

Catalytic oxidation of benzyl alcohol by Al³⁺ doped manganese oxide of the type OMS-2 using molecular oxygen or air

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The oxidation of benzyl alcohol to benzaldehyde using molecular oxygen over manganese oxides of the type OMS-2 is reported. It is observed that Al³⁺-doped OMS-2 has significantly higher activity (~ 58%) as compared to pure OMS-2 (~ 43 %). The catalysts are characterized by XRD, IR, H⁺ ion exchangeability, thermal analysis, BET surface area and temperature programmed desorption (TPD) of ammonia. Catalytic activity depends on the ease of availability of lattice oxygen and presence of Mn⁴⁺/Mn³⁺ redox couple. The activity of the catalysts has been correlated with various physicochemical characteristics, like surface area and concentration of acid sites.

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Catalytic partial oxidation of alcohols to produce aldehydes or ketones is an industrially important process and a fundamental reaction in organic synthesis. Heterogeneous catalytic oxidation using air or molecular oxygen is of increasing importance due to its environmentally friendly nature, unlike the use of H₂O₂, Cr(VI) compounds, etc. which are hazardous. Benzyl alcohol and its derivatives find extensive use in perfume industry. However benzyl alcohol gives different oxidation products over various catalysts, both homogeneous and heterogeneous. Various catalytic systems have been investigated both for liquid phase and vapour phase oxidation of benzyl alcohol. Viswanathan *et al.*^{1,2} have investigated vapour phase oxidation of benzyl alcohol, both in presence and absence of molecular oxygen over perovskite oxides. They observed formation of benzaldehyde and toluene in absence of oxygen, while in presence of oxygen; some benzoic acid and benzyl benzoate were also detected. Catalytic activity up to 50-60% at ~ 400°C has been reported with high selectivity to benzaldehyde. Catalytic activity was found to be inversely proportional to the M-O bond length; bond strength and role of lattice oxygen were

explained on the basis of Langmuir-Hinshelwood mechanism. Similar results were also obtained over copper chromite catalyst³.

Increased catalytic activity for oxidation of benzyl alcohol has been recently reported over ruthenium oxo complex phase transfer catalysts with oxychloride (OCl⁻) as co-oxidant^{4,5} or H₂O₂⁶ and over Pd(II)-hydrotalcite using molecular oxygen⁷. Selective catalytic oxidation with over 90% conversion is reported over ruthenium-copper bifunctional system, also using molecular oxygen as oxidant.

The present investigation reports liquid phase oxidation of benzyl alcohol using air over pure and Al³⁺-doped manganese oxides, mainly of the type OMS-2 (OMS-octahedral molecular sieves). Mn(IV) oxides are of several types and are characterized by tunnels of varying dimensions analogous to zeolites. Unlike zeolites, which are built from silica and alumina tetrahedra, Mn(IV) oxides are built from [MnO₆] octahedra. Depending upon how the octahedra are connected, the manganese oxides with monodirectional channel structures are todorokite (OMS-1, 3×3 channels), cryptomelane (OMS-2, 2×2 channels), pyrolusite (1×1 tunnels), ramsdellite (1×2 channels) and nsutite, which has ramsdellite-pyrolusite intergrowth structure⁸. Suib *et al.*^{9,10} have developed simple synthetic procedures to obtain OMS materials particularly OMS-1⁹, OMS-2¹⁰ and studied their various properties and applications¹¹. It is well-known that the efficiency of oxidation of benzyl alcohol depended on the crystal phase of manganese dioxide used. The oxidation of benzylic alcohols with manganese dioxides generally stops at the carbonyl stage but further oxidation can occur in hot aqueous solutions or in neutral media. On the basis of isotope exchange studies using α , α -dideuteriobenzyl alcohol, it is shown that the rate determining step during catalytic oxidation of benzyl alcohol over active manganese dioxide catalysts, is due to C-H bond cleavage¹². They suggested on the basis of ¹⁸O₂ isotopellabeling experiments that the catalytic activity of OMS materials should be inversely related to Mn-O bond strengths. They further observed that the active OMS-2 material exchanged ¹⁶O of the lattice with ¹⁸O more easily. The present investigation describes high activity of Al³⁺ doped manganese

OMS-2 for selective oxidation of benzyl alcohol. A reaction mechanism is proposed

Experimental

Catalyst synthesis

OMS-2 (sample S) was synthesized by KMnO_4 oxidation of MnSO_4 in nitric acid medium. Thus 0.037 M KMnO_4 was added to hot MnSO_4 (aq., 0.052 M) containing 3 ml of conc. HNO_3 , and refluxed for 24 hrs¹². Similarly, the Al-doped OMS-2 (sample SA) was prepared by adding 0.015 M $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ during the synthesis of OMS-2. The results were compared with reference to a standard pyrolusite sample (sample P) prepared by thermal decomposition of Mn(II) nitrate at 180°C.

Catalyst characterisation

Chemical analysis of the synthesized samples was carried out to obtain the composition of MnO_{1+x} ; % MnO_2 was determined by standard ferrous ammonium sulphate method and % Mn was determined by EDTA method.

The FTIR spectra of the samples were run in the range 400–4000 cm^{-1} on Shimadzu FTIR spectrometer. XRD analysis of the samples was carried out on a Shimadzu labX-100 diffractometer to confirm the phase of the samples synthesized. The thermal analysis of the samples was carried out in air using NETZCH STA 409 PC TG/DSC instrument, at a heating rate of 10°C min^{-1} . Surface areas of the samples were obtained by BET method using SMART SORB 91 surface area analyser. The acid sites of the synthesized samples were determined by temperature programmed desorption, using ammonia as the probe molecule in a continuous flow type reactor.

Catalytic activity studies

Active manganese dioxides are known to undergo H^+ ion exchange when stirred with KI solution in an aprotic solvent such as dimethyl formamide (DMF). This liberates a proportionate amount of I_2 from I. I_2 is then estimated by titration with sodium thiosulphate. The volume of thiosulphate thus consumed, indirectly gives the H^+ ion exchangeability of the active MnO_2 . In the present investigation, therefore, the H^+ ion exchange capacity was determined in DMF medium and is expressed as volumes of thiosulphate consumed. $\text{V S}_2\text{O}_3^{2-}$ increased with the increase in catalytic activity. The H^+ ion

exchange capacity is directly related to the presence of acidic 'OH' groups attached to Mn^{3+} in the host Mn(IV) oxide lattice. The catalytic activity should therefore depend on the presence of active $\text{Mn}^{4+}/\text{Mn}^{3+}$ redox couple. The catalytic activity was evaluated for the chemical oxidation of benzyl alcohol as per the method illustrated in literature¹³, wherein 1 ml of benzyl alcohol was taken in a round-bottomed flask along with 0.5 g catalyst and 10 ml *n*-hexane. These were refluxed for 1 hr in an oil bath and the products were analysed by Chemito 8610 GC using SE-30 column. Only benzaldehyde was detected as the product.

Results and discussion

Chemical analysis of the OMS-2 samples revealed that the chemical composition was $\text{MnO}_{1.86}$ corresponding to average oxidation state of manganese 3.72. These values are close to the values reported by DeGuzman *et al.* for materials obtained using different precursors¹⁰. In comparison, the pyrolusite sample prepared by thermal decomposition of Mn(II) nitrate showed stoichiometric composition of MnO_2 wherein the oxidation state of manganese is +4.

The XRD patterns are shown in Fig. 1 and the corresponding *d* and *h*/*k*/*l* and the lattice parameters

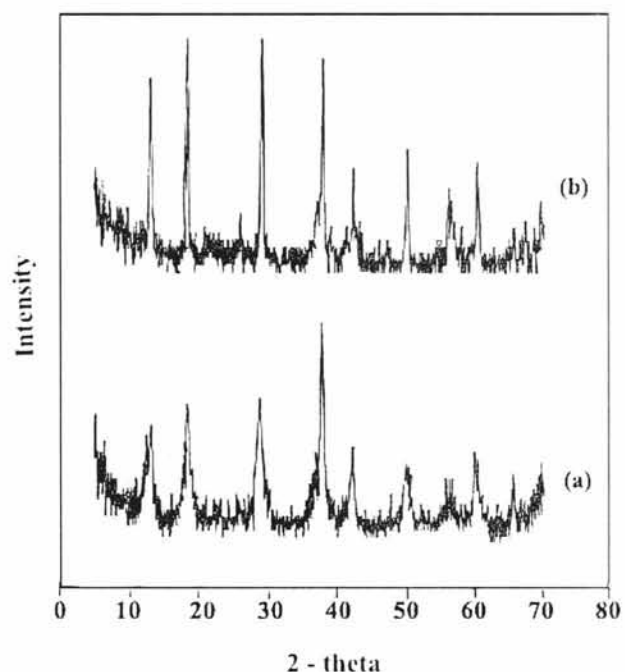


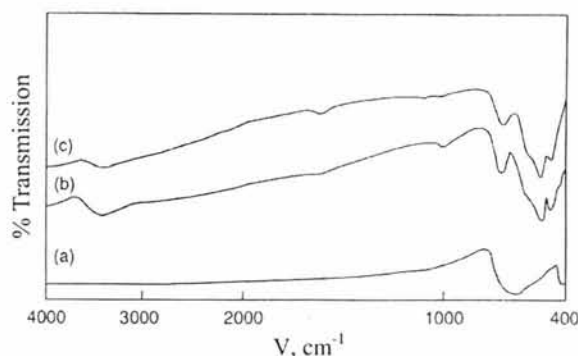
Fig. 1—XRD profiles of the OMS-2 catalysts; (a) Sample S; (b) Sample SA

Table 1—X-ray diffraction data of the OMS-2 catalysts

S		SA		JCPDS 20-908		Ref.14	
<i>d</i>	<i>I/I_o</i>	<i>d</i>	<i>I/I_o</i>	<i>d</i>	<i>I/I_o</i>	<i>d</i>	<i>I/I_o</i>
6.7786	84.24	6.5057	49.31	6.9	90	9.93	s
4.8572	67.98	4.7163	47.77	4.9	80	4.90	vs
3.1186	93.47	3.0406	77.66	3.1	80	3.1	vvs
2.3811	100	2.3482	100	2.39	100	2.39	vvs
2.1373	38.79	2.1206	44.36	2.25	60	2.14	s
1.8227	34.48	1.8025	39.45	1.80	40	1.83	s
1.6274	35.22	1.6209	49.31	1.63	60	1.63	w
1.5406	45.44	1.5234	56.09	1.54	60	1.54	w
1.4210	-	1.4134	24.65	1.35	50	1.42	w
<i>a</i> = <i>b</i> = 9.7584 <i>c</i> = 2.8463		<i>a</i> = <i>b</i> = 9.5683 <i>c</i> = 2.9176		<i>a</i> = <i>b</i> = 9.84 <i>c</i> = 2.86		<i>a</i> = <i>b</i> = 9.81 <i>c</i> = 2.85	

Table 2—Catalytic activity of the Mn(IV) oxides in relation to their physicochemical characteristics

Catalyst	<i>x</i> ' in MnO _x	Crystal phase	BET (m ² /g)	Thermal analysis			Decomp. temp. (°C)	Acidity (mmol g ⁻¹)	V _{S2O3.2} (ml)	% Conversion
				O ₂ loss (%)						
				120-300 (°C)	300-500 (°C)	500-570 (°C)				
S	1.86	Cryptomelane (OMS-2)	77	4.45	4.44	2.4	600	1.66	3.3	43
SA	1.86	Cryptomelane (OMS-2)	84.2	6.15	5.44	2.8	600	2.55	5.9	58
P	2	Pyrolusite	7	2.8	3.29	1.2	597	0.78	0	2

Fig. 2—FTIR profiles of; (a) Pyrolusite (P), (b) OMS-2 (S) and (c) Al³⁺-doped OMS-2 (SA)

calculated on the basis of tetragonal unit cell are given in Table 1. These are in agreement with the literature values¹⁴ and also compare well with JCPDS file 20-908 for cryptomelane KMn₈O₁₆. The peak at *d* ~ 1.80 Å^o, which is a characteristic of cryptomelane OMS-2, is seen to have higher relative intensity in Al-OMS-2 (*I/I_o* = 49%) than in pure OMS-2 (*I/I_o* ~ 35%). It is further seen from Table 1 that the lattice parameter '*c*' for the Al³⁺ doped sample is significantly higher (~ 2.91 Å^o) as compared to the other three cryptomelane samples having an average value of ~ 2.85 Å^o. This suggests enhanced Mn–Mn internuclear distance along the *c* direction, implying slight lattice

dilation following Al³⁺ doping. It could probably be due to lattice substitution of Al³⁺ in place of Mn⁴⁺, the ionic radii in octahedral environments being 67.5 pm and 67.0 pm respectively¹⁵. Figure 2 gives the FTIR profiles of the samples which also showed OMS-2 characteristic bands at ~ 700 cm⁻¹. The prominent absorption peak at 700 cm⁻¹ is generally not seen in pyrolusite and nsutite forms of manganese oxides¹⁶.

Table 2 gives catalytic activity of the samples in relation to their other physico-chemical characteristics, viz, surface area, O₂ loss by TG, acidity levels and volumes of thiosulphate (as a measure of H⁺ ion exchange capacity of the OMS-2). The catalytic activity is expressed in terms of % conversion of benzyl alcohol to benzaldehyde. Al-OMS-2 shows significantly higher conversion (~58 %) as compared to pure OMS-2 (~ 43%). In comparison, the stoichiometric pyrolusite sample is practically inactive for the reaction.

It is known that oxidation of benzyl alcohol follows Mars-van-Krevelen mechanism involving participation of lattice oxygen¹². In such a case, one could hypothesize the higher catalytic activity to be associated with the extent of participation of lattice oxygen. In order to confirm this hypothesis, TG/DSC studies were carried out. Mn(IV) oxides are known to lose (i) bound water and some physisorbed oxygen up to 300°C¹⁷ and thereafter (ii) chemisorbed oxygen and some lattice oxygen up to the temperature of about 500°C. (iii) The

oxygen loss beyond 500°C till the decomposition temperature is more reflective of only lattice oxygen loss^{16,17}. At around 600°C, thermal decomposition of the type $\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3$ occurs¹⁶. In the present case, this decomposition occurs at $\sim 600^\circ\text{C}$. Table 2 gives various TG weight losses in the temperature range from 120-570°C; since beyond this the OMS-2 structure will not be stable. The weight loss between 500-570°C will be pure lattice oxygen loss. The catalytically active Al-OMS-2 sample shows greater oxygen loss in all the three temperature intervals. Therefore, the catalytic activity can be directly related to the rate of oxygen evolution as evident from the TG analysis. The mechanism of oxidation involving anion vacancy generation may thus be explained through loss of lattice oxygen.

It is also evident from Table 2 that the H^+ ion exchange capacity expressed as volumes of thiosulphate consumed, $\text{VS}_2\text{O}_3^{2-}$ increases with increase in catalytic activity. The H^+ ion exchange capacity depends on the presence of acidic 'OH' groups attached to Mn^{3+} in the host Mn(IV) oxide lattice. The lattice dilation associated with the lengthening of Mn-O bond may have enhanced the proton exchangeability of the dioxides. The mobile proton of the MnOOH group could then hop onto the neighbouring Mn^{4+} sites to generate new Mn^{3+} centers; $\text{H}^+ + \text{MnO}_2 \leftrightarrow \text{MnOOH}$. The catalytic activity may therefore, be directly related to the presence of active $\text{Mn}^{4+}/\text{Mn}^{3+}$ redox couple, which may be responsible for the acid centers in the catalysts as evident in the TPD profiles (Fig. 3). Presence of such strong Lewis acid

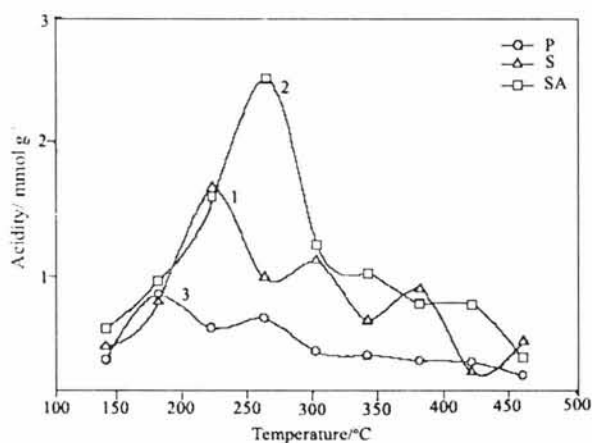
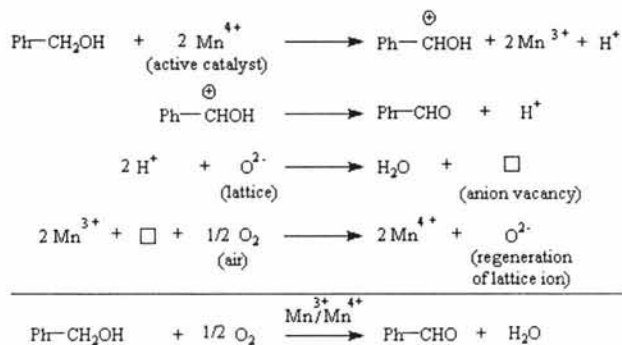


Fig. 3—Temperature programmed desorption of ammonia of OMS-2 catalysts S (curve 1) and SA (curve 2) in relation to pyrolusite (curve 3)



Scheme 1

centers has been in fact suggested by Suib *et al.*¹². It is further seen from Table 2 and the TPD profiles that the Al^{3+} -doped sample has higher concentration of acidic centers, which are also stronger than in the undoped sample as well as in the pyrolusite. Hence the catalytic oxidation of benzyl alcohol may be mediated by: (i) lattice oxygen (ii) $\text{Mn}^{4+}/\text{Mn}^{3+}$ redox couple, as shown in Scheme 1.

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