Infrared Study of Ozone Adsorption on CeO₂

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Ozone (O₃) adsorption on CeO₂ pretreated under different conditions and characterized by low-temperature CO adsorption was studied by Fourier transform infrared (FTIR) spectroscopy at 77–300 K. Preliminary exposure to CO₂, pyridine, acetonitrile, or methanol at 293 K or to CO at 77 K, as well as adsorption of ¹⁸O substituted O₃ were used to clarify the nature of adsorption sites and the structure of the surface species. In addition to physisorption and weak H-bonding with the most acidic OH groups of the ceria surface, O₃ forms coordinate complexes with two kinds of Lewis acid sites. These complexes have the bands of the ν_1 and ν_3 modes of O₃ at 1096 and 1018–1015 cm⁻¹, or 1104 and 1012–1008 cm⁻¹, respectively. The coordinated O₃ molecule is no longer symmetric but is bound to a surface Ce⁴⁺ ion via one of its terminal oxygen atoms. Basic surface sites of the samples pretreated at 773 K account for O₃ decomposition, which occurs almost explosively at 77 K but could be inhibited if O₃ adsorption is performed from the solution in liquid oxygen. Formation of ozonide O₃⁻ (bands at 792 and 772 cm⁻¹) and superoxide O₂⁻ (band at 1128 cm⁻¹) species was detected; these species are believed to be the intermediates of O₃ decomposition on basic sites. On ceria, O₃ does not react at 77 K with adsorbed CO, but ozonolysis of surface methoxy groups proceeds slowly, leading to a formate surface species.

Introduction

Despite the great importance of ozone (O₃) for ecology, it has been studied in the adsorbed state by infrared (IR) spectroscopy only on a few materials. After the IR bands of adsorbed O₃ were first reported for MgO,^{1,2} thorough investigations using Fourier transform infrared (FTIR) instruments were performed for SiO₂³, TiO₂ (anatase),⁴ and CaO.⁵ Preliminary data were also obtained for several other metal oxides with surface acid sites of different strength.^{6,7}

Ozone interaction with silica surface³ has demonstrated the basic character of the O_3 molecule, which is capable of forming weak hydrogen (H)-bonds with the silanol groups. Frequencies of H bonded O_3 almost coincided with those for liquid or dissolved state or those for O_3 physically adsorbed on the surface of any other oxide. From the analysis of the half-width values of O_3 bands for different isotopic modifications it was concluded that the O_3 molecule interacts with OH group proton via its terminal oxygen atom.³

The basic character of O₃ also manifests itself in its interaction with Lewis acid sites of metal oxides.^{4,6} With weaker sites, O₃ forms coordinative complexes bound via a terminal oxygen atom. Large frequency shifts reveal strong distortion of coordinately bound molecules. On stronger Lewis sites, O₃ dissociates, leaving oxygen atoms that participate in further O₃ decomposition or oxidation of other molecules.^{4,7} Ozone adsorption on a activated CaO surface⁵ leads to appearance of surface ozonide O₃⁻ ions, apparently as a result of interaction with the same basic oxygen atoms that account for the formation of 'carbonite' CO₂²⁻ ions when CO is adsorbed in small doses at 300 K.⁸ A weak complex with basic surface OH groups was established as well.

Cerium dioxide (CeO₂) is known as an active catalyst for O_3 decomposition and CO oxidation by O₃ at 283-343 K.⁹ Adsorbed phenol ozonolysis already occurs on ceria at 77 K.10 Cerium dioxide acts as a catalyst of low-temperature ethylene oxidation by surface oxygen,¹¹ and it is one of the most commonly used 'oxygen storage' components in automotive exhaust catalysts.¹² Different active forms of surface oxygen were established for pure or supported ceria after dioxygen adsorption; for examples, superoxide O2⁻ ion, characterized by an IR band at 1126–1128 cm⁻¹;^{13–15} surface peroxides O_2^{2-2} ;¹³ basic O2-, capable of forming the 'carbonite' ions on CO addition;¹⁶ and surface O⁻ species.^{9,11} A quantum chemical study¹⁷ has shown that atomic oxygen strongly adsorbs on ceria, only on the surface basic sites, whereas dioxygen adsorption takes place on both acid or basic centers. Acidic properties of ceria were characterized by electron spin resonance (ESR),¹⁸ revealing the coordinately unsaturated Ce4+ ions acting as Lewis acid sites. From the FTIR spectra of adsorbed pyridine,^{19,20} several kinds of comparatively weak Lewis sites were distinguished and characterized by bands due to the ν_{8a} vibration at 1593 and 1585 cm^{-1} . The surface basicity of active ceria is attributed mostly to coordinately unsaturated oxygen ions. In addition to the above-mentioned CO adsorption,¹⁶ such sites are believed to account for the low-temperature chemisorption of acetonitrile.21

It could be expected that on ceria, O_3 adsorption occurs not only in molecular form but also leads to other products, different from those established for silica or titania. To this end, in this work we have studied ${}^{16}O_3$ and ${}^{18}O_3$ adsorption on cerium oxide either activated at high temperature or hydroxylated. To find out the nature of active sites and the mechanism of simple

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molecule oxidation, experiments with O_3 adsorption on the surface that was exposed in advance to CO, pyridine, acetonitrile, and methanol were carried out as well.

Experimental Section

The stainless steel cell for studying the IR spectra of adsorbed species at liquid nitrogen temperature used in this study was described elsewhere.⁸ To broaden the observable spectral region up to the limit of the bulk CeO₂ absorption at \sim 600 cm⁻¹, the cell was equipped with ZnSe inner windows. The pressure inside the cell was monitored during experiments by a Barocel capacitante manometer (Datametrix 600).

Ozone was prepared from gaseous ${}^{16}\text{O}_2$, ${}^{18}\text{O}_2$, or their mixtures in electric discharge and manipulated as described previously.^{2–5} When mixtures of ${}^{16}\text{O}_2$ and ${}^{18}\text{O}_2$ were used, random isotopic distributions were obtained. To eliminate CO₂ contamination that is always present in thus prepared O₃, the O₃ was purified by distillation before introduction into the cell, and only the first fraction was used.

The CeO₂ samples (from Rhône-Poulenc, with specific BET surface area of 160 m² g⁻¹), pressed into ~10 mg cm⁻² pellets, were first treated in oxygen and under reduced pressure at 773 K and then cooled to ambient temperature either in ~5 Torr of oxygen to have the oxidized surface, or under reduced pressure to obtain a partially reduced sample. Reduced ceria was prepared by treating in CO (5–10 Torr) at 773 K for 20 min.

Oxidized samples were studied at different states of dehydration. To prepare the completely hydrated surface, the oxidized sample was brought into contact with the saturated water vapor (H₂O or D₂O) for several minutes, then the excess of water was removed up to the residual pressure of ~0.1 Torr, and the sample was cooled with liquid nitrogen. Partial dehydration was achieved by following evacuation at 300 K for ~10 min. Samples pretreated under reduced pressure at 973 K and cooled in oxygen were studied as well.

Methylated samples were prepared by exposing the sample to saturated methanol vapor with subsequent pumping at 400 K.

The spectra were recorded with a Nicolet FT-IR 710 spectrometer with 4 cm⁻¹ spectral resolution. A germanium filter was installed in the beam before the cell to reduce sample heating by IR radiation. For better thermal contact of the sample with the cooled environment, $\sim 0.5-1$ Torr of helium was introduced in the sample compartment before recording spectra at the liquid nitrogen temperature. To study adsorption from the solution in liquid oxygen, O₂ was first condensed in the sample-containing volume of the cell at 77 K, and the background spectrum of the sample immersed in the liquid was registered. After that, O₃, preliminarily trapped in a U-trap, was added and carried in by a flux of oxygen. Then, spectra of the solution were run, as described previously,²² to separate the bands of dissolved and adsorbed species.

Results

Surface Characterization by Low-Temperature CO Adsorption. The IR spectra of CO adsorbed on oxidized or reduced CeO₂ are presented in Figure 1. Oxidized samples were studied at four stages of dehydration: completely hydrated or evacuated at 300, 773, and 973 K (the last one not shown in the figure). The only band observed in the spectrum of the completely hydrated sample in the presence of several Torr of CO at \sim 2145 cm⁻¹ disappears immediately on the removal of the CO gas, and is due to the physisorbed molecules. If after water adsorption the sample is pumped for several minutes, even



Figure 1. The IR spectra of CO adsorbed at 77 K on CeO_2 (1) preexposed to D_2O , (2) evacuated for 20 min at 300 K, (3) at 773 K and (4) after reduction by heating in CO at 773 K. Key: (solid line) in the presence of CO (several Torr); (dotted line) after removal of the gas phase at 77 K.

at ambient temperature, one more band arises in the spectrum of adsorbed CO at 2152 cm^{-1} . This band persists after removal of gaseous CO, but disappears after prolonged evacuation in the cooled cell when the sample is heated slightly by IR radiation through the cold inner windows.

The samples used have very low transmission in the OH stretching region. However, in the presence of CO, there is an increase of absorption at \sim 3600 cm⁻¹. For deuterated samples, the disappearance of the band at 2703 cm⁻¹ and the growth of a band at 2680 cm⁻¹ are more apparent.

If CeO₂ is pretreated at 773 K, one more CO band arises at 2169 cm⁻¹, which grows in intensity after pumping off the gas and shifts its maximum to 2172 cm⁻¹. This band, as well as that at 2152 cm⁻¹ disappear completely after raising the temperature up to 300 K or evacuation at ~150 K.

After dehydration at 973 K, the sample becomes less transparent, which results in an increased level of noise, and the intensity of the bands of adsorbed CO decreases due to the sintering.

Reduction of the sample by heating it under CO at 773 K modifies the spectrum of adsorbed CO; that is, the high-frequency band does not appear at all, and only a broad band is visible in the presence of gaseous CO at 2154 cm^{-1} , which moves slightly to higher wavenumbers after evacuation.

Effect of Surface Dehydration on Ozone Adsorption. The IR spectra of the surface species produced by O_3 adsorbed on CeO₂ depend on the conditions of sample pretreatment, as can be seen from Figure 2. Adsorption of O_3 on the completely hydrated sample results in the appearance of a strong band at ~1035 cm⁻¹, accompanied by much less intense features at 2105, 1106, and 705 cm⁻¹. After raising the temperature up to ~170 K, these bands disappear completely.

If the sample is evacuated at 300 K, new O_3 bands appear at 1019 and 712 cm⁻¹, whereas instead of one peak at 1106 cm⁻¹, a doublet with maxima at 1116 and 1104 cm⁻¹ arises. On raising the sample temperature, the bands at 1116, 1035, and 705 cm⁻¹ are the first to disappear. Meanwhile, one more maximum shows up at 792 cm⁻¹ that remains in the spectrum on further heating the cell up to ~150 K, when the group of bands at 1104, 1019, and 712 cm⁻¹ is already gone. A gradual pressure increase inside the cell after ozone admission at 77 K



Figure 2. The IR spectra of ${}^{16}O_3$ adsorbed at 77 K on CeO₂ (1) preexposed to D₂O, and evacuated for 20 min at (2) 300 K, (3) at 773 K, and (4) at 973 K. Curves 2–4 were registered after removal of weakly sorbed O₃ by pumping at ~100 K for 5 min.

indicates a detectable rate of O_3 decomposition on \mbox{CeO}_2 evacuated at 300 K.

Adsorption of small portions of O₃ on ceria activated at 773 K leads to the appearance of bands at 1116, 1104, 1012, 712, and 1033 cm⁻¹; the latter band is rather weak in this case. The rate of pressure increase due to O₃ decomposition is much higher than for the sample evacuated at 300 K. After ~20 min after O₃ addition, the adsorbate band intensities, which increased gradually before, start to diminish and finally come to zero in ~2 h, when the pressure value indicates almost complete O₃ conversion into oxygen. The band of surface hydroxyl groups perturbed by adsorbed O₃ arises at 3630 (OH) and 2669 (OD) cm⁻¹, which should correspond to the most intense band of unperturbed hydroxyls observed for such pretreatment conditions at 3663 (OH) and 2702 (OD) cm⁻¹. Thus, for both OH and OD groups, O₃ adsorption results in a frequency shift of ~33 cm⁻¹.

If O_3 is added in excess, in several minutes an abrupt change of pressure occurs and the pellet is completely destroyed and transformed into a layer of powder covering the walls and windows of the cell. Such explosions of adsorbed O_3 happened several times with fresh samples, despite the presence of gaseous helium to stabilize the temperature. It is interesting to note that several minutes after sample explosion the bands of adsorbed O_3 at 1116, 1104, 1033, 1010, 714, and 704 cm⁻¹, although weaker than before, appear again. This result demonstrates ozone adsorption and further transformations on the ceria powder covering the cold windows, which is identical to what was observed with the pellet if it wasn't destroyed.

While O_3 is present, a gradual growth of one more band occurs at 792 cm⁻¹. On raising the temperature, the bands at 1116, 1033, and 704 cm⁻¹ are the first to disappear, leaving those of strongly held molecules at 1104, 1010, and 714 cm⁻¹. After complete desorption of molecular O_3 at ~130 K, exhibited by disappearance of the strong v_3 bands at 1035–1010 cm⁻¹, a band at 1128 cm⁻¹ remains, and the 792 cm⁻¹ band intensity diminishes simultaneously with the growth of another band at 772 cm⁻¹. Heating up to 200 K removes all the aforementioned bands.

Addition of O_3 at 140 K to the sample pretreated at 773 K does not lead to the spectrum of molecular adsorption of O_3 , however a band at 1128 cm⁻¹ arises. Ozone adsorption on CeO₂ pretreated at 973 K leads to appearance of a strong band at 1008 cm⁻¹ with a shoulder at 1019 cm⁻¹ and weaker maxima at 1116, 1098, and 1035 cm⁻¹. A gradual pressure increase implies the decomposition of O_3 and, in ~30 min, bands of weakly bonded molecules at 1116 and 1035 cm⁻¹ disappear, finally leaving the bands of more strongly held species. After



Figure 3. Effect of isotopic substitution on the spectrum of O_3 chemisorbed on CeO₂ pretreated at 773 K. Spectra are recorded at 77 K ~10 min after admitting O_3 , with the following isotopic content: (1) pure ¹⁶O₃; (2) pure ¹⁸O₃; (3) O₃ with 50% ¹⁸O.

 \sim 1 h, the bands at 1098 and 1019 are also gone. The last peaks remaining at 1102 and 1008 cm⁻¹ disappear after a slight raising of the temperature.

Adsorption from the solution in liquid oxygen, inhibits O_3 decomposition. In this case, the bands of adsorbed molecules at 1096, 1008, and 710 cm⁻¹ are the most intense in the spectrum of the sample pretreated at 973 K, and their intensities increase or remain unchanged during at least 2 h, whereas the band at 772 cm⁻¹ grows continuously.

Reduction of the sample in CO does not affect the spectrum of adsorbed O_3 too much; that is, the bands at 1010 and 772 cm⁻¹, although weaker than before, do appear.

Adsorption of ¹⁸O₃ and Isotopically Mixed Ozone Molecules. The IR spectra of isotopically substituted O₃ adsorbed on oxidized CeO₂ pretreated at 773 K are illustrated in Figure 3. The spectra were recorded when the bands of physisorbed O₃ have almost disappeared due to decomposition, and those of chemisorbed O₃ remain practically alone. Then, the bands of ¹⁸O₃ molecules, corresponding to those of ¹⁶O₃ observed in such conditions at 1103 and 1012 cm^{-1} , arise at 1043 and 957 cm^{-1} , respectively. Adsorption of isotopically mixed O₃ with \sim 50% ¹⁸O results in the appearance of a third broad maximum of the high-frequency band at $\sim 1071 \text{ cm}^{-1}$, whereas the 1103 cm^{-1} peak shifts to 1099 cm⁻¹. In the region of the v_3 mode, four bands of almost equal intensities appear at 1009, 992, 977, and 960 cm⁻¹. We were not able to resolve the splitting of the bands due to v_2 and the v_1+v_3 combination for the 50% isotopic mixture, but for pure ¹⁸O₃, a band at 675 cm⁻¹ was detected simultaneously with the bands of chemisorbed molecules.

The band, corresponding to the one growing slowly at 792 cm⁻¹ after ${}^{16}O_3$ adsorption, was found at 748 cm⁻¹ for ${}^{18}O_3$ and appeared as a broader band at intermediate position after adsorption of a 50% isotopic mixture. A peak analogous to that at 772 cm⁻¹ appeared at 733 cm⁻¹ after ${}^{18}O_3$ adsorption.

As illustrated in Figure 4, the band at 1128 cm⁻¹, which arises after ${}^{16}O_3$ addition at ~ 140 K to the sample pretreated at 773 K, moves to 1062 cm⁻¹ after ${}^{18}O_2$ adsorption. Furthermore, in the case of mixed ${}^{16/18}O_3$, this band splits into three maxima, with the additional maximum in the middle at 1096 cm⁻¹.

Effect of Surface Poisoning by Different Preadsorbed Test Molecules on Ozone Adsorption. Effect of Pyridine and



Figure 4. Isotopic splitting of the 1128 cm⁻¹ band of ozone adsorbed at 140 K on CeO₂ pretreated at 773 K. Key: (1) pure ¹⁶O₃; (2) pure ¹⁸O₃; (3) O₃ with 50% ¹⁸O.

 CH_3CN . Pyridine adsorption on the oxidized ceria sample that was pretreated at 773 K and had excess adsorbate pumped off for ~25 min at 300 K, gives rise to bands at 1627, 1598, 1573, 1069, 1035, and 1004 cm⁻¹, which are characteristic of species coordinated to weak Lewis acid sites. The last two peaks are exactly in the region of the ν_3 mode of adsorbed O₃, which impedes their observation; however, the appearance of a band near 1020 cm⁻¹, approximately half as intense as the ν_3 band in the spectrum of a pure sample pretreated at the same temperature, was noticed after O₃ was admitted into the cell. Other bands of adsorbed O_3 molecules arise at 2104, 1113, 1107, and 706 with a shoulder at 711 cm^{-1} . These bands disappear after a slight increase of temperature, whereas a band at 776 cm⁻¹ and its shoulder at 794 cm⁻¹, which do not display any intensity redistribution as observed for pure CeO2, remain in the spectrum.

The spectrum of adsorbed CH₃CN, recorded at 77 K after removal of the excess adsorbate by short pumping at ambient temperature, reveals strong bands at 2287, 2096, 1538, 1516, and 1451 cm⁻¹ and several weaker maxima. Subsequent O₃ adsorption gives rise to the band at 1012–1015 cm⁻¹, again with lower intensity than that observed after adsorption on pure ceria. Bands at ~794 and ~776 cm⁻¹ appear as well; these bands are broader with respect to the case of the pure sample and display no intensity redistribution on sample heating. The overall intensity of these bands does not differ significantly from that observed without preadsorbed molecules. We have not detected any new bands assignable to the products of pyridine or acetonitrile ozonolysis at 77 K.

*Effect of CO and CO*₂. After CO adsorption on the oxidized sample pretreated at 773 K and removal of gas at 77 K, bands of CO remain at 2172 and 2152 cm⁻¹. The addition of O₃ to such a sample results in bands at 1105, 1012, and 785 cm⁻¹, at almost the same positions as for the sample without CO. However, the intensity of the 1012 cm⁻¹ band is <25% of its maximal value for the sample without CO, whereas the intensity of the 785 cm⁻¹ band is only slightly diminished. No bands due to oxidation products were detected at 77 K. However, after raising the temperature up to ~120 K, new bands arise at



Figure 5. Effect of CO_2 preadsorption on the IR spectrum of O_3 adsorbed at 77 K on oxidized CeO_2 preactivated at 773 K. Key: (1) ${}^{16}O_3$ adsorbed on pure sample; (2) ${}^{16}O_3$ adsorbed on the sample preliminarily exposed to CO_2 at 300 K.

900

Wavenumbers (cm⁻¹)

800

700

1000

1100

1200

 \sim 2350, \sim 1610, and \sim 1280 cm⁻¹. These new bands become much stronger on further heating the sample and are evidently due to adsorbed molecular CO₂ and surface carbonate ions.

Preliminary adsorption of CO_2 at ambient temperature on CeO_2 pretreated at 773 K leads to strong bands of surface carbonates. Nevertheless, as seen from Figure 5, these strong bands do not affect other bands of adsorbed O₃, but those at 792 and 772 cm⁻¹ that do not arise at all on such a sample. It should also be noted that no pressure increase was detected in the cell after admitting O₃, thus demonstrating the elimination of the catalytic decomposition of O₃ on a ceria surface by preadsorption of CO₂ at 300 K.

Ozone Interaction with Methanol Adsorbed on Ceria. After methanol adsorption on ceria activated at 773 K and pumping off the excess adsorbate at 400 K, three characteristic bands due to C–O vibrations of methoxy groups arise at ~1110, ~1058, and ~1016–1010 cm⁻¹. In the spectrum of methanol adsorbed on the reduced sample, the intensity of the high-frequency band observed at 1102 cm⁻¹ is much lower, whereas a new band appears at 1070 cm⁻¹ with a shoulder at ~1030 cm⁻¹.

The effect of reduction on the spectrum of methoxy groups is partially reversible. Even dioxygen adsorption at roomtemperature results in the increase of the high-frequency band intensity and in a shift of the band at 1070 cm⁻¹ to lower wavenumbers. A similar effect was observed after introduction of O₃ at 77 K; that is, the 1070 cm⁻¹ band disappears immediately and is replaced by bands at 1058 and 1033 cm⁻¹. The latter continues to grow with time together with the band at 1093 cm⁻¹, and after raising the temperature up to 250 K only a pair of strong bands at 1093 and 1033 cm⁻¹ remains in this region.

Admission of O_3 to the oxidized sample at 77 K, illustrated in Figure 6, results in the appearance of bands at 1035 and 1013 cm⁻¹ and at 714–709 cm⁻¹. These bands are at almost the same positions as those for nonmethylated samples, however the highest peak intensity of the 1013 cm⁻¹ band observed in this experiment did not reach a half of the maximum value obtained for the pure sample. One more band that arises at 785 cm⁻¹ is not less intense than that at 772 cm⁻¹ for the



Figure 6. The IR spectrum of CeO_2 (1) methylated in CH₃OH at 400 K after cooling to 77 K, (2) after ¹⁶O₃ addition at 77 K and waiting for 1 h, and (3) after subsequent raising the temperature to 250 K.

nonmethylated sample. A gradual growth of new bands at $\sim 1568-1560$, ~ 1373 , and ~ 1357 cm⁻¹ occurs at 77 K; those new bands apparently are due to the products of ozonolysis.

Raising the sample temperature leads to both the increase of the bands due to the ozonolysis products and to the disappearance of those due to adsorbed O₃. On further heating to \sim 200 K, new maxima arise at 1575, 1300, and 860 cm⁻¹, and a broad one at 930 cm⁻¹. At \sim 250 K, one more peak grows at 1550 cm⁻¹, accomplishing the complicated structure of the band. Bands of methoxy groups diminish in intensity, whereas the low-frequency band at 1012 cm⁻¹ almost disappears, remaining as a weak shoulder.

Almost the same bands of ozonolysis products arise on the reduced methylated sample; that is, a strong band at 1575 cm^{-1} , those at 1300 and 930 cm⁻¹, and a couple of weak maxima at 1373 and 1357 cm⁻¹.

Discussion

Weakly Bound Ozone and OH Group Perturbation. Physisorbed or weakly bound O_3 accounts for the bands at ~2105, ~1116-1105, ~1033, and ~705 cm⁻¹, that disappear together as a result of decomposition at 77 K or desorption at slightly higher temperatures. The positions of these maxima are practically the same as those for O_3 dissolved in liquid $O_{2,}^{22}$ adsorbed on SiO₂³, or physisorbed on TiO₂.⁴

The shift of the band of surface OH or OD groups by \sim 33 cm⁻¹ with O₃ adsorption shows that part of adsorbed O₃ molecules form a weak complex with surface OH groups. The H-bond formation of O₃ with surface hydroxyls was established earlier for SiO₂, TiO₂, or zeolites,²³ and it was found that the frequency shifts observed with O₃ and CO adsorption were very close to each other, thus accounting for the basicities of these two molecules. In the case of CeO₂, the shift caused by perturbation with O₃ is also close to that caused by CO adsorption (23 cm⁻¹ for OD groups), and we can conclude that O₃ forms a weak H-bond with the acidic OH groups, but not a

complex with the oxygen atom of basic hydroxyls as was recently found for CaO.⁵ The most intense ν OD band at 2703 cm⁻¹ in our experiments corresponds to that at 2696 cm⁻¹ reported in ref 24. This band is assigned to bridged hydroxyls that are slightly more acidic than the terminal groups, and thus, could form a weak H-bond with O₃ or CO.

The v_1 band at 1116–1113 cm⁻¹, observed after pretreatment at 300 K, is shifted by 10–13 cm⁻¹ with respect to the gas phase. Such a great frequency shift and the absence of this band in the spectrum of totally hydrated sample does not enable us to assign it to physisorbed molecules. The band was, however, detected for the sample dehydroxylated at 973 K, and hence, cannot belong to H-bonded O₃. The CO₂ adsorption at 300 K does not eliminate this band, and we should, thus, exclude interaction with basic oxygen ions. We have to conclude that this band is due to weak chemisorption on certain kind of surface cationic sites that accounts for the high position of the v_1 band, whereas the v_3 and v_2 frequencies (1035 and 704 cm⁻¹) are still typical of physisorption.

Molecular Ozone Chemisorption. Another molecular O₃ species arises at the CeO₂ surface that was pumped at 300 K or higher to desorb water; this species has absorption bands at 1105–1096, 1019–1008, and 714–712 cm⁻¹. On raising the pretreatment temperature, the overall intensity of these bands and, hence, the number of sites that account for this form of adsorption, increases. Data on the sample pretreated at 973 K, for which the bands are better resolved, suggest the existence of at least two kinds of these species with the bands of ν_1 and ν_3 modes at 1096 and 1019, or 1102 and 1008 cm⁻¹, respectively, whereas the ν_2 band of both appears at near 714 cm⁻¹. The multiplicity of bands implies site heterogeneity when dehydroxylation at higher temperature produces stronger sites.

The nature of the sites could be cleared up by the results of surface poisoning with preadsorbed gases, which could be classified as three different kinds: (i) those interacting with basic sites only, such as CO₂; (ii) those that adsorb on Lewis acid sites, such as CO, pyridine, or acetonitrile; and (iii) those that dissociate on coordinatively unsaturated cation—oxygen pairs as water or alcohols. One could also take into account that acetonitrile could also interact with strong basic O^{2—} sites of CeO₂, leading to the formation of CH₂CN[—] (band at 2096 cm⁻¹) and CH₃CNO^{2—} (bands at 1516 and 1451 cm⁻¹) species.²¹

The adsorption of CO₂ occurs on surface basic oxygen ions or on basic OH groups with the formation of carbonate or bicarbonate ions, respectively. Although preadsorption of CO₂ at 300 K completely eliminates the bands at 794-772 cm⁻¹, it does not affect at all the intensities of other bands due to the O3 species already mentioned. Pyridine or acetonitrile preadsorption at 300 K does not result in the disappearance of these bands, but causes their intensity diminution and slightly affects the peak position of the ν_3 band. To our mind, this result means that O₃ adsorption takes place on weak Lewis sites that could be partially liberated from coordinatevely bound water molecules at 300 K, which accounts for the band at 2155 cm^{-1} in the spectrum of adsorbed CO. The intensity increase of both the CO just mentioned or adsorbed O3 bands on raising the pretreatment temperature enables us to reject the surface OH groups as active sites that account for this form of adsorption. Because of a low electron-accepting ability of these sites, either originally weak or influenced by strong repulsive interaction between the adsorbed molecules, pyridine, acetonitrile, or coordinately bound water at 300 K, and CO at 77 K could not be held strongly on all of them and at least part of the sites are free after removal of the excess adsorbate.

Strong repulsive interaction between CO molecules coordinated to Ce⁴⁺ ions could be illustrated by the decrease of the 2172 cm⁻¹ band intensity observed at high surface coverages and the shift of its maximum to lower wavenumbers (see Figure 1). Partial occupation of these sites with preliminary adsorbed CO almost does not affect the band positions in the spectrum of chemisorbed O₃, and only causes intensity diminution. Unlike the case of strong Lewis sites on TiO₂, where O₃ dissociation followed by reaction of atomic oxygen with CO was established,⁴ here CO adsorbed on Lewis sites does not react with O₃, and the O₃ decomposition reaction is not stopped by CO adsorption. We can suggest that O₃ adsorption on the sites that account for the 2172 cm⁻¹ band of CO results here in the same molecular form as that with the largest shift of ν_3 vibration peak to 1008 cm⁻¹.

Our results suggest that there is no strong repulsion between coordinated O_3 and other coadsorbed electron-donor molecules such as CO, pyridine, or acetonitrile. Earlier, it was demonstrated, that repulsive static interaction between the adsorbed dipoles prevents occupation of all the Lewis sites and, for instance, CO molecules adsorbed on ZnO at saturating conditions occupy only each second-surface cation.²⁵ In our case, the static dipole moment of O_3 , coordinated to a surface Lewis site via its terminal oxygen atom, is oriented parallel to the surface and should not interact with perpendicularly directed dipoles of other molecules. The direct repulsion has to be weaker and we could expect, therefore, O_3 adsorption on the remaining sites of the surface to be poisoned by electron-donating molecules.

Adsorption of water or methanol also does not completely poison the sites of molecular O_3 chemisorption when the excess of the adsorbate is removed by pumping at 300 K. It is only when the surface is totally hydrated by cooling in the presence of water vapor traces and when the band at 1630 cm⁻¹ of coordinately bound molecular water is strong enough that the bands of chemisorbed O_3 at 1020–1008 cm⁻¹ region do not appear.

Isotope Splitting Analysis. More information about the structure of chemisorbed O_3 species could be obtained from the results of isotopic substitution. Splitting of ν_1 into three components instead of six for a free molecule in a gas phase was found earlier when mixed^{16 18}O₃ was adsorbed on titania.⁴ This result was regarded as evidence for the strong distortion of the molecules adsorbed on weak Lewis sites via the terminal oxygen atom as in the following scheme:



In such molecules, there are no equivalent oxygen atoms and the shifts produced by the substitution of every oxygen by ¹⁸O are no longer equal. As a result, we have two possible isotopes in the three different positions and, thus, each band should be split into eight maxima. In general, the shift values caused by substitution of each oxygen do not substantially depend on the masses of the others, thus, the additivity of the shift values can be used to predict the whole picture of splitting.

Three bands with the intensity ratio close to 1:2:1 for 50% substitution are typical of the structures with two equivalent atoms. So, splitting of the 1128 cm^{-1} band for the sample

pretreated at 773 K into three maxima separated by \sim 33 cm⁻¹ is exactly what is expected for the dioxygen species and thus supports the assignment of this band to the superoxide O₂⁻ ion.

In the case of chemisorbed O₃, splitting of the high-frequency stretching band in such a manner means that now this vibration is localized on the stronger bond; for example, between O¹ and O² atoms in the above scheme, the substitution of each one produces almost equal shifts of $\sim 30 \text{ cm}^{-1}$. The third oxygen atom O³ practically does not participate in this mode and its substitution does not result in the resolved splitting, but rather in a slight low-frequency shift of each band on increasing the ¹⁸O concentration.

Four peaks of the same intensities for the 50% isotopic mixture could arise for the same species if the shift caused by one atom, as already mentioned, is too small for the observation of the resolved splitting, but the substitution of the two others results in shifts of different values. In our scheme, the low-frequency stretching vibration is localized on the weaker bond between nonequivalent O^2 and O^3 atoms. To account for the observed splitting, their substitution should lower the frequency by ~25 and 17 cm⁻¹. The small difference of the positions of maxima for the 50% isotopic mixture with respect of those for pure isotopes could be explained if the shift caused by the exchange of O^1 atom is ~8 cm⁻¹. The total shift caused by complete substitution will then be ~50 cm⁻¹, which is close enough to the observed value.

The frequency of $\nu_1 + \nu_3$ combination should be sensitive to the substitution of all three atoms, so a complex structure of up to six or eight bands could be expected. Such a structure with at least six resolved maxima was in fact observed for O₃ chemisorbed on titania,⁴ where this combination band could be registered for isotopic mixtures with better signal-to-noise ratio.

Interaction of Ozone with Basic Sites. The bands in the $794-772 \text{ cm}^{-1}$ region observed after O₃ adsorption (792 and 772 cm⁻¹ for pure ceria sample, 794 and 776 cm⁻¹ for samples with preadsorbed pyridine and acetonitrile, and 785 cm⁻¹ after CO or methanol preadsorption), like those of chemisorbed O₃ molecules, are due to species formed on sites produced by surface dehydroxylation. These sites could be completely poisoned by adsorbed CO₂, and are, evidently, basic oxygen ions that participate in carbonate formation.

According to Spiker and Andrews²⁶ and Hesse et al.,²⁷ ozonide O_3^- ions of alkali ozonides have strong absorption bands at ~818-802 cm⁻¹. Our results have shown that ozonides formed from O_3 on a CaO surface⁵ absorb at 812 cm⁻¹, which is close enough to the bands in question. The values of isotopic shifts observed after adsorption of ¹⁸O₃ ($\Delta \nu = 44$ cm⁻¹ as compared with 47 cm⁻¹ for CaO) or for ozone isotopic mixtures are also consistent with the assignment of these bands to surface ozonides. Still not understood is the existence of two maxima and the phenomenon of intensity redistribution between them on O₃ desorption from the CeO₂ sample pretreated at 773 K.

Naidenov et al.⁹ supposed ozonide formation to be a result of Ce^{3+} oxidation:

$$\underline{\operatorname{Ce}}^{3+} + \operatorname{O}_3 \rightarrow \underline{\operatorname{Ce}}^{4+} + \underline{\operatorname{O}}_3^{-}$$

Our data show, however, that ceria reduction does not promote ozonide formation, and site poisoning by CO_2 suggests basic oxygen ions to be the sites of ozonide formation, as found earlier for CaO.⁵ The supposed mechanism should lead, in addition to ozonides, to surface superoxide ions formation and liberation of oxygen molecules:

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$$\underline{O}^{2^-} + 2O_3 \rightarrow \underline{O_4}^{2^-} + O_3 \rightarrow \underline{O_4}^- + \underline{O_3}^- \rightarrow \underline{O_2}^- + O_3^- + O_2^{\uparrow}$$

Formation of superoxide, characterized by the band at 1128 cm⁻¹, was in fact observed together with strong ozonide bands for the samples pretreated at 773 K after O₃ desorption, or at \sim 140 K after O₃ adsorption. Moreover, for such samples, oxygen emission, evidently due to O₃ decomposition, was indeed observed, and its rate increases in time, as could be expected for the last step of the proposed reaction as if the accumulation of intermediate products is needed. The fact that oxygen emission could be poisoned together with ozonide formation by preadsorbed CO₂ is also in agreement with the proposed scheme.

Adsorbed Ozone Reactivity. The data obtained enable us to draw information about CeO₂ activity and the nature of the active sites in the reactions of O₃ decomposition and ozonolysis of other adsorbed molecules. The rate of O₃ decomposition on ceria can be followed by the gradual pressure increase with time after O₃ adsorption. As for the oxides studied earlier, such as TiO₂ or CaO, the rate of O₃ decomposition for ceria also depends on the temperature of pretreatment. Ozone decomposition was detected already after ceria evacuation at 300 K, increased dramatically after heating under reduced pressure at 773 K, and diminished somewhat after treatment at 973 K. There are three kinds of sites that are formed in such conditions and could account for O₃ decomposition; these are, rather strong Lewis sites, characterized by the band of adsorbed CO at 2172 cm^{-1} ; weak Lewis sites, responsible for the CO band at 2152 cm⁻¹, and basic sites that lead to ozonide formation. The former could be poisoned, at least, partially, by CO adsorption at 77 K, but CO adsorption does not influence O₃ decomposition.

On the other hand, preadsorbed CO_2 eliminates O_3 decomposition and completely blocks the basic sites, but does not affect O_3 coordination on weak Lewis sites. To our mind, this result means that O_3 decomposition on ceria mainly occurs on basic oxygen ions, which account for ozonide formation, according to the schema already proposed, or on the cation—anion pairs including these oxygen ions.

Adsorbed CO oxidation by O_3 , which readily occurs at 77 K on TiO₂,⁴ was not detected on CeO₂ at 77 K. The bands of molecular CO₂ and surface carbonates arise only after heating the sample up to ~120 K. This result means that the mechanism reaction established for TiO₂, when O₃ decomposition on strong Lewis sites is followed by CO interaction with atomic oxygen, is not valid here. Intermediates of O₃ decomposition on ceria (that are not inhibited by CO adsorption and occur at 77 K) are evidently not sensitive to the presence of the excess CO coordinated to both strong and weak Lewis sites. This result is in accord with the aforementioned conclusion that the mechanism of O₃ decomposition on ceria differs from that on TiO₂ and involves interaction with surface basic oxygen ions.

Our data about the spectra of methoxy groups are in agreement with those reported earlier²⁸ for oxidized and reduced ceria at 300 K. The three ν OC bands at 1112, 1060, and 1013 cm⁻¹ are due to the on-top, bridged and triply bridged (type I, II, and III) methoxy groups, respectively. The intensity decrease of these bands and disappearance of the 1012 cm⁻¹ methoxy band after treatment with O₃ indicate that all types of methoxy species are oxidized, but their reactivity toward O₃ is not the same. Although the type III groups disappear almost completely, the bands of the two others undergo only certain intensity decreases.

The results of methoxy ozonolysis on reduced CeO₂ show that the main products are the same. Changes of the spectrum of methoxy groups with O₃ introduction could be explained by a partial reoxidation of ceria surface already at 77 K by first doses of O₃, however, even after heating to 250 K, the spectrum is never identical to that of initially oxidized sample; that is, the strong bands due to methoxy groups remain shifted by $10-20 \text{ cm}^{-1}$.

The bands at 1568, 1560, 1373, 1357 cm⁻¹ of the ozonolysis products that arise by 77 K and grow on further raising the temperature could be assigned to surface formate ions.²⁹ The peak at 1550 cm⁻¹, which appears on heating to almost 300 K, is characteristic of such species formed at 293 K.²⁹ Bands at 1300 and 860 cm⁻¹ that show up at ~200 K when molecular CO₂ appears in the gas phase, together with a band at 1575 cm⁻¹, could be attributed to bidentate carbonates observed earlier at almost the same frequencies with CO₂ adsorption on ceria.²⁹

Conclusions

This study demonstrated that IR spectroscopy at low temperatures is a powerful method to study O_3 adsorption and reactivity on ceria. Several different surface species were observed, depending on the activation state of CeO₂ Their structure was clarified using adsorption of ¹⁸O-substituted ozones. The relevant surface sites were characterized by lowtemperature CO adsorption or O₃ adsorption on the surface preliminary exposed to CO₂, pyridine, acetonitrile, or methanol at 293 K or to CO at 77 K.

The FTIR spectra of CO adsorbed at 77 K on oxidized CeO_2 revealed two kinds of Lewis acidic sites characterized by the bands at 2172–2168 and 2156–2152 cm⁻¹, respectively. The latter disappeared after water adsorption, but could be partially liberated by pumping at 300 K, whereas the former arose after evacuation at elevated temperature, and were rather abundant after pretreatment at 773 K. Reduction in CO at 773 K results in disappearance of the stronger sites.

Molecular O₃, weakly adsorbed on CeO₂, has a rather high ν_1 band peak position (1116 cm⁻¹). Some adsorbed O₃ forms a weak H-bond with the most acidic OH groups of the surface.

Ozone forms coordinative complexes with the two kinds of Lewis acid sites of ceria, with the bands of the ν_1 and ν_3 modes shifted to 1096 and 1018–1015 cm⁻¹, or to 1104 and 1012–1008, respectively. Data obtained with ¹⁸O-substituted O₃ show that a coordinated O₃ molecule is no longer symmetric and is bound to a surface Ce⁴⁺ ion via one of terminal oxygen atoms.

On basic surface sites, formation of ozonide O_3^- species has been detected; they are characterized by the bands at 792 and 772 cm⁻¹ that grow slowly after O_3 adsorption on samples pretreated at 773 K. These basic sites could be completely poisoned by preadsorbed CO₂ and may account for the explosive O₃ decomposition that occurs at 77 K on the samples pretreated at 773 K.

It should be noted that on acidic oxides such as alumina and titania, O_3 activation and decomposition was shown to occur via dissociation on strong Lewis sites.^{4,7} In the case of ceria, another, nondissociative mechanism of O_3 decomposition, therefore, takes place. This other mechanism has been suggested earlier for CaO and involves unstable ozonide formation on surface basic oxygen sites. Ozone adsorption from the solution in liquid oxygen diminishes the rate of decomposition and enables us to obtain the highest surface coverages by chemisorbed O_3 .

On ceria, O_3 does not react with adsorbed CO at 77 K, as it does on TiO₂. Reaction of O_3 with surface methoxy groups proceeds slowly at 77 K, leading to formate surface species. The rate of ozonolysis is different for different types of methoxy groups: triply bridged groups were found to be the most reactive toward O_3 .

We have not found any serious manifestations of ceria redox properties studying O_3 adsorption or reactivity on the reduced samples. The preliminary results of methoxy groups ozonolysis on reduced CeO₂ could be explained by a rapid partial reoxidation of ceria surface at 77 K by O₃, and further reaction as on the oxidized sample. Thus, in the presence of O₃, the ceria surface seems to be always in an oxidized state.

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References and Notes

(1) Alekseev, A. V.; Babaeva, M. A.; Bystrov, D. S.; Tsyganenko, A. A.; Yushkov, V. A. All-Union symposium on photochemical processes in the Earth atmosphere. Moscow, 1986. Tchernogolovka, 1986. *Abstracts*; p 27 (Russ).

(2) Alekseev, A. V.; Babaeva, M. A.; Bystrov, D. S.; Tsyganenko, A. A.; Yushkov, V. A. In *Photochemical Processes in the Earth atmosphere*; Nauka: Moscow, 1990; p 20 (Russ).

- (3) Bulanin, K. M.; Alekseev, A. V.; Bystrov, D. S.; Lavalley, J. C.; Tsyganenko, A. A. J. Phys. Chem. **1994**, *98*, 5100.
- (4) Bulanin, K. M.; Lavalley, J. C.; Tsyganenko, A. A. J. Phys. Chem. 1995, 99, 10294.
- (5) Bulanin, K. M.; Lavalley, J. C.; Tsyganenko, A. A. J. Phys. Chem. B 1997, 101, 2917.
- (6) Bulanin, K. M.; Lavalley, J. C.; Tsyganenko, A. A. Colloids Surf., A. Physicochem. Eng. Aspects 1995, 101, 153.
- (7) Thomas, K.; Hoggan, P. E.; Mariey, L.; Lamotte, J.; Lavalley, J. C. *Catal. Lett.* **1997**, *46*, 77.

- (8) Babaeva, M. A., Bystrov, D. S., Kovalgin, A. Yu., Tsyganenko, A. A. J. Catal. **1990**, *123*, 396.
- (9) Naidenov, A.; Stoyanova, R.; Mehandjiev, D. J. Mol. Catal. A: Chemical 1995, 98, 9.
- (10) Mariey, L.; Lamotte, J.; Lavalley, J. C.; Tsyganenko, N. M.; Tsyganenko, A. A. *Catal. Lett.* **1996**, *41*, 209.
 - (11) Li, C.; Qin Xin; Xie-xian Guo. Catal. Lett. 1992, 12, 297.
 - (12) Yao, H. C.; Yao, Y. F. Yu. J. Catal. 1984, 86, 254.
- (13) Li, C.; Domen, K.; Maruya, K.; Onishi, T. J. Am. Chem. Soc. 1989, 111, 7683.
- (14) Li, C., Domen, K.; Maruya, K.; Onishi, T. J. Catal. 1990, 123, 436.
- (15) Haneda, M.; Mizushima, T.; Kakuta, N. J. Chem. Soc., Faraday Trans. 1995, 91, 4459.
- (16) Binet, C.; Badri, A.; Boutonnet-Kizling, M.; Lavalley, J. C. J. Chem. Soc., Faraday Trans. 1994, 90, 1023.
- (17) Zhanpeizov, N. U.; Staemmler, V.; Baerns, M. J. Mol. Catal. 1995, 101, 51.
- (18) Makaryan, G. L.; Lunina, E. V. Kinet. Catal. 1996, 37, 133.
- (19) Zaki, M. I.; Hussein, G. A. M.; Mansour, S. A. A.; El-Ammawy, H. A. J. Mol. Catal. **1989**, *51*, 209.

(20) Jadi, A. Thesis, Université de Caen, 1990.

- (21) Binet, C.; Jadi, A.; Lavalley, J. C. J. Chim. Phys. Phys.-Chim. Biol. 1992, 89, 31.
- (22) Bulanin, K. M.; Bulanin, M. O.; Tsyganenko, A. A. Chem. Phys. (Amsterdam) 1996, 203, 127.
- (23) Mariey, L.; Lamotte, J.; Hoggan, P.; Lavalley, J. C.; Bulanin, K. M.; Tsyganenko, A. A. Chem. Lett. 1997, 835.
- (24) Badri, A.; Binet, C.; Lavalley, J. C. J. Chem. Soc., Faraday Trans. 1996, 92, 4669.
- (25) Tsyganenko, A. A.; Denisenko, L. A.; Zverev, S. M.; Filimonov, V. N. J. Catal. 1985, 94, 10.
- (26) Spiker, R. C., Jr.; Andrews, L. J. Chem. Phys. 1973, 59, 1851.
 (27) Hesse, W.; Jansen, M.; Schnick, W. Prog. Solid State Chem. 1989,
- 19, 47.(28) Badri, A.; Binet, C.; Lavalley, J. C. J. Chem. Soc., Faraday Trans.
- **1997**, *93*, 1159.
- (29) Binet, C.; Jadi, A.; Lavalley, J. C. J. Chim. Phys. Phys.-Chim. Biol. 1992, 89, 1779.