

An Infrared Spectroscopic Study of the Adsorption and Surface Reactions of Oxygen on Supported Manganese Oxides

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Received September 1, 1983; revised January 24, 1984

An ir study of the MnO_x supported on various supports, TiO_2 anatase, γ -alumina and CeO_2 has been performed to complement previously reported evidence that sharp differences in catalytic properties were effected by the contributions of the support. Adsorption studies of O_2 on these catalysts at 573 K indicate that hydrated surfaces are allowed to continue to exist partially and that more highly oxidized manganese oxyhydroxide overlayers are produced. The adsorption and desorption of the oxygen is reversible and appears to take place at carbonate and hydroxyl sites.

INTRODUCTION

The application of ir spectroscopy to the study of surfaces has brought major insights into surface chemistry. Areas in which new information can be gained include the structure of adsorbed species, the mode of interaction between the surface and the adsorbed species, surface structures and the nature of adsorption sites (1-3).

The surface structure of oxides always consists of a combination of oxygen anions, hydroxyl groups, and cations associated with anion vacancies. These cations, exposed through anion vacancies to the gas phase, are suitable "sites" for the adsorption of reactants. Oxygen anions are also the chemisorption centers of substances, either in the adsorption of oxygenated compounds and in oxidative chemisorptions.

However, the chemistry of the oxide surfaces is, to a large extent, dominated by the quantity and type of both physically and chemically adsorbed water, and the efforts

to explicitly determine the number of such groups, their dissociative behavior and the nature of their interaction with the components of the surrounding medium have been enormous in the past decades.

We have recently reported the preparation of highly dispersed manganese oxide overlayers on a series of supports with widely different physical and chemical properties for their study as novel oxide-hydrogenation catalysts (4). We have also showed that the deep oxidation properties of these catalysts—as exemplified by the oxidation of carbon monoxide—are a strong function of the support used (5).

The ir characterization of the formation and transformation of surface compounds during dehydroxylation and reactive chemisorption of O_2 on the series of TiO_2 (anatase)-, Al_2O_3 (type γ)-, and CeO_2 -supported manganese oxide(s) catalysts is the purpose of this work. The ir experiments were planned to complement and assist in interpreting the reaction studies presented in previous publications (4-6).

The adsorption of oxygen on supported MnO_x is expected to produce surface cation-oxygen bonds with dissimilar thermal and chemical stability as well as the formation of surface species related to the surface

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hydroxyls and residual carbonates arising from contamination by atmospheric CO_2 .

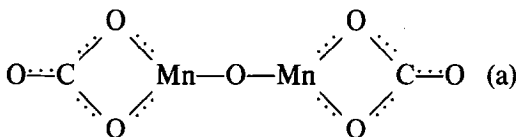
No ir studies on the hydroxylation and dehydroxylation of manganese oxides are available. On pure manganese dioxide the dissociative chemisorption of oxygen produces bands at 1120, 1070, 1040, and 980 cm^{-1} with different stabilities (7) and a spectral range of the stretching vibrations of the surface cation–oxygen bonds which vary from single to double bonds.

Adsorption studies of CO and CO_2 on TiO_2 , Al_2O_3 , CeO_2 , and bulk manganese oxides indicate that there are difficulties for unambiguous band assignments in the spectra of supported manganese oxide catalysts. Several causes are identified among other possible sources of ambiguity:

(a) Carbonates on anatase have absorption maxima at 1580 and 1320 cm^{-1} ; carbonates on MnO_2 also show maxima at 1580 – 1500 and 1320 – 1300 cm^{-1} (8).

(b) Formates and carboxylates give bands at 1580 – 1560 and 1400 – 1350 cm^{-1} . They decompose at $\sim 553\text{ K}$ on some oxides, to give CO and H_2O . Bands at $\sim 2900\text{ cm}^{-1}$ are also observed upon heating when formates are present on the surfaces, and thus they can be identified unambiguously. The simultaneous presence of carboxylates can never be ruled out if only ir spectroscopy is used, though.

(c) The structure,



“dimer carbonate,” is known to absorb ir radiation at 1420 – 1470 cm^{-1} (9). It forms at low temperatures and does not decompose at 573 K . Free carbonates also give an absorption band at 1440 cm^{-1} .

(d) Bicarbonates also absorb at 1440 cm^{-1} . The species are removable upon evacuation above 473 K (10) and thus thermal treatments can be used as an identification tool.

APPARATUS AND PROCEDURES

For the ir studies samples of $\text{MnO}_x/\text{TiO}_2$, $\text{MnO}_x/\text{Al}_2\text{O}_3$, and $\text{MnO}_x/\text{CeO}_2$ were ground in an agate mortar and sieved through a 325 mesh to minimize radiation scattering effects (11). The finely dispersed powders were pressed into pellets by using a hardened stainless-steel die (12 mm diameter). Wafers were pressed between two disks of Mylar; the average pellet thickness was 10 mg/cm^2 , and an average pressure of 5 MPa/cm^2 was required to have a good mechanical resistance.

The ir measurements were carried out in portable vacuum quartz cells with water-cooled NaCl windows (12). The cells could be heated to 773 K for pretreatments and measurements. A set of two twin interconnected cells were placed in the front and back beams of a Nicolet 7199 FT–ir spectrometer. The cells were attached to a conventional high-vacuum system equipped with a manifold for gas flow which permitted performing all pretreatments and measurements *in situ*.

The catalyst wafers were placed only in the front cell. Spectra were always recorded for both the sample and blank cells and were subsequently ratioed, yielding the spectrum of the catalyst and adsorbed species on the surface. The bandwidth used was adjusted to cover the spectral range 4000 – 700 cm^{-1} , at a resolution of 4 cm^{-1} .

Table 1 summarizes the experimental procedure that was used to study the adsorption and desorption of oxygen on each catalyst of the series at different temperatures and pressures. Spectra were routinely taken and stored after each change of conditions. Purified U.H.P. oxygen and helium (The Matheson Co.) were used.

Each specimen was pretreated with 100 cc/min of pure oxygen at 473 K for 4 h; then the temperature was raised to 573 K and held for 2 h to uniformly oxidize the surface and eliminate adsorbed water. This pretreatment is identical to the one used during

TABLE 1

Experimental Procedure for O₂ Adsorption on Catalyst Specimens Outgassed at 573 K

Treatment ^a	Gas composition	Time (h)	Pressure (Torr)	Temperature (K)
Pretreatment	Pure O ₂ (100 cc/min)	4	760	473
	Pure O ₂ (100 cc/min)	2	760	573
	Pure O ₂ (100 cc/min)	Overnight	760	Cooled to RT
Evacuation	—	2	2 × 10 ⁻⁵	573
	—	½	2 × 10 ⁻⁵	573 ^c
	—	½	2 × 10 ⁻⁵	473 ^c
	—	½	2 × 10 ⁻⁵	373 ^c
	—	½	2 × 10 ⁻⁵	RT ^c
Adsorption of O ₂	Pure O ₂ (static)	½	0.2	RT ^c
	Pure O ₂ (static)	½	1	RT ^c
	Pure O ₂ (static)	½	5	RT ^c
	Pure O ₂ (static)	½	15	RT ^c
	Pure O ₂ (static)	½	40	RT ^c
	Pure O ₂ (static)	½	100	RT ^c
	Pure O ₂ (static)	¾ ^b	100	373
	Pure O ₂ (static)	¾ ^b	100	473
	Pure O ₂ (static)	¾ ^b	100	573
Desorption of O ₂	—	2	100	Cooled to RT
	—	Fast	1	RT
	—	Fast	0.02	RT
	—	1	4 × 10 ⁻⁵	RT
	—	¾ ^b	4 × 10 ⁻⁵	373
	—	¾ ^b	4 × 10 ⁻⁵	473
	—	¾ ^b	4 × 10 ⁻⁵	573
Cooling after O ₂ desorption	—	½	2 × 10 ⁻⁵	573 ^c
	—	½	2 × 10 ⁻⁵	473 ^c
	—	½	2 × 10 ⁻⁵	373 ^c
	—	½	2 × 10 ⁻⁵	RT ^c

^a Spectra taken after each change of experimental conditions.^b Heating time = 30 min.^c Used as a reference spectrum for absorbance measurements.

reaction experiments with the catalyst series (6).

After cooling to room temperature — RT— under flowing oxygen (100 cc/min), the catalyst wafer was heated to 573 K under high vacuum —HV— (10⁻⁵ Torr) and held for 2 h at that temperature. The specimen was cooled under evacuation and reference spectra were taken at 573, 473, 373, and 298 K. These reference spectra represent the surface under “clean” conditions and were subtracted from absorbance spectra in the adsorption and desorption experiments using background subtraction mathematical routines. Thus, surface

changes due to adsorbed species are greatly enhanced.

To study the adsorption and desorption of O₂ at different pressures and temperatures the gas was adsorbed at increasing pressures of 1, 5, 15, 40, and 100 Torr at RT, and then the temperature was increased to 373, 473, and 573 K and held for three-quarters of an hour at each value under a pressure of 100 Torr of pure O₂. Spectra were taken 15 min after each pressure or temperature change.

The sample was then cooled to RT under 100 Torr of O₂ and evacuated for 1 h (final vacuum = 8 × 10⁻⁵ Torr) to desorb the

weakly held oxygen. Spectra were taken every 15 min during this procedure. It was then heated to 373, 473, and 573 K under high vacuum to follow the desorption of oxygen at those temperatures. Each heating step was made at ~ 3 K/min.

ESR was also used as a complementary tool for band assignments (6).

RESULTS AND DISCUSSION

MnO_x/TiO_2

The untreated MnO_x/TiO_2 had a large amount of adsorbed molecular water, together with different carbonate and bicarbonate impurities from contamination by atmospheric CO_2 .

The preoxidized sample (outgassed at 573 K for 2 h, to 2×10^{-5} Torr) showed a moderate dehydration, with bands that are typical of residual carbonate species (located at 1578, 1560, 1541, 1525, 1488, 1412, 1378, and 1349 cm^{-1}) (7), the bending mode of molecular water coordinated to surface cations (1617 cm^{-1}) and bending vibrations of surface OH groups ($1265, 1177\text{ cm}^{-1}$) (Fig. 1). After cooling to 373 K under HV new carbonate bands appeared at 1685 and 1367 cm^{-1} , and the band at 1267 cm^{-1} increased in intensity. After cooling to RT under high vacuum the small bands were also observed at 1695, 1653, and 1617 cm^{-1} . At high temperatures an appreciable proportion of the surface molecules is thermally excited into the higher vibrational states. Weaker bands are then likely to be observed for some vibrational modes of structures still present on the catalyst surface (1) (Fig. 1).

The adsorption of pure O_2 at room temperature and pressures from 10^{-5} to 10^2 Torr caused an increase of the coordinated water band (1620 cm^{-1}) and a transformation of residual bidentate carbonates to their geminal form (appearance of a new band at 1222 cm^{-1} ; increase of the 1689, 1585, and 1419 cm^{-1} bands). This can be explained recalling that geminal carbonates are more stable at low temperatures (13). The coordination to metal cations by disso-

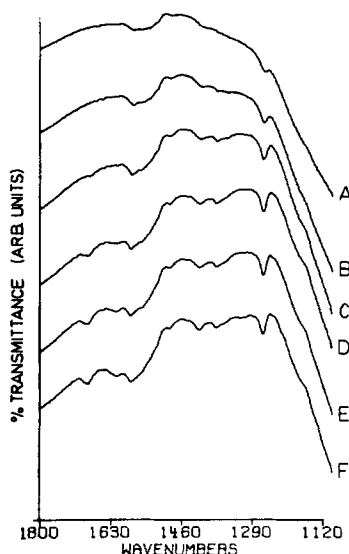
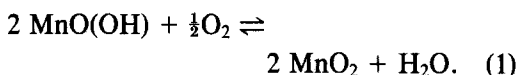


FIG. 1. Infrared spectra of the carbonate region after oxygen adsorption on MnO_x/TiO_2 , preoxidized at 573 K, and evacuated to 2×10^{-5} Torr (HV): (A) Evacuated cell, HV, 573 K; (B) evacuated cell, HV, 473 K; (C) evacuated cell, HV, 373 K; (D) evacuated cell, HV, RT; oxygen adsorption; (E) 1 Torr, RT; (F) 100 Torr, RT.

ciatively chemisorbed oxygen explains the enhancement of molecular water bands, e.g.,



When the adsorption temperature was increased to 373 K (under 100 Torr O_2) the spectrum changed slightly (Fig. 2). The increase in temperature reversed the transformation of the geminal bidentate carbonates to the bridged type, with an increase in the intensity of the bands at 1570–1500 and $1377\text{--}1364\text{ cm}^{-1}$ (2). When the adsorption temperature was raised to 573 K almost all bands lost intensity, and the initial spectrum (i.e., before chemisorption of O_2) was restored (Figs. 1 and 2).

After cooling to RT (in 100 Torr of O_2) the ir cells were evacuated to 8×10^{-5} Torr to observe the desorption of oxygen and oxygenated surface species. The cooling process revealed that the formation of water coordinated to cations (Eq. (1)) upon

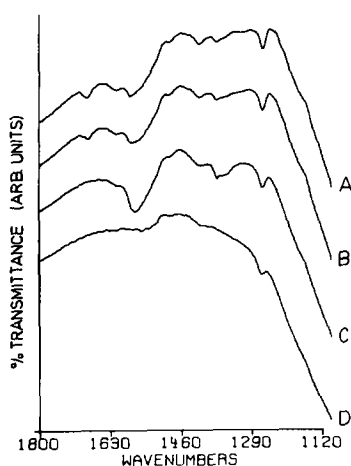


Fig. 2. Infrared spectra of the carbonate region after oxygen adsorption on $\text{MnO}_x/\text{TiO}_2$: (A) 100 Torr, RT; (B) 100 Torr, 373 K; (C) 100 Torr, 473 K; (D) 100 Torr, 573 K.

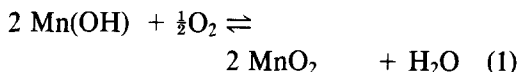
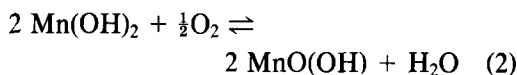
exposure to O_2 at high temperatures had been substantial (band at 1619 cm^{-1}). The evacuation at 373 K under high vacuum removed this water and again caused the transformation of geminal to bridged carbonates (decrease in the bands at 1685 and 1619 cm^{-1}). After evacuation at 473 K the bands at 1685 and 1619 cm^{-1} disappeared.

When compared with the spectrum of adsorbed O_2 (100 Torr) at 473 K, it is apparent that some decomposition of surface contaminants was caused by the evacuation; bands due to carbonate groups, at 1580–1500 and $1380\text{--}1350\text{ cm}^{-1}$ had then much less intensity (Fig. 3). Further heating *in vacuo* at 573 K essentially recovered the original spectrum. No strong indication of irreversibility or transformation of bicarbonate to carbonate surface residual structures can be extracted from this adsorption/desorption sequence.

The experimental results offer direct evidence about the surface and adsorbate transformations that follow the preoxidation pretreatment and the oxidation reactions on $\text{MnO}_x/\text{TiO}_2$:

—The untreated catalyst surface is covered with adsorbed water and carbonate contaminants. The initial contamination by atmospheric CO_2 to give various surface

carbonate species is only partially reversed after the preoxidation at 573 K in 20% O_2 –80% He. The pretreatment drives off physisorbed and structural water,



but some coordinated water may remain on the surface as a ligand of exposed cations (Fig. 1).

—The adsorption of oxygen at various pressures (from 10^{-5} to 10^2 Torr) and temperatures (from RT to 573 K) causes an increase in the amount of coordinated water, probably via a direct oxidation of the manganese oxyhydroxide overlayer (Eq. (1)), but the process appears to be reversed upon further cooling and evacuation. The water molecules held to the surface as coordinated ligands can form the oxyhydroxide again.

—The adsorbed O_2 does not interact with the residual surface carbonates at low temperatures. At higher temperatures the residual geminal bidentate carbonates (b) are transformed into the more stable bridged bidentate carbonates (c)

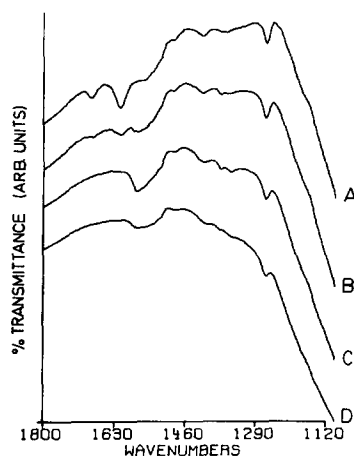
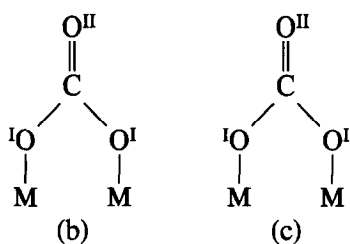


Fig. 3. Infrared spectra of the carbonate region after oxygen desorption on $\text{MnO}_x/\text{TiO}_2$: (A) 8×10^{-5} Torr (HV), RT; (B) HV, 373 K; (C) HV, 473 K; (D) HV, 573 K.



This process occurred at each increase of temperature above 373 K, and it is not due to the presence or absence of adsorbate gases.

The transmittance of this catalyst, MnO_x/TiO_2 , was very low below 1100 cm^{-1} and so the formation of metal–oxygen bonds could not be observed. It can be speculated that oxygen undergoes a dissociative adsorption to replenish anion vacancies caused by the evacuation at 573 K and 10^{-5} Torr.

MnO_x/CeO_2

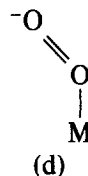
Cerium dioxide belongs to the group of oxides that can be reduced *in vacuo* at moderate to high temperatures. Supported CeO_2 on silica and alumina, calcined and evacuated at 773 K, has paramagnetic surface defects (Ce^{3+}) and on this nonstoichiometric cerium oxygen adsorption takes place by electron transfer from quasi-free electrons (14–17) with formation of O_2^- species at 77 K (18). No spectral ir data for oxygen adsorption on CeO_2 is available in the literature, but it is known that on evacuated specimens the exposure to this gas produces reversible changes (19).

The untreated catalyst had a large amount of physisorbed water (zero transmittance in the region $3800\text{--}3000\text{ cm}^{-1}$), cation coordinated H_2O (band at 1608 cm^{-1}), adsorbed oxygen (peroxo bands, $M\text{--}O\text{--}O\text{--}M$, or O_2^- , at 809 cm^{-1}), surface OH groups (bending vibrations at 1295 and 1148 cm^{-1}), and a large amount of residual carbonates, bicarbonates, and/or carboxylates of different types, with bands located at 1758 , 1730 , 1687 , 1551 , 1517 , 1375 , 1092 , 842 , and 825 cm^{-1} .

The preoxidized sample (outgassed at 573 K for 2 h) showed a fair dehydration,

with bands that are typical of strong hydrogen bond interactions (3652 , 3628 , and 3505 cm^{-1}) (20), very small amounts of coordinated water (band at 1626 cm^{-1}), bending vibrations of surface OH groups (1284 and 1140 cm^{-1}), and residual carbonates, bicarbonates, and carboxylates (bands at 1591 , 1559 , 1518 , 1464 , 1365 , 1352 , 1222 , 1068 , 1024 , and 833 cm^{-1}). The bands from the CeO_2 -support lattice are very weak (1160 and 970 cm^{-1}) (21) (Figs. 4 and 5).

After adsorption of oxygen at room temperature and pressures from 10^{-5} to 10^2 Torr all the cation–oxygen bands remained unchanged with the exception of a new $M\text{--}O$ band, located at 1123 cm^{-1} that appeared after exposure to 15 Torr of the gas. This band has been assigned by Nakamoto (22) to a superoxo bond, in molecular oxygen complexes, and can be represented as



When the adsorption temperature was increased to 373 K (under 100 Torr O_2) this superoxo vibration disappeared and a new $M\text{--}O$ bond was formed (band at 952 cm^{-1}).

The adsorption of 100 Torr of pure O_2 at higher temperatures caused significant modifications on the catalyst: After heating to 473 K and then 573 K new metal–oxygen bonds were formed (new bands appeared at 956 , 949 , and 903 cm^{-1} —symmetric peroxo bonds) while others were broken (the bands at 1123 and 992 cm^{-1} disappeared) (Fig. 4). The adsorption of O_2 at higher temperatures caused also a thermal activation of the residual carbonates on the surface, with strong interaction with the surface OH groups, as shown in various spectral regions: the surface hydroxyl bands located at 3652 , 3628 , and 3505 cm^{-1} shifted to 3642 , 3626 , and 3499 cm^{-1} , respectively, after the ir cell was heated to 473 K (100 Torr O_2); their shape became entirely different.

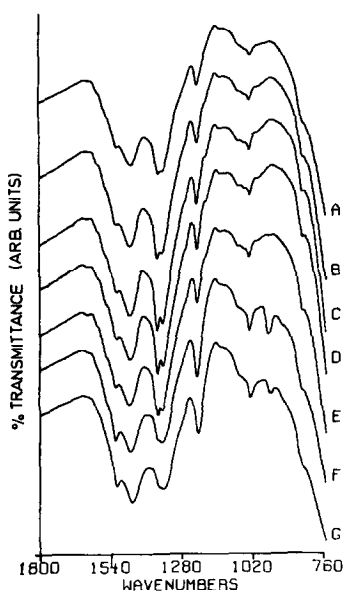


FIG. 4. Infrared spectra of the carbonate region after oxygen adsorption on $\text{MnO}_x/\text{CeO}_2$, preoxidized at 573 K, and evacuated to 2×10^{-5} Torr (HV): (A) Evacuated cell, HV, 473 K; (B) evacuated cell, HV, 373 K; (C) evacuated cell, HV, RT; oxygen adsorption: (D) 100 Torr, RT; (E) 100 Torr, 373 K; (F) 100 Torr, 473 K; (G) 100 Torr, 573 K.

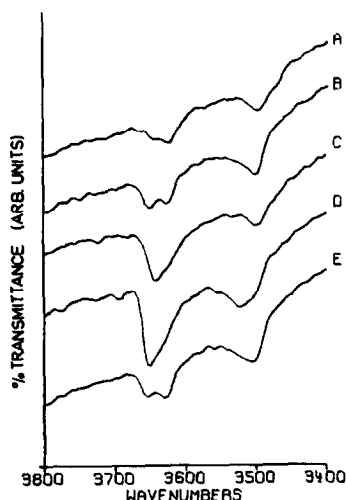


FIG. 5. Infrared spectra of the hydroxyl region upon adsorption and desorption of oxygen on $\text{MnO}_x/\text{CeO}_2$: (A) Evacuated cell, HV, 473 K; (B) evacuated cell, HV, RT; oxygen adsorption: (C) 100 Torr, 473 K; (D) 100 Torr, cell cooled to RT; oxygen desorption; (E) HV, RT.

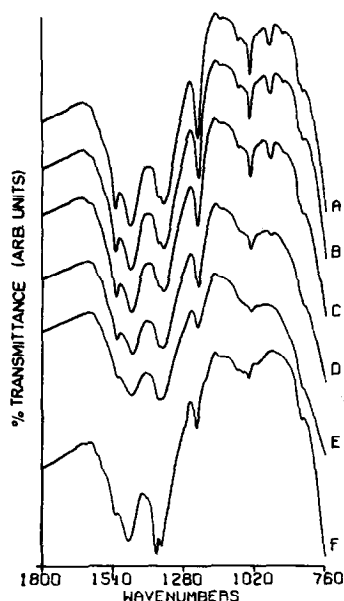
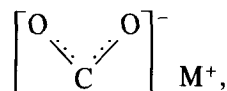


FIG. 6. Infrared spectra of the carbonate region upon oxygen adsorption and desorption on $\text{MnO}_x/\text{CeO}_2$: Oxygen adsorption, (A) 100 Torr, after it was cooled to RT; oxygen desorption: (B) 2×10^{-5} Torr (HV), RT; (C) HV, 373 K; (D) HV, 473 K; (E) HV, 573 K; (F) cooled to RT under HV.

A comparison of the spectra of $\text{MnO}_x/\text{CeO}_2$ before and after the exposure to O_2 at higher temperatures (Figs. 4C and 6A), both taken at RT, shows that cation-coordinated water (band at 3657 cm^{-1}), geminal bidentate carbonates (bands at 1222, 1033, and 834 cm^{-1}), monodentate carbonates (bands at ~ 1470 , 1349, 1073, and 849 cm^{-1}), bridged bidentate carbonates (bands at ~ 1527 and 1284 cm^{-1}), symmetric peroxo metal-oxygen bonds (bands at 962, 954, and 909 cm^{-1}), and bridged M-O-O-M structures (bands at 799 cm^{-1}) were either formed or increased their amount on the surface after the adsorption or oxygen.

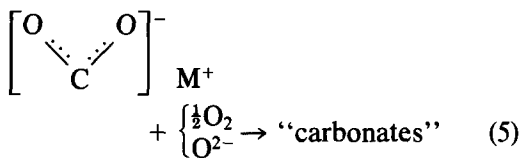
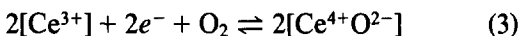
Surface carboxylates



with bands at $\sim 1369\text{ cm}^{-1}$, were greatly reduced, and might be the precursors of the newly formed carbonates. In addition, metal-oxygen species with different bond orders (23) may be postulated to have

formed during the adsorption of the gas (bands at 1073, 1052, and 1033 cm^{-1}). The tiny bands at ~ 1592 and 1570 cm^{-1} also suggest the formation of bicarbonates during the adsorption process (Fig. 6).

The chemistry of these changes can be written as a combination of several processes, in addition to those described by Eqs. (1) and (2):



The desorption of O_2 (4×10^{-5} Torr) at increasing temperatures revealed that all the surface rearrangements that followed the adsorption of the gas were reversible. After increasing the temperature to 573 K under HV the spectrum became identical to the initial one (Figs. 4 and 6). In addition, the evacuation sequence showed that the surface rearrangements that followed the adsorption and desorption of O_2 are activated processes and require temperatures around or above 473 K to proceed at appreciable rates.

The experimental results indicate that the untreated catalyst is heavily contaminated by atmospheric CO_2 that forms stable carbonates on its surface. This contamination is only partially reversed after preoxidation treatments in 20% O_2 –80% He at 573 K. The preoxidation treatment drives off physisorbed and structural water (Eqs. (1) and (2)) that may remain on the surface as a coordinated ligand of surface cations (Figs. 4–6).

The adsorption of oxygen at room temperature and at various pressures (from 10^{-5} to 10^2 Torr) is accompanied with production of superoxides, O_2^- . These superoxides decompose at 373 K, but new metal–oxygen bonds of various bond or-

ders are formed: symmetric peroxides, bridging $\text{M}-\text{O}-\text{O}-\text{M}$ and single to double $\text{M}-\text{O}$ bonds. The adsorption of O_2 (100 Torr) at temperatures between 373 and 573 K is a reactive chemisorption that involves a direct oxidation of the manganese oxyhydroxide overlayer, the oxidation of the support, CeO_2 , with replenishment of the anion vacancies created by the evacuation at 573 K (6), and the thermal activation of the carbonate residues with transformation of carboxylates into carbonates.

The process is described by Eqs. (1) to (6). The surface carbonates can react with coordinated water to give bicarbonates when the temperature is lowered to 298 K (Eq. (6)), and it is possible that coordinated water may restore some of the manganese oxyhydroxide overlayer via the reverse of Eq. (1). The adsorption of oxygen does not cause irreversible chemical changes on the catalyst surface, but the surface transformations that occur after adsorption of O_2 at high temperatures are reversed only after evacuation to 2×10^{-5} Torr above 473 K, i.e., these surface reactions have high activation energies.

$\text{MnO}_x/\text{Al}_2\text{O}_3$

The adsorption of oxygen on $\text{MnO}_x/\text{Al}_2\text{O}_3$ was studied to analyze the formation of surface species associated with the OH groups and residual carbonates from the usual contamination by atmospheric CO_2 as well as the formation of surface cation–oxygen bonds. Oxidation at 473 K in 20% O_2 –80% He (100 cc/min) removed geminal bidentate carbonates (bands above 1650 cm^{-1}) as well as some molecular and coordinated water. The catalyst surface was only moderately free of residual impurities after 2 h of oxidation at 573 K using the same gas mixture.

The transmittance of the catalyst below 1100 cm^{-1} and at 3400 – 3000 cm^{-1} was nearly zero. Thus, some molecular water was still present on the surface and no direct observation of metal–oxygen was then possible (Fig. 7).

Additional (weak) spectral bands indi-

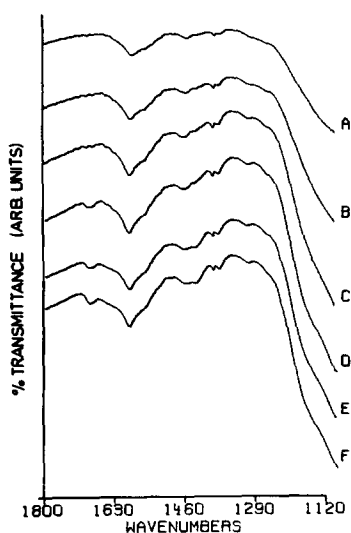
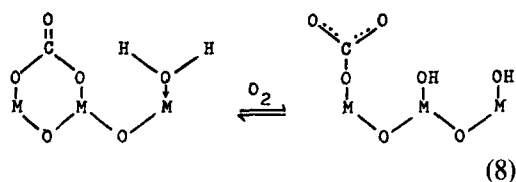


FIG. 7. Infrared spectra of the carbonate region after oxygen adsorption on $\text{MnO}_x/\text{Al}_2\text{O}_3$, preoxidized at 573 K, and evacuated to 2×10^{-5} Torr (HV): (A) Evacuated cell, HV, 573 K; (B) Evacuated cell, HV, 473 K; (C) evacuated cell, HV, 373 K; (D) evacuated cell, HV, RT; oxygen adsorption: (E) 0.11 Torr, RT; (F) 100 Torr, RT.

cated the presence of hydration or coordination water (3667, 1634, 1268, and 1162 cm^{-1}), surface OH groups (3721 cm^{-1}), "alumina" bands and residual carbonates (bands at 1589, 1559, 1542, 1523, 1457, 1432, 1376, and 1304 cm^{-1} (10, 24, 25)). After cooling to RT a new band appeared at 1690 cm^{-1} , typical of the transformation from bridged bidentate carbonates to geminal bidentate moieties, the preferred form at low temperatures:



The adsorption of O_2 (100 Torr) at RT caused small changes: the alumina bands (1434 and 1376 cm^{-1}) were enhanced and the band at 1634 cm^{-1} was eliminated. It can be postulated that monodentate carbonates are the preferred surface structures after adsorption of the gas:



This would account for the elimination of coordinated water bands. Free and dimer carbonates—(a) structures—also give bands at 1440 cm^{-1} and it is plausible that they may be formed upon adsorption, from other residual carbonate structures initially present, such as the bridged bidentate carbonates in Eq. (8) (Fig. 7).

When the adsorption temperature was increased to 373 K (under 100 Torr O_2) no geminal bidentate carbonates remained on the catalyst surface (the band at 1691 cm^{-1} disappeared). At this temperature the bands at 1594, 1557, and 1437 cm^{-1} were enhanced. A distinct shoulder appeared at 1228 cm^{-1} . When the temperature was raised to 473 K the bands at 1657, 1228, and 1163 cm^{-1} were eliminated, the band at 1437 cm^{-1} was sharply reduced; the peaks at 1394 and 1378 cm^{-1} almost doubled in intensity. Further heating to 573 K under 100 Torr O_2 reduced the intensity of all bands, but the initial spectrum was not fully recovered (Figs. 7 and 8).

The adsorption bands that appeared upon O_2 adsorption at higher temperatures cannot be identified unambiguously. Bridged bidentate species (bands at 1590 and 1307 cm^{-1}) and their "dimer" (1437 cm^{-1}) could have been formed, as well as monodentate (8) species, as outlined in Eq. (8). However, the appearance at 373 K of new bands at 1657 and 1228 cm^{-1} strongly suggests the formation of labile bicarbonates via Eq. (6) as the most plausible reason of the spectral changes at 373 K. They decompose later at 473 K.

This statement is supported by the spectral data: strong bicarbonate-type bands (1650, 1437, and 1226 cm^{-1}) dominate the spectrum (Fig. 8E), with absence of geminal bidentate carbonate bands at 1690 cm^{-1} , when the $\text{MnO}_x/\text{Al}_2\text{O}_3$ is cooled to

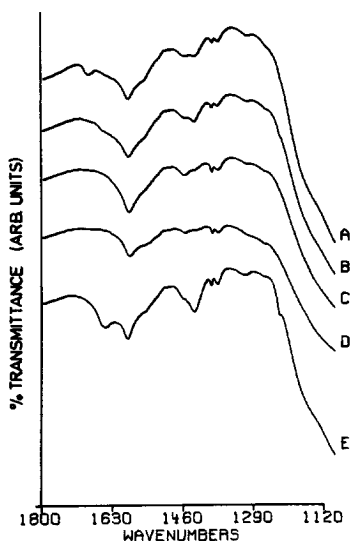
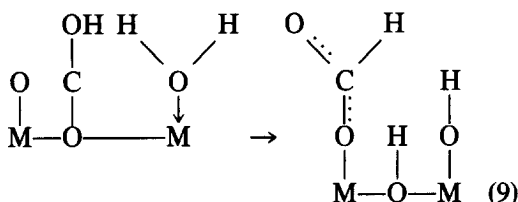


FIG. 8. Infrared spectra of the carbonate region after adsorption of oxygen on $\text{MnO}_x/\text{Al}_2\text{O}_3$. Spectra taken after adsorption of 100 Torr O_2 at (A) RT; (B) 373 K; (C) 473 K; (D) 573 K; (E) after it was cooled to RT.

ambient temperature under 100 Torr O_2 after the adsorption of the gas at 573 K.

The thermal activation of OH-groups or coordinated water, with formation of formates (bands at 1598, 1394, and 1377 cm^{-1}) above 473 K, at the expense of the surface bicarbonates is another possible reaction to be considered:



The desorption of O_2 at room temperature (2×10^{-5} Torr) showed that the surface changes caused by the adsorption at high temperatures could not be reversed by simple evacuation. All the bands associated with bicarbonates (1653, 1437, and 1226 cm^{-1}) were partially removed at this temperature and almost disappeared with further evacuation to 373 K. The bands associated with formates and/or monodentate

carbonates (1590, 1394, 1378, and 1437 cm^{-1}) only disappeared after evacuation at 573 K, but even this treatment was not enough to reverse the surface changes caused by the exposure to O_2 . A comparison of the spectra obtained under high vacuum at room temperature before and after the adsorption/desorption cycle reveals that less residual geminal bidentate carbonates and more formates and monodentate carbonates were left (Figs. 7 and 9), but there is no evidence of anything but surface rearrangement of the residual contamination.

The experimental results of the adsorptions of O_2 offer direct evidence of the chemical transformations of the surface—and adsorbates—that follow the preoxidation treatment and the oxidation reactions on $\text{MnO}_x/\text{Al}_2\text{O}_3$. This type of support presents typical “alumina bands,” absorbance regions at 1570 and 1440 cm^{-1} , and 1480 and 1370 cm^{-1} that interfere with the carbonate, formate or bicarbonate bands of

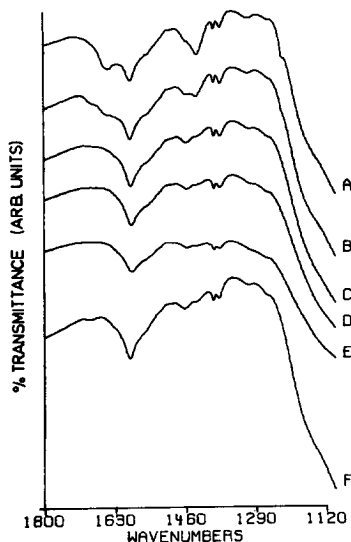


FIG. 9. Infrared spectra of the carbonate region upon adsorption and desorption of oxygen on $\text{MnO}_x/\text{Al}_2\text{O}_3$: Oxygen adsorption, (A) 100 Torr, after cooling to RT; oxygen desorption: (B) 4×10^{-5} Torr (HV), RT; (C) HV, 373 K; (D) HV, 473 K; (E) HV, 573 K; (F) HV, after it was cooled to RT.

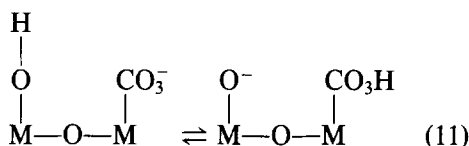
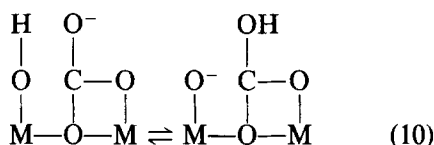
interest and make difficult the interpretation of the ir spectra.

However, it is possible to extract some valuable information, as follows:

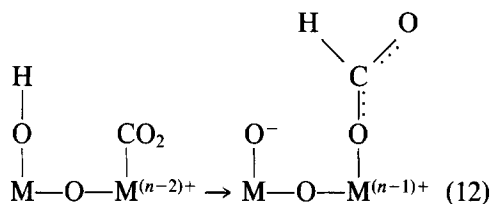
—The untreated catalyst has a large amount of adsorbed molecular water and a significant contamination from atmospheric CO_2 . The pretreatment in 20% O_2 at 473 and then 573 K partially dehydrates the surface. The manganese oxihydroxide overlayer is expected to be oxidized by this procedure (Eqs. (1) and (2)) with production of additional amounts of H_2O driven off by the reactions. The evolution of this newly formed water could not be observed due to the partial dehydration of the catalyst. Residual carbonates are also only partially decomposed in the preoxidation pretreatment. When the $\text{MnO}_x/\text{Al}_2\text{O}_3$ is cooled under a flow of 20% O_2 –80% He, these residual carbonates react with neighbor water molecules to give labile bicarbonates (Fig. 7 and Eq. (6)).

—The adsorption of oxygen at various pressures (from 10^{-5} to 10^2 Torr) and temperatures (from RT to 573 K) offers only indirect evidence of the actual incorporation of O_2 to the catalyst lattice, as postulated in Eq. (8). The transformation of geminal bidentate residual carbonates into monodentate species at RT, with the participation of coordinated water is, then, a consequence of the adsorption of the gas. No metal-to-oxygen bonds could actually be observed due to the poor transmittance of the catalyst below 1100 cm^{-1} .

—The residual surface species can experience additional transformations upon heating under O_2 atmosphere. Bicarbonates can easily form 373 K (Fig. 8E), but they decompose to give stable formates (Eq. (9)) at higher temperatures. This pattern of surface transformations is typical of the $\text{MnO}_x/\text{Al}_2\text{O}_3$ catalyst and was observed after each thermal treatment while adsorbing either O_2 or CO (6), on surfaces outgassed at room temperature or at 573 K. The abundance of surface water and OH groups may help explain this phenomenon, via



for the bicarbonates formation, and Eq. (9) and



for the formates formation.

SUMMARY AND CONCLUSIONS

The adsorption of oxygen on the series of TiO_2 -, CeO_2 -, and Al_2O_3 -supported manganese oxides undergoing the same pretreatments used in operational flow microreactors has been studied using ir spectroscopy.

The preoxidation pretreatment with flowing 20% O_2 –80% He, at 473 and then 573 K, leaves partially dehydrated catalyst surfaces, with simultaneous oxidation of the manganese oxihydroxide overlayer. The catalyst surfaces are usually contaminated with residual carbonates, bicarbonates, and/or formates from exposure to atmospheric CO_2 . The preoxidation pretreatment removes most but not all of these moieties.

The adsorption and desorption of oxygen is a reversible process on $\text{MnO}_x/\text{TiO}_2$ and $\text{MnO}_x/\text{CeO}_2$. Adsorption and desorption on the second catalyst is a highly activated process. Oxygen adsorption involves reactions with surface carbonates and hydroxyl groups.

Table 2 summarizes the observed ir spectral changes on the catalyst series.

TABLE 2

Observed ir Spectral Changes upon Oxygen Adsorption from Room Temperature to 573 K on Supported MnO_x Catalysts

Phenomenon ^a	Catalyst		
	MnO _x /TiO ₂	MnO _x /Al ₂ O ₃	MnO _x /CeO ₂
Totally reversible spectrum after desorption at 300°C	Yes	No	Yes
Filling of anion vacancies upon adsorption	Yes	No	Yes
Enhancement of coordinated water after RT adsorption	Yes	Yes	—
Bicarbonates formation	No	Yes	No
Cation-oxygen species	—	—	Yes
Enhancement of carbonate bands	Yes	Yes	Yes
Geminal/bridged bidentate carbonates swing upon heating	Yes	Yes	Yes
Decomposition of surface contaminants	Yes	No	Yes

^a The catalysts were subjected to the following pretreatments: (i) pre-oxidized under 100 cc/min O₂ for 4 h at 473 K, then 2 h at 573 K; (ii) outgassed (10⁻⁵ Torr) for 2 h at 573 K; (iii) cooled to RT under high vacuum (10⁻⁵ Torr).

ACKNOWLEDGMENTS

This work was supported by a National Science Foundation grant from the Industry University Cooperative Research Program and by the Industrial Sponsors of the Center for Catalytic Science and Technology.

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