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Ag doped MnOx catalyst for formaldehyde removal at room temperature

Munzar Badshah*, Shozab Mehdi, Imran Abbas, Saqib Mujtaba, Muhammad Usman, Kamran Alam

Ghulam Ishaq Khan Institute of Engineering Sciences and Technology, Topi, Pakistan

Corresponding Author E-mail: munzar.khan11@gmail.com

ABSTRACT

The abundant amount of formaldehyde gas in the indoor public places from the building materials such as furniture, and consumables have a severe health effect on the human. Research indicated that long-term exposure to such an environment even with a low concentration of less than 0.5 ppm can damage the central nervous system and cause severe carcinogenic effects. Therefore, it is vital to develop such a method that can oxidize the formaldehyde at ambient temperature. Here in this research work, a novel ambient temperature metal oxide catalyst (MnOx) was synthesized with silver doping to enhance its efficiency and activity. The said catalyst was synthesized using the Co-precipitation method at pH 7 and calcined at 450ºC. Doping the catalyst with Ag enhanced the surface area and crystallinity of the catalyst which in turn improved the efficiency of the prepared catalyst. Thermal stability, crystallinity, and surface area were analyzed using TGA/DSC, XRD, and BET respectively. The surface area of undoped MnO2 was increased from 27.431 m^2 g^{-1} to 33.481 m^2 g^{-1} for the doped MnOx catalyst. Formaldehyde was tested at ambient temperature in the elongated reactor with a diameter of 0.5 inches and length of 5 inches. The initial concentration of Formaldehyde taken in the reactor was 20 ppm. The removal efficiency of Undoped MnO2 was 83% efficiency while the Ag-doped MnOx catalyst removal efficiency was 94%. The enhanced efficiency was due to the higher surface area and higher crystallinity of the doped catalyst. The present work thus exploited an inexpensive approach to enhance the catalytic activity of transition metal oxides via doping them with a suitable metal.

Keywords:

Formaldehyde
MnO_2
Catalytic oxidation
Co-precipitation

1. Introduction

Indoor air pollution's health effects have garnered considerable attention currently, especially because of our mostly spending time in indoors working. Indoor volatile organic compounds (VOCs) such as formaldehyde (HCHO), acetaldehyde, and toluene, which are released by household and decorating materials, are now the most significant indoor hazards. HCHO seems to be the most abundant and severe indoor air contaminant among them[1][3].Unfortunately, both people and animals are very poisonous to HCHO. Ingestion of 30 mL of a solution containing 37 percent formaldehyde, regardless of how HCHO is consumed, has been

documented to cause mortality in an adult person, according to a study by the Agency for Toxic Substances and Disease Registry. People would experience nasal tumors, eye and skin inflammation, and nasopharyngeal cancer if exposed to HCHO for an extended period, even at a low concentration of a few ppm. At around 0.5 ppm, people start to feel eye discomfort. As a result, in 1977, the German Federal Agency of Health suggested a recommendation maximum value of 0.1 ppm in air to restrict human exposure in buildings[3], [4].

To avoid long-term health effects, WHO recommendations recommend a short-term HCHO exposure limit of 0.1 mg/m^3 and a long-term exposure limit of 0.2 mg/m^3 [2]. Various detoxification approaches have been investigated to eliminate formaldehyde from ambient air, including physical adsorption, chemical adsorption, photocatalytic oxidation (PCO), catalytic oxidation (thermal and non-thermal), Plasma catalytic oxidation, and biotechnical breakdown. However, they have a few flaws that prevent them from being used indoors: Adsorption is the most basic technique, with a high rate of elimination, high efficiency, and cheap cost however adsorbents have limited capabilities and must be replaced on a regular basis, when cleaning indoor pollutants. Under specific temperature and pressure, a porosity sorbent was used to achieve adsorption. When employed without strategy modification, traditional sorbents' sorption performance of FA is typically poor due to high fugacity (i.e., greater vapor pressure: 3883 mmHg) [5].Plasma-catalytic and photocatalytic oxidation techniques, on the other hand, require additional energy input and plasma- or light-generation equipment's. This complicates the procedure and raises the footprint expenses significantly[2], [3]. Hazardous byproducts may also be produced by PCO and plasma. In alternative biological breakdown [6], the life cycle of microbes is still an issue that might impact purifying effectiveness. Because of its high removal efficiency, energy savings, and moderate reaction conditions, catalytic oxidation is the most promising of these methods. The removal of formaldehyde by catalytic oxidation using catalysts has recently been described. Among the methods, room-temperature catalytic oxidation is thought to be the most cost-effective, easy, and comprehensive method for removing HCHO. Room temperature catalytic oxidation does not demand UV light or plasma, and the catalyzed process takes place throughout the catalyst rather than only on the UV-activated surface. Because of these benefits, it is more suited for indoor formaldehyde elimination than other methods[3], [7],[8]. The development of high-efficiency catalysts to maintain reaction at ambient temperature is a crucial enabling element for room-temperature HCHO degradation. Catalytic oxidation can convert HCHO to H_2O and CO_2

completely without the formation of hazardous by-products or secondary pollutants. This can be done at ambient temperature, especially with noble metal catalysts, making it the most potential HCHO elimination method[9]. The overall reaction of this method is represented as reaction[10].

$$HCHO+O_2=CO_2+H_2O$$

The development of high-efficiency catalysts to maintain reaction at ambient temperature is a crucial enabling element for room-temperature HCHO degradation. Different catalytic oxidation catalysts, such as metal oxides, supported non-noble metals, and supported noble metals on metal oxides, have been studied for their HCHO removal efficiency. As the advancement of catalytic oxidation methods is critical. Many significant studies on HCHO removal catalytic materials have been published. Supported noble metal on metal oxide catalyst and transition metal oxide catalyst are the two most common types. Transition-metal oxides have received a lot of interest because they are inexpensive, abundant, and have high thermal stability. A variety of meso/macroporous metal oxide catalysts have also been investigated for catalytic removal of HCHO [1]–[5], [11], [12]. Some of the currently, the oxide-supported noble metal catalytic materials (Ag, Pt, Pd and Au) used in catalytic removal of formaldehyde such as Ag/Co3O4 [13], Ag/SBA-15 [14], Ag/Beta-Si[15], Ag/HMO[16], Ag/CeO2[17], Ag/MnOx-CeO2[18] Pt/MnOx-CeO_2[19], Pt/TiO_2[20], Pt/MnO_2, Pt/Fe_2O_3[20], Pt/SiO_2[21], PdMn/Al2O3[22], Pd/TiO2[23], Pd/Beta[24], Au/Fe2O3[25], Au/ZrO_2[26], Au/CeO_2[27] , Au/Co_3O_4-CeO_2[28]. A number of metal oxide catalysts for the removal of Formaldehyde have also been developed, including MnOx-SnO_2[29], Co-Mn[30], KxMnO_2[31], MnOx-CeO_2[32].

Supported transition metal oxide catalysts, such as VOx, MnOx, and WOx, have been used frequently and efficiently in recent investigations.[38].Manganese oxide materials have the highest efficiency among these transition metal oxides catalysts due to their exceptional oxygen storage capability and appealing properties (e.g., favorable porous structure, large surface area, and tunability pore diameter) for improved gaseous VOC removal (e.g., FA). Even at ambient temperature, manganese oxide proved successful in removing formaldehyde, resulting in the selective generation of carbon dioxide and other gases, with no hazardous by-product gases produced. As a result, without the need of heat or electric energy, this metal oxide can be employed as an active component in the elimination of formaldehyde [2], [9]. In a static reaction tank, Sekine et al. first catalytically oxidized HCHO across various metal oxides (Ag2O, PdO, MnO2, TiO2, and CeO2), with MnO2 exhibiting the highest removal efficiency, oxidizing high percentage of

formaldehyde at room temperature and suggesting that MnO_2 might be employed as an active component in the elimination of HCHO from indoor air. [33]. Pyrolusite (0.23 nm x 0.23 nm), cryptomelane (0.46 nm x 0.46 nm), and todorokite (0.46 nm x 0.46 nm) are three manganese oxides developed by Chen et al. with varied square tunnel dimensions. Cryptomelane's effective tunnel diameter is the same as the dynamic diameter of the HCHO molecule, which may account for its exceptional catalytic activity [34]. However, several disadvantages, including as poor stability, and agglomeration prohibit more widespread use. Manganese oxides and manganese composite oxides, also have a low HCHO removal efficiency at low temperatures. As a result, despite their potential and cheap prices, there are limitations to indoor HCHO removal [24]. Since, because most practical catalytic processes are so complex that single component catalysts struggle to fulfill the challenges for superior efficiency, such as high activity, notable selectivity, and higher deactivation resistance, composite catalysts, which integrate two or more materials, are much more researched and used[2], [3], [12], [44].

The benefits of noble metal nanoparticles (NPs) based catalysts in heterogeneous catalysis for VOC degradation have recently been identified[45]–[47]. The advantages of dispersing noble metal NPs on supports include increase the number of surface atoms and therefore active sites, providing synergistic activity between the NP and the support, avoiding NP agglomeration even at relatively high particles densities, and decreasing the cost of catalysts[48].Because of their increased activity for the break of C-C link, and C-H bonds, noble metals such as Pt, Au, and Ag are used and improve the oxidation of VOCs and boost the anti-toxicity of the catalyst, according to recent articles[38]. For example, according to Xuehua Yu., the improved Pt/MnO2 catalyst's strong metal-support interaction, widely dispersed Pt nanoparticles with tiny particle sizes, and high surface area resulted in increased formaldehyde oxidation activity.[24].Similarly, Li et al. synthesis Au/ CeO_2 catalysts with a large specific surface area (261 m2 g1) and high Au loading (5 wt% notional; 3 wt% measured) that converted 500 ppm HCHO to 92 percent at 37 °C. The large specific surface area of the CeO_2 support supplied more oxygen vacancies as catalytic active sites, making the stimulation of adsorbed O_2 molecules simpler[49].Ag-supported catalysts, which are significantly less costly than the noble metals listed above, have been shown to exhibit effective low-temperature catalytic activity for HCHO oxidation, according to current research. On the Sigma-Aldrich website, the price of Pt per gram for $H_2PtCl_6.6H_2O$ is nearly 20 times that of Ag per gram for $AgNO_3$. At temperatures as low, full oxidation of HCHO was achieved over

Ag/MnOx–CeO_2 catalysts; the catalysts were produced using a deposition precipitation technique[18]. Preparing atomically dispersed metal catalysts, which theoretically have the greatest metal dispersion (i.e., 100 percent) and may offer numerous active sites for catalytic reaction, is another efficient method for increasing the activity of Ag-based HCHO oxidation catalysts. For example, silver nanoparticles supported on Hollandite-type manganese oxide nanorods demonstrated good activity for HCHO oxidation, according to Huang et al. With an initial HCHO concentration of 400 ppm, the conversion was 100 percent at 383K [15]. Because of the development of strong metal-metal contacts between Ag and Co, Qu et al. described a bimetallic AgCo/APTES@MCM-41 catalyst that could accomplish full oxidation of HCHO at temperatures as low as 90 ºC. Due to increased surface OH supplied by K+ ions, Bai et al. reported that K–Ag/Co_3O_4 revealed full conversion of HCHO at 70 C[13]. He and Zhang experimented with a variety of supports (TiO_2, Al_2O_3, and CeO_2) and determined that the Ag/TiO_2 catalyst had the greatest catalytic performance (100 percent HCHO conversion at 95 °C) [42]. However, as compared to other noble metal catalysts, the performance of Ag-supported catalysts at room temperatures still needs to be improved.

Doping the Ag and measuring the HCHO removal efficiency at room temperature are critical since supported Ag catalysts have such a broad range of application.

In this study, we used a co-precipitation technique to produce Ag-based catalysts with MnOx supports, and then evaluated their performance for catalytic oxidation of HCHO at room temperature to that of undoped MnOx. On the two catalysts, a significant variation in catalytic activity was detected. With a gas hourly space velocity of 32000, Ag/MnOx had the best activity, recording 91 percent conversion of 110ppm HCHO at ambient temperature. The catalysts were then characterised by X-ray diffraction (XRD), TGA/DSC, and Brunauer-Emmett-Teller (BET). The intrinsic laws affecting the activity of Ag-based catalysts were explored and explained based on the findings.

2. Materials and methods

2.1. Catalyst preparation

$Mn(NO_3)_2$, $AgNO_3$, and Na_2CO_3 were chosen as raw materials for the AgMnOx catalysts, which were made via a co-precipitation technique. The following is the synthesis procedure for Ag/MnOx

catalysts; In 1000 ml of distilled water, make a 1 molar solution of $Mn(NO_3)_2$ with a molecular mass of 178.95 g. Similarly, make a 0.1 molar $AgNO_3$ solution by dissolving 0.124 g in 7.3 ml distilled water. For Ag/MnOx, dissolve 7.3 mL of 0.1 M $AgNO_3$ solution in 90 mL $Mn(NO_3)_2$ solution under stirring to get homogeneous solution A; 105.988 g of Na_2CO_3 was dissolved in 1000 mL deionized water under stirring to obtain homogeneous solution B. Pour the combination A into a funnel, then the solution B into a second funnel. In a beaker, add 100 mL distilled water and dropwise add both mixtures A and B, maintaining a pH of 7-8 with the digital pH meter along the continuous string. As the reaction proceeded, a mixed precipitate of MnCO3 and Ag_2CO_3 was formed. Add Na_2CO_3 solution until solution combination A is completed finish. The pH of the supernatant liquor was around 8. The precipitates were then put to a Buchner funnel and filtered, then washed until the pH of the solute was constant, then dried in an oven at 100°C for 12 hours and calcined at 450°C for 4 hours. Ag/MnOx was the term given to the above-mentioned catalysts. Similarly, for MnOx catalyst preparation same method is used without adding $AgNO_3$.

2.2. Catalyst characterization

The thermostability of precipitates was evaluated using a thermal gravimetric analyzer/dynamic stability control STARe system (TGA/DSC 1 STARe system, METTLER TOLEDO, Switzerland) at a 20°C/min heating rate from 0°C to 900°C under 50 mL/min of flowing argon gas. $MnCO_3$ and Ag_2CO_3-containing precipitates made comprised the test sample. The crystalline structure of catalysts was determined using Xray powder diffraction (XRD) (D8-Advance, Bruker, Germany) with Cu K (wavelength = 0.15406 nm) radiation at a tube voltage of 40 kV and current of 40 mA in the 2Ɵ range 10–80° with a step size of 0.05. The specific surface area and pore structure of the catalysts were determined using a Quantachrome physisorption analyzer (Autosorb-iQ-1MP, Quantachrome, USA). Before measuring, the catalysts were degassed for 6 hours at 280°C. The surface area (SBET) was calculated using data from the 0.05–0.5 partial pressure range using the Brunauer–Emmett– Teller (BET) equation.

2.3. Catalytic testing

The catalysts (0.156 g) for catalytic oxidation of HCHO were used in a fixed-bed continuous flow reactor tested at ambient temperature. The Flowing N_2 through a para-formaldehyde container produced gaseous HCHO. Flowing O_2 through a water bubbler produced water vapor. At room temperature (30 °C), a gas mixture containing 100 sccm pure O_2, 90 sccm HCHO/N_2 (balanced by N_2), and humidified air O_2 of 50 sccm (this flow rate bubbled through water to maintain relative

humidity of 50%) was provided for the reaction in reactor 0.5 inches diameter and length of 5 inches . Flowing nitrogen through paraformaldehyde in a round-bottomed flask at 40 °C in a water bath produced gaseous HCHO. The feed stream's HCHO content and relative humidity were maintained by adjusting the make-up gas flowrate with GHSV of 35,000 sccm $gcat^{-1}$. In the thoroughgoing procedure, the initial HCHO concentration of 20 ppm is maintained. The formaldehyde elimination efficiency was determined using a Multi-Gas Analyzer (GASERA ONE, Gasear, Finland) using the following formula:

$$C_{HCHO}=([HCHO]in - [HCHO]out])/[HCHO]in * 100\%$$

where C_{HCHO} represent removal efficiency, [HCHO]in formaldehyde initial concentration, and [HCHO]out represent final concentration the formaldehyde.

The CO_2 yield was defined as follows:

$$CO_2 \text{ Yield } (\%) = [CO_2]out/[HCHO]in * 100\%$$

where [HCHO]in denotes the HCHO concentrations in the inlet, and $[CO_2]$ denotes the CO_2 concentration at the output.

3. Results and discussion

3.1. Calcination temperature Effect

The thermal stability of the MnOx catalyst precursor (MnCO3) was investigated using thermogravimetry/DSC (TG/DSC) curves, as illustrated in Fig. 01. TGA was performed in the temperature range of ambient temperature to 900 °C in argon environment to investigate thermal stability and the presence of water in co-precipitation routed $MnCO_3$. Weight loss may be classified into three types. Also, the purpose of the thermal gravimetric investigation was to examine how Ag nanoparticles doped on MnOx varied in thermal behavior from undoped MnOx. Weight loss below 300 °C is caused by the removal of physically adsorbed water and the desorption of chemically bonded water. Notice that the weight loss in MnCO3 below 350°C is 7 %. In the temperature range of 300 to 480 °C, a rapid reduction in weight loss of about 30% is seen, which may be attributed to the conversion of metal carbonate to metal oxides and the evolution of CO_2 gas. The growth of lattice oxygen and the phase change from MnCO3 to MnO_2

to Mn2O3 to Mn3O4 when the temperature rises to 480°C. Notice that the maximum weight loss is shown below 500 °C. There is no weight loss after that until the temperature reaches 900 °C. When calcined at elevated temperatures, MnOx tended to lose carbon dioxide and oxygen ($MnCO_3$ → MnO_2→ Mn_2O_3→ Mn3O4), according to the TG/DSC findings. Similarly, the curve of Ag/MnOx is also shown and clearly indicating that MnOx less weight loss is decreased after the doping the Ag. The TGA indicates a progressive degradation phase with an initiation temperature of 50 °C when the same conditions are applied to the research of an Ag/MnO_x catalyst, which is attributed to volatile impurities and moisture breakdown. Until the catalyst reaches a temperature of 370 °C, it does not lose weight. There is rapid weight loss in the temperature range of 380–480 °C. There was a 28% loss in this region. As a result, the catalyst may be assumed to be thermally stable up to 400 °C, with a significant loss in thermal stability as the temperature rises. The Ag/MnOx is more thermally stable as shown.

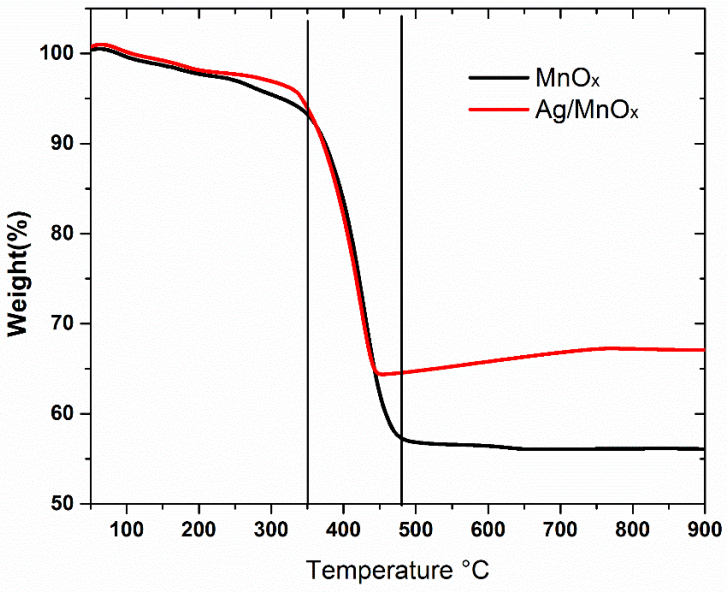

Fig. 01: TGA analysis

3.2. Structural analysis

XRD was used to identify the crystalline phase of as-prepared samples (Fig. 02). Both the catalyst shows the peak 18.2 (101), 29.2(112), 31.1(200), 32.6(103), 36.6(202), 38.3 (009), 44,6, 51.3, 58.7 (321), 60.1 (224), 64.9(400) show the differential peaks of tetragonal Hausmanite Mn_3O_4 (JCPDS 008-0017). In the diffraction peaks some of peaks 27.4(111), 46.4(210), 56.1(211), 68.5 (211), 69.8(102) are the differential peaks of MnO_2 (JCPDS 024—0735). It is pyrolusite in nature There

are no Ag crystalline phases for the catalysts, indicating that Ag is evenly distributed in the MnOx support. All the peak intensity of Ag/MnO2 gets high intensity when Ag is added. Their small peak widths and strong intensities indicate great crystallinity of Ag/MnOx. There are also some peaks shifts in Xrd after adding Ag which is indicated that the dopant was successfully incorporated.

3.3. BET Analysis

The surface area of the as-synthesized catalysts was examined using BET surface area analysis to measure the surface area and evaluate the relationship between surface area and catalytic activity for the oxidation of HCHO. N_2 adsorption-desorption experiments showed the pore size, surface area and total porosity (total surface pore volume) of both synthesized nanostructures as shown in Table. 01. The surface area of the un-doped catalyst MnOx was around 22.431 $m^2 g^{-1}$ and exhibited 88% HCHO conversion, but after doping Ag nanoparticles, i.e., Ag/MnOx, the surface area has been significantly increased to 30.481 $m^2 g^{-1}$ and the HCHO conversion has been significantly increased to 94 %.

The presence of Ag NPs on the surface of MnOx is responsible for the significant increase in surface areas. The surface area is increased from 26.731 $m^2 g^{-1}$ to 32.481 $m^2 g^{-2}$. The BJH formula from the N_2 adsorption isotherms desorption branch was used to calculate the average pore size. Both the catalyst shows the average pore diameter of 10.18 nm and 10.18 nm which indicated that the difference in the catalyst efficacy is due to different surface area.

Table 01: BET analysis of Samples

Sample (nm)	Surface area(m2/g)	Pore volume (cm3/g)	Average pore diameter
MnOx	22.731	0.1319	10.18
Ag/MnOx	30.481	0.1704	10.18

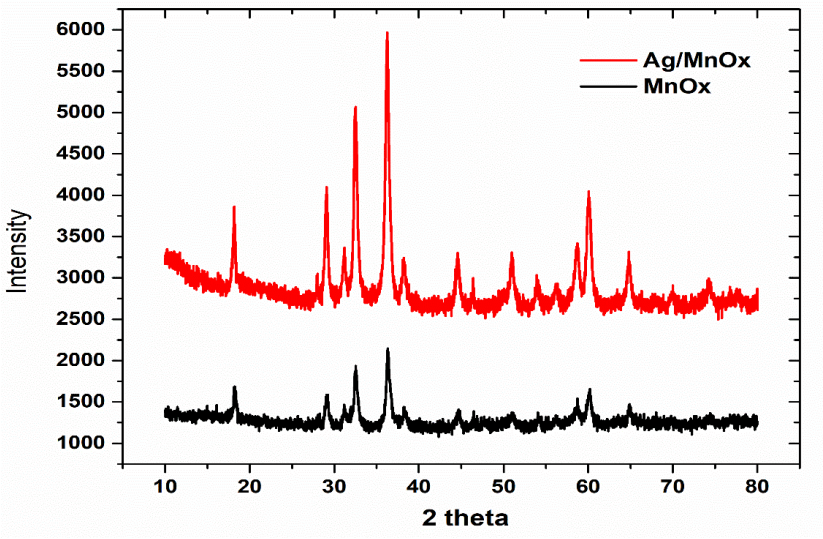

Fig. 02: XRD patterns

3.4. Catalytic oxidation of HCHO

The as-obtained MnO2 and Ag/MnO2 was used for the catalytic oxidation of formaldehyde at room temperature (30 °C), and the results are shown in Fig. 03. Both catalysts exhibited superior activity for formaldehyde removal with efficiencies more than 70% at the initial stage (first 20 min). As the time passes, Ag/MnOx maintained a high catalytic activity of ca. 91% while MnO2 started to decline the removal efficiency after 40minThe maximum removal efficiency of mnO2 88% after 40 minutes. After that MnOx catalyst start to deactivation. The main reason of deactivation is the adsorption of intermediate and H2O.Notice that CO_2 production begins to decline sharply at 60 minutes and then begins to rise again up to 100 minutes. HCHO conversions on Ag/MnOx are diminishing, which might be related to the buildup of intermediate species or changes in active species on the catalyst surface. The major intermediates in HCHO oxidation are dioxymethylene (DOM) and HCOO species, which are mostly adsorbed on the MnOx surface. It is demonstrated that the composition and reactivity of active species have a significant impact on the production and transformation of intermediate species. As a result, activity variations and the emergence of an inflection point on Ag/MnOx catalysts should be due to changes in active species[20], [23], [26], [40].The maximum removal efficiency of 94%.The removal efficiency is shown in Fig. 04. After 100 minutes Ag/MnO_2 also start deactivation have same reason of deactivation of MnO2. The CO_2 produced by formaldehyde oxidation across various MnOx and Ag/MnOx catalysts throughout the reaction is shown in fig. In the beginning, the produced CO_2 over MnOx and Ag/MnO2x was around 15.02 ppm and 14.369 ppm, respectively, and then

progressively decreased to 3.1 ppm and 3.5 ppm as the reaction progressed for 250 minutes. The result indicates that Ag/Mnox is more favorable for the catalytic oxidation of HCHO as it is more thermally stable, high crystallinity and high surface area. It is proposed that Ag nanostructure improve the removal efficiency.

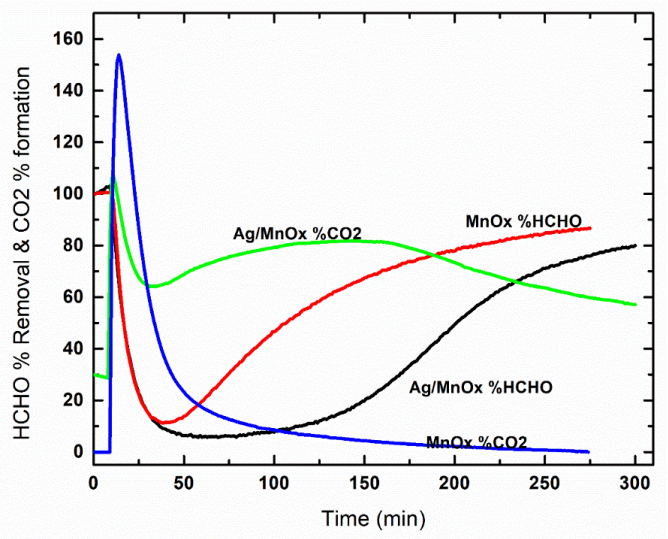

Fig. 03: HCHO removal efficiency as a function of time over MnOx and Ag/MnOx

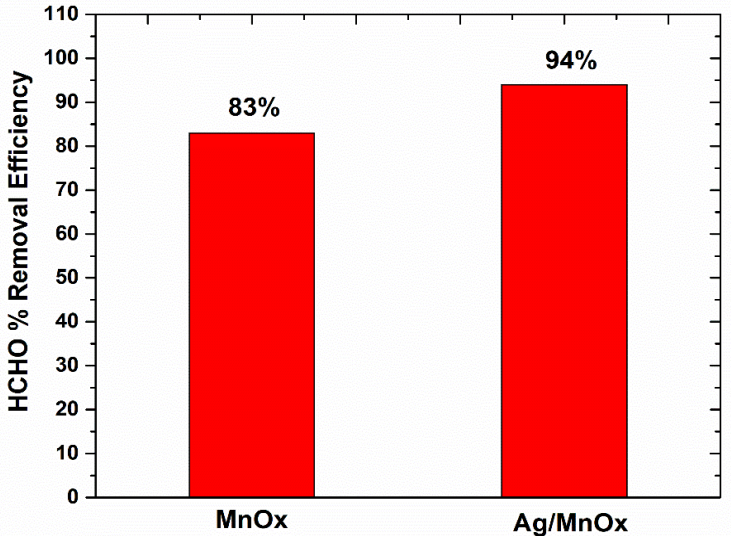

Fig. 04: HCHO % Removal Efficiency

4. Conclusions

In conclusion, we described a technique for preparing MnOx and Ag/MnOx by adding Ag to a co-precipitation process. An Ag/MnOx is favorable for the removal of HCHO due its high crystallinity, high thermally stability. At ambient temperature, this kind of Ag/MnOx was very

effective for HCHO oxidation, converting 20 ppm HCHO at 30 °C under a WHSV of 35000 sccm $gcal^{-1}$. The inclusion of Ag nanostructure in MnOx was essential for generating high surface area and surface-active sites, which allowed HCHO to be converted to intermediates effectively. This research presents a co-precipitation method for synthesizing crystallized Ag/MnOx for effective HCHO oxidation, as well as identifying active sites for the transformation of the reactant and intermediates, allowing for the rational design of MnOx for HCHO oxidation with long-term activity and high stability.

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