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Excellent product selectivity towards 2-phenyl-acetaldehyde and styrene oxide using manganese oxide and cobalt oxide NPs for the selective oxidation of styrene



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ABSTRACT

 MnO_x and Co_3O_4 nanoparticles (NPs) were synthesized using the temperature controlled co-precipitation method and were immobilized on the mesoporous metal oxide supports that were synthesized using the inverse surfactant micelle method. The synthesized catalysts were characterized using TEM, SEM, pXRD, N2-sorption, XPS, and H2-TPR. From TEM the well-dispersed metal oxide NPs were observed and the interaction of the NPs with the support was confirmed with H2-TPR. These metal oxide NPs and immobilized metal oxide NPs were employed in the selective oxidation of styrene using tert-butyl hydrogen peroxide (TBHP) as an oxidant. Higher selectivity towards styrene oxide was obtained using Co₃O₄ NPs. MnO_x NPs gave higher selectivity towards 2phenyl-acetaldehyde while the immobilized metal oxide NPs gave a mixture of products. The catalytic activities of the compared catalysts followed the following decreasing order of MnO_x NPs (646.9 h⁻¹) > Co_3O_4 NPs $(338.1\,h^{-1}) > \text{Co-MnO}_2350 \ (54.1\,h^{-1}) > \text{Mn-Co}_3\text{O}_4350 \ (44.1\,h^{-1})^{>}\text{MnO}_2350 \ (35.8\,h^{-1}) > \text{Co}_3\text{O}_4350 \ (35.8\,h^{-1}) >$ (21.3 h⁻¹) after 8 h of reaction. The catalytic activities and selectivity profiles under various reaction conditions such as solvent type, catalyst amount, styrene to TBHP ratio and temperature are discussed. The catalytic recyclability of immobilized metal oxide NPs on mesoporous metal oxides showed that they are stable, and the structure of the catalyst was retained.

1. Introduction

The development of heterogeneous catalysts has been an area of great interest over the past decades, due to the ease of recycling of these heterogeneous catalysts. However, there have been great strides in the field of catalysis such as the successful drive to move from the traditional complex compounds to nanoscale materials [1]. The ability to prepare NPs with well-defined shapes, with sizes that range between 1-100 nm in diameters, have attracted great attention from researchers [2]. These NPs have unique properties such as electronic, magnetic and catalytic properties that distinguish them from their corresponding bulk materials [2-4].

The selective oxidation of styrene to its products has been much studied in the past decades as its products are of industrial importance [5]. It has been also used as a model reaction for ethylene epoxidation due to it being a liquid at room temperature [3]. Styrene oxidation produces multiple products such as styrene oxide, benzaldehyde, 2phenyl-acetaldehyde, acetophenone, benzoic acid [3,6-8], depending on the reaction conditions and the type of catalyst used. Benzaldehyde and benzoic acid are a result of further oxidation of styrene oxide while 2-phenyl-acetaldehyde and acetophenone are a result of the isomerization of styrene oxide. The schematic illustration of styrene oxidation is given in Scheme 1.

Styrene oxide is mainly used in the epoxy resins industry as a plasticizer and also, as a raw material for phenethyl alcohol, styrene glycol, and its derivatives. It is also used as a chemical intermediate for cosmetics, surface coatings, treatment of fibers and textiles, and agricultural and biological chemicals and is, therefore, an important product for the pharmaceutical and fine chemical industry [9-11]. While, 2-phenyl-acetaldehyde, the isomer of styrene oxide, is mainly used in the agricultural industry for monitoring and controlling insects because of its aroma that attracts them. It is also used as an intermediate in the biochemical pathways, including those involved in the metabolism of carbohydrates, vitamins, steroids, amino acids, benzylisoquinoline alkaloids, hormones, and lipids [12]. Therefore, it is important to selectively oxidize styrene to styrene oxide and 2-phenylacetaldehyde while achieving high styrene conversion.

We intend to exploit the properties of manganese oxide (MnOx) NPs

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Styrene oxide 2 - Phenylacetaldehyde Benzaldehyde Benzoic acid

Scheme 1. Schematic illustration of the catalytic oxidation of styrene.



Fig. 1. HR-TEM images of (A): MnO_x NPs, (C): Co₃O₄ NPs, and their particle size distribution histograms in (B) and (D) respectively.

and cobalt oxide (Co₃O₄) NPs which include high surface to volume ratio and excellent processability to selectively produce styrene oxide and 2-phenylacetaldehyde. From literature, it can be noted that different forms of manganese oxide catalysts have been employed in styrene oxidation and different products were observed. Benzaldehyde and styrene oxide were the major products observed using manganese oxide catalytic systems [13-18]. For example, the role of manganese oxide octahedral molecular sieves in styrene epoxidation [19], manganese catalyzed epoxidation of alkenes in bicarbonate solutions [20], etc. The Mn₃O₄ and Co₃O₄ nanocrystals which were synthesized using the sonochemical method were used for the epoxidation of styrene

[21]. The MnO_x NPs have also been used in hydrogenation reactions such as reduction of carbon dioxide to methanol [22] and also as electrocatalysts for the oxygen reduction reaction in alkaline medium [23]. However, in this work, the manganese oxide nanoparticles which were synthesized using the heat mediated co-precipitation method was investigated for the oxidation of styrene.

Different forms of cobalt catalysts which include cobalt complex, cobalt nanocrystals, cobalt oxides, etc, have also been employed in the oxidation of styrene to styrene oxide and benzaldehyde as major products [7,16,17,24,25]. However, cobalt oxide NPs synthesized using the heat mediated co-precipitation method has not been used for studying



Fig. 2. TEM images A: Mn-Co₃O₄_350 and B: Co-MnO₂_350.

Table 1

The table of BET surface areas, BJH pore sizes, pore volumes and crystallite sizes of the synthesized mesoporous metal oxides catalysts.

Catalyst	BET Surface	BJH pore	Pore Volume	Crystallite size ^a	
	areas (m ² /g)	size (nm)	(cm ³)	(nm)	
MnO ₂ _ 350	37	22.4	0.21	11.5	
Co-MnO ₂ _350	36	22.1	0.20	12.0	
Co ₃ O ₄ _ 350	42	26.4	0.27	20.8	
Mn-Co ₃ O ₄ _ 350	38	25.9	0.32	19.5	

^a Crystallite sizes were calculated from p-XRD using the Scherer equation.

the oxidation of styrene. Cobalt NPs have been used as an efficient electrocatalyst for oxygen evolution reactions [26,27]. Other transition metal NPs that have been investigated in styrene oxidation include Pt and Pd by Noh [3] and supported gold NPs [2,28,29]. Therefore, it is important to investigate the behavior of our unsupported MnO_x and Co_3O_4 NPs in styrene oxidation. Also, supporting these NPs on an active metal oxide support will enhance our knowledge on the influence of the created interface between the support and the metal NPs. The MnO_x NPs were supported on mesoporous cobalt oxide, while Co_3O_4 NPs was supported on mesoporous manganese oxide to investigate the influence of the interfacial domain that is created by the change in electronic structure through the exchange of electrons between the two metals [22]. Hence, exploration of the catalytic behavior of MnO_x and Co_3O_4 NPs in catalytic oxidation of styrene in this study will enrich the scientific knowledge in the field of oxidation by colloidal metal oxide NPs.

2. Experimental details

2.1. Materials and instrumentation

All chemicals were used as received without further purification and were of the analytical grade. Styrene (\geq 99%), TBHP (70% in water), styrene oxide (\geq 97%), benzaldehyde (\geq 99%), acetophenone (\geq 99%), 2-phenyl-acetaldehyde (\geq 98%), dichloromethane (DCM) (\geq 99.8%), dimethyl carbonate (DMC) (\geq 99%), methanol (\geq 99.5%), cyclohexane (\geq 99.8%), 1-butanol (\geq 99.5%), dichlorobenzene (\geq 99%), ethanol (\geq 99.8%), n-hexane (\geq 97%), 1-octadecene (\geq 98%), toluene (\geq 99.8%), chloroform (\geq 99%), and acetonitrile (\geq 99.9%), manganese(II) nitrate tetrahydrate (\geq 97%), cobalt(II) nitrate hexahydrate (\geq 98%), MnCl₂·4H₂O (\geq 98%), dichlorobenzene (DCB) (\geq 99%) sodium oleate (\geq 82%), Co₂(CO)₈ (stabilized with 1–5% hexanes), oleic acid (\geq 99%), and poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) (P123) were all purchased from Sigma-Aldrich.

2.2. Synthesis of manganese oxide NPs (MnO_x)

Manganese oxide NPs were synthesized using Mn-oleate as a source of manganese. Mn-oleate was synthesized by dissolving 7.92 g (40 mmol) MnCl₂.4H₂O and 24.36 g (80 mmol) sodium oleate in a mixture of 30 mL of ethanol, 40 mL of water, and 70 mL *n*-hexane that was preheated to 70 °C. The mixture was left to react for 4 h at 70 °C under magnetic stirring. The solution of Mn-oleate was collected using a separation funnel. Then, the Mn-oleate salt was collected using a rotary evaporator.

The MnO_x NPs were synthesized by dissolving 1.24 g of Mn-oleate in 12.67 mL of 1-octadecene in a 50 mL round bottom flask. The solution was stirred at 70 °C and degassed under nitrogen for 1 h. The temperature of the reaction mixture was ramped to 260 °C (1.9 °C/min). The color of the solution changed from pink to dark brownish. The solution was left to cool for 10 min. The MnO_x NPs were collected by centrifugation and they were dispersed in 10 mL of chloroform [22,30].

2.3. Synthesis of cobalt oxide NPs

Cobalt oxide NPs were synthesized by degassing $150 \,\mu$ L of oleic acid under nitrogen for 1 h that was placed in a Schlenk tube connected to a condenser. Then, 12 ml of dichlorobenzene (DCB) was transferred into the flask and the temperature was raised to 169 °C (5 °C/min). Finally, 0.444 g of Co₂(CO)₈ dissolved in 3 mL DCB was injected into a reaction vessel using an airtight syringe and the reaction was left to react for 20 min before the heat was turned off. DCB (13 mL) was poured into the flask, and the colloidal suspension was left to cool. The Co₃O₄ NPs were collected by centrifugation and redispersed in 10 mL chloroform for further use [22].

2.4. Immobilization of NPs on mesoporous metal oxides

Immobilization of the NPs was achieved using the capillary inclusion method. Briefly, 5 mL (0.570 mmol) of colloidal MnO_x NPs dispersed in chloroform was diluted with 40 mL *n*-hexane and mixed with 1 g of mesoporous cobalt oxide. The mixture was sonicated for 3 h at room temperature. The precipitate was collected by centrifugation and washed with a 50/50 v/v mixture of ethanol and acetone five times. The resultant pellet was dried overnight at 80 °C. The same procedure was followed for immobilizing Co_3O_4 NPs on mesoporous manganese oxide [22]. The synthesis of mesoporous metal oxides is detailed in the supplementary information. The description of the instruments used for characterization is found in the supplementary information.



Fig. 3. Characterization of immobilized metal oxide NPs on MMOs. A: N2 sorption isotherms; B: BJH pore volume distributions, and C: BJH pore sizes distributions.



Fig. 4. Characterization of immobilized metal oxide NPs mesoporous metal oxides. A: graphs of low angle p-XRD and B: graphs of wide angle p-XRD patterns.

2.5. Experimental procedure for styrene oxidation

The oxidation of styrene was conducted under aerobic conditions using a 25 mL 2-neck round bottom flask equipped with a magnetic stirrer, thermometer, and a heated silicon oil bath. For colloidal MnO_x and Co_3O_4 NPs, 0.114 mmol of each was used. For immobilized MnO_x and Co_3O_4 NPs on mesoporous metal oxides, typically 0.1 g of catalyst, 1 mmol styrene, and 2 mmol TBHP as an oxygen source was added to a 25 mL 2-neck round bottom flask filled with 5 mL DMC as a solvent. The

silicone oil bath was heated to 90 °C prior to the reaction and the reactions were heated under reflux with stirring. The reaction was sampled after every 2 h for 8 h. The catalytic conversion of styrene and selectivity was determined using a Shimadzu GC-2010 Plus equipped with a flame ionization detector (FID) using a Restek - 800-356-1688 capillary column (30 m * 0.25 mm, the film thickness of 0.25 µm). Temperatures of 250 °C and 300 °C were used for injection port and FID respectively. The column oven temperature was set at 300 °C and nitrogen was used as a carrier gas. Reaction products were confirmed



Fig. 5. H2-TPR profiles of mesoporous metal oxides and when immobilized with metal oxide NPs. A: cobalt oxide and B: manganese oxide.

using a Shimadzu gas chromatography (GC–MS) using a Rxi-5Sil MS capillary column ($30 \text{ m} \times 0.25 \text{ µm}$ film thickness) and injection port temperature of $200 \degree$ C was used. The ion source and interface temperature were $200 \degree$ C and $250 \degree$ C, respectively.

3. Results

3.1. Synthesis and characterization

The metal oxide NPs were successfully synthesized using the temperature-controlled co-precipitation method. The synthesized MnO_x NPs were well dispersed as noted from the TEM image in Fig. 1A and were found to have an average size of 6.2 nm as shown in Fig. 1B. The synthesized Co_3O_4 NPs were also well dispersed, and they were found to have an average size of 8.4 nm. The purity of the metal oxide NPs was confirmed using EDX as shown in Fig. S1. From Fig. S1A, the manganese and oxygen peaks were observed in the EDX spectrum which confirms the presence of pure MnO_x NPs. The copper peaks which were observed came from the Cu grid. In Fig. S1B, the cobalt and oxygen peaks were observed which confirms the presence of Co_3O_4 NPs

The elemental analysis of immobilized metal oxide NPs on mesoporous metal oxide supports was confirmed using EDX as shown in Fig. S1. From the ICP-OES analysis, 1.2 wt% of Mn was found to be supported on mesoporous cobalt oxide and 1.2 wt% of Co was found to be supported on mesoporous manganese oxide support. Fig. 2 shows the TEM images of the immobilized NPs on the metal oxides support. It is important to note the difficulty in observing the supported NPs on the support and measuring them since the NPs suffer from low contrast due to the high electron density from the support. The difference in focal planes of the NPs and the support when acquiring images adds to the difficulty of measuring the NPs [31]. In Fig. 2A and B) the small black dots are observed on the support which signifies the presence of the MnO_x NPs and Co₃O₄ NPs on the support respectively. The SEM images in Fig. S2A and B show the morphology of the immobilized MnO_x NPs and Co₃O₄ NPs on the support respectively.

The nitrogen sorption experiments showed that the BJH pore sizes decreased from 22.4 nm for mesoporous MnO_2 350 to 22.1 nm after the Co_3O_4 NPs were immobilized on it. For mesoporous Co_3O_4 _350 it decreased from 26.4 to 25.9 nm after MnO_x NPs were immobilized, as shown in Table 1. The surface area for mesoporous MnO_2 _350 decreased from 37 to 36 m²/g after immobilization of Co_3O_4 NPs. While the surface area of Co_3O_4 _350 decreased from 42 to 38 m²/g after immobilization of MnO_x NPs. These changes in the physical properties of the mesoporous metal signify successful immobilization of metal oxide

NPs. Fig. 3A shows that both immobilized mesoporous metal oxides exhibited the characteristic type IV adsorption isotherms, with a hysteresis loop of the ordered mesoporous structure.

From Fig. 4A, it was observed that the synthesized materials diffract in a low angle region. The peak observed at around 20 showed that both immobilized metal oxide NPs on mesoporous metal oxides are crystalline in nature. The crystallite sizes increase did not change significantly after immobilization of the metal oxide NPs as shown in Table 1. These crystallite sizes were calculated from wide angle p-XRD shown in Fig. 4B, using the Scherrer equation. Fig. 5 shows the H₂-TPR profiles of mesoporous metal oxides and when immobilized with metal oxide NPs and it can be noted that two bands are observed. It is observed that immobilization of metal oxide NPs on the mesoporous metal oxide support increases the reduction temperature of the mesoporous metal oxides.

X-ray photoelectron spectroscopy (XPS) was carried to provide information on the electronic structure of the catalysts. The O 1s spectra for all four catalysts are as expected [32]. The largest peak in Fig. 6, at the lowest binding energy, is due to stoichiometric oxygen. The peak at around 531 eV is due to oxygen vacancies and/or other defects [33,34]. Finally, the peak at highest binding energy is known to be from chemisorbed oxygen [35]. In a similar way the Mn 2p spectra, shown in Fig. 6, show spin-orbit split peaks. These are due to Mn in a 2 + oxidation state, a 3 + oxidation state and a satellite at high binding energy. Note that for Mn the 2 +oxidation state is at lower binding energy, which is the opposite to what occurs with Co [36]. The oxidation state % ratio of Mn 2p are presented in Table 2. It can be noted that the two samples with MnO₂ have similar oxidation states, whereas the MnO_x NPs samples have a slightly different oxidation state. Fig. 6 shows the Co 2p spectra of those catalysts with Co present. The spectra were fitted with three components. Each component is split into the Co $2p_{3/2}$ and $2p_{1/2}$ peaks. These components are due to Co in the 3 + oxidation state (at lower binding energy), Co in the 2 +oxidation state (at higher binding energy) and a satellite at high binding energy. The spectra are consistent with what is expected from literature [32]. The oxidation state % ratio of Co 2p are presented in Table 2, and they were found to be similar across all 3 samples.

3.2. Optimization of the reaction conditions

The oxidation of styrene in the presence of air using metal oxide NPs and immobilized metal oxide NPs on mesoporous metal oxides support as catalysts were conducted with various experimental parameters such as solvent type, catalyst amount, *etc*, to obtain the optimum conditions.





Fig. 6. The O 1 s, Mn 2p, and Co 2p core level electrons XPS spectra for pure mesoporous metal oxides and for immobilized metal oxide nanoparticles on a mesoporous metal oxide support.

Tab	le	2	
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The percentage composition of the oxidation states of the synthesized catalysts.

Orbital type	Catalyst	Oxidation state $(2+)$ %	Oxidation state (3+) %
Co 2p	Co ₃ O ₄ _350	28	72
	Mn-Co3O4 _350	21	79
	Co-MnO _{2_} 350	24	76
Mn 2p	MnO2_350	66	34
	Co-MnO _{2_} 350	62	38
	Mn-Co3O4 _350	53	47

3.2.1. Solvent type

The influence of solvent on the oxidation of styrene was investigated using various types of solvents. Chloroform was found to give the highest styrene conversion of 67.8%, however, its selectivity towards 2phenyl-acetaldehyde was lower (81.6%) than that of DMC (90.6%) as shown in Fig. 7A. From Fig. 7A, it is noted that DMC as a solvent gave high selectivity (90.6%) towards 2-phenyl-acetaldehyde while its styrene conversion is moderate as compared to others. Solvents with a high polarity index such as acetonitrile (polarity index 5.8) and methanol (polarity index 5.1) showed low styrene conversion of 50.9% and 38.7% respectively while their product selectivity was moderate compared to others. Toluene and cyclohexane which are nonpolar solvents with a polarity index of 2.4 and 0.2 respectively gave a relatively high styrene conversion and a moderate selectivity towards 2phenyl-acetaldehyde as shown in Fig. 7A. After 4 h of reaction, small brown particles were observed in methanol while in acetonitrile, large black particles were observed. The overall results showed that DMC as a solvent gave the highest product selectivity and a moderate styrene conversion, hence it was selected as an optimum solvent for further



Fig. 7. Optimization of the reaction conditions. A: solvent variation; B: catalytic amount variation; C: mole ratio of styrene to TBHP variation; D: temperature variation. Reaction conditions: catalyst (0.114 mmol of MnO_x NPs), solvent (5 mL DMC), 1 mmol styrene, 2 mmol TBHP, T = 90 °C, time = 4 h, except when the condition is investigated.

investigations.

3.2.2. Optimum amounts of reagents

The influence of the catalyst amount on the styrene conversion and product selectivity was investigated and it was observed that the styrene conversion and product selectivity towards 2-phenyl-acetaldehyde increase as the catalyst amount is increased as shown in Fig. 7B. The reaction was performed without the catalyst under the same reaction conditions and a conversion of 8.5% was observed. When the catalyst amount was increased beyond 0.114 mmol, a large decrease in selectivity towards 2-phenyl-acetaldehyde was observed. Hence 0.114 mmol was chosen as the amount of catalyst for further research on styrene oxidation.

3.2.3. The optimum ratio of styrene to TBHP

The influence of styrene to TBHP ratio in the styrene conversion and product selectivity was examined by keeping the concentration of styrene constant while varying the amount of TBHP. From Fig. 7C, it is noted that the styrene conversion increases with an increase in TBHP amount. Also, the selectivity towards 2-phenyl-acetaldehyde was affected to a lower extent. However, a large decrease in selectivity towards 2-phenyl-acetaldehyde was observed when the styrene to TBHP ratio is at 1:4 as shown in Fig. 7C. Hence, the ratio of 1:1 was found to be the optimum condition for further research on the styrene oxidation.

3.2.4. The optimum temperature

The influence of temperature on the styrene conversion and product selectivity was investigated. Styrene conversion was found to increase with increase in temperature. The highest selectivity towards 2-phenyl-acetaldehyde (91.7%) was achieved at 80 °C. From the observed results, no correlation can be deduced between temperature and product selectivity as the product selectivity remains relatively constant as shown in Fig. 7D. Therefore, 90 °C was used as the reaction temperature for further investigations on styrene oxidation considering the boiling point of the solvent and styrene conversion.

3.3. Styrene oxidation catalyzed by various catalysts

From Fig. 8 it can be noted that styrene conversion increases with an increase in reaction time for all catalysts. The highest styrene conversion (59.3%) was obtained using MnO_x NPs as a catalyst after 8 h. The catalytic activities of the compared catalysts were decreasing in the order of MnO_x NPs (646.9 h⁻¹) > Co_3O_4 NPs (338.1 h⁻¹) > Co- MnO_2_350 (54.1 h⁻¹) > $Mn-Co_3O_4$ _ 350 (44.1 h⁻¹) > MnO_2_350 (35.8 h⁻¹) > Co_3O_4 _ 350 (44.1 h⁻¹) > MnO_2_350 (35.8 h⁻¹) > Co_3O_4 _ 350 (21.3 h⁻¹) after 8 h of reaction. The turnover frequency (TOF), which is defined as the number of moles of styrene converted to all products per mole of the catalyst per hour were calculated after 8 h of reaction. When the mesoporous metal oxide supports were used in styrene oxidation as catalysts, poor styrene



Fig. 8. The comparison of styrene conversion and product selectivity for different metal NPs and after being immobilized on mesoporous metal oxide supports. A: MnO_x NPs, B: Co_3O_4 NPs, C: $Mn-Co_3O_4$.350, D: $Co-MnO_2$.350, and E: turnover frequency. Reaction conditions: catalyst (1 mL for metal oxide NPs and 0.1 g for immobilized metal oxide NPS), solvent (5 mL DMC), 1 mmol styrene, 1 mmol TBHP, T = 90 °C.

conversion and product selectivity were observed. From Fig. 8E it can also be noted that immobilizing metal oxide NPs on the mesoporous metal oxides supports reduces the activity of the metal oxide NPs in styrene oxidation. From the obtained results, it can be noted that the selectivity of the products formed during oxidation of styrene depends on the catalyst used.

When colloidal MnOx NPs were used, 2-phenyl-acetaldehyde was

observed as a major product while when colloidal Co_3O_4 NPs were used, styrene oxide was obtained. When these metal oxide NPs were immobilized on the mesoporous metal oxides support they lost their selectivity and a mixture of products were obtained as shown in Fig. 8 (C and D). For metal oxide NPs, the product selectivity remains constant towards one product over the course of the reaction from 2 to 8 h. However, with immobilized metal oxide NPs, the product selectivity



Fig. 9. The influence of catalyst recycles test on styrene conversion and product selectivity. A: $Mn-Co_3O_4_350$ and B: $Co-MnO_2_350$. Reaction conditions: 100 mg catalyst, Solvent (5 mL DMC), 1 mmol styrene, 1 mmol TBHP, T = 90 °C, Time = 4 h.

changed with the change in time. When Mn-Co₃O₄_350 was used as a catalyst, the formation of 2-phenyl-acetaldehyde increased while the formation of styrene oxide decreased with an increase in reaction time. For the Co-MnO₂_350 catalyst, the formation of other products increases with increase in reaction time while product selectivity towards styrene oxide and 2-phenyl-acetaldehyde decreased from 4 to 8 h. Hence, immobilizing metal oxide NPs on mesoporous metal oxide supports decreased both styrene conversion and product selectivity. Representative GC-MS spectra of 2-phenyl-acetaldehyde and styrene oxide are given in Figs. S3 and S4, respectively of the supplementary materials.

3.3.1. Catalyst recycle test

The influence of catalyst recycling on styrene conversion and product selectivity was investigated by recycling the catalysts four times for immobilized metal oxide NPs. From Fig. 9, it can be noted that styrene conversion diminished, and product selectivity showed insignificant changes even after the 4th cycle for Co-MnO2_350. Mn-Co₃O₄_350 showed higher selectivity towards 2-phenylacetaldehyde in the first two cycles and then, the selectivity changed towards styrene oxide for the third and fourth cycles. The immobilized metal oxide NPs on mesoporous metal oxide catalysts remained unchanged as shown in the TEM images (Fig. 10E and F). The TEM images taken after 8 h of the reaction showed slight agglomeration for Co₃O₄ NPs while most of the NPs remain well dispersed in solution as seen in Fig. 10A. The Co₃O₄ NPs increased in size from 8.4 to 9.7 nm during the reaction. The shape of MnOx NPs remained unchanged after the reaction as shown in Fig. 10C and their particle size also increases from 6.2 to 7.8 nm after the reaction. This showed the stability of the metal oxide NPs in the reaction.

4. Discussion

4.1. Synthesis and characterization of colloidal NPs and MMOs immobilized with metal oxide NPs

The mesoporous metal oxide supports used to immobilize metal oxide NPs in this study were synthesized using the inverse micelle solgel method. The principle behind this method is that it uses HNO_3 to prevent condensation while the metal oxo-clusters are stabilized and the clusters are formed inside hydrated inverse micelles and they interact with the surfactant via hydrogen bonding [37–39].

The synthesized materials were characterized using a range of

techniques. From the nitrogen, sorption experiments the observed Type IV adsorption isotherms signify the regular ordered mesoporous nature. The presence of the regular ordered mesoporous structure was supported by the presence of a low angle peak observed in the p-XRD [38]. After immobilization of metal oxide, NPs on the mesoporous metal oxides, the surface area, and pore volumes decreased. This is because the metal oxide NPs occupy space inside pores. [40]. The purity of the metal oxide NPs and immobilized metal oxide NPs on the support was confirmed by EDX analysis which showed only the peaks of oxygen and the corresponding metals under investigation as shown in Fig. S1.

The H2-TPR was performed to investigate the differences in redox properties of the immobilized metal oxide NPs on mesoporous metal oxide supports because the catalytic activity of the catalyst towards redox reactions depends on the reducibility. For spinel metal oxides, usually, the first reduction signal is assigned to the most electropositive cation. The first band appearing at 268 °C for mesoporous cobalt oxides can be ascribed to the reduction of Co^{3+} species to Co^{2+} while the second band at 348 °C can be ascribed to the reduction of Co²⁺ to metallic cobalt [37,39]. For mesoporous manganese metal oxide, the first band appearing at 272 °C can be ascribed to the reduction of Mn³⁺ to Mn^{2+} while the second band 405 °C can be ascribed to the reduction of Mn^{2+} to metallic manganese [38,41]. The obtained oxidation states are supported by the data obtained from the XPS measurements shown in Table 2. From Fig. 5, the increase in reduction of the mesoporous metal oxide supports after immobilization of the metal oxide NPs can be attributed to the change in the electronic structure of the material due to the interaction of the NPs with the support [22].

4.2. Selective oxidation of styrene

4.2.1. Optimization of the reaction conditions: solvent type, catalyst amount, the ratio of styrene to TBHP and temperature variation

In literature, the influence of solvent type used for the oxidation of styrene was found to influence the styrene conversion and the product selectivity of the reaction. Higher styrene conversion was reported to be obtained for solvents with a high polarity such as acetonitrile, DMF etc [17,18,24,42,43]. Therefore, considering the results of these papers, polar solvents and non-polar solvents were investigated. The lower styrene conversion obtained using acetonitrile and methanol as solvents can be attributed to the agglomeration of NPs in solution which results in them being inactive catalysts. DMC which is also a polar solvent with a polar index of 3.9 gave higher 2-phenylacetaldehyde selectivity and moderate styrene conversion. The good dispersion of NPs in DMC and



Fig. 10. TEM images were taken after the recycle test of styrene oxidation: A: Co_3O_4 NPs, C: MnO_x NPs E: $Mn-Co_3O_4_350$, F: $Co-MnO_2_350$. B and D are particle size distribution histograms of Co_3O_4 NPs and MnO_x NPs respectively.

chloroform can be attributed to the absorption of these solvents to the surface of the NPs which inhibit aggregation of the NPs [44]. The brown and black particles observed when methanol and acetonitrile were used as solvents are a result of NP aggregation [3]. While non-polar solvents gave moderate selectivity towards 2-phenylacetaldehyde and styrene conversion which can be attributed to the interaction of the solvent with the reactants and catalyst.

The increase in styrene conversion with an increase in catalyst amount can be attributed to the increase in the active site of the catalyst for the reaction to take place before they are saturated. When the temperature of a catalyzed reaction is increased, it increases the collision frequency of the reactants by supplying them with kinetic energy which results in an increase in the collision of reactants with catalyst hence an increase in styrene conversion was observed with increase in temperature. A similar trend of results had been reported by Noh et al [3]. The decrease in 2-phenylacetaldehyde selectivity can be attributed to further oxidation of the product and hydrolysis to form other products [45].



Scheme 2. The proposed reaction mechanism for styrene oxidation using metal oxide nanoparticles and immobilized nanoparticles [46].

 Table 3

 Comparison of metal NPs for selective oxidation of styrene.

Catalyst	oxidant	Con. (%)	Product selectivity			TOF (h ⁻¹)	Ref.	
			STO	PHA	BZA	others	(11)	
MnO _x NPs	TBHP	59.3	-	90.6	-	9.4	646.9	This work
Co ₃ O ₄ NPs	TBHP	42.3	100	-	-	-	338.1	This work
G5-OH Pd ₈₀	TBHP	64.3	67.4	-	30.2	2.4	285.1	[3]
G6-OH Pt ₁₆₀	TBHP	33.4	59.5	-	33.6	6.8	271.4	[3]
$Pd w_o = 10$	TBHP	47.2	73.3	-	23.8	2.9	209.3	[3]
$Pt w_o = 5$	TBHP	27.2	70.5	-	25.0	4.0	219.5	[3]
Au NPs@XAD- 4-G _{3.0}	02	9.5	48	-	33	19	63.4	[47]
Au/MgO (HDP)	TBHP	62.6	54.3	16.8	10.8	18.1	297.1	[48]
Au/SrO (HDP)	TBHP	53.0	44.8	26.0	11.7	17.4	373.8	[48]
Co/N-HCS300	0 ₂	99	86	-	-	-	232.6	[7]
1% Ag- METMS	H_2O_2	60	> 99	-	-	-	129.2	[10]
Mn- Co₃- O₄ 350	TBHP	31	30.4	46.3	-	23.3	44.1	This work
Co-MnO _{2_} 350	TBHP	38.9	32.3	22.5	-	45.1	54.1	This work

Con. = conversion of styrene, STO = styrene oxide, PHA = 2-phenyl-acetaldehyde, BZA = benzaldehyde. G₅-OH and G₆-OH mean fifth and sixth generation hydroxyl terminated polyamidoamine dendrimers. W_0 = water to surfactant ratio, HDP = homogeneous deposition precipitation, METMS = methyltrimethoxysilane, XAD-4-G_{3.0} = third generation PAMAM dendrimers on the surface of amberlite XAD-4 resin, N-HCS300 = nitrogen doped carbon hollow spheres.

4.2.2. Comparison of the catalytic activities of the synthesized catalysts

The increase in styrene conversion with the increase in reaction time for most catalysts shows that styrene oxidation requires time for the reaction to take place. The higher styrene conversion observed with colloidal metal oxide NPs as compared to the immobilized metal oxide particles may be attributed to the high surface area to volume ratio of the metal oxide NPs, thus more active sites are available for the reaction to take place. The immobilized metal oxide NPs have lower activities, which can be attributed to the NPs passivation [3]. Also, the change in binding energy due to metal to metal interaction after immobilization of the metal oxide NPs influenced the activities of the catalysts.

The higher styrene conversion obtained with MnOx NPs as compared to Co₃O₄ NPs can be ascribed to the fact that Mn has a lower reduction potential (+1.51) for Mn³⁺ to Mn²⁺ as compared to Co (+1.81) for Co³⁺ to Co²⁺. Hence based on the reduction potentials, Mn is expected to be a better catalyst for the oxidation reaction compared to Co. The obtained results give an insight that the product selectivity of styrene oxidation depends mainly on the type of the metal used. The difference in the structure of MnO_x and Co₃O₄ NPs might be responsible for different product selectivity. The structure of MnOx NPs allows the opening of the ring through the rearrangement of hydrogens which gave rise to 2-phenyl-acetaldehyde. This can be explained by the XPS data which showed that for Mn the 2 + oxidation state is at lower binding energy, which is the opposite to what occurs with Co [36]. Hence after, immobilizing the metal oxide NPs, a mixture of products was observed because both the metal oxide NPs and the support played a role in influencing the product formed. Moreover, the interaction between the metal oxide NPs and the support played a role in the product formed. The decrease in selectivity and conversion that was observed after the third and fourth cycles can be attributed to the leaching of the nanoparticles from the support to the solvent [3]. The oxidation of styrene using metal oxide NPs and immobilized NPs on mesoporous metal oxide supports was expected to follow the mechanism shown in Scheme 2 which was proposed by Nepak et al [46]. The two bonds between the TBHP oxygen and the nanoparticles are formed due to enhanced electron density on the oxygen π^* orbitals caused by the positive inductive effect of the alkyl groups. The oxygen will donate electrons to the empty d orbitals of the metal oxide nanoparticles. This eventually weakens the O-O bond which results in the formation of nanoparticle oxo species. On the metalloepoxy intermediate, oxygen is transferred to the olefin double bond to form styrene oxide. ß- hydride elimination at the metalloepoxy results in the formation of 2-phenyl-acetaldehyde [46].

The catalytic activities of the colloidal MnO_x and Co_3O_4 NPs in styrene oxidation were compared with other reported catalysts, both colloidal and supported NPs systems as shown in Table 3. It was observed that MnO_x and Co_3O_4 NPs showed higher catalytic activities as compared to other catalytic systems. The selectivity towards styrene oxide and 2-phenyl-acetaldehyde were excellent with Co_3O_4 and MnO_x NPs respectively. The immobilized metal oxide NPs on the mesoporous metal oxide showed poor product selectivity as compared to reported data, while its activity is comparable to literature.

5. Conclusion

Well-defined MnO_v and Co₃O₄ NPs were successfully synthesized within a narrow range of 6.2 nm and 8.4 nm respectively. The metal oxide NPs were successfully immobilized on the MMOs. The colloidal NPs showed higher activities in the catalytic oxidation of styrene as compared to the immobilized metal NPs on the mesoporous metal oxide support. The catalytic activities of the compared catalysts in decreasing order of MnO_x NPs (646.9 h⁻¹) > Co_3O_4 NPs (338.1 h⁻¹) > Co- $MnO_{2}350 (54.1 h^{-1}) > Mn-Co_{3}O_{4} = 350 (44.1 h^{-1}) > MnO_{2}350$ $(35.8 h^{-1}) > Co_3O_4$ _ 350 (21.3 h⁻¹) after 8 h of reaction was observed. MnOx NPs showed high selectivity towards 2-phenyl-acetaldehyde while the Co₃O₄ NPs showed 100% selectivity towards styrene oxide. The immobilized metal oxide NPs did not show any selectivity towards a specific product. After 8 h of reaction, the TEM images of the NPs showed their stability. Therefore, the catalyst in this study can be recycled and used for further reactions. Also, the recycle test showed that the immobilized metal oxide NPs are stable, and the product selectivity and styrene conversion did not change much. Therefore, styrene oxidation using these metal oxide NPs can contribute to the scientific knowledge and development of Co₃O₄ NPs and MnO_x NPs based catalytic systems in the field of oxidation catalysis.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcata.2018.04.027.

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