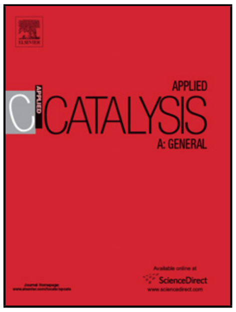

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Effective and selective oxidation of 2-butanol over Mn supported catalyst systems

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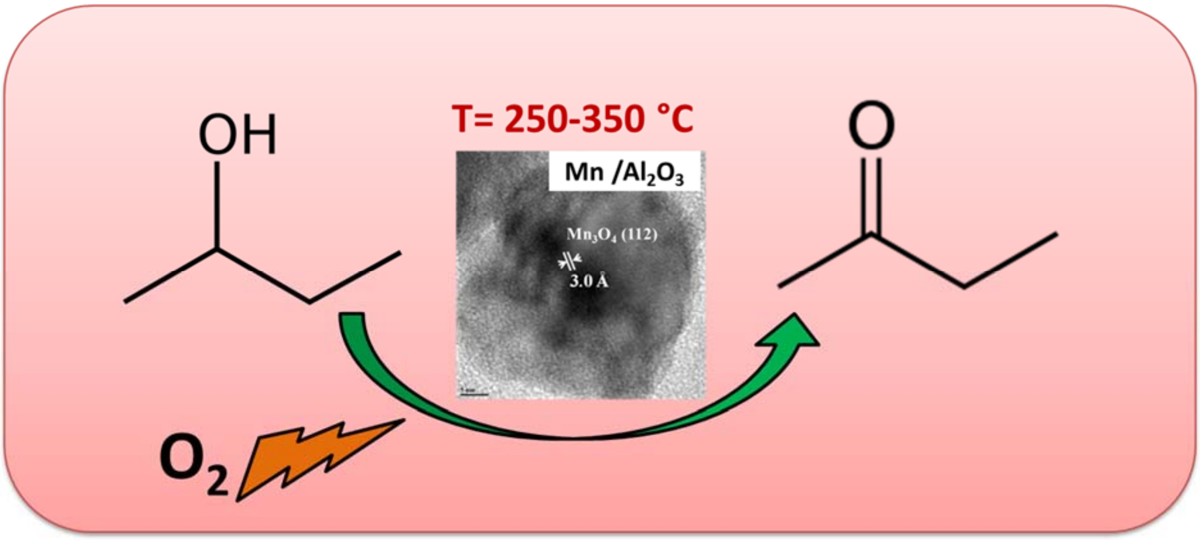
GRAPHICAL ABSTRACT



Highlights:

- A series of Mn_xO_y-Al_2O_3 (MA), Mn_xO_y-CeO_2 (MC), Mn_xO_y-ZrO_2 (MZ) and Mn_xO_y-SiO_2 (MS) catalysts were prepared by co-precipitation followed by hydrothermal method
- Selective oxidation of 2-butanol to MEK over Mn supported on different oxide supports was studied
- Presence of Mn_3O_4 species in MA and MZ catalysts is responsible for maximum catalytic activity towards 2-butanol oxidation
- MA catalyst conferred a maximum 2-butanol conversion of 51 % and selectivity of 88 % towards MEK

Abstract: *Oxidation of alcohols to their corresponding aldehydes/ketones is an important reaction in industries as well as in academic perspective. Selective oxidation (Selox) of alcohols like methanol, ethanol and propanol are well studied in literature; however, alcohols like butanol, pentanol, octanol is a challenging task. Selective oxidation of 2-butanol to methyl ethyl ketone (MEK) is an important reaction due to its wide range of applications. Herein, we demonstrated the selective oxidation of 2-butanol to MEK over Mn supported on different oxide supports. A series of* Mn_xO_y-Al_2O_3 *(MA),* Mn_xO_y-CeO_2 *(MC),* Mn_xO_y-ZrO_2 *(MZ) and* Mn_xO_y-SiO_2 *(MS) catalysts were prepared by co-precipitation followed by hydrothermal method. As synthesised catalysts were characterised by various physico-chemical characterisation techniques. It was found that the presence of* Mn_3O_4

species in MA and MZ catalysts is responsible for maximum catalytic activity towards 2-butanol oxidation. MA catalyst conferred a maximum 2-butanol conversion of 51 % and 88 % selectivity towards MEK. XPS analysis revealed that Mn in MA catalyst exists in +2 and +3 oxidation states and responsible for 2-butanol oxidation. Moreover it was found that the acidity of the catalyst also plays an important role in catalytic activity.

Keywords: Selective Oxidation, 2-butanol, Methyl Ethyl ketone, Mn based catalysts

1. Introduction

Oxidation of alcohols to their corresponding aldehydes/ketones is one of the important processes in chemical industries, as well as in academia, for the production of value added chemicals. Conventionally, aldehydes/ketones were prepared by the oxidation of alcohols using stoichiometric amount of oxidants, such as salts of permanganates [1], chromates [2,3] and bromates [4]. Due to the generation of enormous quantity of metal wastes, conventional methods are replaced by catalytic method for the production of aldehydes/ketones. In homogeneous catalytic method, high catalytic activity towards desired product was achieved; however, it has a major drawback in separation and reuse of the catalysts. To overcome these difficulties, heterogeneous catalytic method was used. It plays a vital role in separation and reuse of the catalysts; but the challenging task was the synthesis of catalysts with high selectivity towards desired products. Preparing high active catalysts and selective towards desired products with sustainability is an interesting area of research in heterogeneous catalysis. Hence, it provides further details about the physical and chemical properties of the catalysts.

Alcohols such as methanol, ethanol, propanol and butanol are the raw materials for the production of renewable and sustainable energy sources [5].Compared to lower carbon chain alcohols such as methanol, ethanol and propanol, butanol shows less hygroscopic, high energy density, low vapor pressure, and low affinity to water [6-9]. n-Butanol is one of the promising biofuels, which has received much attention due to its renewability over other biofuels [5]. Methyl ethyl ketone (2-butanone) (MEK) is one of the important products, which has wide spectrum of applications in industries. Commercially, MEK is produced by dehydrogenation of 2-butanol using copper, zinc catalysts but it requires harsh reaction conditions [10-11]. There are some other processes examined for the production of MEK such as oxidation of 2-butene [12] and oxidation of isobutyl benzene [13]; however, these processes are not commercialized. Owing to its less impact to environment and mild reaction conditions, oxidation of 2-butanol using an oxidant is an alternative method for production of MEK. In such a process alternative oxidant gases are like air, CO_2, O_2 and N_2O is co-fed to oxidize butanol to 2-butanone. There are seldom a few reports for the production of MEK using above said oxidants. Mistry et al. reported that catalytic activity of 2-butanol oxidation depends upon the morphology of 'Pt' nanoparticles supported on γ-Al_2O_3 [13]. Mapa et al employed a solid solution of ZnO and InN for selective oxidation of 2-butanol to MEK, but at high temperatures between 350-450 ^{0}C [14]. Hou et al. reported that liquid phase oxidation of 2-butanol using oxygen as oxidant over Au:Pd bimetallic nanoparticles shows higher selectivity towards 2-butanone at 60 °C [15]. Several d-block metals like Pt, Ru, Rh, Au, Co, Ni, Ag and Ir [16-17] were tested as catalysts for oxidation of alcohols in liquid [17] as well as in gas phase [16] reactions.

In many oxidation reactions metals like V, Cr, and Mn were used due to their redox properties, oxygen storage capacity, etc.[18-20]. Apart from redox properties, certain ratio of different oxidation states in such metals can alter the catalytic activity. Mn supported catalysts were used in many field of research due to its redox properties. Controlling an active oxidation state in Mn-based materials is a challenging task in heterogeneous catalysis. In this paper we stabilized and maintained the oxidation states of Mn during the selective oxidation of 2-butanol. In eletrocatalytic [21] and photocatalytic [22] reactions, Mn-based mixed oxide catalysts showed better catalytic activity with suitable supports in many reactions. In this work, manganese oxide on Al_2O_3, CeO_2, ZrO_2 and SiO_2 mixed oxide catalysts were prepared by co-precipitation and sol-gel methods. Catalysts which has certain ratio of Mn^{+2}/Mn^{+3} shows better catalytic activity towards oxidation of 2-butanol. This reaction was performed in fixed bed reactor (FBR) system and characterized by several techniques. Powder X-ray diffraction (PXRD), Raman spectroscopy, N_2 adsorption desorption, temperature programmed desorption (NH_3-TPD), transmission electron microscopy (TEM) confirmed the structural and textural properties. Presence of different oxidation states in the active catalyst was confirmed by X-ray photoelectron spectroscopy (XPS). Maximum conversion of 51% and 88% selectivity towards MEK was achieved by Mn_xO_y-Al_2O_3 catalyst over 12 hours. By using surface characterization techniques, surface species on the catalysts were confirmed.

2. Experimental

2.1. Catalyst synthesis

All the chemicals used to synthesize catalyst were of reagent grade. Manganese (II) nitrate ($Mn(NO_3)_2.4H_2O$, 98%), aluminium (III) nitrate ($Al(NO_3)_3.9H_2O$, $\geq$ 95%), cerium (III) nitrate ($Ce(NO_3)_3.6H_2O$, 99.5%), zirconyl (IV) nitrate ($ZrO(NO_3)_2.H_2O$), TEOS ($Si(OC_2H_5)_2$, 98%), sodium hydroxide (NaOH, 98%), ethanol (C_2H_5OH) and hydrochloric acid (HCl) were used as precursors for catalyst synthesis. All the chemicals were purchased from Alfa Aesar and Merck.

2.2. Hydrothermal method

Mn supported catalysts were synthesized by co-precipitation followed by hydrothermal method [23].The procedure is as follows: Metal nitrates precursors (Mn^{2+}, Al^{3+}, Ce^{3+}, Zr^{4+}) were dissolved in water and precipitating agent (NaOH) were added simultaneously drop wise at constant pH (9.5±0.2). The solution was transferred into a teflon lined autoclave for hydrothermal synthesis kept at 150 °C for 12 hours. Then the solid was filtered, washed and dried at 110 °C for overnight followed by calcination at 450 °C for 6 hour in air. As-synthesized Mn_xO_y-Al_2O_3, Mn_xO_y-CeO_2 and Mn_xO_y-ZrO_2 catalyst were labelled as MA, MC and MZ, respectively.

2.3. Sol-gel method

Mn supported SiO_2 catalyst was synthesized by sol-gel method [24]. Mn $(NO_3)_2.4H_2O$ and TEOS was diluted using ethanol and the solution was stirred at room temperature to get homogeneous clear solution. Half of the alcohol was used for this and another half was used to dilute the water and acid. The mixed solution of EtOH-H_2O-HCl was added drop wise to the above Mn-TEOS-EtOH solution with constant stirring. After complete addition, the solution was stirred at 40 °C for 12 hours. Then the solution was dried at 110 °C for overnight and calcined at 450 °C for 6 hours in presence of air. Finally, Mn_xO_y-SiO_2 catalyst was labelled as MS.

2.4. Characterization

PXRD pattern of synthesized catalysts were collected by PANanalyticalX'pert Pro dual goniometer diffractometer at a step size of 0.008°and a scan rate of 0.5° min^{-1}. X-ray was generated by using Cu Kα (1.5418Å) with Ni filter and the flat holder in Bragg–

Brentango geometry used for data collection. Autosorb 1C Quantachrome USA was used to collect Nitrogen adsorption/desorption isotherms for the catalysts. The surface area from the adsorption branch was calculated by using Brunauer–Emmett– Teller (BET) equation. High resolution transmission electron microscopy (HRTEM) of all catalysts was recorded by FEI TECNAI F30 electron microscope operating at 300 kV. Samples were prepared by dispersion powder catalysts in isopropanol before depositing onto a holey carbon grid. Raman spectra were recorded on a Horiba JY LabRAMHR800 Raman spectrometer coupled with microscope in reflectance mode with 514nm excitation laser sources and a spectral resolution of 0.3 cm^{-1}. Oxidation states of manganese and aluminium was studied by ambient pressure photoelectron spectrometer (APPES) [25]. X-ray was produced by using Mg Kα with the energy of 1253.6 eV.

2.5. Catalytic activity

The activity of the catalyst was performed in fixed bed continuous down flow reactor (FBR) over a temperature range of 200-350 °C atmospheric pressure. 1 ml catalyst was loaded at the centre of Inconel reactor (13mm X 510 mm), packed with ceramic beads on either sides of the catalyst bed. Temperatures of the catalyst bed were measured by k-type thermocouple. 2-butanol and oxygen feed flow were monitored by using isocratic pump (Lab Alliance series II) and Brook's Mass flow controllers (5850 series) respectively. The volume of the gaseous products was measured by a wet gas flow meter (Ritter Drum-Type Gas Meter). The reaction liquid products were condensed and analysed by Agilent 6890N gas chromatography (FID) with HP-5 (5.5% phenyl methyl siloxane) column and gaseous products were analysed by customised Thermo Fisher 1110 GC with (Molecular Sieve) TCD detectors.

3. Results and discussion

3.1. Powder x-ray diffraction

PXRD is one of the primary techniques which offer the detailed information about catalyst nature and structure. Fig.1. shows the PXRD pattern of as-calcined MA, MZ, MC and MS catalysts. It is clearly seen from Fig.1 (a), MS mixed oxide catalyst shows the presence of SiO_2 phase at 21˚ and manganese oxide in the form of Mn_2O_3 phase which matches with JCPDS No.78-0390. MZ mixed oxide catalyst shows peaks at 18˚, 28˚, 32˚, 36˚, 38˚, 50˚ and 60˚ correspond to Mn_3O_4 (JCPDS No.24-0734). In MC mixed oxide catalyst, a high intensity peak at around 28° corresponds to ceria (JCPDS No. 75-0151) and the other peaks correspond to Mn_2O_3 phase (JCPDS No.78-0390) which reveals that manganese is well dispersed in ceria. Fig.1. (d) shows MA mixed oxide catalyst, which offer information about presence of Mn_3O_4 phase. The presence of active sites in MA mixed oxide catalyst reveals that dispersion of manganese oxide in alumina is very well than other catalysts. Presence of Mn_3O_4 phase was further confirmed by JCPDS data -24-0734.

3.2. Surface area

Catalytic activity of the reaction depends upon different parameters, one of important parameter is BET surface area. All the as-synthesized catalysts were analysed by N_2-adsorption desorption isotherms. Table.1. provides the details about textural properties of as-synthesized catalysts. Surface area of manganese containing mixed oxide catalysts increased in the order, Mn_xO_y-Al_2O_3<Mn_xO_y-CeO_2<Mn_xO_y-ZrO_2<Mn_xO_y-SiO_2 respectively. Mn_xO_y-Al_2O_3 mixed oxide catalyst shows the lowest surface area (84 m^2/g) compared to other catalysts due to be bigger crystallite size [26]. Mn_xO_y-SiO_2 mixed oxide catalyst exhibit the highest surface area in comparison with other catalysts (339 m^2/g). High surface area of Mn_xO_y-SiO_2 catalyst is due to SiO_2 support, where SiO_2 support shows 369 m^2/g surface area which decreases to 339 m^2/g after Mn was incorporated.

Mn_xO_y-CeO_2 and Mn_xO_y-ZrO_2 catalysts showed 89 and 103 m^2/g surface area respectively. Both catalysts showed near 5±1.0 nm crystallite size. Compared to other catalysts, Mn_xO_y-Al_2O_3 showed high pore volume (0.32 cc/g) and this may be the one of the reasons for the maximum catalytic activity of 2-butanol.

3.3. X-ray photoelectron spectroscopy (XPS)

To explore the chemical composition of the catalyst surface and the oxidation state of the elements, XPS was used. Fig.2. shows XPS spectra of Mn 2p core level of pure manganese oxide, fresh and used Mn_xO_y-Al_2O_3 catalysts. XPS spectra of Mn containing mixed oxide and pure manganese oxide catalysts reveal the information about active species on the surface and oxidation states of manganese oxide. XPS was recorded to know about surface chemical composition of manganese oxide in Mn containing mixed oxide catalysts. Multiple peaks corresponding to Mn^{+2}, Mn^{+3} and Mn^{+4} were observed which was deconvoluted by peak fitting method with Shirley background removal in Mn 2p core level spectrum. Mn $2p_{3/2}$ deconvolution shows three peaks at 640.4, 641.7 and 643.3 eV binding energy which corresponds to Mn(II), Mn(III) and Mn(IV) respectively [27]. It clearly shows that manganese in pure manganese oxide has multiple oxidation states. Fig.2. (b) shows the XPS spectra of Mn $2p_{3/2}$ core level for fresh Mn_xO_y-Al_2O_3 catalyst at 641.7 eV [27,28]. The peaks at 640.4 and 641.7 eV clearly indicate the presence of Mn in Mn^{+2} and Mn^{+3}oxidation states. This satellite structure, noticeable on the higher binding energy of Mn $2p_{3/2}$ core-level in the XPS spectrum of the manganese compounds originates from the charge transfer from oxygen ligand to unfilled 3d orbital of Mn during the final state of photoelectron emission process [29]. It is further confirmed that fresh Mn_xO_y-Al_2O_3 catalyst shows both Mn^{+2} and Mn^{+3}oxidation states. The catalytic activity of M_xO_y-Al_2O_3 catalyst was evaluated for 2-butanol oxidation, and it shows maximum conversion (51 %) and selectivity (88 %) than other tested catalysts. To study the surface chemical composition of the catalyst, the spent Mn_xO_y-Al_2O_3 catalyst was analysed by XPS measurement. Spent catalyst analysis reveals the presence of peaks at 640.4 and 641.7 eV proving that there is no significant change in the catalyst after reaction. It is also confirmed that the catalyst possess stable oxidation state even after 12 hour on time on stream under optimum reaction conditions.

O 1s spectra of all fresh and used MA catalyst were recorded. Fresh Mn_xO_y-Al_2O_3 catalyst showed peaks around 530, and 531.5 eV corresponds to lattice oxygen, surface hydroxyl species [30, 31]. On the surface of spent catalyst, presence of lattice oxygen and surface hydroxyl species was confirmed by peaks at 530 and 531.5 eV respectively. Catalytic activity of Mn_xO_y-Al_2O_3 catalyst showed maximum yield due to surface oxygen species which favours selective oxidation of 2-butanol. In spent catalyst O 1s spectrum, it is clear that the intensity of surface oxygen species is more which confirms the role of these species.

3.4. Raman spectroscopy

Fig. 4 shows the Raman spectral data of Mn_xO_y-Al_2O_3, Mn_xO_y-CeO_2, Mn_xO_y-ZrO_2 and Mn_xO_y-SiO_2 catalysts. Raman spectroscopy provides detailed information about vibration modes of catalysts/materials. Characteristic peaks for Mn_xO_y-ZrO_2 catalyst is in the range of 300-700 cm^{-1}. High intensity peak is at 660 cm^{-1} and two small intensity peaks at 317 and 372 cm^{-1}corresponds to Mn_3O_4. These characteristic Raman bands support the results obtained in PXRD. In Mn_xO_y-Al_2O_3 catalyst presence of broad peak at 645 cm^{-1} corresponds to Mn_3O_4 [32].The characteristic Raman band at 630 and 680 cm^{-1} is not seen which confirms that there is no formation of Mn_2O_3. There was no characteristic peaks observed for Mn_xO_y-SiO_2 catalyst. Mn_xO_y-CeO_2 catalyst showed four characteristic peaks in the range of 300-700 cm^{-1}. The high intensity peak at 457 cm^{-1} corresponds to vibration mode of cubic fluorite (F_{2g}) CeO_2 lattice [33, 34] and other peaks corresponds to Mn(III)-O and Mn(IV)-O bonds.

Used Mn_xO_y-Al_2O_3 was analysed to observe the nature of catalyst after reaction and to see what type of coke is formed during reaction. The Raman characteristic peaks of used-Mn_xO_y-Al_2O_3 catalyst was compared with fresh Mn_xO_y-Al_2O_3 catalyst, noticeably strong vibration band at 650cm^{-1}which corresponds to Mn_3O_4 and smaller band at 313 and 367 cm^{-1} corresponds to high surface area manganese oxide were observed [35]. No peaks corresponding to D and G bands [36] were observed which suggests that there is no graphitic coke formation after long time on stream (12 and 30 hours) reaction conditions.

3.5. Temperature programmed desorption (NH_3-TPD)

Acidity is one of the parameter which plays an important role in the catalytic activity of 2-butanol oxidation. To find the acidity of the catalysts, NH_3-temperature programmed desorption was carried out for all calcined catalysts and the results are given in Fig. 6. Mn_xO_y-CeO_2 and Mn_xO_y-ZrO_2 catalysts showed no peaks which confirmed that both the catalysts has no acidity. In Mn_xO_y-SiO_2 catalyst the peak at 650 °C corresponds to strong acidic centres and very little amount of weak acid sites (200-300 °C) from the SiO_2 were also observed. Mn_xO_y-Al_2O_3 catalyst showed two major peaks in which the peak observed at lower temperature (~200 °C) is due to weak acidic centres present in the catalyst and peak observed at a higher temperature (~650 °C) is due to strong acid site. MA exhibits more number of weak as well as strong acid sites in comparison to MS emphasizes that the former possess more acidic centres. This important feature associated with MA helps in enhancing the catalytic activity of MA catalyst, which showed maximum and stable catalytic activity over a period of 30 hours.

3.6. Transmission electron microscopy (TEM)

Fig. 7. shows the TEM images of fresh and used Mn_xO_y-Al_2O_3 catalyst. TEM images reveal the information about the morphology and lattice of the catalysts. Fig.7. (a), and (b) and (c) displays TEM images of fresh Mn_xO_y-Al_2O_3 catalyst in low and high resolutions, respectively. Fig.7. (a) and (b) TEM images clearly confirmed the dispersion of manganese oxide on Al_2O_3. Indeed, a nice decoration of alumina by nano Mn_xO_y has been directly demonstrated from the TEM results. The d-spacing value of Mn_xO_y-Al_2O_3 catalyst is 3.0 Å which is in agreement with the value obtained from PXRD results. Used Mn_xO_y-Al_2O_3 catalysts TEM image (Fig. 7 (d)) shows a thin layer of coke deposited on the surface of the catalyst and there was no other changes in the morphology of the catalyst. Highly dispersed

manganese oxide on Al_2O_3 showed maximum yield on 2-butanol oxidation using molecular oxygen.

3.7. Effect of supports

Support has an important role in any catalytic activity of a reaction. Choosing a suitable support is a critical part in heterogeneous catalysis. To study the influence of the support for 2-butanol to MEK reaction, manganese oxide catalyst was loaded on four different supports . Manganese oxide on Al_2O_3, CeO_2, ZrO_2 and SiO_2 mixed oxide catalysts were subjected to oxidation of 2-butanol at optimized reaction conditions and the results are given in Fig. 8 and Table 2. MC catalyst shows maximum 2-butanol conversion and MEK selectivity of 41 and 81 %, respectively. MS catalyst shows better conversion (54 %), but selectivity towards MEK is very low due to complete oxidation of 2-butanol to undesired products. Minimum selectivity (33 %) towards MEK was observed with MS catalyst. MA and MZ catalysts shows about 50 % conversion and 88 % selectivity towards MEK. MA and MZ catalysts show similar pattern up to certain time on stream. However after certain time on stream, MA catalyst shows slight increase in catalytic activity but in MZ the catalyst activity decreases at the end of 12 h. This decrease in catalytic activity may be due to coke formation which might block the catalytic active centres. MA catalysts shows better activity than other tested catalysts. There is no conversion of 2-butanol to MEK was observed over alumina, which confirms that bare alumina is not active for 2-butanol oxidation. 2-butanol conversion on MA increases dramatically to 51 %. MA shows high conversion as well as yield of MEK, which is attributed to synergistic effect of manganese and alumina. Conversion of 2-butanol and yield towards MEK is stable up to 30 hours. Catalytic activity of 2-butanol is further carried out using MA catalyst for optimization of different parameters.

3.8. Effect of temperature

Temperature is one of the main important factors which affect the catalytic activity. To examine the influence of temperature, oxidation of 2-butanol was carried out at three different temperatures ranging from 250, 300 to 350 °C in FBR and the results are shown in Fig. 9. Oxidation of 2-butanol was carried out at LHSV = 1.8 h^{-1} with respect to 2-butanol, and GHSV = 1200 h^{-1} with respect to oxygen at atmospheric pressure. At low temperature (250 °C), conversion towards 2-butanol and selectivity towards MEK was observed to be 30 and 80 %, respectively. Further increase in temperature to 300 °C, conversion and selectivity increased to 51 and 88% respectively and remains constant for 30 hours time on stream. At the high temperature (350 °C), very less conversion but high selectivity (90 %) towards MEK was observed, which is higher than other two temperatures. Decrease in conversion and yield may be due to complete oxidation of 2-butanol to undesired products like CO_x, methanol, acetone and water at higher temperature. An appropriate and suitable reaction condition was always required for partial oxidation. At 300 °C maximum conversion and selectivity was observed due to appropriate temperature and active centres to activate the reactants. Maximum catalytic activity was observed at 300 °C and it is optimised for oxidation of 2-butanol.

3.9. Effect of 2-butanol flow

To study the effect of contact time between reactants and catalytic active centres, reaction was performed at different 2-butanol flow and the results are shown in Fig. 10. Oxidation was carried out at three different 2-butanol flow (LHSV 1.8, 3.6 and 5.4 h^{-1} with respect to 2-butanol), at 300 °C, GHSV = 1200 h^{-1} respect to oxygen at atmospheric pressure. At LHSV 1.8 h^{-1}, 51% conversion of 2-butanol was observed with maximum selectivity (88 %) of MEK. At this flow, 2-butanol has optimum contact time to react with adsorbed oxygen on the surface of the catalyst. While increasing the 2-butanol flow to LHSV 3.6 h^{-1} conversion of 2-butanol was decreased to 26 % but the selectivity of MEK was increased to 90 %. At LHSV 5.4 h^{-1} conversion as well as selectivity decreased to 20 and 89 %, respectively. Due to decreasing contact time between reactants and active centres a decrease in yield was observed at higher LHSV of 2-butanol viz. 3.6 and 5.4h^{-1}. The maximum conversion of 2-butanol (51 %) and selectivity towards MEK (88 %) was obtained at appropriate flow rate (LHSV 1.8 h^{-1}), which favours selective oxidation.

3.10. Effect of oxygen flow

To understand the effect of oxidant on catalytic activity, this reaction was carried out at three different molecular oxygen flows and the results are shown in Fig. 11. In any oxidation reaction, the change in catalytic activity depends upon the flow of oxidants. In this work, reaction was carried with three different oxygen flow rates (GHSV 600, 1200 and 1800 h^{-1}). At GHSV = 600 h^{-1} the conversion towards 2-butanol was 35 %, and 70 % MEK selectivity was observed. Further increase in oxidant flow to GHSV = 1200 h^{-1} conversion attained the maximum (51%) and selectivity (88%) which favours the partial oxidation of 2-butanol to MEK. Further increase in GHSV to 1800 h^{-1} relatively low conversion and selectivity was obtained which may be due to complete oxidation of 2-butanol to CO_x and undesired side products. Based on the above results GHSV 1200 h^{-1} (O_2) was optimized for oxidation of 2-butanol.

3.11. Catalyst stability and reaction sustainability

To understand the stability and durability of the MA catalyst, the optimization study was carried out with long time on stream (TOS) with optimised reaction parameters. The reaction conditions are GHSV 1.8 h^{-1} with respect to 2-butanol and GHSV 1200 h^{-1} with respect to molecular oxygen at 300 °C .The activity of the catalyst remains same for longer duration (30 h) the result shown in Fig.12.Gradual increase in catalyst activity in the first few hours under wide variety of reaction conditions demonstrated a change in the nature of the catalyst under reaction conditions towards higher active form for this particular selective oxidation. Both conversion and selectivity linearly increases, till the reaction reaches a steady state. When comparing the oxidation ability of CeO_2 alone as catalyst for this reaction, it gives very less conversion and selectivity (Fig.13.).

4. Conclusion

MA, MC, and MZ catalysts were prepared by co-precipitation followed by hydrothermal method; however, MS was prepared by sol-gel method. All the catalysts were characterized by various analytical techniques like Raman spectroscopy, N_2-adsorption, XPS, TEM and NH_3-TPD. Presence of Mn_3O_4 and Mn_2O_3 phases was revealed by PXRD. Presence of different oxidation states were confirmed by XPS spectra which shows that MA catalyst has Mn^{+2} and Mn^{+3}oxidation states. All the catalysts were subjected to 2-butanol oxidation using molecular oxygen in continuous flow fixed bed reactor. MA catalyst shows maximum catalytic activity of 51% conversion of 2-butanol and 88% selectivity towards MEK. Active centres in the catalysts were confirmed by XPS and Raman spectroscopy. Raman spectroscopy shows the presence of Mn_3O_4 which was correlated with PXRD. Nature of acidity was confirmed by NH_3-TPD. When CeO_2 alone is used as catalyst for this reaction it is less active and deactivates fast. Synergetic effect of appropriate acidity along with active Mn species is responsible for this reaction. Using oxidants like air in oxidation reaction leads to environmental friendly and green reaction. More work is in progress with CO_2 as oxidant for this reaction.

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Figures

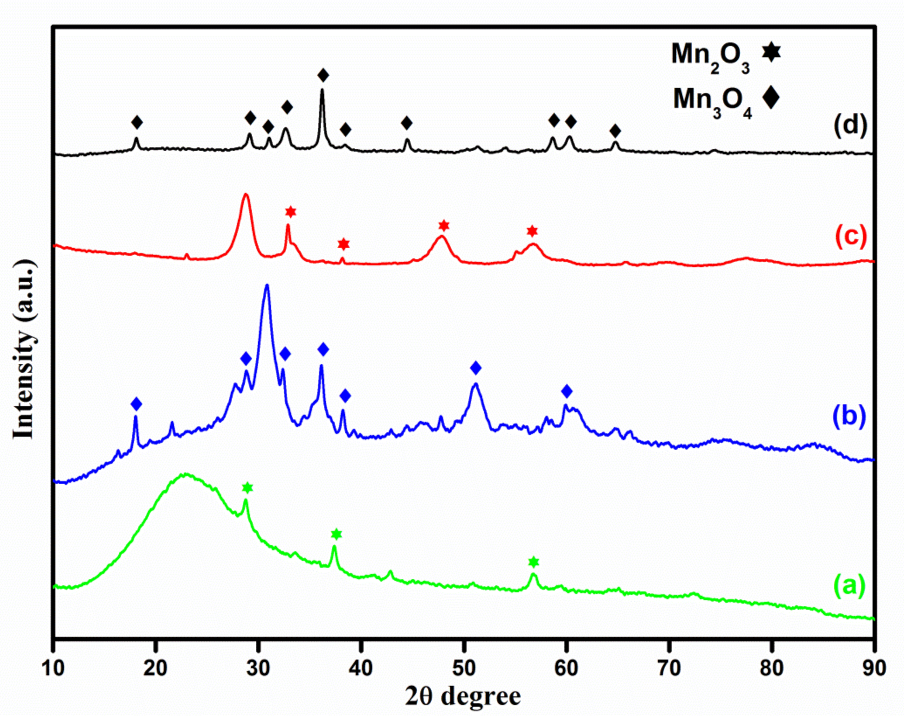

Fig.1. Powder X-ray Diffraction pattern of as-calcined Mn containing mixed oxide catalysts (a) Mn_xO_y-SiO_2, (b) Mn_xO_y-ZrO_2, (c) Mn_xO_y-CeO_2, and (d) Mn_xO_y-Al_2O_3

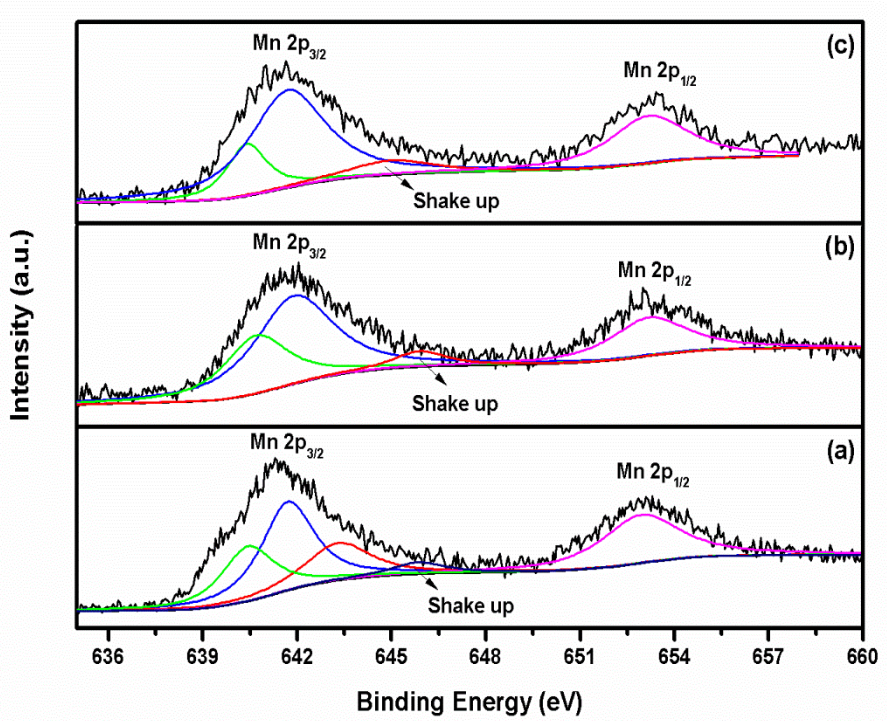

Fig.2. XPS spectra of Mn 2p core levels for (a) Manganese oxide, (b) Fresh-Mn_xO_y-Al_2O_3 and (c) Used-Mn_xO_y-Al_2O_3

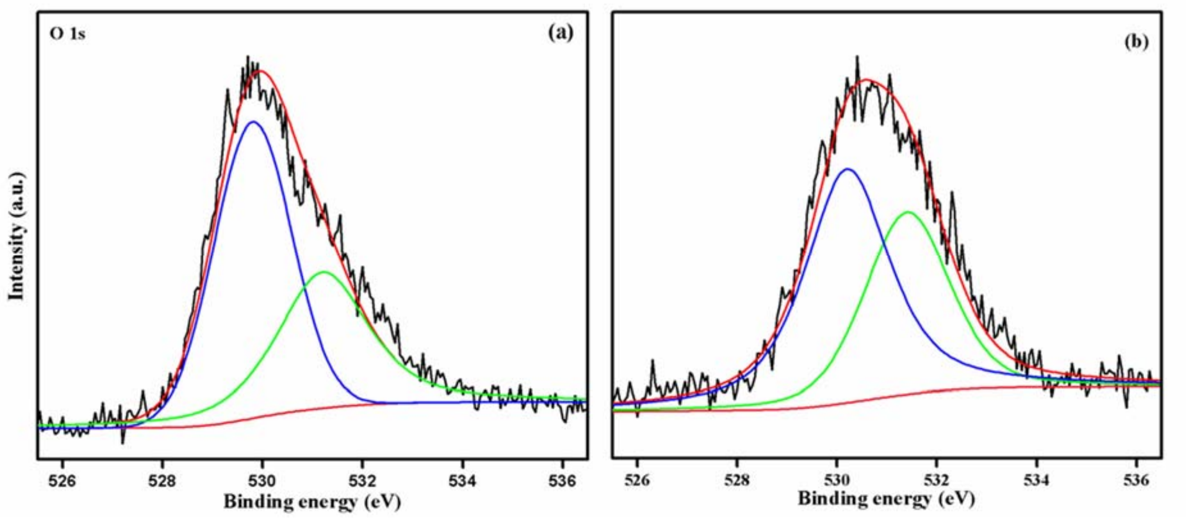

Fig. 3. XPS spectra of O 1s (a) Fresh-Mn_xO_y-Al_2O_3 and (b) Used-Mn_xO_y-Al_2O_3

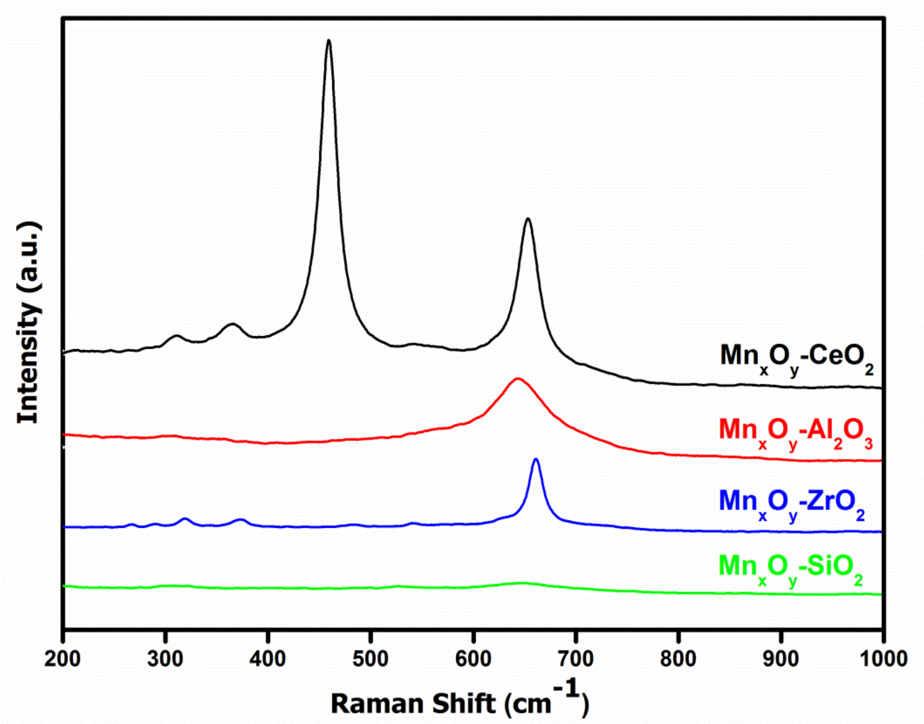

Fig. 4. Raman spectrum of all as-synthesized catalysts calcined in air at 450 °C

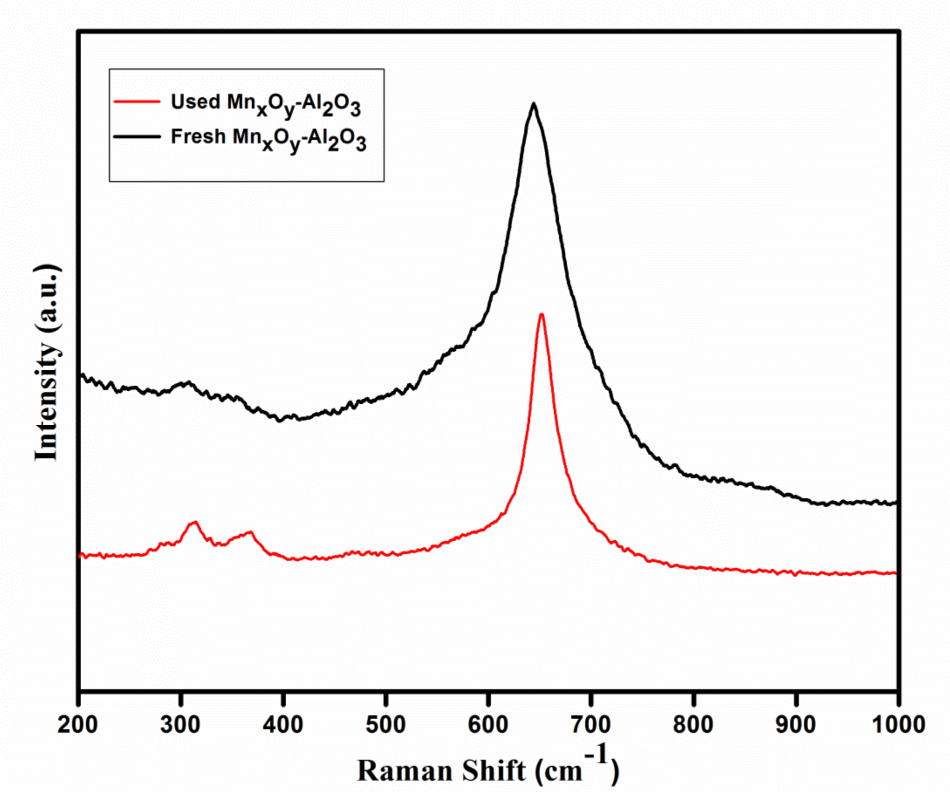

Fig. 5. Raman spectrum of fresh and used Mn_xO_y-Al_2O_3 catalysts.

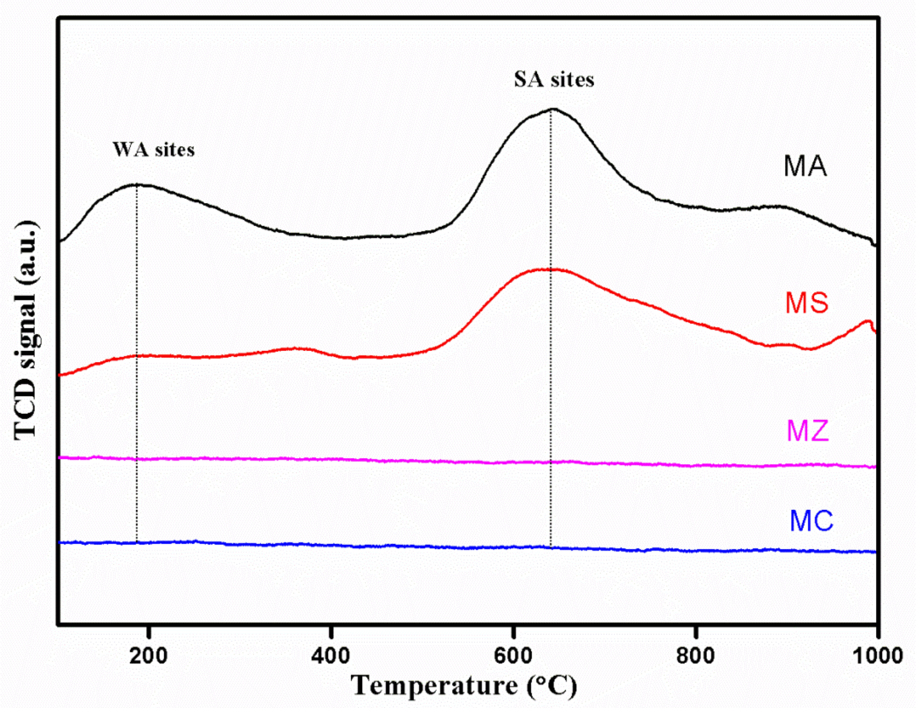

Fig.6. NH_3-Temperature Programmed Desorption profile of as-synthesised catalysts calcined in air at 450 °C

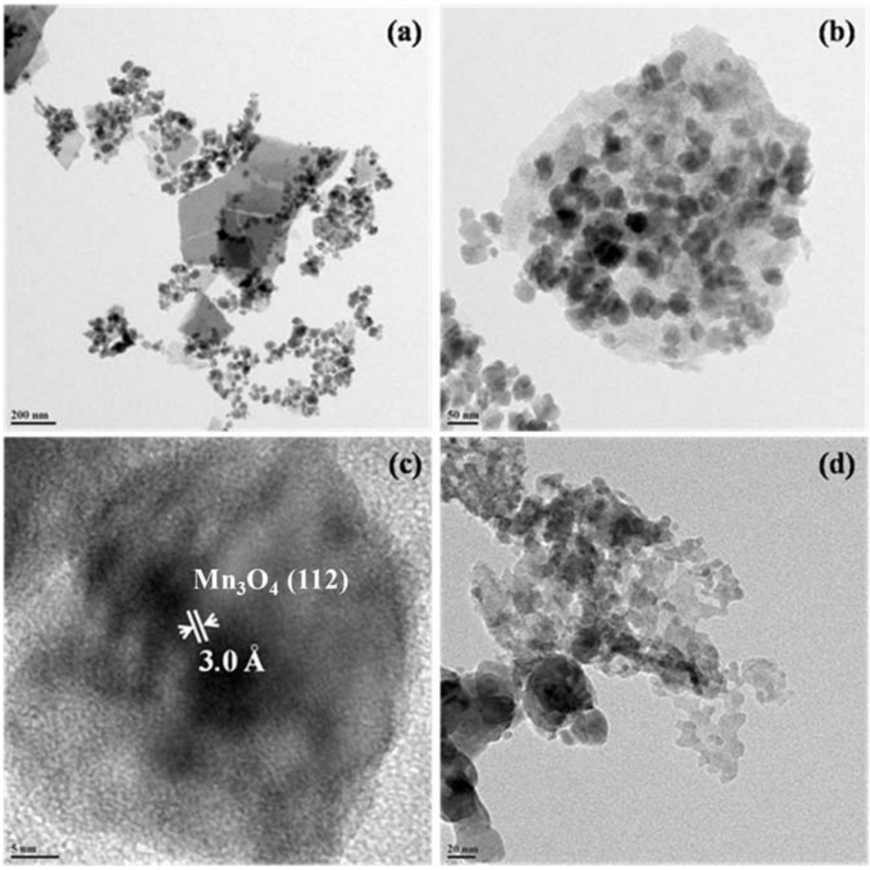

Fig.7. TEM images of Mn_xO_y-Al_2O_3 fresh and spent catalyst (a-c) Fresh Mn_xO_y-Al_2O_3 and (d) Spent Mn_xO_y-Al_2O_3.

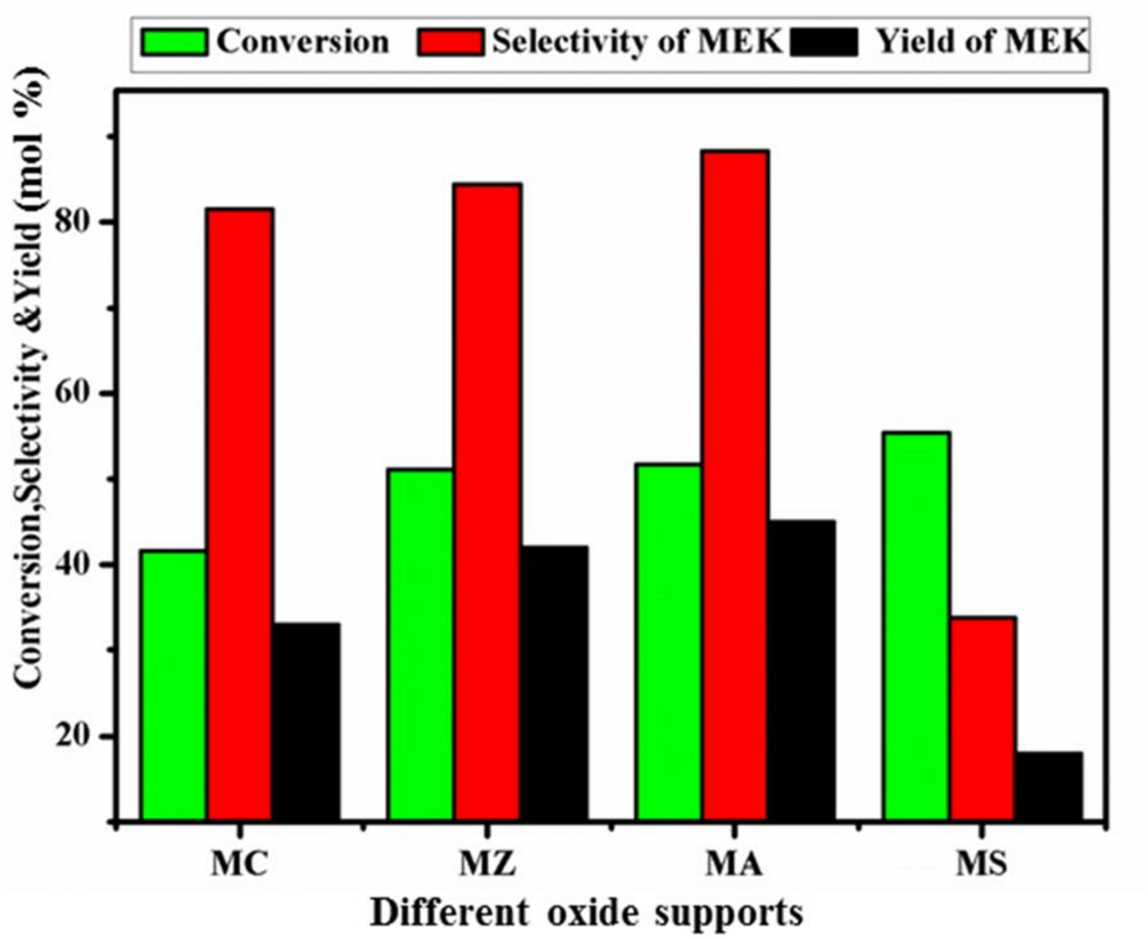

Fig.8. Conversion of 2-butanol and selectivity of MEK at different Mn supported catalysts Reaction conditions: 300 °C, LHSV 1.8 h^{-1} with respect to 2-butanol and GHSV 1200 h^{-1} with respect to oxygen at atmosphere pressure.

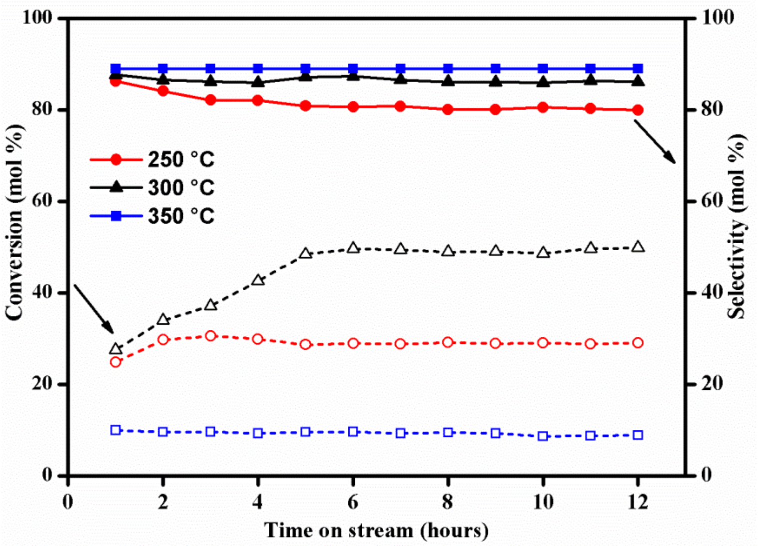

Fig.9. Conversion of 2-butanol and selectivity of MEK at various reaction temperatures over MA. Reaction conditions: LHSV 1.8 h^{-1} with respect to 2-butanol and GHSV 1200 h^{-1} with respect to oxygen at atmosphere pressure.

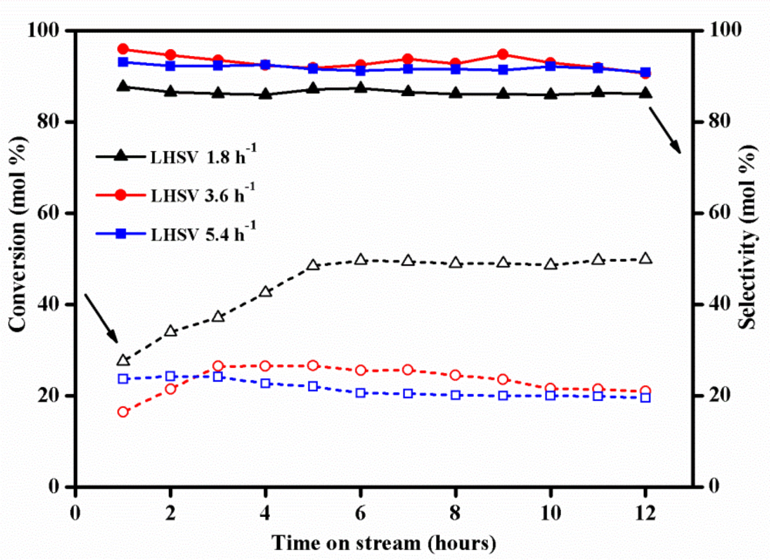

Fig. 10. Conversion of 2-butanol and selectivity of MEK at various 2-butanol flow rates over MA. Reaction conditions: 300 °C, GHSV 1200 h^{-1} with respect to oxygen at atmosphere pressure.

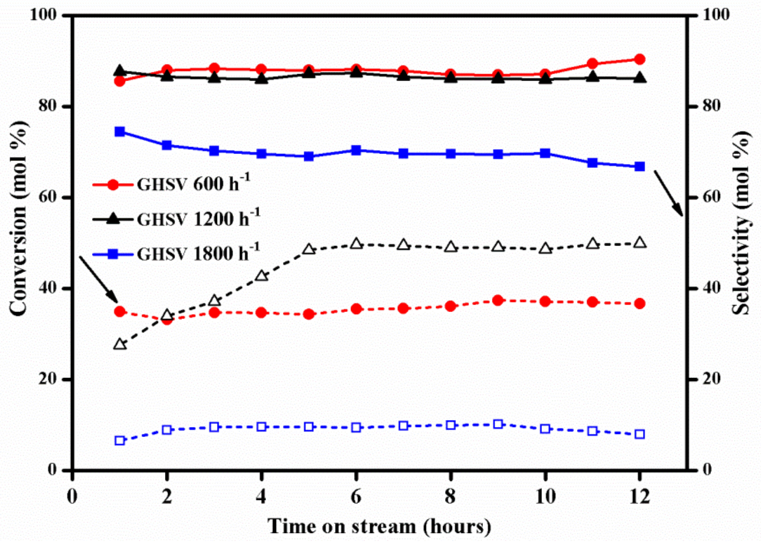

Fig. 11. Conversion of 2-butanol and selectivity of MEK at different oxygen flow rates over MA. Reaction conditions: 300 °C, LHSV 1.8 h^{-1} with respect to 2-butanol at atmosphere pressure.

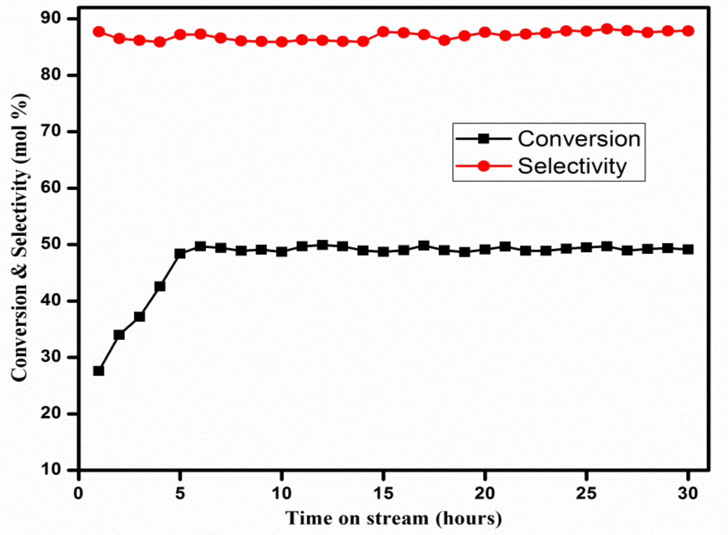

Fig. 12. 30 hours TOS study using MA catalyst. Reaction conditions: 300 °C, LHSV 1.8 h^{-1} with respect to 2-butanol and GHSV 1200 h^{-1} with respect to oxygen at atmosphere pressure.

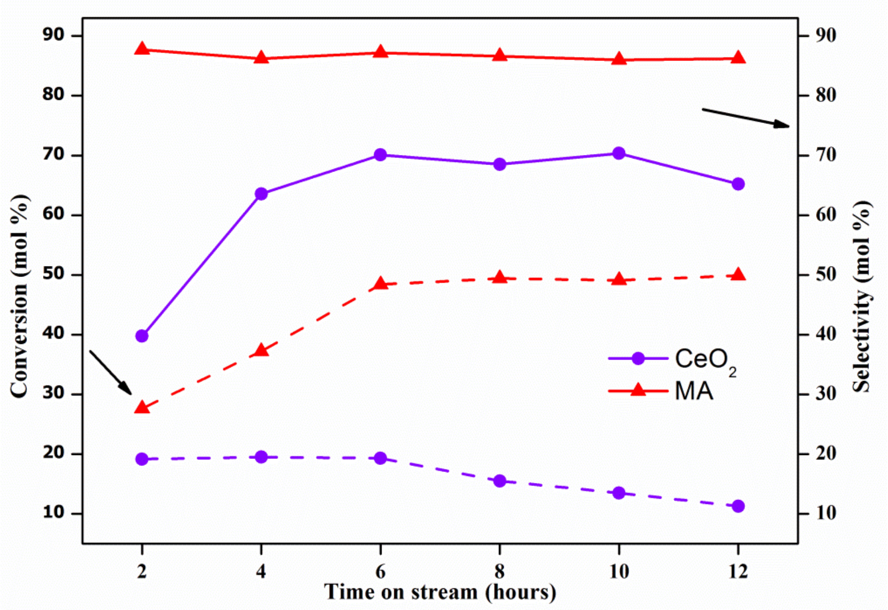

Fig. 13. Conversion of 2-butanol and selectivity of MEK for (i) MA (ii) CeO$_2$. Reaction conditions: 300 °C, LHSV 1.8 h^{-1} with respect to 2-butanol and GHSV 1200 h^{-1} with respect to oxygen at atmosphere pressure.

Table.1. Textural properties of as-synthesised catalysts calcined in air at 450 °C

S.No	Catalysts	Surface area (m^2/g)[a]	Total pore volume (cc/g)[b]	Crystallite size (nm)[c]
1	Mn_xO_y-Al_2O_3	84	0.32	24.7±1.0
2	Mn_xO_y-CeO_2	89	0.18	5.5±1.0
3	Mn_xO_y-ZrO_2	103	0.20	4.6±1.0
4	Mn_xO_y-SiO_2	339	0.25	19.8±1.0

[a] Calculated from BET Surface area analysis. [b] Obtain from BJH analysis. [c] Calculated from PXRD by using Scherer formula

Table. 2. Catalytic activity of Mn_xO_y loaded on different supports

S. No.	Catalysts	Conversion of 2-butanol (mol %)[a]	Selectivity (mol %)				Yield of MEK (mol %)
			MEK	Acetone	CH_3OH	CO_x[b]	
1	Mn_xO_y/CeO_2	41	81	12	02	05	35
2	Mn_xO_y/ZrO_2	51	84	08	07	01	42
3	Mn_xO_y/Al_2O_3	51	88	05	05	02	45
4	Mn_xO_y/SiO_2	55	33	17	14	36	18

[a] Conversion at steady state. Reaction conditions: 300 °C, LHSV 1.8 h^{-1} with respect to 2-butanol and GHSV 1200 h^{-1} with respect to oxygen at atmosphere pressure. [b] CO and CO_2.