic linkers, which mostly are different types of carboxylic acid, are supplied in a polar organic solvent, after combination of these inorganic and organic components under stirring, the metal-organic structures are formed by self-assembly within under high temperature or even solvothermal conditions[3]. MOFs with unique pore structure and large specific surface area crystalline materials are expected to apply in the field of heterogeneous catalysis[4 5 6]. Such as alkene epoxidation[7 8 9], phenol hydroxylation[10], hydrocarbon oxidation[11], Knoevenagel condensation reaction[12 13 14], oxidation of benzyl alcohol[15 16] and so on. Benzaldehyde is a valuable intermediate for many organic compounds, which is wildly used in the pharmaceutical, perfume, plastic, dyestuff and agrochemical industries[17]. Development of catalysts for oxidation benzyl alcohol reaction with O_2 as terminal oxidant is of high actual interesting for academic research and for industrial application[18 19]. The large versatility in the design of MOFs with adequate geometry and pore size makes these materials more promising for liquid phase reactions[20]. The Pd/MIL-101 catalyst was highly active in the liquid-phase aerobic oxidation of benzyl alcohol[21]. The Fe(BTC) catalyst was highly selective in benzyl alcohol oxidations[22].

As a member of MOFs, the structure of two subunits in M(bdc)(ted)$_{0.5}$ contains inorganic coupling parts (secondary building units SBUs)[23], and the secondary building units (SBUs) of the framework structure are paddlewheel binuclear metal clusters (Fig. 1). In the layer of 2D network, each paddlewheel building unit is linked by bdc molecules, while in the 3D porous frameworks and the apical sites of metal ions in the SBUs are bonded by ted molecules[24]. M(bdc)(ted)$_{0.5}$ have aroused great concern not only owing to its structure of paddlewheel binuclear metal clusters, but also due to the high microporosity porous, thermal stability and good catalyst properties[25]. Huang et al[26] reported that a highly hydrophobic and permselective Zn(bdc)(ted)$_{0.5}$ membrane for H_2 and CO_2 separatio. Lee et al[27] synthesized microporous [M(bdc)(ted)$_{0.5}$]·2DMF·0.2H_2O (M = Zn, Cu) that tested argon, hydrogen and hydrocarbon sorption properties at cryogenic and higher temperature.

Herein, we explored the catalytic performance of M(bdc)(ted)$_{0.5}$ (M = Cu, Zn, Ni, Co, bdc = 1,4-

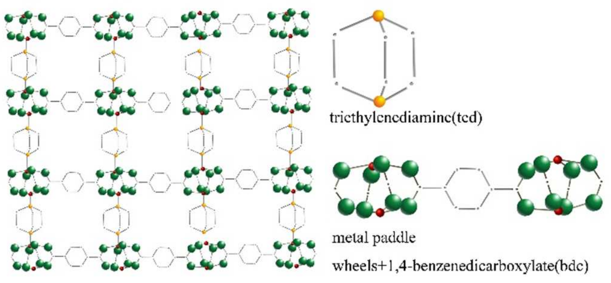

Fig. 1. Schematic presentation for the construction of typical M(bdc)(ted)$_{0.5}$ (M=Co, Cu, Ni, or Zn), M (red),O (green),N (yellow),and C (gray).

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benzenedicarboxylate, ted = triethylenediamine) for the oxidation of benzyl alcohol and found that Co(bdc)(ted)$_{0.5}$ showed high benzyl alcohol conversion and benzaldehyde selectivity.

2. Experimental

2.1 Materials

All chemical reagents used were obtained from commercial sources and used without further purification. Chemicals were used as received: 1,4-benzenedicarboxylic acid (H_2bdc, 98%), triethylenedia mine (ted, 98%), N,N-dimethylformamide (DMF, 99.8%), zinc(II) nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, 99%), cobalt(II) nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$, 99%), copper(II) nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$, 99.5%), nickle(II) chloride hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$, 98%).

2.2 Catalyst preparation

M(bdc)(ted)$_{0.5}$ was synthesized via a facile encapsulation method[28 29]. In a typical synthesis, cobalt nitrate hexahydrate (0.45 mmol) was dissolved in the mixture of H_2bdc (0.36 mmol), ted (0.29 mmol) and 15 mL of DMF by ultrasonic treatment and then transferred to Teflonlined autoclave (20 mL) and heated at 120 ˚C for 2 days. A purple crystalline powder of production was isolated by filtering and washed three times with 10 mL of DMF, and then dried in vacuum at 50 °C for 12 h. In order to remove the guest DMF molecules, the dried powders were kept in a flow of dry nitrogen and heated at 120 ˚C for 12 h. For comparison, Cu(bdc)(ted)$_{0.5}$, Ni(bdc)(ted)$_{0.5}$ and Zn(bdc)(ted)$_{0.5}$ were synthesized by a similar method.

2.3 Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku X-ray diffractometer using Cu Kα radiation carried at 40 kV and 40 mA. Diffraction patterns were a range of 2θ angles from 5 to 40° at a scanning speed of 3°/min. Scanning electron microscopy (SEM) sample images were taken on an S-4800 (Hitachi) with a cold field emission gun. Thermogravimetric analyse (TG) were conducted using a Netzch Sta 449c thermogravimetric analyzer. Samples were heated from 0 °C to 600 °C at a rate of 10 °C min^{-1} under a constant N_2 flow of 60 mL min^{-1}. FT-IR spectra were recorded on IFS-66V/S at room temperature. The Raman measurements were collected using a Nicolet Almega XR Dispersive Raman spectrometer from Thermofisher. N_2 adsorption–desorption isotherms were measured with a Micromeritics ASAP 2010 system at -196 °C. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. Pore size distributions were evaluated from adsorption branches of nitrogen isotherms. The metal content was estimated by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis conducted on a PerkinElmer emission spectrometer.

2.4 Catalytic reaction evaluation

The benzyl alcohol oxidation was tested in 50 mL two-neck flask under continuous magnetic stirrer and reflux condenser. A mixture of 100 mg catalyst, 1 mmol benzyl alcohol and 10 mL DMF were added to vessel. The reactor temperature was kept at 90 °C and the balance made up of O_2 a flow as oxidant. After the reaction was finished, the solid catalyst was filtered, washed with DMF and ethanol, dried and reused without further purification. The reactants and products were analysed online by gas chromatograph (GC-8A) equipped with an HP-5 capillary column and a FID detector. All the experiment was performed three times and the average value was obtained and adopted.

3. Results and discussion

3.1 Characterization of catalysts

The crystalline structure of the M(bdc)(ted)$_{0.5}$ crystals were characterized by using powder X-ray diffraction (Fig.2). The XRD pattern of M(bdc)(ted)$_{0.5}$ samples exhibit a sharp intense peak around 2θ of 8.2^{o} attributed to the (100) plane, while 2θ of 7.1^{o}, 11.6^{o}, 12.2^{o}, and 16.3^{o}, are corresponding to several hump ordered reflections for the (001), (110), (101), and (200) planes, respectively, indicating that all peaks of the material match well with the previous report results[30].

Fig.3 show the SEM images of M(bdc)(ted)$_{0.5.}$ The obtained Co(bdc)(ted)$_{0.5}$ has an approximate width of 13 μm and shows a nearly column shape. Cu(bdc)(ted)$_{0.5}$ shows a messy block, Zn(bdc)(ted)$_{0.5}$ shows a lump structure, while Ni(bdc)(ted)$_{0.5}$ shows a cuboid morphology.

TG analysis was carried out to evaluate the thermal stability of Co(bdc)(ted)$_{0.5}$ as shown in Fig. S1. The TG curve recorded under N_2 atmosphere showed a two-step weight loss at temperatures ranging from 30 to 600 °C. Below 180 °C, weight loss is mainly attributed to the removal of adsorbed water and DMF molecules. Co(bdc)(ted)$_{0.5}$ is stable up to 350 °C. A sharp weight loss occurs after 350 °C, which might be ascribed to the

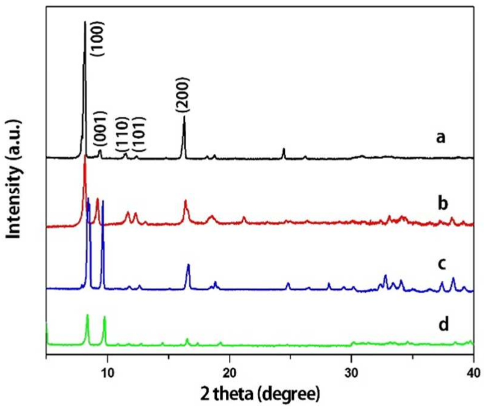

Fig. 2. XRD patterns of (a) Co(bdc)(ted)$_{0.5}$, (b) Cu(bdc)(ted)$_{0.5}$, (c) Zn(bdc)(ted)$_{0.5}$ and (d) Ni(bdc)(ted)$_{0.5}$.

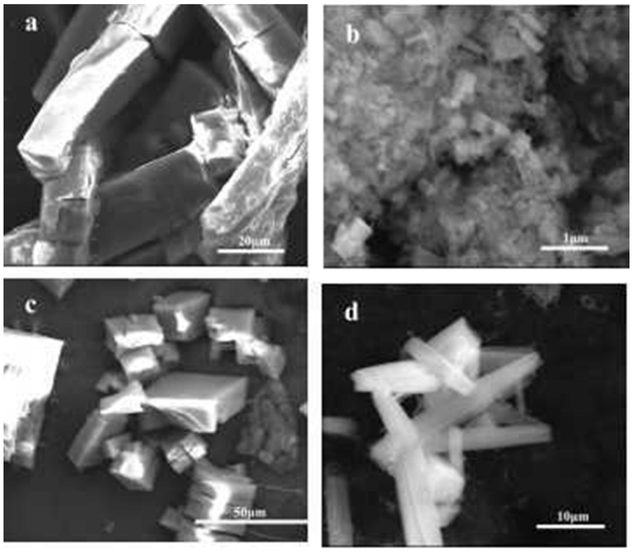

Fig.3. SEM images of (a) Co(bdc)(ted)$_{0.5}$, (b) Cu(bdc)(ted)$_{0.5}$, (c) Zn(bdc)(ted)$_{0.5}$ and (d) Ni(bdc)(ted)$_{0.5}$.

stripping of neutral pillared ligand and indicates the collapse of whole frameworks.

The FT-IR spectra of M(bdc)(ted)$_{0.5}$ were shown in Fig. S2. Four characteristic vibration bands for the paddlewheel structure of MOFs are observed at 1576 cm^{-1}, 1502 cm^{-1}, 1150 cm^{-1} and 1021 cm^{-1}, which are associated with the carbon-carbon double bond and hydrocarbon bond bending motions in the phenyl[31 32]. In addition, the intense band of 1394 cm^{-1} is also attributed to the benzene ring mode. The strong broad peak at 1619 cm^{-1} is attribute to the asymmetric vibrations of ν_{as} (COO). Besides, a considerable shift in frequency is observed for $\nu_{as}(NC_3)$ of the band at 1056 cm^{-1}. The band at 745 cm^{-1} is corresponded to 12 ring deformation[24 26 30].

From Raman spectra (Fig. S3), the band at ca. 1050 cm^{-1} should be associated with the ted ligands[33 34 35]. In the high frequency range (1800 cm^{-1} to 900 cm^{-1}), the Raman bands are primarily related to the vibrational modes of bdc linkers. For example, the band at 1617 cm^{-1} is assigned to the phenyl mode ν_{8a} and it has g parity under C_i symmetry. The bands at 1426 cm^{-1} can be assigned to ν_{sym}(COO). The band at 1018 cm^{-1} band can be correlated to the C-C stretching mode ν_4. While the band at 871 cm^{-1} is attributed to the γ(CH)oop[24 28].

Fig. 4 shows N_2 adsorption-desorption isotherms and pore size distribution of M(bdc)(ted)$_{0.5}$ samples, and Table 1 lists the corresponding surface area and pore size data. According to the IUPAC classification method, the samples display typical I isotherms. There is a large leap when the pressure is relatively low due to the adsorption produced by micropore, while the middle part of the adsorption-desorption isotherms is relatively smooth. The absorption raises fast in the high pressure region. The surface area and pore size of M(bdc)(ted)$_{0.5}$ are in agreement with the reported ones[27 30].

3.2 Catalytic oxidation of benzyl alcohol

The catalytic performance of Co(bdc)(ted)$_{0.5}$ was carried out in benzyl alcohol oxidation to benzaldehyde with O_2 as oxidant. In order to obtain the optimal reaction conditions, we investigated different parameters, such as catalyst amount, solvent, reaction time and temperature. The catalytic results were summarized in Table 2. The temperature has supreme influence on the catalytic behaviour. The benzyl alcohol conversion increased from 58.7% to 81.8% by raising the reaction temperature from 80 °C to 90 °C, while further enhancing reaction temperature would results in the decrease of the benzyl alcohol conversion. Additionally, we investigated the influence of the catalyst amount on the catalytic behaviour. It exhibited negligible catalytic activity without catalyst due to no active sites. The benzyl alcohol conversion reached 70.9% by using 50 mg (containing 20.8 wt.% Co) catalyst after 8 h reaction. The conversion can be enhanced by increasing the catalyst amount up to 100 mg, while further increasing catalyst amount would decrease the conversion. In addition, the reaction time has evident influence on the benzyl alcohol conversion. As the reaction time prolonging from 2 h to 8 h, the benzyl alcohol conversion increased from 54.6% to 81.8% with ~100% benzaldehyde selectivity, while further prolonging reaction time has no significant influence on the benzyl alcohol conversion. Moreover, the solvent has great influence on the catalytic performance. It showed better catalytic performance in DMF than toluene and CH_3CN under the same test conditions. The outstanding yields in DMF

Table 1 The BET parameters of the samples.

Sample	S_{BET}(m^2 g^{-1})	Pore size (Å)
Co(bdc)(ted)$_{0.5}$	1510	5.8
Cu(bdc)(ted)$_{0.5}$	1197	5.9
Zn(bdc)(ted)$_{0.5}$	1592	5.8
Ni(bdc)(ted)$_{0.5}$	1763	5.8

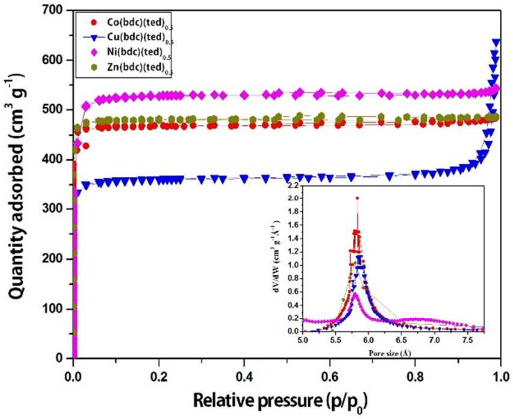

Fig. 4. N_2 adsorption-desorption isotherms and the corresponding pore size distributions of M(bdc)(ted)$_{0.5}$

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Table 2 Catalytic performance of benzyl alcohol oxidation [a].

Entry	Catalyst	Temperature (°C)	Solvent	Time (h)	Quantity (mg)	Conversion (%)	Selectivity (%)
1	No catalyst	90	DMF	8	0	2	>99
2	Co(bdc)(ted)$_{0.5}$	90	DMF	8	50	70.9	>99
3	Co(bdc)(ted)$_{0.5}$	90	DMF	8	150	77.3	>99
4	Co(bdc)(ted)$_{0.5}$	90	DMF	8	100	81.8	>99
5	Co(bdc)(ted)$_{0.5}$	90	DMF	2	100	54.6	>99
6	Co(bdc)(ted)$_{0.5}$	90	DMF	4	100	68.3	>99
7	Co(bdc)(ted)$_{0.5}$	90	DMF	6	100	75.6	>99
8	Co(bdc)(ted)$_{0.5}$	90	DMF	10	100	82.3	>99
9	Co(bdc)(ted)$_{0.5}$	90	CH_3CN	8	100	39.1	>99
10	Co(bdc)(ted)$_{0.5}$	90	Toluene	8	100	6.8	>99
11	Co(bdc)(ted)$_{0.5}$	80	DMF	8	100	58.7	>99
12	Co(bdc)(ted)$_{0.5}$	100	DMF	8	100	76.6	>99

[a] Reaction conditions: benzyl alcohol (1 mmol), solvent (10 mL), and a flow O_2 (50 mL/min) as oxidant.

Table 3 The catalytic behaviour of various catalysts for selective oxidation of benzyl alcohol [a].

Entry	Catalyst	Temperature (°C)	Time (h)	Conversion (%)	Yield (%)	Reference
1	Co(bdc)(ted)$_{0.5}$	90	8	81.8	81.8	This study
2	Cu(bdc)(ted)$_{0.5}$	90	8	8.8	8.8	This study
3	Zn(bdc)(ted)$_{0.5}$	90	8	5.6	5.6	This study
4	Ni(bdc)(ted)$_{0.5}$	90	8	25.2	25.2	This study
5	Co_3O_4/HT-R	100	6	92	75	36
6	Co(TPP)Cl	60	1.5	>99	48	37
7	1.3- Co_3O_4/CMK-3	110	6	82.1	80.2	38
8	Pd/MIL-101	80	1.5	99	98	21
9	Fe(BTC)	90	3	98	97	22

[a] Reaction conditions: catalyst 100 mg, benzyl alcohol (1 mmol), DMF (10 mL), and a flow O_2 (50 mL/min) as oxidant.

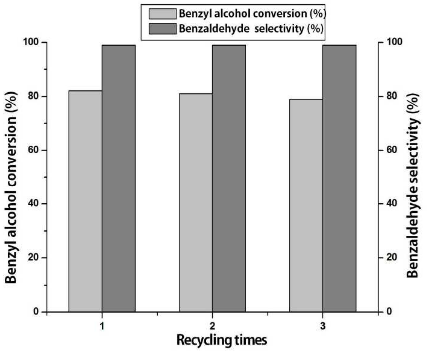

Fig.5 Recycling experiments of the Co(bdc)(ted)$_{0.5}$ for oxidation of benzyl alcohol.

indicate that the solvent plays a special role in the oxidants process. Similar DMF solvent effects have been noted in several oxidation reactions[39 40 41]. Since triplet ground state of O_2 disfavours reactions with singlet organic compounds[42]. Cui et al[43] and Opre et al [44] suggested that the coordinated Co^{2+} sites with DMF played a pivotal role in the activation of oxygen, and DMF was considered a sacrificial solvent that acted as the co-reductant of molecular oxygen in the reaction. Meanwhile, there are a few studies on the coordination of DMF to Co^{2+} complexes that the coordination may affect the ability of O_2 to bind to the cobalt complexes and their redox potential[40]. In a word, when the O_2 as oxidant was used in combination with DMF as the solvent, the amount of 100 mg fresh Co(bdc)(ted)$_{0.5}$ catalyst showed 81.8% benzyl alcohol conversion and ~100% benzaldehyde selectivity after 8 h reaction at 90 °C.

Under the optimized conditions, the catalytic properties of different materials were studied in Table 3. When Cu(bdc)(ted)$_{0.5}$, Zn(bdc)(ted)$_{0.5}$ and Ni(bdc)(ted)$_{0.5}$ were used as catalysts, 8.8%, 5.6% and 25.2% conversion of benzyl alcohol were obtained, respectively, which were much lower than the activity of Co(bdc)(ted)$_{0.5}$ (81.8%). The different catalytic activity observed over iso-structural Cu(bdc)(ted)$_{0.5}$, Co(bdc)(ted)$_{0.5}$, Ni(bdc)(ted)$_{0.5}$ and Zn(bdc)(ted)$_{0.5}$ suggests that the catalytic activity is mainly dependent on the metal ions in the MOFs. Compared with Cu^{2+}, Zn^{2+}, and Ni^{2+}, Co^{2+} sites of Co(bdc)(ted)$_{0.5}$ are the more effective catalytic active sites for the selective oxidation of benzyl alcohol to benzaldehyde. A similar phenomenon has been reported that Co(acac)$_2$ showed better catalytic behaviour than Cu(acac)$_2$, Ni(acac)$_2$, Fe(acac)$_2$ and Mn(acac)$_2$ for selective oxidation of benzyl alcohol[45]. Compared with a series of cobalt based reported heterogeneous catalyst (Table 3), it is obvious that Co(bdc)(ted)$_{0.5}$ possessed excellent catalytic activity, which can be attributed to the high density of fully exposed active sites. Besides, the unique MOF pore structure can avoid blockage and accelerate guest molecules diffusing and the product moving out.

Based on relevant literatures[46 47], the mechanism of the aerobic oxidation of benzyl alcohol over M(bdc)(ted)$_{0.5}$ (M = Cu, Co, Ni or Zn) is proposed. The metal centers of M(bdc)(ted)$_{0.5}$ can activate O_2 to give O_2 adduct of an intermediate, which can abstract hydrogen from benzyl alcohol to form benzaldehyde.

Recycling experiments of Co(bdc)(ted)$_{0.5}$ for oxidation of benzyl alcohol were investigated to examine the stability and recoverability of Co(bdc)(ted)$_{0.5}$ (Fig. 5). The catalysts were recovered by filtration of the reaction solution, washed thoroughly with DMF and dried in vacuum at 50 °C for one night. Compared with the fresh catalyst, the reused catalyst could be successfully recycled for at least three cycles without obvious loss of the catalytic activity and selectivity. Co(bdc)(ted)$_{0.5}$ exhibits basically stable catalytic activity and selectivity (78.3-81.8 conversion and ~100% selectivity). The slight decrease in the conversion might be due to the loss of catalyst by filtration and washing. We further investigated the structure of the recycled catalysts by IR and XRD shown in Fig. S4 and Fig. S5, respectively. No noticeable difference is observed for the initial materials and the reused catalysts, indicating that the structure remained well after running for three times.

To verify the catalysis of Co(bdc)(ted)$_{0.5}$ is heterogeneous during the catalytic process, the reaction was carried out under the optimized conditions (Fig. S6) and the Co(bdc)(ted)$_{0.5}$ solid catalyst was filtered in hot from the reaction mixture at 54.6% formation of benzaldehyde after 2h. The resulting clear solution was sequentially stirred for another 4h. It can be found that only less than 5% conversion was obtained after 4 h if the catalyst was removed. Therefore, it can be concluded that the reaction mainly occurs between the liquid phase and solid phase.

4. Conclusions

MOF catalyst Co(bdc)(ted)$_{0.5}$ is efficient heterogeneous catalyst for the oxidation of benzyl alcohol. Compared with different metals (Cu^{2+}, Zn^{2+}, Ni^{2+}) isostructural MOFs, Co(bdc)(ted)$_{0.5}$ performed better benzyl alcohol conversion (81.8%) and benzaldehyde selectivity (> 99%) than the others. The catalyst can be easily recovered and reused three times without evident loss in catalytic activity.

Acknowledgements

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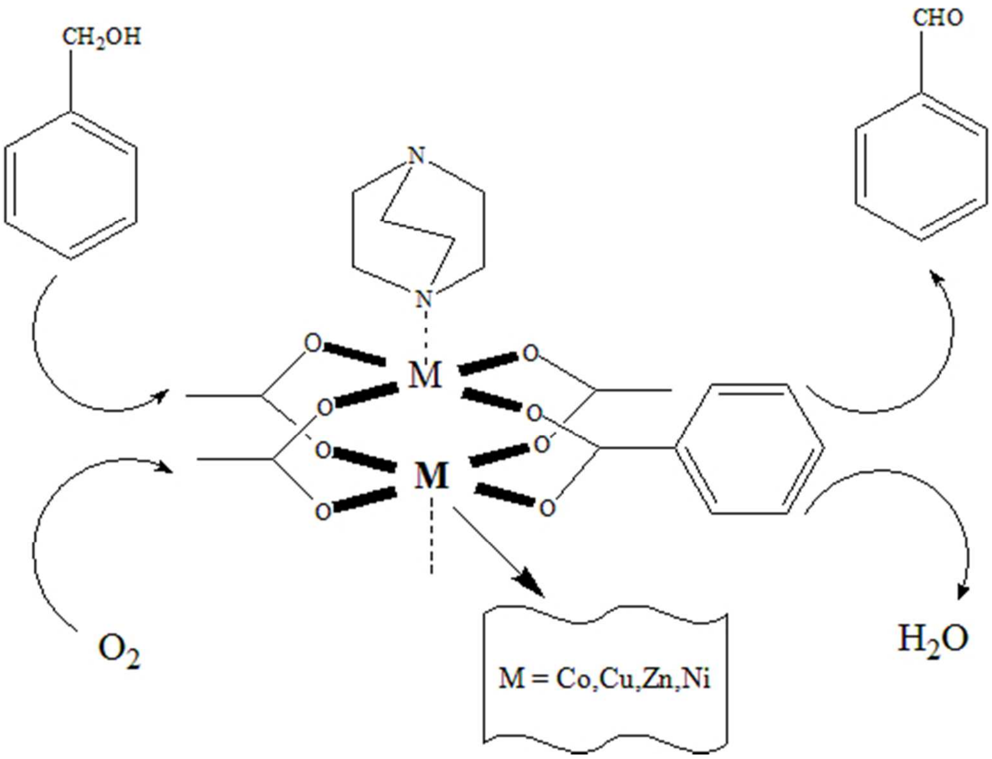

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