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763

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Highly dispersed cobalt oxide nanoparticles on manganese oxide nanotubes

for aerobic oxidation of benzyl alcohol

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Abstract: Hybrid Co_3O_4/MnO_2 nanotube-based catalysts were prepared by a simple hydrothermal synthesis method. The physico-chemical properties of Co_3O_4/MnO_2 catalyst were then studied by different characterization techniques, namely, SEM, TEM and HR-TEM, BET surface area, H₂-TPR and XPS. The hybrid catalyst showed superior catalytic performance toward benzyl alcohol oxidation than pure MnO_2 nanotubes and Co_3O_4 nanoparticles. The uniform dispersion of Co_3O_4 nanoparticles, better redox behaviour, the variable oxidation states of manganese and cobalt ($Mn^{3+/4+}$ or $Co^{3+/2+}$) as well as the abundance of active surface oxygen species were responsible for such a high catalytic activity.

Keywords: Hybrid Co₃O₄/MnO₂; Benzyl alcohol oxidation; High dispersion; Nanotubes

1. Introduction

The selective oxidation of alcohols to aldehydes and carboxylic acids is of critical importance to fine chemicals production. At industrial scale, the oxidation processes were conducted for decades to oxidize toxic organic solvents by deploying hazardous oxidants at least in stoichiometric amounts [1]. While the gas-phase oxidation of simple alcohol molecules has been well practiced, the limitations due to requirements for adequate volatility as well as thermal stability of reactants and products, have directed research to liquid catalytic oxidation processes at mild conditions (temperatures < 150°C, low oxygen pressures) [2].

Benzaldehyde has been extensively used in plastic, pharmaceutical, and agrochemicals industry [3]. It has been traditionally produced by the hydrolysis of benzyl chloride or vapor/liquid oxidation of toluene [4, 5]. At present these processes have little industrial importance and have a major drawback of low conversion to achieve high selectivity. Alternatively, the production through the liquid-phase aerobic catalytic oxidation of benzyl alcohol by oxygen using solid catalysts, presents an environmentally sustainable alternative route [6]. Typically, Pd, Pt, and Au metals supported on various metal oxides such as TiO₂, Al₂O₃, MgO, and CeO₂, have been tested as catalysts, exhibiting promising behavior in terms of both conversion and selectivity [7, 8]. For example, Enache et al. synthesized Au-Pd/TiO₂, which showed excellent catalytic activity at temperatures between 100-160 °C under oxygen pressures in the range of 1-10 bar [9]. However, the deployment of such catalysts at industrial level is rather unfeasible due to the scarcity and consequently prohibitive cost of noble metals [10].

In 2001, Son et al. reported the successful catalytic oxidation of alcohols in the liquid phase using MnO_x as catalyst and O_2 from air as oxidant [11]. According to the authors, the

oxidation could be described by a redox mechanism according to which, Mn^{4+} reduces to Mn^{3+} and then it is re-oxidized by O₂. The same group further showed that the oxidation followed a Mars-van Krevelen type mechanism with the lattice oxygen of the manganese octahedral molecular sieves (OMS-2) participating in the reaction and being replenished by the fluid-phase O₂ [12]. In fact, one of the crystal phases of MnO₂, alpha-phase MnO₂, consists of 2x2 (4.6x4.6 Å) tunnels constructed from double chains of octahedra [MnO₆] is a promising catalyst for oxidation reactions [13]. The tunnel cavity, moderately acidic sites as well as easy release of lattice oxygen of MnO₂ have rendered it promising for various applications [14]. This was confirmed by Su et al. [15] who showed that among the different manganese oxides, α -MnO₂ exhibits a superior catalytic activity in the oxidation of benzyl-alcohol by O₂ under microwave radiation. It is believed in general that the Mn oxidation state, local symmetry and active site-support interaction, play a defining role in the catalytic activity.

Apart from manganese, cobalt oxides (i.e. Co_3O_4) have been evaluated in the selective oxidation of benzyl alcohol [16]. Co_3O_4 nanoparticles were homogeneously dispersed on activated carbon by Zhu et al. [17] and showed ~100% benzyl alcohol conversion as well as 87.3% aldehyde selectivity at 80 °C and atmospheric pressure, with the catalyst exhibiting no significant activity loss even after 4 cycles. Octahedral Co_3O_4 nanocrystals have been utilized by Teng et al. [18], and the incorporation of nanoparticles on alumina [19] and hydrotalcite [20] has resulted in promising results with respect to conversion, selectivity, stability and recyclability. Interestingly, Kamimura et al. [21] prepared cobalt doped MnO₂, which showed up to 89% yield of benzaldehyde at 110 °C under oxygen atmosphere. This verifies, that Co could function as a promoter for the redox behavior of Mn³⁺/Mn⁴⁺ in the presence of oxygen, which is responsible for the conversion of benzyl-alcohol to benzaldehyde.

Herein, we report the employment of Co_3O_4 -decorated α -MnO₂ nanotubes for the liquidphase benzyl-alcohol oxidation in the presence of O₂. The aim of the study was to exploit the synergy between manganese and cobalt oxides, as well as take advantage of a potentially favorable α -MnO₂ morphology, that could significantly boost the oxidation process. Further, the prepared catalysts were thoroughly characterized to enable the elucidation of the oxidation mechanism.

2. Experimental section

2.1 Catalyst synthesis and characterization

 α -MnO₂ nanotubes were prepared hydrothermally via the reduction of KMnO₄. A solution of 0.66 g KMnO₄, 1.5 mL HCl and 75 mL deionized water (DI-H₂O) was stirred at room temperature (RT) to form a homogeneous mixed solution. The solution was then transferred to a Teflon-lined stainless-steel autoclave and kept at 150 °C for 10 h. After it was cooled down naturally to RT, the reaction product was centrifuged and vacuum dried overnight. Following the synthesis of α -MnO₂ nanotubes, the decoration with Co₃O₄ nanoparticles was carried out via a low-temperature hydrothermal method. 5.82 g Co(NO₃)₃·6H₂O (source of Co), 6 g CO(NH₂)₂ (use as template), 0.5 g α -MnO₂ as well as 150 ml DI-H₂O and 50 ml CH₃CH₂OH were added into a solution that was strongly stirred at 80 °C for 2 h. After the process was completed, the product was centrifuged, vacuum dried overnight and finally calcined at 350 °C under air for 2 h with a heating ramp of 2 °C min⁻¹. With the decorating process, Co₃O₄ was successfully coated on MnO₂ nanotubes (represented as Co₃O₄/MnO₂) with a 20 wt.%, which was validated by MP-AES analysis. Materials and characterization details are discussed in supporting information.

2.2 Catalytic activity test

In a typical reaction, 1 mmol of benzyl alcohol, 25 mg of Co_3O_4/MnO_2 catalyst (equals to 291 µmoles (62 µmoles Co+ 229 µmoles Mn)) and 10 mL of solvent were added to a 50 mL round bottom flask with a reflux condenser. For compassion purpose, we have used 291 µmoles of Mn (equals to 25.32 mg of MnO₂) and Co (equals to 51.51 mg of Co₃O₄) for the same reaction. The oxygen gas was supplied to the reaction system with a 10 mL/min flow rate. The reaction was carried out at different temperatures and times. After the reaction, the catalyst was separated by undergoing centrifugation and was analyzed by gas chromatography and mass spectrometry.

3. Results and discussion

3.1 Catalyst characterization

The decoration of Co_3O_4 nanoparticles on MnO_2 nanotubes was examined by scanning electron microscopy (SEM). Fig. 1 shows the morphologies of MnO_2 and Co_3O_4/MnO_2 catalysts, confirming that the MnO_2 particles possessed a nano-tubular shape. The average length and diameter of the MnO_2 nanotubes was calculated $3\pm 2 \ \mu m$ and $60\pm 20 \ nm$, respectively. Fig. 1 clearly shows that the Co_3O_4 nanoparticles ($25\pm 5 \ nm$) were well dispersed on the surface of MnO_2 nanotubes. For comparison, pure Co_3O_4 nanoparticles size was determined from TEM and shown in Fig. S1. It was found that the average particle sizes of Co_3O_4 was $30\pm 2 \ nm$. Moreover, the energy dispersive X-Ray spectrometry (EDS) mapping (Fig. S2) confirmed the presence of Mn, Co, and O elements on the surface of Co_3O_4/MnO_2 catalyst.



Fig. 1. SEM images of MnO₂ and Co₃O₄/MnO₂ catalysts at two different magnifications.

The transmission and high-resolution electron microscopy (TEM and HR-TEM) images of MnO₂ nanotubes are displayed in Fig. S3(a-c), respectively. As it can be observed in Fig. S3a-b, MnO₂ comprises of a nanotubular morphology. Further, in Fig. S2c, the calculated lattice d-spacing of 0.69 nm may be attributed to (110) crystal plane of alpha-MnO₂ phase [22]. Fig. 2 shows the TEM, HR-TEM, and fast Fourier transform (FFT) images of hybrid Co_3O_4/MnO_2 catalyst. The Co_3O_4 nanoparticles were well-dispersed on the surface of MnO₂ nanotubes and it was further confirmed that an interface was formed between the Co_3O_4 nanoparticles and MnO₂ nanotubes. The corresponding HR-TEM image displays the interplanar d-spacing values of 0.28 nm and 0.69 nm, which are in good agreement with the (220) and (110) crystal planes of Co_3O_4 and MnO_2 phases, respectively [22, 23]. Also, the corresponding FFT image shows the coexistence of MnO₂ and Co_3O_4 phases in the hybrid catalyst.



Fig. 2. TEM, FFT, and HR-TEM images of Co₃O₄/MnO₂ catalyst.

Powder X-ray diffraction (XRD) profiles of MnO_2 , Co_3O_4/MnO_2 , and Co_3O_4 are shown in Fig. 3. The diffraction lines appeared for pure MnO_2 and Co_3O_4 catalysts can be attributed to the pure phase of alpha-MnO₂ and Co_3O_4 , respectively [14, 24]. As expected, for the Co_3O_4/MnO_2 catalyst, there are two peaks at 32 and 38° along with MnO_2 diffraction peaks, which can be attributed to the Co_3O_4 phase, indicating the formation of hybrid Co_3O_4/MnO_2 .



Fig. 3. Powder XRD pattern of MnO₂, Co₃O₄/MnO₂, and Co₃O₄ catalysts.

The N₂ sorption isotherms of MnO₂, Co₃O₄/MnO₂, and Co₃O₄ catalysts are displayed in Fig. S4. All catalysts manifested a type III isotherm with the surface of pure MnO₂ nanotubes being 33.3 m² g⁻¹. This was decreased to 25.8 m² g⁻¹ upon the decoration with Co₃O₄ nanoparticles.

X-ray photoelectron spectroscopy (XPS) was employed to determine the oxidation states and surface atomic ratios of elements in the developed catalysts. Fig. S5a shows the O 1s XPS spectra of MnO₂, Co₃O₄/MnO₂, and Co₃O₄ catalysts. The surface atomic ratios of Mn, Co, and O for the catalysts are displayed in Table S2. All catalysts displayed three types of oxygen species that were attributed to lattice oxygen (O_A, 529.5-529.7 eV), surface adsorbed oxygen species (O_B, 531.4-531.9 eV), and oxygen associated with surface hydroxyl or carbonate species (O_C, 532.6-533.7 eV) [25]. Among the three catalysts, the hybrid Co₃O₄/MnO₂ catalyst showed the highest concentration of surface atomic oxygen (47.14%) species, followed by the pure MnO₂ (31%) and Co₃O₄ (24.32%) catalysts. Many reports have suggested that the presence of these surface-active oxygen species offer facile oxidation

reaction sites [26, 27]. Hence, the as-prepared Co₃O₄/MnO₂ catalyst could be expected to exhibit an enhanced catalytic performance when compared to its pure counterparts. Fig. S5b shows the Mn 2p spectra of MnO₂ and Co₃O₄/MnO₂ catalysts. Pure MnO₂ displayed one peak attributable to Mn⁴⁺ (642.2 eV), confirming that Mn⁴⁺ was the main valance state of manganese in MnO₂ [28]. Mn 2p XPS spectrum of Co₃O₄/MnO₂ was deconvoluted into two components. These could be attributed to Mn⁴⁺ (642.0 eV) and Mn³⁺ (640.2 eV) oxidation states, respectively [29]. The co-existence of Mn³⁺ and Mn⁴⁺ ions means that the oxygen vacancies are generated due to the process of charge compensation in MnO₂ lattice [30]. The Co 2p XPS spectra of Co₃O₄ and Co₃O₄/MnO₂ catalysts are shown in Fig. S5c. The two peaks appearing at 779.8 eV and 781.7 eV may be attributed to Co $2p_{3/2}$ and Co $2p_{1/2}$, respectively, indicating in this way that Co ion existed in two different oxidation states (Ha⁴⁺) [29, 30]. It is postulated that the presence of variable oxidation states (Mn⁴⁺/Mn³⁺ and Co³⁺/Co²⁺) along with the oxygen deficiency could enhance catalytic performance in Co₃O₄/MnO₂ catalyst.

Hydrogen-temperature programmed reduction (H₂-TPR) was used to investigate the redox properties of the as-prepared catalysts. H₂-TPR patterns of MnO₂, Co₃O₄/MnO₂, and Co₃O₄ catalysts are shown in Fig. S6. Pure MnO₂ showed a broad peak, centered at 362 °C, which can be attributed to the reduction of MnO₂ to MnO with Mn₂O₃ and Mn₃O₄ as the intermediates, which was similar with other reported MnO₂ systems [31, 32]. Besides, pure Co₃O₄ catalyst exhibits broad peak at 379 °C, which can be attributed to the reduction of Co₃O₄ to CoO and metallic Co [33]. Interestingly, the hybrid Co₃O₄/MnO₂ showed the reduction peak of MnO₂ at 309 °C, whereas the reduction of cobalt oxide peak in between 350 to 550 °C. The observed low temperature peaks of hybrid Co₃O₄/MnO₂ catalyst compared to its counterparts can be referred to the synergistic interaction between Co₃O₄ and MnO₂.

3.2 Catalytic activity results

The catalytic activities of MnO₂, Co₃O₄/MnO₂, and Co₃O₄ were tested in benzyl alcohol oxidation under the presence of O₂. Table 1 illustrates the influence of reaction time in regard to various catalysts' performance towards benzyl alcohol oxidation. Initially, the benzyl alcohol was chosen for a model substrate and the oxidation reaction was performed at room temperature for 6 h in the absence of catalysts and solvents. However, no conversion of benzaldehyde from benzyl alcohol was observed. The same reaction was then conducted under the same conditions except that gaseous O₂ was introduced to the reaction at atmospheric pressure. The conversion of benzyl alcohol approached 1.9% with 81% of selectivity. Further, to determine the temperature effect, the reaction was carried out at 100 $^{\circ}$ C under air, with the product conversion increasing to 4.1%.

Table 1

Optimization of the reaction conditions and catalyst selection for benzyl alcohol oxidation.

Reaction conditions

CHO

Entry	Catalyst	Solvent	Oxidant	Time (h)	Temp. (°C)	Conv. (%)	Select. (%)	
1	Absence	Absence	N_2	6	rt	-	-	
2	Absence	Absence	Air	6	rt	1.9	81	
3	Absence	Absence	Air	6	100	4.1	85	
4	α -MnO ₂	DMF	Air	6	100	58	89	
5	Co_3O_4	DMF	Air	6	100	51	74	
6	Co_3O_4/MnO_2	DMF	Air	6	100	89	95	
7	Co_3O_4/MnO_2	ACN	Air	6	80	84	92	
8	Co_3O_4/MnO_2	Toluene	Air	6	100	81	90	
9	Co_3O_4/MnO_2	THF	Air	6	100	74	88	
10	Co ₃ O ₄ /MnO ₂	1,4- Dioxane	Air	6	100	93	99	

11	Co ₃ O ₄ /MnO ₂	1,4-	Air	12	100	93	99
		Dioxane					

The reactions using pure MnO₂ and Co₃O₄ as well as Co₃O₄/MnO₂ were carried out in DMF solvent for 6 h at 100°C in air. As shown in Table 1, the product conversion was raised to 58, 51, and 89%, respectively, indicating that the conversion and formation of benzaldehyde from benzyl alcohol with Co₃O₄/ α -MnO₂ was more efficient than the respective pure catalysts i.e., MnO₂ and Co₃O₄. No additional conversion was observed by increasing the reaction time from 6 to 12 h. Furthermore, it was reported that the polarity and dipole moment of the solvents can play pivotal role in oxidation reaction [34]. Thus, aprotic polar and non-polar solvents are used to determine the solvent effect on the oxidation reaction. Different solvents like acetonitrile, 1,4-dioxane, toluene, and THF were screened out to determine possible effects when using Co₃O₄/ α -MnO₂ at 100 °C for a 6 h reaction period. It was observed that the maximum conversion (93%) of benzaldehyde was found in the presence of medium polarity with low dipole moment having 1,4-dioxane, with 99% selectivity.

Table 2.	Effect	of	functional	groups	on	conversion	and	selectivity	for	benzyl	alcohol
oxidation											

ACC CO	HO	Co ₃ O ₄ /α–MnO ₂ Solvent 6 h, 100 °C	CHO R
S.No	R	Conversion (%)	Selectivity (%)
1	Н	93	99
2	OMe	94	99
3	3,4-OMe	95	99
4	3,4,5-OMe	96	99
5	F	80	99
6	Cl	80	99

12

7 NO₂ 77 99

In catalytic reactions, the required amount of catalyst may also play a pivotal role especially on large scale industrial processes. In our study, no significant changes were detected by increasing the catalyst amount from 50 to 100 mg. This indicates that the lowest amount of catalyst loading was enough to carry out the benzyl alcohol oxidation reaction under the selected conditions. Furthermore, the effects of functional groups were investigated by introducing various substituents i.e., 4-OMe, 3,4-OMe, 3,4,5-OMe, F, Cl and NO₂ under the same reaction conditions (Table 2). The conversion increased in the presence of electron donating groups, while it decreased when the electron withdrawing groups were present. Therefore, it can be argued that the electron donating groups such as methoxy favored the oxidation reaction. The repeatability of catalyst was investigated by using the Co₃O₄/MnO₂ catalyst 4 times. In each cycle, the catalyst was washed with 1,4-dioxane and dried at 80 °C and reused for the next cycle. The results reported in Fig. 4 show that the catalyst exhibited 80% conversion and 73% selectivity after 4 cycles. Further, the leaching experiment was conducted by testing the filtered solution for benzyl alcohol oxidation after each cycle. The solution did not show any activity, which confirms that the as-prepared hybrid catalyst was not leached and stable during the reaction. The stability of used Co₃O₄/MnO₂ catalyst was validated by further characterization (XRD and SEM). As shown in Fig. S7, the XRD pattern of used Co₃O₄/MnO₂ catalyst is similar to fresh catalyst, which confirms that the crystallinity of material is not changed. The morphology of Co_3O_4/MnO_2 (Fig. S8a-b) indicates that the nanotubular morphology was not perturbed during the reaction.

13



Fig. 4. Recyclability of Co₃O₄/MnO₂ catalyst for benzyl alcohol oxidation.

To further elucidate the reaction mechanism over Co_3O_4/MnO_2 catalyst, XPS analysis was performed. The XPS spectra of the used catalyst was shown in Fig. S5. The calculated surface atomic ratios of Mn^{4+}/Mn^{3+} , Co^{3+}/Co^{2+} , and O_B+O_C/O_A for the used Co_3O_4/MnO_2 catalyst are compared with the fresh catalyst. As shown Table S2, the ratio of Mn^{4+}/Mn^{3+} decreased after benzyl alcohol oxidation, whereas the ratio of Co^{3+}/Co^{2+} increased. It indicates that the redox reaction between Mn and Co ($Mn^{4+} + Co^{2+} \leftrightarrow Mn^{3+} + Co^{3+}$) was benefited benzyl alcohol oxidation. Further, the decreased in ratio of O_B+O_C/O_A indicates that the surface oxygen also participated in the reaction process. Based on these results, the plausible reaction mechanism of benzyl alcohol oxidation by Co_3O_4/MnO_2 to benzaldehyde was illustrated by the schematic presented in Fig. 5. First, the benzyl alcohol molecules are absorbed on the surface of Co_3O_4/MnO_2 due to the presence of abundant surface-active oxygen species. Then, the presence of surface oxygen species leads to the activation of molecular oxygen (O_2) due to the redox reaction between Mn and Co. Consequently, the

absorbed benzyl alcohol molecules transform into benzaldehyde and H₂O by the active oxygen species on Co_3O_4/MnO_2 . Moreover, $Mn(OH)_2$ undergoes rapid oxidation in the presence of O₂ to give back MnO_2 [11]. Thus, the hybrid catalyst becomes reusable for application in subsequent reaction cycles. During the reaction, the ability to activate O₂ is critical for the catalytic activity. As discussed in the characterization section, the hybrid Co_3O_4/MnO_2 catalyst manifested uniform dispersion of Mn, Co, and O elements, oxygen deficiency, good redox behaviour, abundant surface oxygen species, and variable oxidation states ($Mn^{3+/4+}$ and $Co^{2+/3+}$), which are all resulted due to the synergistic interaction between Co_3O_4 and MnO_2 .



Fig. 5. The plausible reaction mechanism for benzyl alcohol oxidation over Co_3O_4/MnO_2 catalyst.

4. Conclusion

In summary, we have reported that highly dispersed Co_3O_4 nanoparticles on the surface MnO_2 nanotubes may act as an efficient catalyst for benzyl alcohol oxidation. The hybrid Co_3O_4/MnO_2 catalyst was able to oxidize different functional groups containing benzyl

alcohol with excellent conversion and selectivity efficiency. Moreover, the hybrid catalyst displayed good repeatability and stability after the reaction. The highest catalytic performance was reported in the absence of soft oxidants such as TBHP and H_2O_2 , clearly demonstrating the green nature of the catalyst. The surface oxygen species, better redox behaviour, and variable oxidation states of Co_3O_4/MnO_2 hybrid catalyst, were responsible for its enhanced activity as compared to its pure constituents.

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Appendix A. Supplementary data

Supplementary data to this article can be found online.

Supplementary data

Supplementary material

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Highlights:

- Co₃O₄ nanoparticles dispersed MnO₂ nanotubes were fabricated by hydrothermal synthesis
- An interface is observed between Co_3O_4 and MnO_2 in the hybrid catalyst
- Co₃O₄/MnO₂ exhibited low temperature redox behaviour due to synergistic interaction
- Surface oxygen species and variable oxidation states are responsible for superior activity

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