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Performance of cobalt titanate towards H_2O_2 based catalytic oxidation of lignin model compound

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Abstract

Mixed metal cobalt titanium oxide ($CoTiO_3$) prepared by solution phase method has been evaluated for the liquid phase catalytic oxidation of vainly alcohol to vanillin using H_2O_2 as an oxygen source. The morphology, phase composition and crystal structure of the freshly prepared and reused $CoTiO_3$ catalyst was studied by SEM, EDX, XRD, XPS and Raman spectroscopy. Vanillyl alcohol conversion was influenced by various experimental conditions such as reaction time, temperature, molar ration of reactants, catalyst loading, nature of solvent and reaction medium. The design a heterobimetallic oxide catalyst which can efficiently perform the high conversion and selective oxidation of vanillyl alcohol into fine chemicals, such as vanillin and vanillic acid. It has been found that during the 5h reaction time in NaOH, the $CoTiO_3$ exhibits remarkable conversion of 99 % and excellent selectivity of 99.8 % to vanillin was achieved in acetic acid and isopropnal solvents respectively. The oxidation reaction mechanism over the catalyst was postulated based on the observation product from the HPLC analysis. $CoTiO_3$ catalyst can retain its performance without significant change in the catalytic activity after four consecutive cycles.

1. Introduction

Lignin, one of the three subcomponents of lignocellulosic biomass (along with cellulose and hemicellulose), represents more than 20 % of the total mass of the Earth's biosphere [1,2]. However, essentially due to its complex structure, this renewable polymer derived from biomass is mainly burned as a source of energy in the pulp and paper industry [1,2]. In the current context of sustainable development and green chemistry [3], lignin valorization represents an important challenge in the biorefinery area in order to diminish the reliance on oil [4,5]. Today, the valorization of lignin into the production of chemical feedstocks represents a real challenge in terms of both sustainability and environmental protection. Because of the complexity of lignin, most of the lignin oxidation studies were performed from model compounds and are very well documented in literature [6,7,8,9,10]. In the past few years, some novel strategies for oxidation of lignin and lignin compounds have been investigated, such as electrochemistry [11,12], use of mesoporous materials [8], photocatalysis [13] and use of vanadium-based catalysis [14].

These studies reveal that some issues need to be resolved, such as the lack of selectivity, decomposition of the catalyst, low amounts of lignin required and difficult separation of products after the reactions are completed. These problems can be overcome by designing suitable heterogeneous catalysts because they offer many advantages over their homogenous counterparts such as easy handling, separation and reusability. Several noble metal-based heterogeneous catalysts such as Au/CeO_2, Pt/C, Ru/TiO_2 etc. have been explored for this purpose and such reactions are mediated by the use of alkali [15,16, 17]. Although noble metal catalysts exhibit high activity for oxidation reactions, they can be expensive, minimizing their potential for commercial applications[18]. Oxides of other transition metals, such as titanium, chromium, manganese, cobalt and copper are also known to be effective catalysts for oxidation reactions. Among these metals, titanium and cobalt are the most attractive because of their strong capability for dioxygen activation (through metal–O_2 adduct formation) and because these are more cost effective compared to noble metals. Recently, a mixed metal oxide catalyst of manganese and cobalt oxide ($CoMn_2O_4$) was found to be an active species for oxidation reactions and catalyzed oxidation of vanillyl alcohol to vanillin [19].

In light of this study, we were attracted and motivated towards the mixed-metal cobalt titanium oxide system as a focus of our present study. We wish to report the preparation, characterization and detailed catalytic performance of $CoTiO_3$ for liquid phase oxidation of vanillyl alcohol mediated with H_2O_2. The catalytic reaction parameters such as time, mass loading of catalyst, mole ratio and reusability of the $CoTiO_3$ catalyst have also been systematically carried out during current study. It has been observed the change of acidic medium to base significantly enhance the selectivity and conversion of vanillyl alcohol to vanillin. Furthermore, the reusability of catalyst has been tested for fourth times and no significant change in the catalytic activity is been observed.

2. Experimental

2.1. Materials and methods

All Chemicals were purchased from various commercial sources such as: Cobalt (II) acetate tetra hydrate (Merck 99%), titanium (IV) iso-propoxide (Sigma-Aldrich 98%), vanilly alcohol (Sigma-Aldrich 98%), hydrogen peroxide (Sigma-Aldrich solution 30% in water), and acetic acid (Merck 96%). The chemicals were used without further purification.

2.1.1. Synthesis of Catalyst

In a typical synthesis, 1.0 g (4.0 mmol) cobalt (II) acetate tetrahydrate was dissolved in 25 mL methanol in a 100 mL Schlenk tube fitted with an inert gas/vacuum line adapter and magnetic stirrer. 1.2 mL titanium (IV) iso-propoxide (4.0 mmol) was added drop by drop via syringe to the solution. The contents were stirred for 4h to obtain a clear purple solution. The reaction mixture was evaporated to dryness under vacuum to produce a deep purple solid.

The as synthesized solid was ground to fine powder and calcined in air at the rate of 2 ˚C/min until 500 ˚C and was kept at this temperature for 6h.

2.2. Characterization

The XRD pattern of the catalysts was recorded on a D8 Advance X-ray diffraction-Bruker AXS using Cu Kα radiation (d= 1.54Å) at a voltage of 40 kV and current of 40 mA at ambient temperature. The surface morphology and chemical composition of the catalyst were analysed by a scanning electron microscope (FEI Quanta 400) equipped with an energy dispersive X-ray spectrometer EDX (INCA Energy 200, Oxford Inst.) operated at an accelerating voltage of 20 kV and a working distance of 9 mm. FT-Raman spectra were recorded with a Reinishaw inVia Raman microscope, using the 514 nm excitation source of Ar^{+1} laser with a 0.01 mw output power. X-ray photoelectron spectroscopy was studied using an ULVAC-PHI Quantera II with a 32-channel Spherical Capacitor Energy Analyzer under vacuum (1 x 10-6 Pa) using Monochromated Al Kα radiation (1486.8eV) and natural energy width of 680meV. The carbonaceous C 1s line (284.6 eV) was used as a reference to calibrate the binding energies.

2.3. Typical method for the oxidation of vanillyl alcohol

The oxidation reaction was carried out in a 50 mL two-necked round bottom flask fitted with a water-cooled reflux condenser. In a typical oxidation reaction, the calculated quantities of vanillyl alcohol (0.15 g, 1.0 mmol) and acetonitrile (25 mL) were added to round bottom flask and kept on magnetic stirrer with oil bath at 358 K. After the desired temperature was attained, the amount of catalyst was added while stirring (850 rpm) followed by H_2O_2 (0.2 mL, 2.0 mmol). About 0.5 cm^3 of reaction mixtures withdrawn periodically by means of a syringe and filtered. The progress of the reaction was monitored by analyzing the filtrate into Agilent HPLC 1100 series liquid chromatography equipped with an ultraviolet detector was used for the analysis. HPLC analysis was performed on a 25 cm RP-18 column. The products and reactant were detected using a UV detector at $\lambda_{max} = 270$ nm. Aqueous acetonitrile (15%) with (1%) acetic acid was used as a mobile phase at a column temperature of 28°C and a flow rate of 1.0 ml min^{-1}.

3. Results and discussion

3.1. Structural and morphological characterization

The phase composition and chemical formula of the as-synthesized Co-Ti oxide catalyst was determined from XRD and the resultant X-ray pattern is presented in **Fig. 1** (blue line). A careful matching of the fresh Co-Ti oxide XRD pattern with the standard inorganic crystal structure database available in PANalytical X'Pert HighScore Plus" software identifies the formation of $CoTiO_3$ as a catalyst product. The cobalt titanium oxide ($CoTiO_3$)crystallizes in the rhombohedral crystal system with cell parameters a = b = 5.0440, c = 13.9610 A˚; α = β = 90°and γ = 120˚and is identified by its peaks at 2θ = 24.0, 32.9, 35.4, 40.6, 49.2, 53.5, 60.3, 63.7, 71.4, 75.3, 84.1 and87.9 produced by their Miller indices (012), (104), (110), (113), (024), (116), (214), (300), (119), (220), (134) and (226) correspondingly. All peaks in XRD pattern show excellent matching with standard pattern (ICSD = 00-001-1040) in terms of their peak position, 2θ value and d-spacing. No possible crystalline impurities such as Co_2O_3, Co_3O_4 and TiO_2 were detected from XRD pattern. This clearly indicates the formation of pure crystalline $CoTiO_3$ at 500 ˚C.

After performing the catalytic oxidation reaction, the reused catalyst was again characterized by XRD (**Fig. 1,** green line) in order to observe any change in its phase composition and chemical identity. It is worth noticing that no significant change in the composition and phase has been detected and finger prints of reused catalyst are similar to the fresh $CoTiO_3$in terms of its peak position and 2θ values. Both the XRD patterns are dominated by the peak at 2θ = 32.9˚ also reveals that $CoTiO_3$ product is well crystallized. However the crystallinity of the reused catalyst has been reduced as compared to the freshly prepared $CoTiO_3$.

Recent literature implies that attempts to synthesize pure $CoTiO_3$ generally require higher temperatures exceeding 600 °C and often produce TiO_2 and Co_2TiO_4as impurity phases.[20,21,22]. Furthermore, it needs prolonged annealing at higher temperature of 700 °C to enhance the crystallinity of the material. On the other hand, in the present case, solution method at a relatively low temperature of 500 °C to furnish a high crystalline $CoTiO_3$ product free from all other titania and cobalt oxide phases.

[Insert Figure 1 about here]

The cobalt titanate phase that was identified from the XRD pattern was further confirmed by Raman spectroscopy as is shown in **Fig.2**.

The Raman scattering vibration modes detected at 193, 208, 237, 267, 335, 383, 480, 521 and 689 cm^{-1} are characteristic of ilmenite $CoTiO_3$. The Raman spectroscopy results are in good agreement with our XRD pattern and also matched well with the previously reported Raman data for the $CoTiO_3$materials [20].

[Insert Figure 2 about here]

The change in surface morphology of the as-synthesized $CoTiO_3$ catalyst before and after vanillyl alcohol oxidation reaction has been studied by scanning electron microscopy and images are shown in **Fig. 3**. Before carrying out the catalytic reaction, $CoTiO_3$catalyst is comprised of large size crystallites (**Fig. 3a**) and high resolution image reveals the rough and stony surface of the catalyst (**Fig. 3b**).It is generally believed that the rough surface of the catalyst because of its high surface area can better perform the catalytic action as compared to smooth and plane surface which has less surface area. After execution of the oxidation reaction the morphology of

$CoTiO_3$ changes to oval shaped crystallites which exhibit smooth and plane surface (**Fig. 3c and d**).

[Insert Figure 3 about here]

The stoichiometric composition of the catalyst before and after the catalytic oxidation reaction was established from energy dispersive X-ray analysis and EDX spectra are shown in **Fig. 4**. It has been erudite that the elemental composition of the catalyst before and after catalytic oxidation reaction remains unchanged and EDX spectra show the expected stoichiometric ratio indicating that the composition of the catalyst before and after oxidation reaction is in fact $CoTiO_3$. The molar ratio of Co/Ti obtained from different peak areas of the EDX spectra is thus close to the expected 1:1 ratio of $CoTiO_3$.

[Insert Figure 4 about here]

Figure 5 indicates the EDX mapping of $CoTiO_3$ catalyst before and after the catalytic oxidation reaction and reveals that Co, Ti and O atoms are homogeneously distributed throughout the catalyst's surface.

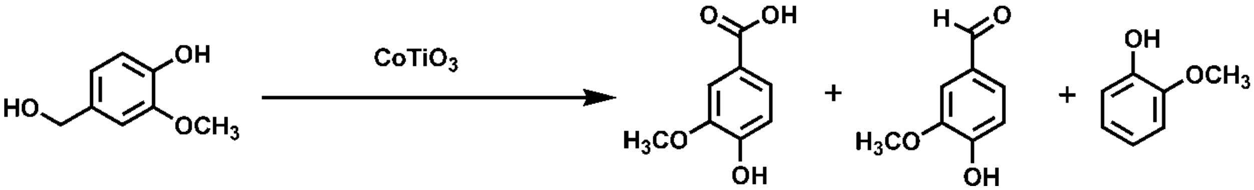
[Insert Figure 5 about here]

The XPS survey san plot (**Fig. 6a**) indicates the presence of the major cobalt, titanium, and oxygen components in on the surface of the catalyst. Figure 6 (**b, c and d**) shows the high resolution XPS spectra in the Co 2p and Ti 2p and O1s region for the catalyst powder. Fig. 4 shows that the binding energies of Co 2p3/2 and Co2p1/2 are 780.0~780.8 eV, and 796.2~796.4eV, respectively. These values are comparable to the 780.7 (2p3/2) And 796.3 eV (2p) that was found in Co_3O_4[23] . The binding energies of Ti 2p3/2 (457.2~458.6 eV) and Ti 2p (463.0~ 464.2 eV) are agreeable with that of the TiO powder (458.5 eV for Ti 2p3/2)[24] and the binding energy of O 1s is between 529.2~530.2 eV. Overall the XPS spectra is in good agreement with the previously reported $CoTiO_3$ prepared by a modified sol-gel method[25].

[Insert Figure 6 about here]

3.2. Liquid phase oxidation of vanillyl alcohol

To determine the optimum reaction condition of vanillyl alcohol oxidation various reaction parameters were studies such as effect of time, catalyst amount, molar ratio of vanillyl alcohol: H_2O_2, reaction temperature, solvent type and the effect of alkaline medium on the reaction. Under the optimum reaction condition, the oxidation of vanillyl alcohol without catalyst did not show any activity and the reusability analyses were also investigated. Moreover, the reactions also were performed under optimum reaction conditions in alkaline medium. The idea behind using base is probably to deprotonate the phenolic-OH to form the phenoxy anion, which is more reactive and easier, favours coordinate to $CoTiO_3$ and resulting more selectivity to vanillin and increasing the activity[26]. The equation for the oxidation of vanillyl alcohol is shown in **Scheme 1**.



Scheme1: liquid phase oxidation of vanillyl alcohol products in $CoTiO_3$ catalyst.

3.2.1 Influence of reaction time

The effect of reaction time on vanillyl alcohol conversion and selectivity to vanillic acid and vanillin were studied for $CoTiO_3$ and the results are shown in **Fig. 7**. The conversion increased slowly from 28 % to 67 % when the time increased from 30 min. to 5 h. Further extending the reaction time to 6 h. did not improve the oxidation. Based on the highest conversion, the 5 h reaction time was selected as an optimum time for this catalytic system. However, the selectivity of vanillic acid was found to be decreased from 87 % to 77 % within time increase, this decrease is consistent with the increased selectivity of vanillin from 10 % to 19 % in reaction time 30 min. to 5 h.

[Insert Figure 7 about here]

3.2.2 Catalytic activity with different mass of catalyst:

The prepared catalyst was tested in liquid phased oxidation of vanillyl alcohol. As illustrated in **Fig. 8**, as the mass of the catalyst increased the conversion of vanillyl alcohol to corresponding product was found to be increased sharply from 24 %, to 67 % when the catalyst mass used was increased from 25 to 100 mg. The selectivity of acid formatting was found to slightly decrease as the catalyst mass was increased. However, further increase in the catalyst mass to 125 mg resulted in a decrease in vanillyl alcohol conversion to 59 %. The reason behind that could be due to the rapid decomposition of H_2O_2 over the large surface area available with a higher mass catalyst [27,28]. As a result, the selectivity of vanillin was observed slightly increased associated with decreased formation of vanillic acid. On the other hand, the absence of the catalyst leads to maximum value of 3% vanillyl alcohol conversion to vanllic acid.

[Insert Figure 8 about here]

3.2.3 Influence of Temperature

The reaction temperature was found to have a great influence on the conversion of the reaction. Thus, in the oxidation of vanillyl alcohol the effect of temperature on the reaction was studied in the range of 338-363 K (**Fig. 9**). The reaction was conducted at a fixed parameter (vanillyl alcohol: H_2O_2 molar ration 1:2 and a catalyst amount of 100 mg in 25 ml acetonitrile). The conversion was found to increase from 51 % at 338 K to 72 % at 363 K. The plausible explanation for this observation could be due to the enhanced decomposition of H_2O_2 at high temperature [27]. However, there is no significant change in the selectivity of vanillic acid and vanillin at different temperature. Therefore, 358 K was preferred as suitable reaction temperature for the subsequent optimization studies, since there are moderate conversion and rapid decomposition of H_2O_2.

[Insert Figure 9 about here]

3.2.4 Influence of H_2O_2 mole ratio

To determine the optimum ratio of H_2O_2 needed for this oxidation of vanillyl alcohol reactions, four different ratio were studied. The results obtained from the reactions are shown graphically in **Fig. 10**. The conversion was ranging from 51-67 % for 1 to 4 H_2O_2 molar ratio. However, the results clearly show that when H_2O_2 is taken in more than equimolar ratio (vanillyl alcohol: H_2O_2:-1:2, 1:3) the conversion significant increased (67 %). Generally, the decomposed of H_2O_2 produced water as by-product [29], and that might poison the catalyst by adsorbing strongly to the catalyst $CoTiO_3$ and blocked the active site, thus inhibiting the conversion of vanillyl alcohol to further products. Furthermore, decomposition of H_2O_2 increased the formation of vanillic acid, on the contrary, the formed of guaiacol which was decreased with increasing of H_2O_2 ratio, while the formed of vanillin did not significantly change. Unlike, it can be seen from **Fig. 10**, which indicates that an increase in H_2O_2 more than 2 equimolar ratio no significant change in the performance of the catalyst.

[Insert Figure 10 about here]

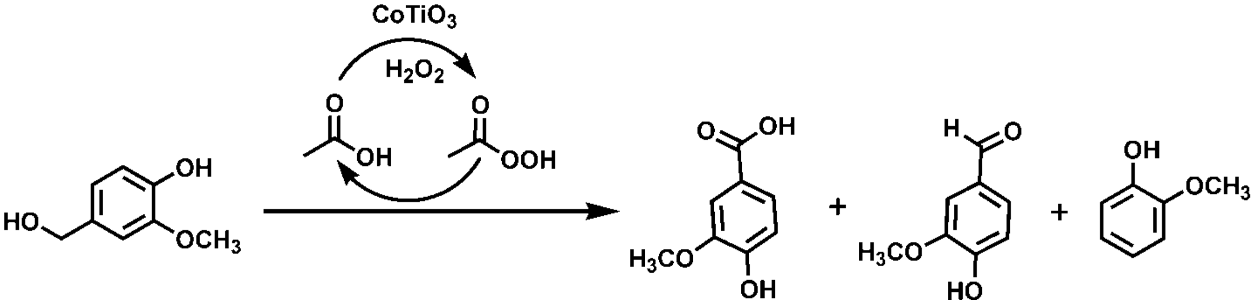
3.2.5 Reusability of the catalyst

In order to study the stability of $CoTiO_3$heterogeneous catalyst the regenerating test carried out. After observing the completion of the reaction over a fresh catalyst which was carried out as mention in typical method for the oxidation of vanillyl alcohol, the liquid contents were removed from the flask and $CoTiO_3$catalyst washed several times with acetone. Then, dried under vacuum at 100 °C for 2 h. This dried catalyst was reused in a second cycle for the oxidation of vanillyl alcohol and a similar procedure was followed for four subsequent oxidation cycles, the result is depicted in **Fig.11**. It can be observed that the vanillyl alcohol conversion decreased *ca.* 15 % and 20 % after the third and fourth reuse, respectively. However, the selectivity of the vanillic acid and vanillin was found with slight changes after third recycle. To further confirm the catalyst nature of $CoTiO_3$ after the fifth reused, the XRD, SEM and Raman were analysed and was described in section 3.1.

[Insert Figure 11 about here]

3.2.6 Influence of solvent

Since the catalytic activity is strongly dependent on the basic character of the solvent, the influence of nature solvent on the oxidation of vanillyl alcohol and vanillin selectivity were investigated over sixth different solvent system with 100 mg catalyst mass and 1:2 vanillyl alcohol: H_2O_2 molar ratio, the result is represented in **Fig. 12.** Based on the experiment, highest conversion was achieved in acetic acid (91 %) followed by ethyl alcohol (70 %), acetonitrile (67 %), *N,N*-dimethyl formaldehyde (35 %), tetrahydrofuran (20 %) and acetone (1%). Keeping the above fact in view, it is understood that the increasing conversion by using acetic acid as a solvent is directly proportional to the formation of peracetic acid, which is in situ generation by reacted acetic acid with H_2O_2 in the presence of an acid catalyst [30]. And this in turn accelerates and acting as an oxidant source for the oxidation reaction, as shown in **Scheme 2**. However, the selectivity of vanillin was significant increased when acetic acid used as a solvent compared to other solvents [31, 32], this could be due to the possibility of formation O_2 higher than radical hydroxide. Nonetheless, acetic acid was chosen as the optimal solvent media due to formation of peracetic acid and this led to higher conversion and increases the selectivity to vanillin. So under these reaction conditions, in the oxidation of vanillyl alcohol to vanillin, a major role is played by peracetic acid conversely to oxidation of vanillyl alcohol to vanillic acid a major role is played by H_2O_2.



Scheme2: Role of formation peracetic acid in oxidation of vanillyl alcohol.

[Insert Figure 12 about here]

3.2.7 Influence of basic medium

The effect of NaOH on the conversion and selectivity of aldehyde product (vanillin) in the oxidation of vanillyl alcohol is displayed in **Fig. 13A**. The adding amount of the base (NaOH) has been used equivalent to H_2O_2 (2.0 mmol). The role of using alkaline is probable to deprotonate the phenolic to form the phenoxyanion, In addition, it seems that the generation of sodium peroxide occurs immediately after adding H_2O_2 to alkaline oxidation reaction mixture (**Eq. 1**). The latter, can be used as an oxidizing agent as well as oxygen source and that enhance and accelerate the reaction activity and the selectivity of aldehyde. However, according to lack solubility of NaOH in acetonitrile the acetic acid and isopropanol were choosing to examine the effect of alkaline on the oxidation of the vanillyl alcohol reaction (referring **Fig. 13B**.) It has been established that conversion and selectivity of vanillin was significantly influenced by the change of the solvent. When the catalytic reactions were studied in acetic acid, a conversion of 99 and 68 % selectivity of vanillin product was obtained. However using isopropanol as a solvent, slightly reduces the conversion to 91% but enhances the selectivity vanillin to 99.8%. A comparable oxidation reaction in the present of isopropanol as solvent and without a base led to much lower conversion (3 %) of vanillyl alcohol. As a result, this hypothesis indicates that the alkaline an important part in the selective oxidation of the vanillyl alcohol process.

$$H_2O_{2\,(aq)} + 2NaOH_{(s)} \longrightarrow Na_2O_2 + 2H_2O$$

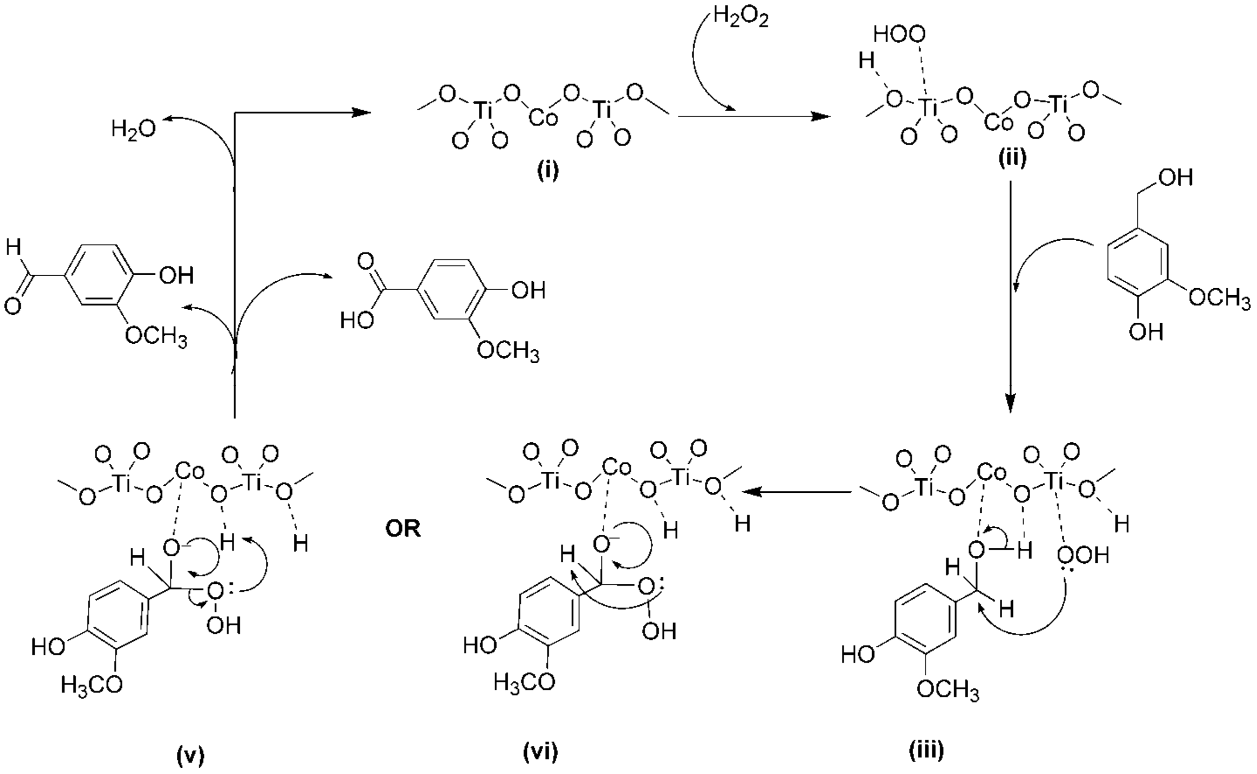
$$Na_2O_2 + 2H_2O \longrightarrow O2 + 4NaOH$$

Equation 1: Reactivity of H_2O_2 in alkaline medium to form oxygen in oxidation reaction.

[Insert Figure 13 about here]

3.2.8 The proposed reaction mechanism

Detection of oxidation products from the HPLC analysis suggests a free radical mechanism may be operating for vanillyl alcohol oxidation under the studied reaction condition. **Scheme 3** illustrates the suggested mechanism for oxidation of vanillyl alcohol in present of H_2O_2. Initially the catalyst reacts with H_2O_2 to form the hydroperoxyl radial which is acting as a source of highly reactive oxidatand, this in turn attack the catalyst forming an intermediate. The hydroperoxyl radial is conjugate acid of superoxide anion ($^{-}O_2$), this is a very important intermediate in combustion chemistry and known to play major roles in the oxidation reaction [33,34]. Moreover, this chemical is more stable at atmosphere than superoxide. On the other hand, its well know the formation of hydroperoxyl radial can be through direct photolysis of H_2O_2 as well as through the Fentons reaction [35]. However, the vanillyl alcohol is activated on the catalyst surface. Then the electron rich hydroperoxyl attack the partial positive carbon and the hydrogen of the hydroxyl group abstraction by the oxygen molecular to produce activated oxygen species, which help to remove the hydroxyl from the hydroperoxyl to produce water as a by-product. Meanwhile, the vanilloxycation releases a proton which is attacked by electron rich oxygen of the hydroperoxyl group and forming the final acid product. Or another possibility the electron rich oxygen of the hydroperoxyl group attacks the proton on activated oxygen species (on catalyst) and forms the final vanilla product. It has found that when the reaction medium more base the formation of aldehyde product increased and that could be due to the formation of superoxide rather that hydroperoxyl radical which is going to prefer attacking the hydrogen on activated oxygen species (on catalyst) than the proton of vanilloxy carbon.



Scheme 3: The suggested mechanism for the formation of main oxidation product (vanillin and vanillic acid) from vanillyl alcohol in presence of $CoTiO_3$.

4. Conclusion

The $CoTiO_3$ catalyst was prepared by mixing equivimolar $Co(OAc)_2$ and $Ti(^{i}Pro)_4$ in methnol and followed by calcination at 500 °C. However the applicability of this process demand a heterogeneous catalyst which can offer potential advantages of easy handling, separation, reusability and cost effectiveness. The as synthesized $CoTiO_3$ material was characterizaed by XRD, SEM, EDX and XPS analyses and employed for the catalytic oxidation of vanillyl model compound with the help of H_2O_2 in acid and base medium. Presence of titanium species were responsible for their enhanced catalytic activity. In the oxidation of vanillyl alcohol, the vanillin product was obtained as the major component in a basic condition (99.8 %) while the highest conversion obtained in the acid medium (99 %). No products were obtained without the presence of the catalyst. However, in the present study, we identified that $CoTiO_3$ possesses these catalytic properties and can be used for practical applications. Through a simple regeneration technique, the prepared catalyst was found to be stable and could be reused several times with minor loss was observed initially.

Acknowledgement

The authors are grateful for the financial support from High Impact Research HIR F-000032 to complete this work.

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Fig. 1. X-ray diffractogram offreshly prepared $CoTiO_3$(blue line) catalyst prepared at 500 ˚C. Green line represents the X-ray diffractogramof reused catalyst after performing the oxidation reaction.

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Fig. 3. Surface topographic images of $CoTiO_3$ catalyst (**a and b**) before vanilline oxidation reaction; (**c and d**) after vanilline oxidation reaction.

Fig. 4. EDX spectra revealing the stoichiometric composition of $CoTiO_3$catalyst (**a-c**) before and (**d-f**) after oxidation reactions.

Fig. 5. EDX mapping revealing the distribution of Co, Ti and O atoms on the surface of catalyst beforeand after oxidation reactions.

Fig 6. XPS spectra of $CoTiO_3$ powder prepared at 500 °C (a) Survey scan plot. (b) Co 2p (c) Ti 2p (d) O1s.

Fig. 7. Effect of time on conversion and selectivity. Reaction condition: amount of $CoTiO_3$ (100 mg); molar ratio of vanillyl alcohol:H_2O_2 (1:2); reaction temperature (358 K); acetonitrile as solvent (25 ml).

Fig. 8. Effect of catalyst loading on conversion and selectivity. Reaction condition: reaction time (5 h); molar ratio of vanillylalcohol :H_2O_2 (1:2); reaction temperature (358 K); acetonitrile as solvent (25 ml).

Fig. 9. Effect of reaction temperature on conversion and selectivity. Reaction condition: reaction time (5 h); molar ratio of vanillyl alcohol:H_2O_2 (1:2); amount of $CoTiO_3$(100 mg); acetonitrile as solvent (25 ml).

Fig. 10. Effect of molar ratio on conversion and selectivity. Reaction condition: reaction time (5 h)**;** amount of $CoTiO_3$ (100 mg); reaction temperature (358 K); acetonitrile as solvent (25 ml).

Fig. 11. Effect of re-used catalyst (reusability) on conversion and selectivity. Reaction condition: reaction time (5 h); amount of $CoTiO_3$(100 mg); molar ratio of vanillyl alcohol:H_2O_2 (1:2); reaction temperature (358 K); acetonitrile as solvent (25 ml).

Fig. 12. Effect of solvent on conversion and selectivity. Reaction condition: reaction time (5 h); amount of $CoTiO_3$(100 mg); molar ratio of vanillyl alcohol:H_2O_2 (1:2).

Fig. 13. Effect of basic medium on conversion and selectivity. Reaction condition: amount of $CoTiO_3$ (100 mg); amount of NaOH (2.0 mmol); molar ratio of vanillyl alcohol:H_2O_2 (1:2); reaction temperature (358 K); solvent **A)**: acetic acid (25 ml), **B)**: isopropanol (25 ml).

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Figure 1

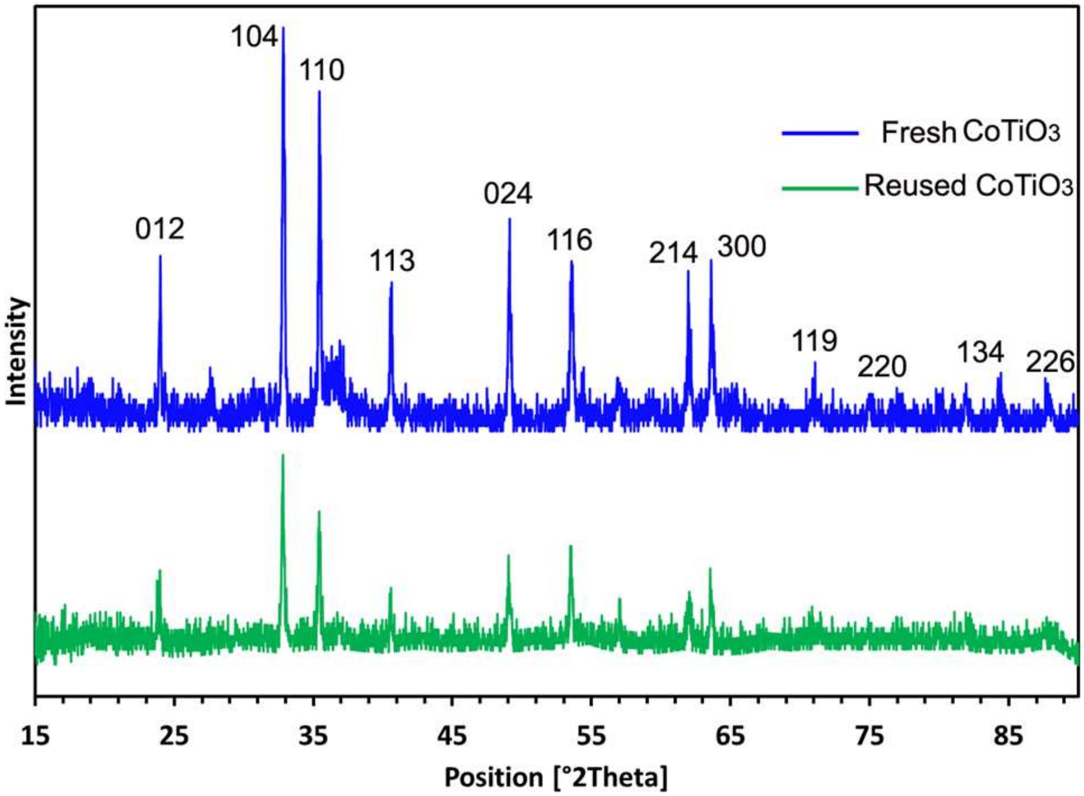

104
110
012
113
024
116
214
300
119
220
134
226
Fresh CoTiO3
Reused CoTiO3
Intensity
15
25
35
45
55
65
75
85
Position [°2Theta]

Figure 2

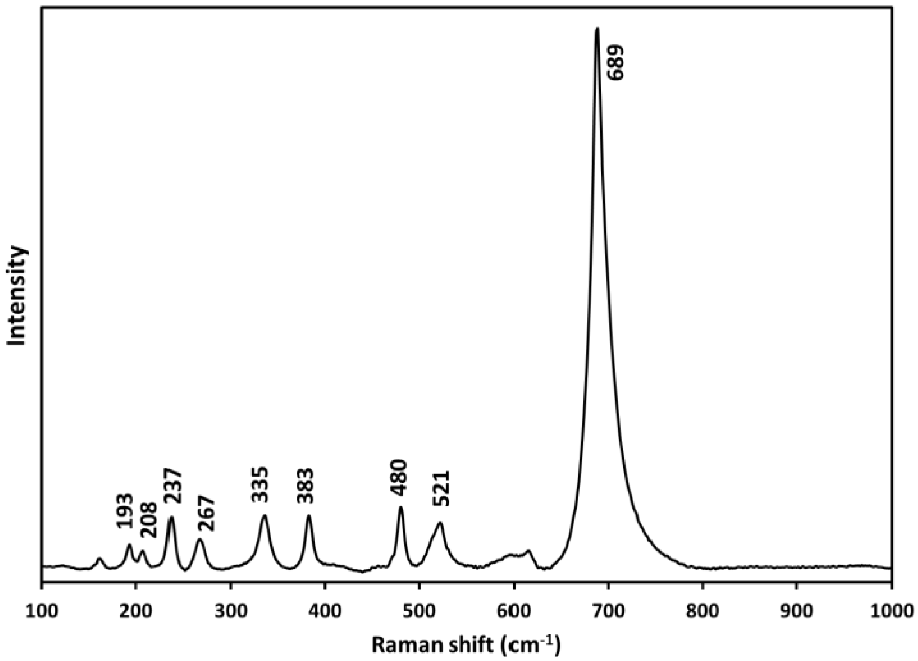

689
193
208
237
267
335
383
480
521
Intensity
100
200
300
400
500
600
700
800
900
1000
Raman shift (cm-1)

Figure 3

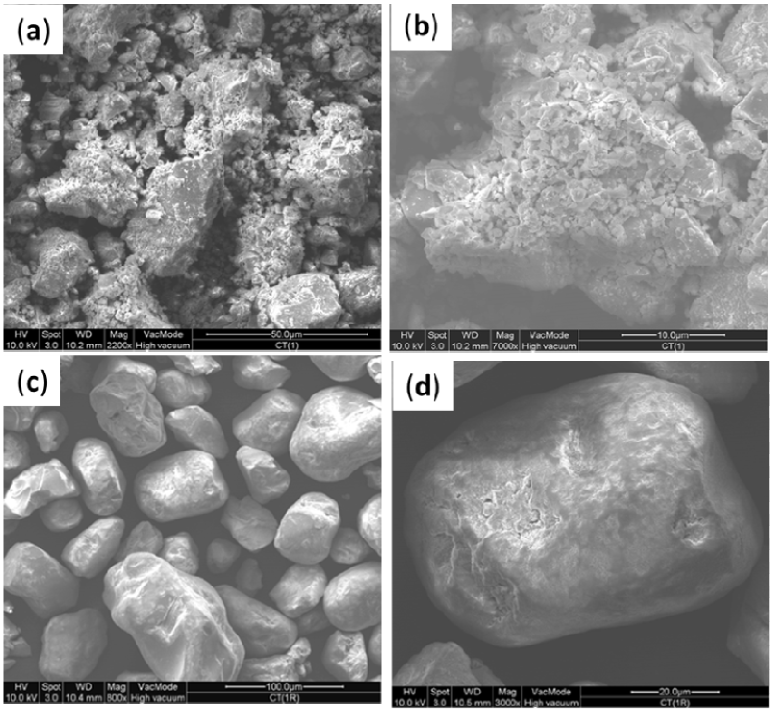

(a)
HV Spot WD Mag VacMode
10.0 kV 3.0 10.2 mm 2200x High vacuum
50.0µm
CT(1)
(b)
HV Spot WD Mag VacMode
10.0 kV 3.0 10.2 mm 7000x High vacuum
10.0µm
CT(1)
(c)
HV Spot WD Mag VacMode
10.0 kV 3.0 10.4 mm 800x High vacuum
100.0µm
CT(1R)
(d)
HV Spot WD Mag VacMode
10.0 kV 3.0 10.5 mm 3000x High vacuum
20.0µm
CT(1R)

Figure 4

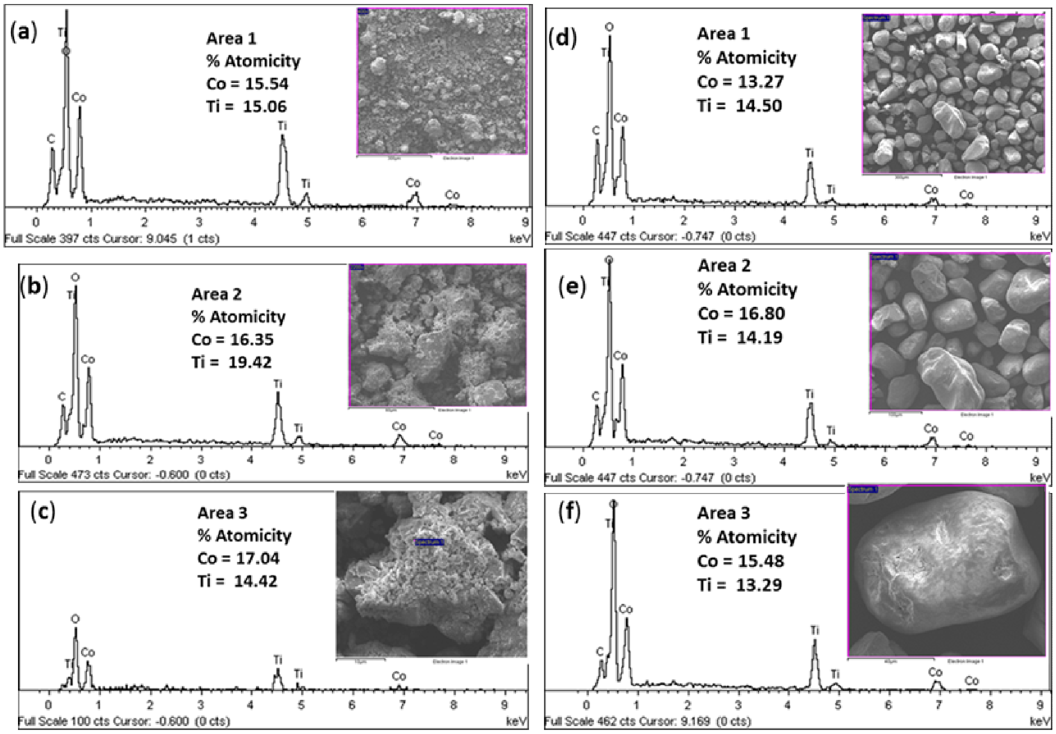

(a)
Area 1
% Atomicity
Co = 15.54
Ti = 15.06
Full Scale 397 cts Cursor: 9.045 (1 cts)
(b)
Area 2
% Atomicity
Co = 16.35
Ti = 19.42
Full Scale 473 cts Cursor: -0.600 (0 cts)
(c)
Area 3
% Atomicity
Co = 17.04
Ti = 14.42
Full Scale 100 cts Cursor: -0.600 (0 cts)
(d)
Area 1
% Atomicity
Co = 13.27
Ti = 14.50
Full Scale 447 cts Cursor: -0.747 (0 cts)
(e)
Area 2
% Atomicity
Co = 16.80
Ti = 14.19
Full Scale 447 cts Cursor: -0.747 (0 cts)
(f)
Area 3
% Atomicity
Co = 15.48
Ti = 13.29
Full Scale 462 cts Cursor: 9.169 (0 cts)
C
O
Ti
Co
0 1 2 3 4 5 6 7 8 9
keV

Figure 5

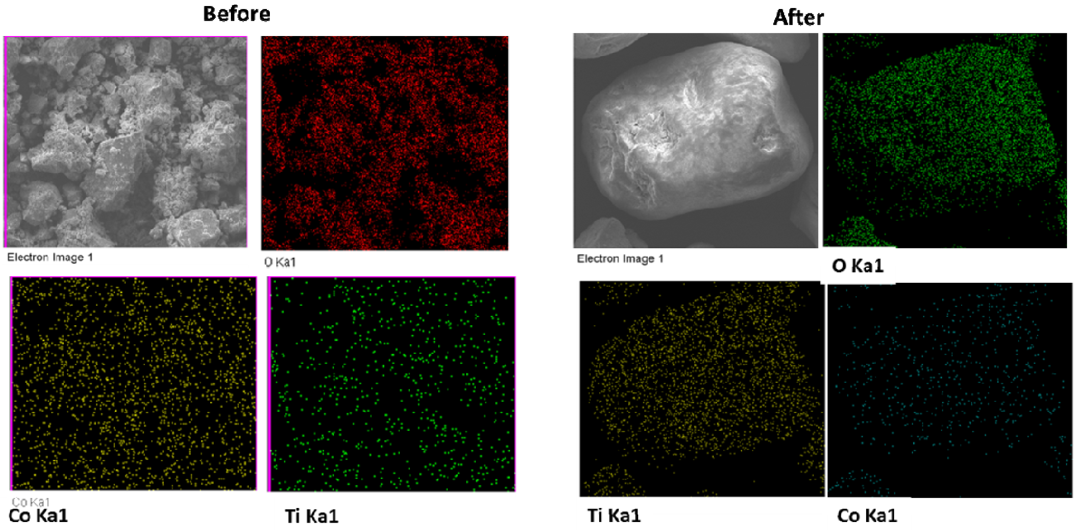

Before
Electron Image 1
O Ka1
Co Ka1
Co Ka1
Ti Ka1
After
Electron Image 1
O Ka1
Ti Ka1
Co Ka1

Figure 6

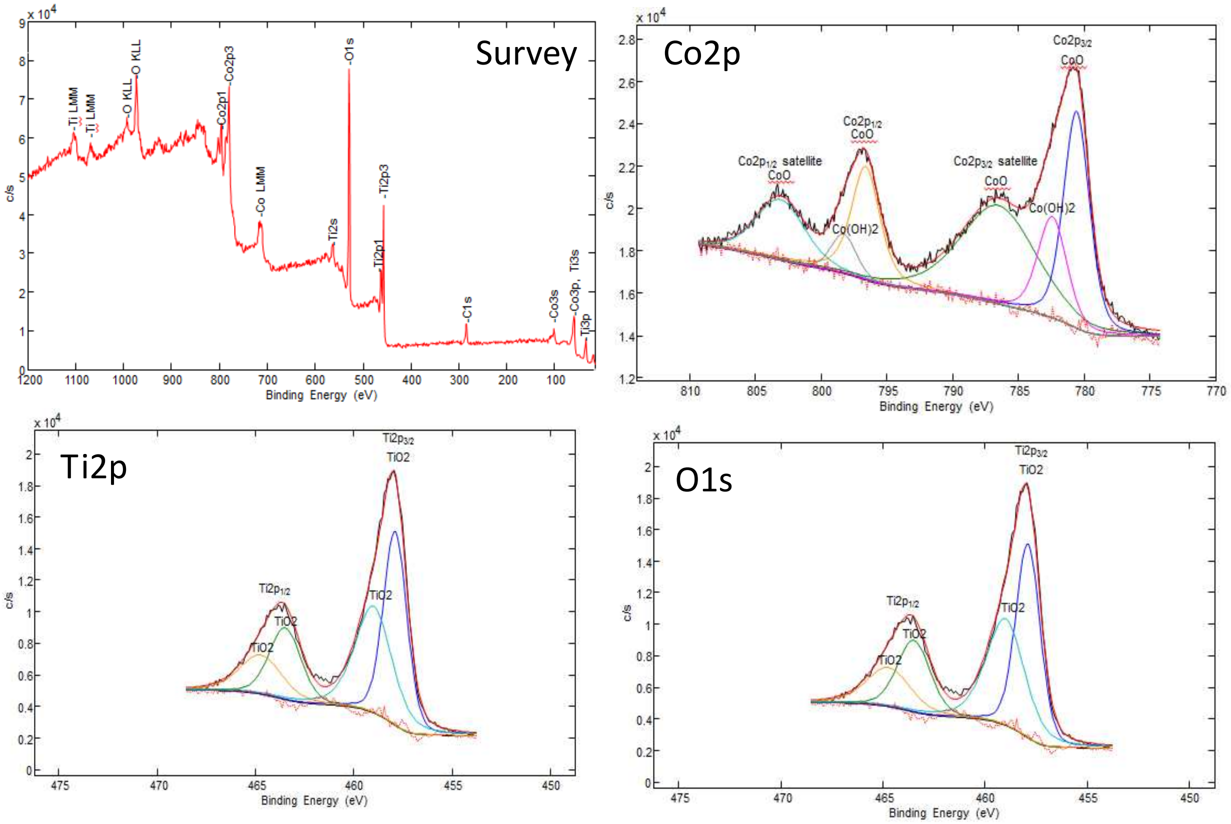

Survey
x 10^4
c/s
Binding Energy (eV)
Ti LMM
Ti LMM
O KLL
O KLL
Co2p1
Co2p3
Co LMM
Ti2s
O1s
Ti2p1
Ti2p3
C1s
Co3s
Co3p, Ti3s
Ti3p
Co2p
Co2p3/2 CoO
Co2p1/2 CoO
Co2p1/2 satellite CoO
Co2p3/2 satellite CoO
Co(OH)2
Co(OH)2
Ti2p
Ti2p3/2 TiO2
Ti2p1/2
TiO2
TiO2
TiO2
O1s
Ti2p3/2 TiO2
Ti2p1/2
TiO2
TiO2
TiO2

Figure 7

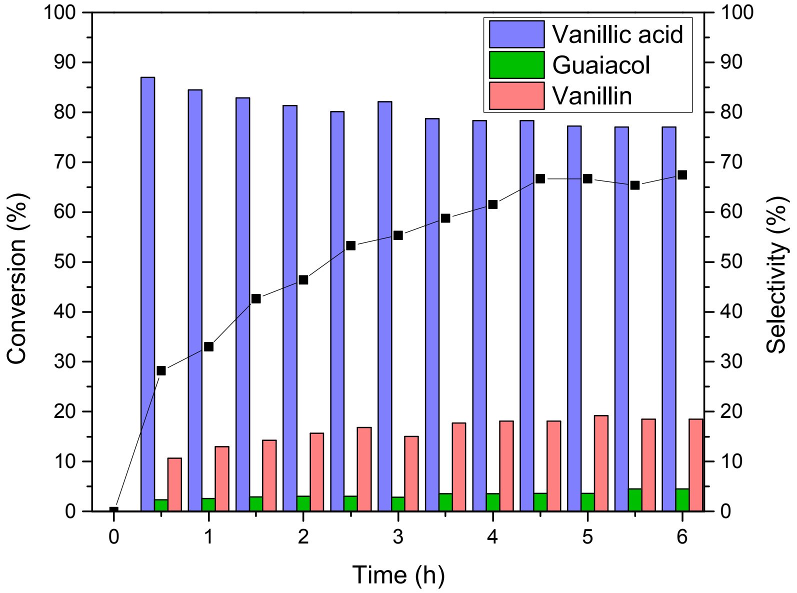

100
90
80
70
60
50
40
30
20
10
0
Conversion (%)
Selectivity (%)
Time (h)
0
1
2
3
4
5
6
Vanillic acid
Guaiacol
Vanillin

Figure 8

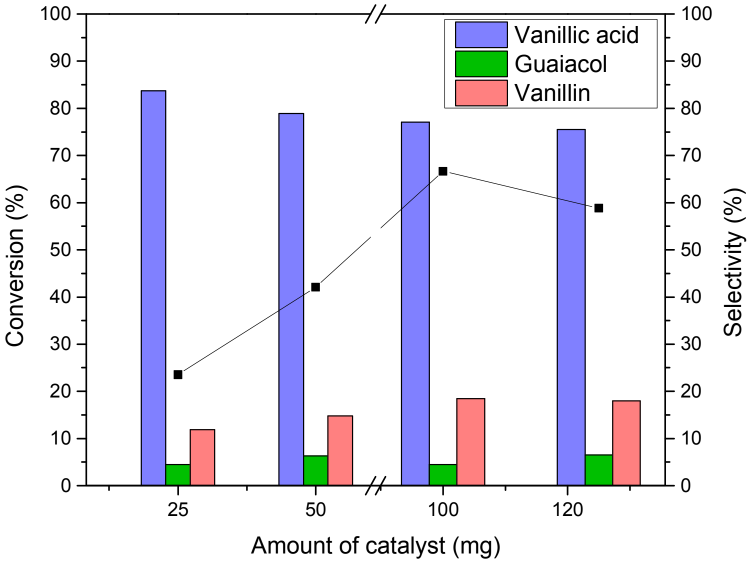

Vanillic acid
Guaiacol
Vanillin
Conversion (%)
Selectivity (%)
Amount of catalyst (mg)
25
50
100
120
0
10
20
30
40
50
60
70
80
90
100

Figure 9

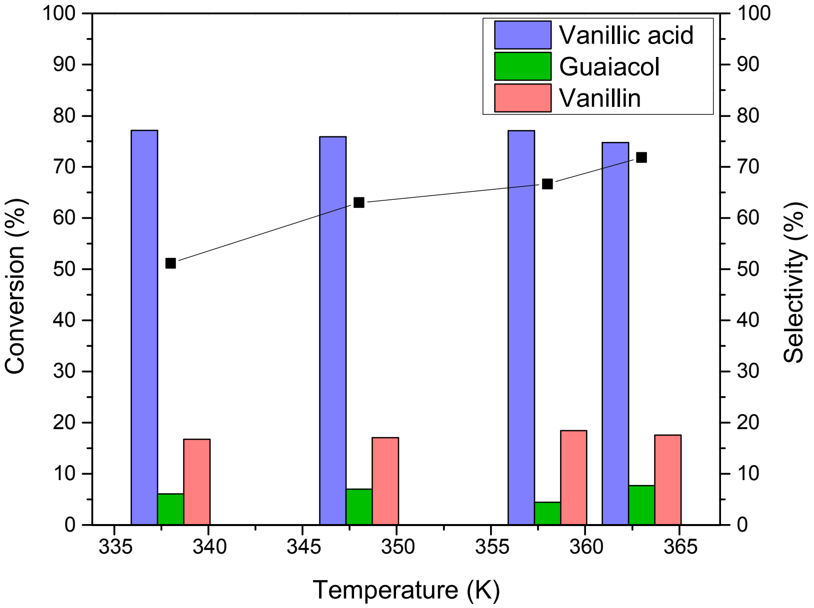
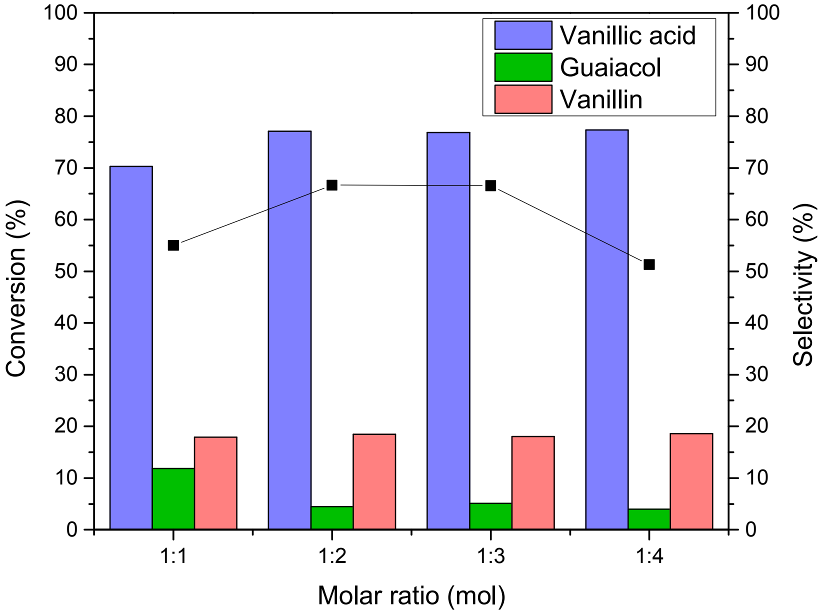

Vanillic acid
Guaiacol
Vanillin
Conversion (%)
Selectivity (%)
Temperature (K)
0
10
20
30
40
50
60
70
80
90
100
335
340
345
350
355
360
365

Figure 10



100
90
80
70
60
50
40
30
20
10
0
Conversion (%)
Selectivity (%)
🟦 Vanillic acid
🟩 Guaiacol
🟥 Vanillin
1:1
1:2
1:3
1:4
Molar ratio (mol)

Figure 11

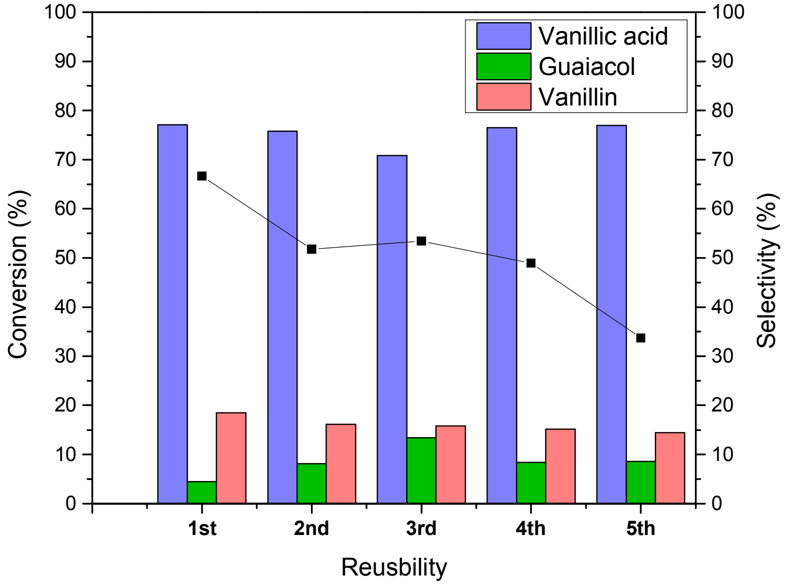

Vanillic acid
Guaiacol
Vanillin
Conversion (%)
Selectivity (%)
0
10
20
30
40
50
60
70
80
90
100
1st
2nd
3rd
4th
5th
Reusbility

Figure 12

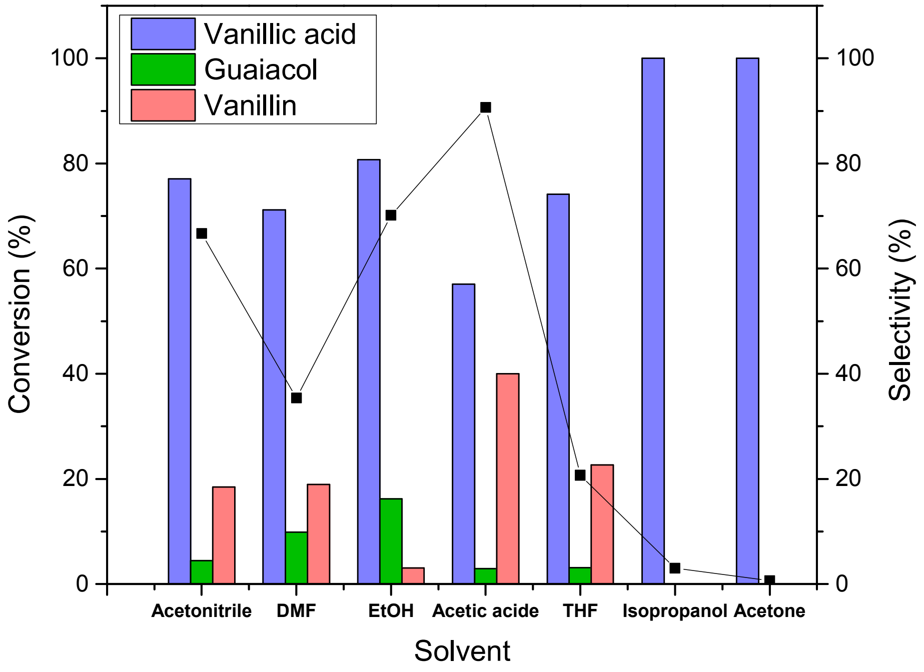
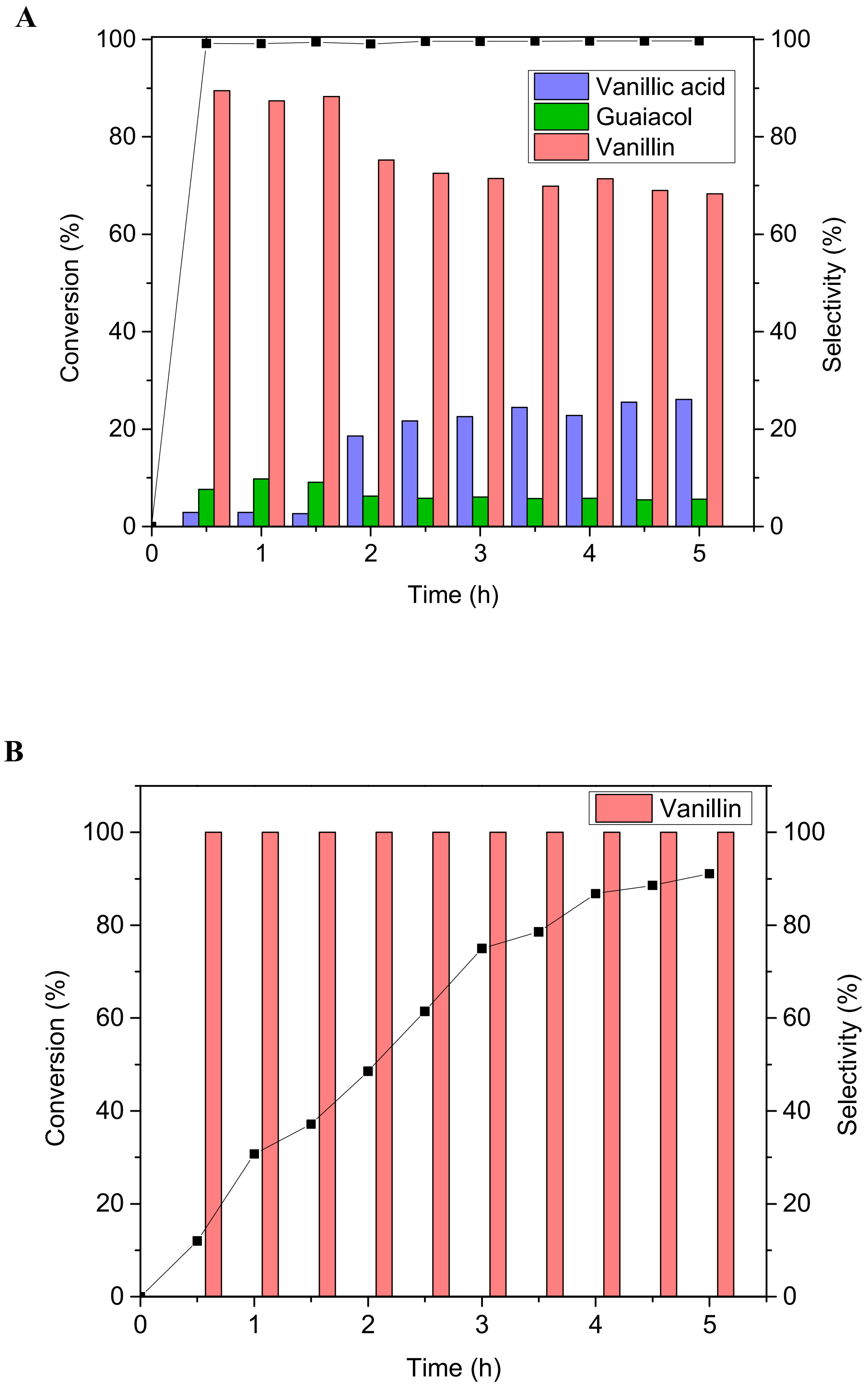

Vanillic acid
Guaiacol
Vanillin
Conversion (%)
Selectivity (%)
0
20
40
60
80
100
Acetonitrile
DMF
EtOH
Acetic acide
THF
Isopropanol
Acetone
Solvent

Figure 13


A
Vanillic acid
Guaiacol
Vanillin
Conversion (%)
Selectivity (%)
Time (h)
0
20
40
60
80
100
0
1
2
3
4
5
B
Vanillin
Conversion (%)
Selectivity (%)
Time (h)
0
20
40
60
80
100
0
1
2
3
4
5

Graphic abstract