

Role of Manganese Oxide Octahedral Molecular Sieves in Styrene Epoxidation

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Manganese oxide octahedral molecular sieves having 2×2 tunnel structure (OMS-2) and synthesized by different methods were used for studying styrene oxidation with *tert*-butyl hydroperoxide (TBHP) as the oxidant. The catalytic activity of the as-synthesized OMS-2 materials was investigated. The physical and chemical properties of the OMS-2 materials are related to their activity in styrene oxidation. This particular study emphasizes the acid–base properties and the porous nature of these materials, and their role in styrene oxidation. Results of styrene oxidation reveal that acidity coupled with high porosity play a crucial role in these catalytic reactions. A desired acidity coupled with pore volume found in OMS-2 synthesized by reflux methods (OMS-2_R) and high-temperature methods (OMS-2_{HT}) produces materials with higher styrene conversion and styrene oxide selectivity when compared with OMS-2 synthesized by solvent free (OMS-2_S), microwave (OMS-2_{MW}), or hydrothermal methods (OMS-2_{HY}). Transition metal doped OMS-2 catalysts show better selectivity of styrene oxide when compared to their undoped catalysts.

1. Introduction

Manganese oxides are one of the largest families of porous materials with various structures existing all over the world. There are two major structures: (1) layered materials constructed by edge sharing of MnO_6 octahedra to form sheets with cations such as Na^+ and K^+ and one layer or two layers of H_2O present between any two adjacent sheets and (2) tunnel structures constructed by both edge and corner sharing of MnO_6 octahedra to form 1×1 tunnels (pyrolusite), 1×2 tunnels (Ramsdellite), $1 \times 1/1 \times 2$ intergrown tunnels (Nsutite), 2×2 tunnels (Hollandite or Cryptomelane with Ba^{2+} or K^+ in the tunnel, respectively), 2×3 tunnels (Romanechite), 3×3 (Todorokite), and 2×4 (synthesized in our laboratory).^{1–7} This diversity of manganese oxides in atomic architectures and structures will in turn result in the diversity of manganese oxides in chemical properties and activities for potential applications such as cation exchange, ion and molecule separation, chemical sensor, battery, catalysis, and patterning. OMS materials exhibit various nanoscale tunnel sizes from $2.3 \text{ \AA} \times 2.3 \text{ \AA}$ to $4.6 \text{ \AA} \times 11.5 \text{ \AA}$. Several manganese oxide nanoscale materials of 3×3 (OMS-1), 2×2 (OMS-2), 2×3 (OMS-6), 2×4 (OMS-5), and 1×1 (OMS-7) have been synthesized in our laboratory and reported.^{1–8}

Some of the several catalytic applications of manganese oxide OMS materials that have been reported are partial oxidation of butene,⁹ conversion of ethanol to aldehyde,¹⁰ conversion of 2-propanol to acetone and propylene,¹¹ conversion of ethylbenzene to styrene,¹² conversion of *n*-paraffin to *n*-olefin, oxidative dehydrogenation of cyclohexane,^{13,14} partial oxidation of cycloalkanes,¹⁵ oxidation of alcohols,¹⁶ and partial epoxidation of olefins.¹⁷

In this study the catalytic performances of OMS-2 (Figure 1) materials with respect to styrene oxidation under particular experimental conditions have been investigated. The ingenuity of this research lies in the correlation of styrene epoxidation to the synthesis conditions for the catalyst along with catalyst properties. The study is to determine some properties of the catalyst, which play a significant role in styrene oxidation. No similar studies have previously been published.

2. Experimental Section

2.1. Apparatus. All epoxidation reactions were carried out in a 50-mL one-necked round-bottomed slurry batch reactor with stirring, under reflux, and open to the atmosphere. Only in the case of kinetic measurements was a two-necked slurry batch reactor used with all other conditions remaining the same.

2.2. Synthesis of OMS-2 Catalysts. OMS-2 (2×2) (Figure 1) with the overall composition $\text{KMn}_8\text{O}_{16} \cdot n\text{H}_2\text{O}$ used for the various reactions were prepared by different methods in order to study their catalytic properties with respect to epoxidation reactions. OMS-2_R was synthesized by the reflux method according to literature procedures.¹⁸ In a 500-mL round-bottom flask with condenser, 225 mL of potassium permanganate solution (0.4 M) was added to a mixture of 67.5 mL of manganese sulfate hydrate solution (1.75 M) and 6.8 mL of concentrated nitric acid. The dark brown slurry was refluxed for 24 h, then filtered and washed with distilled deionized water several times until the pH was ~ 7.0 . The catalyst was dried at 120°C overnight before use. Other OMS-2 materials used for the catalytic studies have been synthesized by hydrothermal methods,¹⁸ solvent free methods,⁶ high-temperature methods,¹⁹ and the constant frequency microwave technique.²¹

In the solvent free technique (OMS-2_S), 9.48 g (0.06 mol) of KMnO_4 and 22.05 g (0.09 mol) of $\text{Mn}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ (stoichiometric ratio of $\text{KMnO}_4:\text{Mn}(\text{Ac})_2 \cdot 4\text{H}_2\text{O} = 2:3$) powders were mixed and ground homogeneously in an agate mortar. The mixed powders were then placed in a capped glass bottle and

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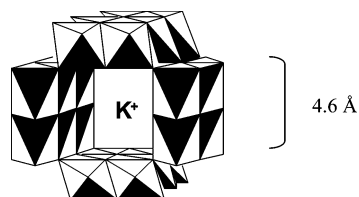


Figure 1. Structure of OMS-2 catalysts.

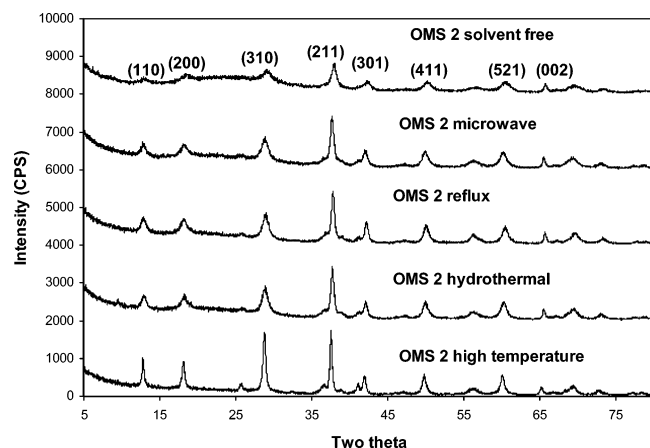


Figure 2. X-ray diffraction of various as-synthesized OMS-2 catalysts.

maintained at 80 °C for 4 h. The resulting black powder was thoroughly washed with distilled deionized water several times to remove any ions which may remain in the product, and finally dried at 80 °C in air overnight. The metal doped solvent free method (M-OMS-2_S, M = Cu, Fe) samples were prepared by mixing $\text{KMnO}_4\text{:Mn}(\text{Ac})_2\cdot 4\text{H}_2\text{O}\text{:metal(II) acetate}$ in the molar ratio of 1:3:0.4 and following the same procedure.

The same precursors used for the solvent free method with the same molar concentrations in aqueous solution were packed in Teflon autoclaves at 100 °C for 24 h for the hydrothermal (OMS-2_{HY}) method.¹⁸ For the microwave method the precursor mixture for the hydrothermal method was poured in microwave safe Teflon autoclaves and placed in a microwave oven at 120 °C for 3 h (OMS-2_{MW}).²¹

The high-temperature OMS-2_{HT} was prepared by a combination of sol-gel and combustion methods except with the source of Mn as manganese nitrate.¹⁹ KNO_3 and $\text{Mn}(\text{NO}_3)_2$ in a molar ratio of 1:5 were dissolved in DDW (solution A). Glycerol and KNO_3 were mixed in a 10:1 molar ratio (solution B). Solution A and solution B were mixed in DDW with vigorous stirring to form a clear solution and then heated to 120 °C to form a gel (usually ~5 h) depending on the DDW amount. The gel was then heated to 250 °C for 2 h to complete the combustion reaction. The black powder was then calcined at 600 °C for 3 h to obtain the final OMS-2_{HT}. Metal doped OMS-2_{HT} (M-OMS-2_{HT}, M = Fe, Ni and Co) were prepared by mixing metal precursors with the $\text{Mn}(\text{NO}_3)_2$ in a 1:5 molar ratio in the initial mixture.

2.3. Characterization Methods. The as-synthesized catalyst was characterized by XRD methods. The XRD patterns were obtained with use of a Scintag 2000 PDS instrument with $\text{Cu K}\alpha$ radiation with a beam voltage of 45 KV and 40 mA beam current. The X-ray patterns of the catalyst were compared with that of actual standard material and were found to be pure (Figure 2). The average oxidation state (AOS) of manganese was obtained with a potentiometric titration method that has already been described (Table 1).²² The average oxidation states of the as-synthesized OMS-2 were obtained by the potentiometric titration method. The catalyst was dissolved in concen-

TABLE 1: Average Oxidation Number of the As-Synthesized OMS-2 Catalysts^a

catalyst	av oxidation state (AOS)
OMS-2 _R	3.90
OMS-2 _{HT}	3.85
OMS-2 _S	3.72
OMS-2 _{MW}	3.92
OMS-2 _{HY}	3.73

^a OMS-2_R refers to OMS-2 synthesized by the reflux method, OMS-2_{HT} that synthesized by the high-temperature method, OMS-2_S that synthesized by the solvent free method, OMS-2_{MW} that synthesized by the microwave method, and OMS-2_{HY} that synthesized by the hydrothermal method.

TABLE 2: Properties of the As-Synthesized OMS-2 Catalysts^a

catalyst	surface area (m ² /g)	crystallite size (nm)	mesopore vol (cm ³ /g)	total pore vol (cm ³ /g)	% mesopore vol
OMS-2 _R	90	18	0.29	0.46	63
OMS-2 _{HT}	13	20	0.027	0.037	73
OMS-2 _S	156	10	0.48	0.52	92
OMS-2 _{MW}	80	18	0.48	0.49	98
OMS-2 _{HY}	70	17	0.22	0.27	85

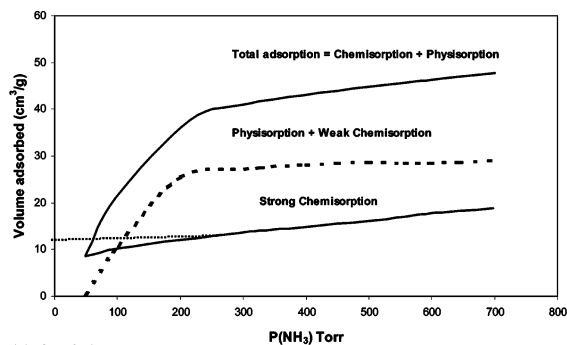
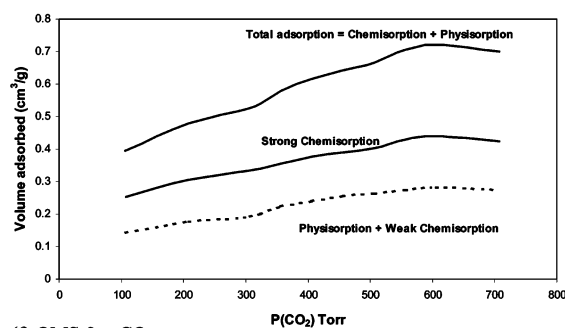
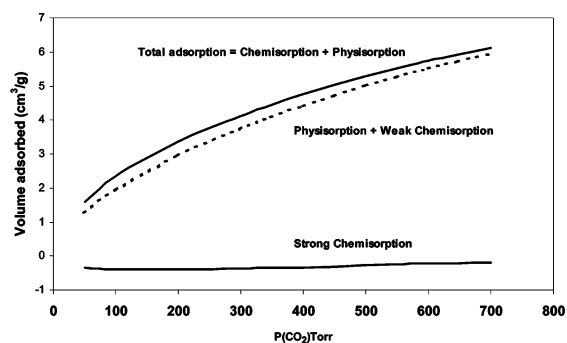
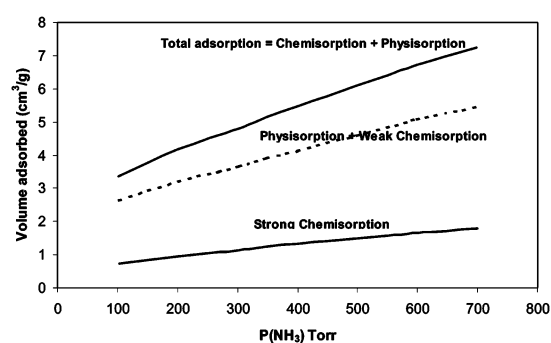
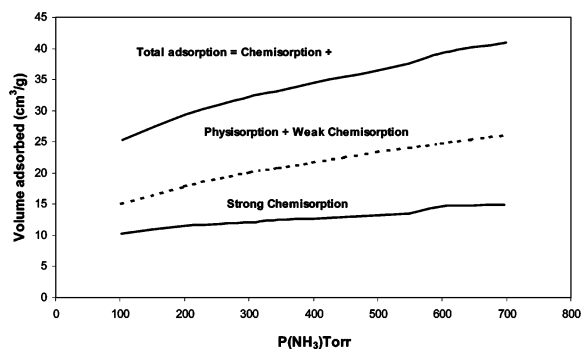
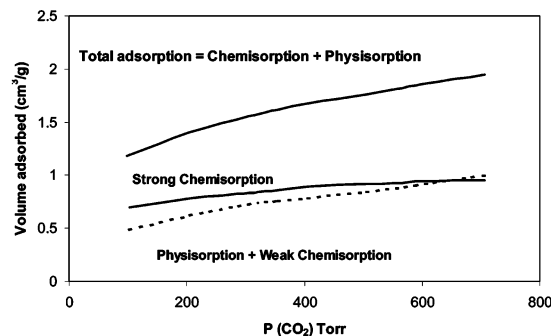
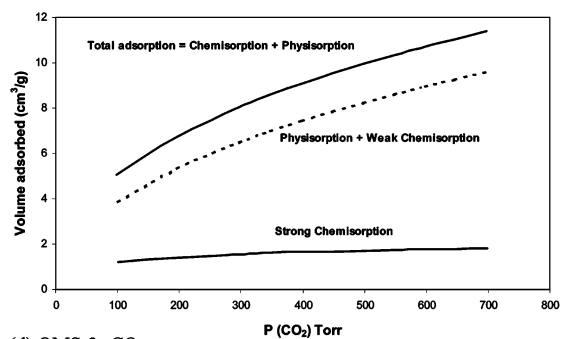
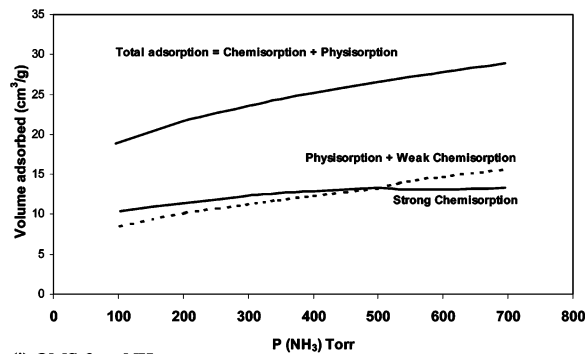
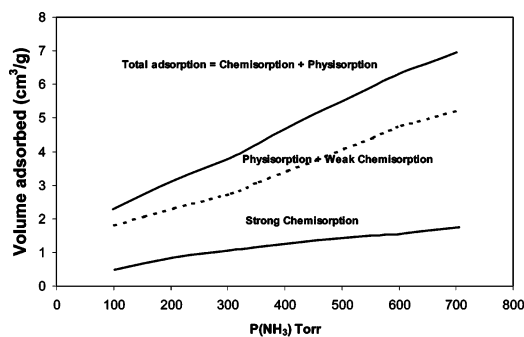
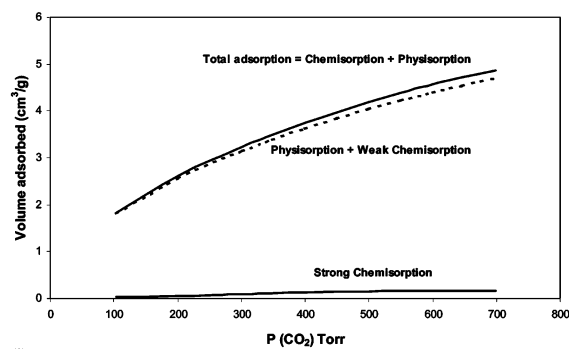
^a OMS-2_R refers to OMS-2 synthesized by the reflux method, OMS-2_{HT} that synthesized by the high-temperature method, OMS-2_S that synthesized by the solvent free method, OMS-2_{MW} that synthesized by the microwave method, and OMS-2_{HY} that synthesized by the hydrothermal method.

trated hydrochloric acid so as to convert all the manganese into Mn^{2+} , and titrated to Mn^{3+} complex by sodium pyrophosphate versus potassium permanganate. This gave the total Mn content, based on which AOS was determined by reducing the solid to Mn^{2+} by ferrous ammonium sulfate and back-titrating the excess Fe^{2+} by the permanganate standard.

A Micromeritics ASAP 2010 instrument was used to measure the surface areas and pore size distributions of the materials (Table 2). Samples were predegassed at 150 °C for about 10 h to remove water and other physically adsorbed species. The N_2 isothermal adsorption and desorption experiments were performed at relative pressures (P/P_0) from 10^{-3} to 0.995 to 0.01, respectively.

Ammonia and carbon dioxide chemisorptions were conducted with a Micromeritics ASAP 2010 instrument (chemisorptions attachment) to quantitatively measure the amount of strong Lewis acidic and basic sites, respectively, in the catalytic materials.²³ Approximately 0.5 g of the fresh material was first evacuated at 150 °C for 2 h to remove the adsorbed species from the surface and reveal the acidic and basic sites. Evacuation was followed by adsorption measurements at 35 °C at gas pressures ranging from 100 to 700 mmHg. After the first adsorption measurement, the catalyst was evacuated at the analysis temperature (35 °C) for 1 h, and then a second adsorption was measured. The first adsorption actually furnishes the total amount of gas adsorption resulting from physisorption, weak chemisorption, and strong chemisorption (Figure 3a–f). The second measurement furnishes the amount of adsorption resulting from physisorption and weak chemisorption. The difference in adsorption between the two measurements is the amount of strong chemisorption. In this method Lewis acid/base sites are mainly measured as the adsorption and desorption of the ammonia and carbon dioxide have been conducted at room temperature.

The second method for estimating the strength of the acidic sites along with the number of acidic sites was done by

(a) OMS-2_R NH₃(f) OMS-2_{HT} CO₂(b) OMS-2_R CO₂(g) Co-OMS-2_{HT} NH₃(c) OMS-2_S NH₃(h) Co-OMS-2_{HT} CO₂(d) OMS-2_S CO₂(i) OMS-2_{MW} NH₃(e) OMS-2_{HT} NH₃(j) OMS-2_{MW} CO₂

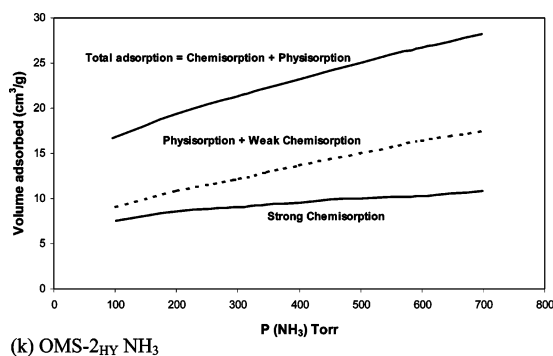
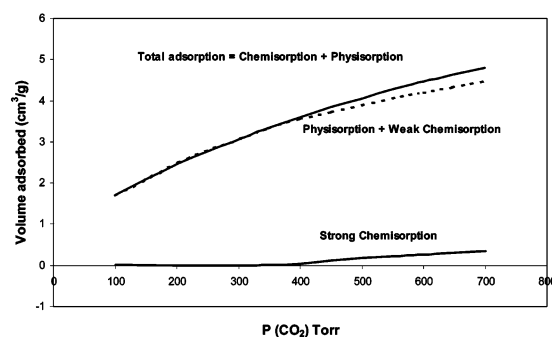
(k) OMS-2_{HY} NH₃(l) OMS-2_{HY} CO₂

Figure 3. (a–l). Chemisorptions of as-synthesized OMS-2 catalysts.

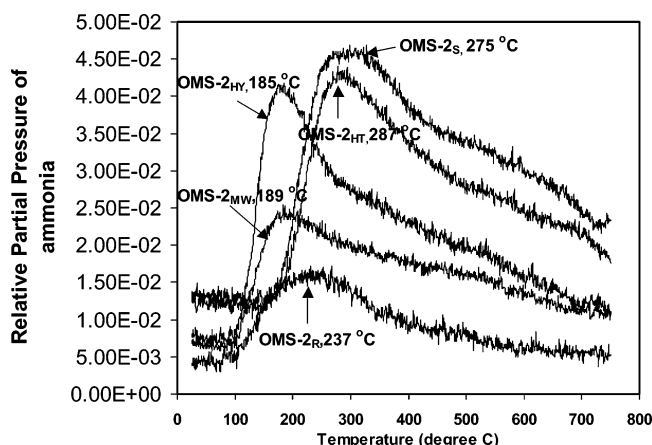


Figure 4. Acidity profiles of OMS-2 materials by ammonia-TPD.

temperature programmed desorption of ammonia (Figure 4). Around 30–40 mg of the sample was loaded in a plug flow quartz reactor. The sample was heated from room temperature to 120 °C under a steady flow of helium at 40 mL/min. This pretreatment was done for 3 h in order to remove any surface moisture. For all catalytic experiments the OMS-2 was preheated at 120 °C. After the pretreatment, ammonia adsorption was done at 80 °C for 3 h by passing 5% ammonia in helium gas mixture at a flow rate of 40 mL/min. The sample was then allowed to cool to room temperature and flushed with a steady flow of helium (flow rate of 40 mL/min) to remove any of the surface physisorbed ammonia. After helium flushing, the sample was heated under a flow of helium from room temperature to 750 °C with a temperature ramp of 10 deg/min. The desorbed ammonia was monitored with a MKS-UTI PPT quadrupole mass spectrometer. This method gives an indication of both Lewis and Brønsted acid sites and strengths.

2.4. Styrene Oxidation Studies. All epoxidation reactions were carried out in a 50-mL one-necked round-bottomed slurry batch reactor with stirring and under reflux and open to the atmosphere, only in the case of time-dependent product distribution measurements, a two-necked slurry batch reactor was used with all other conditions remaining the same. All experiments were carried out at 60 °C, open to the atmosphere, in a round-bottomed flask equipped with a condenser and a magnetic stirrer and placed in an isothermal paraffin oil bath. A typical reaction mixture was composed of the following: catalyst (50 mg); styrene (5 mmol); TBHP (5 mmol; 70 wt % in water); and acetonitrile (15 mL as solvent). The reactions were carried out for 24 h. All catalysts were pretreated at ~100–120 °C overnight before being used in the reaction. For all product analysis purposes, cyclohexylbenzene was used as an internal standard.

Gas chromatography–mass spectrometry (GC-MS) was used for the identification and the quantification of the reaction

products. The analyses were done in an HP 5890 series II gas chromatograph coupled with an HP 5971 mass detector. The column used was an HP-1 (nonpolar cross-linked siloxane) with dimensions of 12.5 m × 0.2 mm × 0.33 μm.

3. Results

The X-ray diffraction patterns (Figure 2) of the as-synthesized OMS-2 catalysts show that the catalysts are in their pure phase and the peaks match the JCPDS database. The average oxidation states (AOS) of the various as-synthesized OMS-2 catalysts did not show a wide variation in values but ranged between 3.72 and 3.92 (Table 1).

Isotherms of ammonia and carbon dioxide on the various OMS-2 materials are shown in Figure 3a–l. Extrapolation of the total adsorption isotherms to zero pressure produces the quantitative estimates of the total acidic and basic sites of the catalysts. Since the oxidation of styrene may be driven by both physisorbed and chemisorbed sites the total value of the active sites related to acidic/basic sites may have some implication in the reaction mechanism. The amounts of the Lewis acidic and Lewis basic sites at STP have been quantified based on the chemisorption measurements done at room temperature (Table 3). The results show a wide variation in values for the same family of manganese oxide molecular sieve catalysts. From the ammonia/carbon dioxide chemisorption results, total Lewis acidity due to chemisorption is maximum in OMS-2_S and least in OMS-2_{HT}. However, if the percentage of the Lewis acid sites due to chemisorption alone is calculated based on the total Lewis acidity then OMS-2_{MW} has the maximum percentage of Lewis acidic sites and OMS-2_{HT} has the minimum.

The temperature programmed desorption (TPD) of ammonia data (Figure 4) show that all OMS-2 materials have acidic sites distributed on their surfaces. The strongest acidic strengths are found to be associated with OMS-2_{HT} and in OMS-2_S. All the OMS-2 materials have at least one strong acidic (which can be both Lewis/Brønsted acidity) site.

From a catalytic study point of view, the surface areas, crystallite sizes, and pore volumes with special emphasis on the mesopore volume have been tabulated in Table 2. Surface area, mesopore volume, and crystallite size can all be affected by temperature, time of exposure, and the nature of the synthesis. As can be seen from Table 2, OMS-2 synthesized by various methods show a wide variation in surface area. However, the surface areas have a good correlation with the temperatures of synthesis. OMS-2_{HT} synthesized at 600 °C bear the lowest surface area while OMS-2_S synthesized at 80 °C displays the highest surface area. The higher the temperature of synthesis is the lower the expected surface area is. Table 1 gives the average oxidation states (AOS) of the as-synthesized OMS-2 catalysts. The average oxidation states (AOS) of the various as-synthesized

TABLE 3: Chemisorption Values of Lewis Acidity/Lewis Basicity in the OMS-2 Sample^a

	OMS-2 _R	OMS-2 _{HT}	OMS-2 _S	OMS-2 _{MW}	OMS-2 _{HY}
total Lewis acidity (mmol/g) STP	0.7	0.06	0.98	0.75	0.63
Lewis acidity due to chemisorption only (mmol/g) STP	0.4	0.02	0.4	0.44	0.3
total Lewis basicity (mmol/g) STP	0.05	0.02	0.2	0.08	0.07

^a OMS-2_R refers to OMS-2 synthesized by the reflux method, OMS-2_{HT} that synthesized by the high-temperature method, OMS-2_S that synthesized by the solvent free method, OMS-2_{MW} that synthesized by the microwave method, and OMS-2_{HY} that synthesized by the hydrothermal method

TABLE 4: Conversion of Styrene by Various As-Synthesized OMS-2 Catalysts^{a,b}

catalyst	conversion (%)	selectivity (%)		
		benzaldehyde	styrene oxide	phenyl acetaldehyde
OMS-2 _R	48	69	31	<i>c</i>
OMS-2 _{HT}	39	58	33	9
OMS-2 _S	21	75	25	<i>c</i>
OMS-2 _{MW}	26	68	32	<i>c</i>
OMS-2 _{HY}	25	69	31	<i>c</i>

^a OMS-2_R refers to OMS-2 synthesized by the reflux method, OMS-2_{HT} that synthesized by the high-temperature method, OMS-2_S that synthesized by the solvent free method, OMS-2_{MW} that synthesized by the microwave method, and OMS-2_{HY} that synthesized by the hydrothermal method. ^b Reaction conditions: 5 mmol of styrene + 5 mmol of TBHP + 50 mg of as-synthesized OMS-2 in a stirred batch reactor under reflux for 24 h at 60 °C. ^c Product not detected.

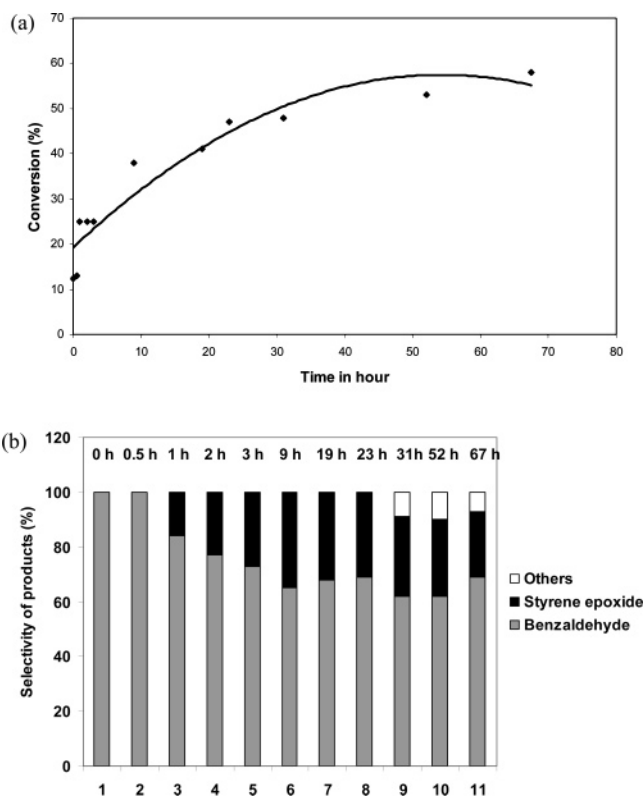
TABLE 5: Conversion of Styrene by Doped OMS-2_{HT} and OMS-2_S Catalysts^a

catalyst	conversion (%)	selectivity (%)		
		benzaldehyde	styrene oxide	phenyl acetaldehyde
OMS-2 _S	21	75	25	<i>b</i>
Fe-OMS-2 _S	22	69	31	<i>b</i>
Cu-OMS-2 _S	23	66	34	<i>b</i>
OMS-2 _{HT}	39	58	33	9
Fe-OMS-2 _{HT}	34	63	37	<i>b</i>
Ni-OMS-2 _{HT}	31	58	42	<i>b</i>
Co-OMS-2 _{HT}	39	50	50	<i>b</i>

^a Reaction conditions: 5 mmol of styrene + 5 mmol of TBHP + 50 mg of as-synthesized OMS-2 in a stirred batch reactor under reflux for 24 h at 60 °C. ^b Product not detected.

OMS-2 catalysts did not show a wide variation in values but ranged between 3.72 and 3.92. The pore volume with special emphasis on the mesopore volume has been given, as mesopore volume comprises more than half of the total pore volume, which may have an effect in catalytic activity especially where two reactants are interacting on the catalyst surface. The highest mesopore volumes are shared by OMS-2_S and OMS-2_{MW}, followed by OMS-2_{HY}, OMS-2_R, and OMS-2_S. The higher the amount of mesopore volume is the lower the styrene conversion for the OMS-2 materials is (Table 4).

The oxidation of styrene was studied on a variety of as-synthesized OMS-2 materials with different properties (Tables 1–3, Figures 3 and 4). The results of the styrene oxidation are shown in Tables 4 and 5. As can be seen from the results, OMS-2_R shows the best results with respect to conversion while OMS-2_{HT} shows a better selectivity with respect to styrene epoxide but also shows the formation of benzene acetaldehyde. OMS-2_S shows very poor conversion of styrene with highest selectivity to benzaldehyde. Comparing the results of doped OMS-2_S and doped OMS-2_{HT} in Table 5, the conversion of styrene is maximum in undoped OMS-2_{HT} and Co-OMS-2_{HT}. Cu-OMS-2_S showed better conversion of styrene and styrene epoxide selectivity compared to undoped OMS-2_S.

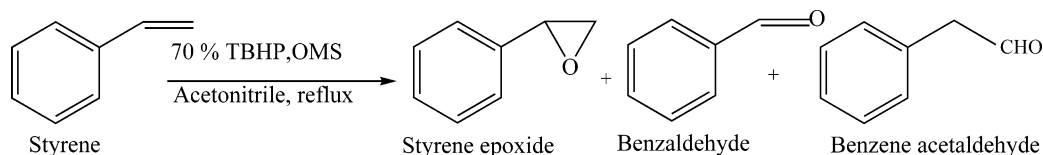
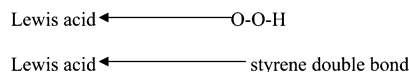
**Figure 5.** Time dependent (a) conversion and (b) distribution of styrene oxidation products by OMS-2_R as catalyst.

The time dependent product distribution (Figure 5a,b) of styrene oxidation furnishes us the result that benzaldehyde is formed from the beginning of the reaction time with styrene epoxide formation after a short induction period of ~1 h. The benzaldehyde formation reaches a decline with time with the appearance of extra products, which may be from styrene epoxide as the selectivity of styrene epoxide gradually decreases. The selectivity of benzaldehyde seems to reach a reasonable steady value around 52 h.

4. Discussion

To search for factors that contribute to the optimization of conversion and selectivity of styrene epoxide (based on reaction Scheme 1) several kinds of the same family of manganese oxide octahedral molecular sieves as catalysts were tried for the styrene oxidation reaction. The size of the reactants that participate in the reaction has also been taken into consideration. Styrene has dimensions of ~6 Å and TBHP has dimensions of ~4.0 Å.

Frequently solid catalysts containing transition metals are called redox catalysts, although they may act in reality as solid Lewis acids.²⁴ Literature evidence²⁵ shows that a Lewis acid can catalyze oxidation reactions by forming acid–base adducts either with the substrate or with the oxidizing agent (in our case TBHP), enhancing their reactivity and thereby acting as catalysts for the oxidation. From ammonia and carbon dioxide chemi-

SCHEME 1: Reaction of Styrene Oxidation by OMS-2 Catalysts**SCHEME 2: Lewis Acids as Oxidation Catalysts**

sorption results (Figure 3a–l), all OMS-2 catalysts have strong Lewis acid sites also accompanied by Lewis basicity. The physisorption (reversible) curve in Figure 3a–l may be attributed to weak acidic/basic sites. The interaction of weakly basic unsaturated hydrocarbons (i.e., styrene) with transition metal ions can be considered as weak base (hydrocarbon/styrene)–strong acid interactions or weak base–weak acid interactions.^{26–28} The selectivity of the products mainly depends on the activity and the accessibility of the transition metal (in our case Mn or the doped metal in the OMS-2 material). Acid–base adducts with the oxidizing agent or the substrate may be represented as Scheme 2.

A Lewis base is any molecule or ion that can form a new coordinate covalent bond by donating a pair of electrons. The term *base* is ambiguous. A nucleophile is a Lewis base. Lewis bases do not require hydroxide ion as an electron acceptor. For the different OMS-2 catalysts, isotherms of CO₂ (Figure 3a–l) chemisorption suggest that the physisorption isotherm profile is similar to the total adsorption isotherm, thus eliminating the fact that Lewis basic sites are not inside the bulk of the catalyst but on the surface. However, for OMS-2_{HT} (Figure 3f) and in cobalt doped OMS-2_{HT} (Figure 3h) the physisorption isotherm profile in the CO₂ chemisorptions isotherms graphs are not necessarily similar to the total adsorption profile, indicating that different Lewis basic sites may be present in the system as compared to other OMS-2 materials, which may be a contributing factor for the better selectivity in styrene epoxide in these oxidation reactions (Tables 4 and 5). The ammonia chemisorption isotherms do not display chemisorption or physisorption isotherm profiles that are very similar to the total isotherm profile, which can thereby be interpreted that there are different acidic sites on OMS-2 materials that contribute to physisorbed (surface acidity) or chemisorbed (bulk acidity) ammonia species.

The temperature programmed desorption (TPD) of ammonia profiles (Figure 4) distinctly suggests that OMS-2_{HT} and OMS-2_S have stronger acid sites compared to OMS-2_R, OMS-2_{HY}, and OMS-2_{MW}. A higher temperature of desorption of ammonia is related to stronger acid sites. OMS-2_{HT} and OMS-2_S have the highest strengths of acid sites followed by OMS-2_R > OMS-2_{MW} > OMS-2_{HY}. Although the total acidity from chemisorption results of OMS-2_{HT} was found to be low, from the TPD–ammonia results strong acid sites are associated with this material. On the basis of the acid–base adduct theory the performance of OMS-2_{HT} materials (possessing low surface area and low pore volume) for styrene oxidation is then well justified.

The adsorption and activation of hydrocarbons in oxidation processes can be regarded as acid–base interactions. Therefore, the total pore volume and pore size of all the as-synthesized OMS-2 catalysts along with Lewis acidity also have roles to play. All the as-synthesized OMS-2 catalysts have a micropore tunnel opening of $4.6 \times 4.6 \text{ \AA}^2$, which leaves a diagonal length of 6.9 \AA . On the basis of the micropore tunnel dimensions, the

reactants can have easy access to the tunnel. Mesopores form 92% of the total pore volume in OMS-2_S, 98% of the total pore volume in OMS-2_{MW}, 83% of the total pore volume in OMS-2_{HY} as compared to 62% in OMS-2_R, and 74% of the total pore volume in OMS-2_{HT}. These mesopores may be responsible for the difference in behavior between the various catalysts although they belong to the same family. Although 74% of the total pore volume in OMS-2_{HT} is contributed by the mesopore volume, the absolute number corresponding to total pore volume is very low (Table 2).

Easy access of the oxidant (TBHP) to the active metallic sites (strong Lewis acidic sites) of the OMS-2_S, OMS-2_{MW}, and OMS-2_{HY} catalysts may result in rapid decomposition of the oxidant leading to loss in activity and also to loss of selectivity. In other words, physical adsorption of TBHP and styrene in strongly acidic mesopore sites may cause an increased rate of reaction, where the action is that of bringing close a large volume of reactants on the Lewis acidic active sites of the catalyst surface, rather than forming a chemisorbed intermediate among the reactants.

In such cases too strong adsorption of styrene/TBHP on the oxidation acid sites will result in a large volume contact of reactants on the pore walls with corresponding loss of selectivity. A similar argument is also valid for the styrene oxidation performance of OMS-2_{MW} and OMS-2_{HY}. The Mn precursor in all three of the samples may also have a role to play in the poor styrene oxidation conversions by OMS-2_S, OMS-2_{MW}, and OMS-2_{HY} (Table 4). Although the OMS-2 catalysts were prepared by different methods, for OMS-2_S, OMS-2_{MW}, and OMS-2_{HY} similar molar ratios of precursors were used under different synthesis conditions. Surprisingly, all three have similar acidic properties (Table 3) and similar catalytic results.

The results of oxidation by OMS-2_S, OMS-2_{MW}, and OMS-2_{HY}, coupled with their acidity/basicity properties, and pore volume suggest that strong Lewis acid sites alone may not be solely responsible for higher styrene conversions. Instead there may be some synergetic effects due to several parameters. In fact, styrene conversions are substantially lower in the case of OMS-2_S, OMS-2_{MW}, and OMS-2_{HY} when compared to OMS-2_R and OMS-2_{HT}. OMS-2_S shows the least percent conversion and lowest percent selectivity to oxide. In the cases of OMS-2_S, OMS-2_{MW}, and OMS-2_{HY} bubbles were observed in the reaction mixture whenever TBHP was added at the beginning of the reaction. This is only possible if there is a fast decomposition of TBHP on coming in contact with the as-synthesized OMS-2 catalysts. No such observations were seen when TBHP was added to reaction mixtures containing OMS-2_R and OMS-2_{HT}. After reaction, when the reaction mixture was tested with peroxide test strips, a qualitative estimate of the presence of undecomposed peroxide was obtained in the cases of reactions with OMS-2_R and OMS-2_{HT}. No peroxide was seen in cases of reactions with OMS-2_S, OMS-2_{MW}, and OMS-2_{HY}. This gives sufficient evidence that the conversion with product distribution may well be related to chemical/physical properties of the catalysts although they all belong to the same OMS-2 family. This also gives evidence

that an intimate association between the catalyst and TBHP actually drives the reaction to higher conversions.

Comparing the surface areas of OMS-2 materials with the results of styrene conversion, oxidation of styrene by as-synthesized OMS-2 may not be a reaction controlled by surface area. OMS-2_{HT} with very low surface area (13 m²/g) displayed reasonably good (39%) conversion of styrene when compared with very high (156 m²/g) surface area OMS-2_S. This suggests that chemical properties of these materials are responsible for differences in oxidation results rather than surface area effects.

From the time dependent conversion and product distribution studies (Figure 4), the initial rate of reaction is rapid with 12% conversion even at the very beginning of the reaction, suggesting that small forces such as physisorption initially have a role to play. Styrene epoxide forms only after an initial induction period of 1 h, which suggests that chemisorption of the reactants on the OMS-2_R catalyst forming a chemisorbed intermediate has a role to play in the formation of product. The product distribution and conversion with time also show that the behavior is typical of a catalytic system. The constant formation of benzaldehyde with a decrease of epoxide selectivity and formation of side products with time suggests that two competitive mechanisms may have a role to play in the formation of products. The benzaldehyde selectivity is not altered very much as compared to epoxide selectivity with time, suggesting that there may be competitive reactions.

The early formation of benzaldehyde in the product distribution studies also demonstrates that benzaldehyde may be formed by an oxidative cleavage of a double bond mechanism and not from epoxide as there was no formation of styrene epoxide in the initial time of the reaction. An intimate intermediate between TBHP (nucleophile) and OMS-2 (electrophile) with the styrene as a substrate may lead to the formation of benzaldehyde. Reactions with styrene oxide as the starting material with TBHP and under similar reaction conditions did not show any benzaldehyde. As a result, benzaldehyde is not formed from styrene oxide but formed through a different route. Solid Lewis acids have high affinity toward the π bond of the double bond in styrene. This may lead to the electrophilicity of styrene for TBHP and thereby cleavage of the double bond. The other product that may be formed is formaldehyde and it is not observed in GS-MS analysis.

Another observation in the behavior of the metal-doped OMS-2 samples is that the conversion of styrene has not changed substantially but the selectivity to the products has changed remarkably (Table 5). In these OMS catalysts the metallic cations act as the Lewis acid sites, and the basic sites are surface O²⁻ or OH⁻ species. Higher valent incompletely coordinated metal ions or anionic vacancies on oxide surfaces can also act as acidic sites. The influence of the acid–base properties on the selectivity for oxidation reactions has been reported in the literature.^{29–33} The generation of added acidic sites by the metal ions leads to better selectivity to styrene oxide in the metal doped OMS-2 catalysts. M–O bonding might have changed substantially if Mn is being replaced by M (M = Fe, Co, Ni, or Cu). A change in the bond strength will also result in a change in the Lewis acidic/basic properties, which has led to substantial change in product selectivity.

5. Conclusions

The behavior of OMS-2 catalyzed styrene oxidation is very much dependent on the type of OMS-2 generated by different synthetic methods. Different synthetic routes for OMS-2 have different physical and chemical properties, which in turn show

different catalytic activity on the same substrate. On the basis of the catalytic activity besides the physical characteristics of the catalyst, the acid–base properties along with the catalyst pore volumes have a dominant role to play in the oxidation via acid–base adduct formation. Although surface areas, particle sizes, and average oxidation states of the Mn in the OMS-2 have been considered for catalytic activity, they by themselves cannot explain the observed results of styrene oxidation.

As a result, OMS-2_R materials having the desired acidic properties and pore volumes show a good conversion of styrene and higher selectivity to styrene oxide when compared with the rest of the catalysts. Similarly OMS-2_{HT} systems with low pore volumes but with good acid strengths (based on ammonia-TPD results) show good catalytic behavior and selectivity to styrene oxide. OMS-2_S, OMS-2_{MW}, and OMS-2_{HY} catalysts synthesized with similar precursors having high acidity (based on chemisorption results) and high pore volumes have been unable to give comparable styrene conversions and selectivity to styrene oxide. The acidic properties coupled with pore volumes of the OMS-2 materials play a crucial role in styrene oxidation. Transition metals doped in OMS-2_S and OMS-2_{HT} may not have increased styrene conversion but have higher selectivity for styrene oxide when compared to undoped counterparts. Transition metals may alter the acidic properties of these OMS-2 materials leading to higher selectivity to styrene oxide.

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