On the Basicity of Ozone

Laurence Mariey, Jean Lamotte, Philip Hoggan, Jean-Claude Lavalley,* Kirill Boulanine,† and Alexei Tsyganenko†
Laboratoire Catalyse et Spectrochimie, UMR CNRS 6506, ISMRA-Université, 14050 Caen Cedex, France
†Institute of Physics, St. Petersburg University, St. Petersburg 198904, Russia

(Received April 21, 1997; CL-970299)

Comparison of IR spectra of species formed from adsorption of different bases on the acidic OH groups of zeolites (HY, MFI) indicates that O_3 basicity is close to that of CO. Calculations confirm such a result ; in particular they involve that the terminal oxygen atoms of ozone are the basic centers.

Ozone is an important compound, due to its atmospheric role and its uses in depollution of water and air. In spite of that, very few fundamentals data are known about it[1].

The aim of this article is to reach the basicity of O_3 using IR spectroscopy. According to an abundant literature[2], when a base gives H-bonded species with hydroxyl groups of metal oxide, the shift of the hydroxyl band grows with the strength of the base.

A recent study[3] suggests that basicity of O_3 is about the same as that of carbon monoxide, because on silica, the shift of the OH band is very close for the two bases (about 100 cm^{-1}). However the shift of the OH band due to ozone depends on the ozone pressure in the cell (from 80 to 100cm^{-1} in this experimental conditions), which makes the study rather unprecise. We present here the results obtained on much acidic materials, HY and MFI zeolites. Their higher acidity leads to a greater $\Delta\nu$(OH) shift and therefore to a more accurate result. We have checked that, in the conditions used (adsorption at liquid nitrogen temperature), no ozone decomposition occurs. In the first part (HY) we compare the results obtained from ozone with those observed with various gases of different basicity. In the second part, we check the analogy between ozone and CO using the MFI sample. Finally calculations are performed to confirm such an analogy.

The stainless steel cell for studying infrared spectra at 77K was described previously[4]. Zeolite samples were pressed into pellets (10-15 mg) and pretreated under vacuum at 673K (HY, prepared from a low sodium form of a NH_4Y zeolite, Zeocat E2268, by ammonium hexafluorosilicate treatment , Si/Al = 5.4). or 723K (MFI, Conteka, Si/Al = 18) during four hours. All spectra were recorded on a 710 Nicolet FT-IR spectrometer. Gas adsorption was performed at 77K, excepted for COS (293K). Ozone was prepared from gaseous O_2 in an electric discharge at room temperature and introduced into the cell at 77K.

The spectrum of the HY zeolite presents two ν(OH) bands at 3640 cm^{-1} (HF) and 3554 cm^{-1} (LF), the HF hydroxyl groups being more acidic than the LF ones and more accessible to adsorbates since they are situated in the supercages.Figure 1 shows the IR spectra obtained by adsorption of various molecules on the HY (all reported spectra were subtracted from those of the pretreated sample).

The quantities of adsorbent were chosen to perturb only the HF(OH) band. We notice during these experiments that the shift does not depend on the adsorbent quantity introduced. The HF(OH) band shifts are reported in Table 1.

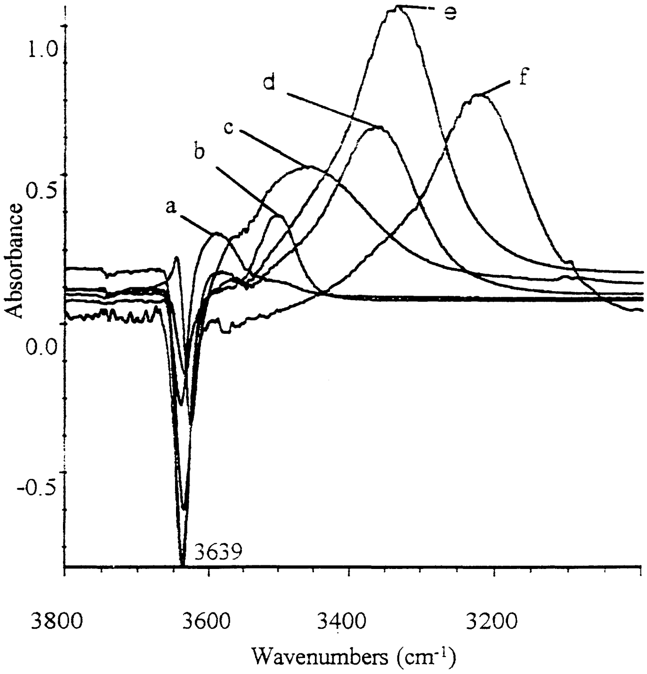

Figure 1. I.R. spectra of species formed from adsorption of : a - O_2 ; b - N_2O ; c - COS ; d - O_3 ;e - CO ; f - C_2H_4, on HY.

Table 1. OH band shifts for various bases

	O_2	N_2O	COS	O_3	CO	C_2H_4
$\Delta\nu$(OH) (cm^{-1})	43	137	170	277	306	419

We deduce that the basicity increases in the following order :

$O_2 < N_2O < COS < O_3 < CO < C_2H_4$

For the selected probe molecules, $\Delta\nu$(OH) varies of a great factor from O_2 to C_2H_4, but it is worthwhile noticing that the results obtained from O_3 and CO are very close (only 30 cm^{-1} between them).

To verify our results, we proceeded to the same experiments with another zeolite (MFI), known to be more acidic than HY. Its spectrum reveals after evacuation at 723K, two bands in the ν(OH) region : 3750 cm^{-1} assigned to silanol groups, and 3623 cm^{-1} assigned to zeolitic hydroxyls (Figure 2a). By adsorption

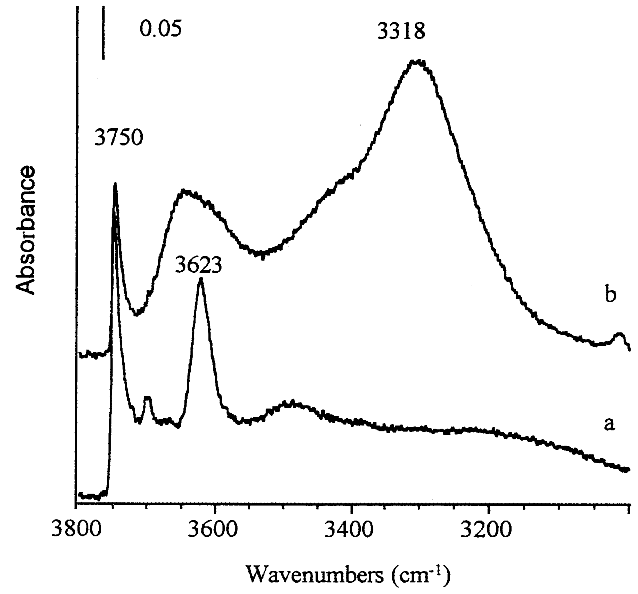

Figure 2. I.R. spectra obtained on the MFI zeolite ;
a - reference at 77K ; b - after O_3 adsorption at 77K.

of ozone at 77K (Figure 2b), these two bands shift of about 100 cm^{-1} and 305 cm^{-1} respectively· Carbon monoxide adsorption produces a shift of the same order (315 cm^{-1} for the acidic hydroxyls[5]).

Using a model for zeolite cage hydroxyl groups suggested by Sauer et al.,[6] careful MNDO-PM3 calculations[7] were carried out to obtain quantitative indicators of basicity for CO and O_3 molecules.

Literature results indicate that the terminal oxygen atoms of O_3 are more basic than the central oxygen[3, 8]. On the other hand, it has been shown that CO interacts with zeolite acidic OH groups via the electron doublet of the carbon[9]. So the calculations have been performed with the following complexes in which one terminal atom of the basic molecule (O_3 or CO) was approached at a distance " d " to the acidic proton in the site (Figure3).

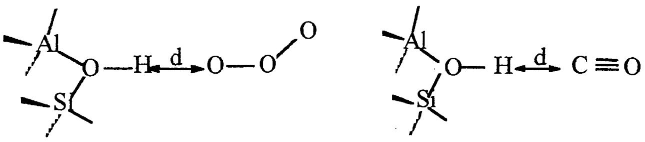

Figure 3. Ozone and CO complexes formed with the zeolite OH group.

The chosen quantitative indicators are i) I_{OH}, the bond order for the weakening OH bond which is lowered from an initial value of 0.92 (separate molecules), ii) the partial atomic charge on the proton ΔC_H (initially +0.2385), and iii) the change in the partial negative charge ΔC_B of the Lewis base donor atom (O in O_3 and C in CO)

Table 2. Indicators of basicity for O_3 and CO

	I_{OH}	ΔC_H	ΔC_B
d = 1.75 Å (O_3) (CO)	0.8638 0.8735	+0.2604 +0.2596	- 0.024 - 0.027
d = 2,0 Å (O_3) (CO)	0.8949 0.8973	+0.2527 +0.2524	- 0.011 - 0.013
d = 2.5Å (O_3) (CO)	0.9139 0.9141	+0.2461 +0.2455	- 0.002 - 0.002

The calculated complexation enthalpies are :
ΔH_{comp} (O_3) = - 19.86 Kcal/mol
ΔH_{comp} (CO) = - 21.40 Kcal/mol
The CO complex is slightly stabler, suggesting CO should be a little more basic, in complete accordance with the IR results.

As shown in Table 2, for values of d from 1.75 to 2.75 Å the indicators of basicity are very similar for CO and O_3. Besides, the ΔC_B results confirm that terminal oxygens of O_3 are basic sites.

References

1 B. Dhandapani and S.T. Oyama, *Appl. Catal. B*, **11**, 129 (1997).
2 H. Knözinger, in "The hydrogen bond" , ed by Schuster et al., North-Holland Publ., Amsterdam , Vol III, 1265 (1976).
3 K.M. Bulanin, A.V. Alexeev, D.S. Bystrov, J.C. Lavalley, and A.A. Tsyganenko, *J. Phys. Chem.*, **98**, 5100 (1994).
4 M.A. Babaeva, D.S. Bystrov, A.Y. Kovalgin, and A.A. Tsyganenko, *J. Catal.*, **123**, 396 (1990).
5 S. Bordiga, E.E. Platero, C.O. Areàn, C. Lamberti, and A. Zecchina, *J. Catal.*, **137**, 179 (1992).
6 J. Sauer, *Chem. Rev.* **89**, 199 (1989).
7 J. P. Stewart, *J. Comput. Chem.*, **10**, 209 (1989).
8 K. Thomas, P.E. Hoggan, L. Mariey, J. Lamotte, and J.C. Lavalley, *Catal. Lett.*, submitted.
9 L. Kubelkova, S. Beran, and J.A. Lercher, *Zeolites*, **9**, 539 (1989).