ESRF

Experiment title:

Cation location and its environment in Rb-exchanged zeolites.

Experiment number:

CH-107

Beamline: **D8 GILDA**

Date of Experiment: from: November 01 to:November **04, 1995**

Date of Report: Feb. 29, 1996

Shifts: 9

Local contact(s): Francesco D'Acapito

Received at ESRF:

Names and affiliations of applicants (*indicates experimentalists):

C. Lamberti*, S. Bordiga*, C. Panze*, G. Spano*#, A. Zecchina

Dipartimento di Chimica Inorganic, Chimica Fisica e Chimica dei Materiali, University' di Torino, Via P. Giuria 7,1-10125, Torino Italy.

F. Geobaldo*
Dipartimento di Scienza dei Materiali ed Ingegneria Chimica, Politecnico di Torino, Corso Duca degli Abruzzi 24, I- 10129 Torino Italy.

Current address: ENICHEM Ricerche Novara, via G. Fauser 4 Novara Italy.

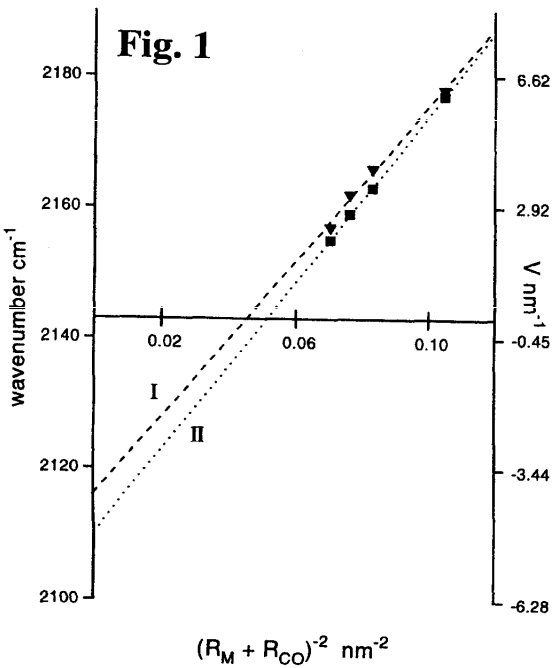
Report:

In the last few years our group has performed an ongoing research program in the characterization of alkali-metal exchanged zeolites, mainly using infrared (IR) spectroscopy of adsorbed mulecules [1-4]. In particular, a linear blue shift of the C-O stretching frequency of M+.. .CO adducts in zeolites (M= Cs, Rb, K, Na, Li), see Fig. 1, was found as a function of $(R_M + R_{CO})^{-2}$, being R_M the cation radius and R_{CO} the molecule radius. This trend enable us to adfirm that the interaction is mainly of electrostatic nature and to infer the geometry of the M+. ..CO adsorption site, see Fig.2. We have thus performed XAFS measurements on Rb-ZSM-5 and Rb-mordenite to verify our previous findings. The complexity of the experiment is remarkable because: **i)** a crytical outgassing procedure at 700 K must be followed to assure the evacuation of undesired adsorbed molecules; **ii)** after the dosage of a desired ammount of CO (or N_2), the obtained pure atmosphere must be preserved during the XAFS data acquisition (4 h for sample cooling, cell location and 3 spectra collection); **iii)** being the Rb^+.. .CO interaction very weak, adducts can not be formed at RT and measurements at 77 K are required. To fulfill those requests, as planned in the proposal, we have realized an improoved version of our EXAFS cell previously used at ADONE and LURE to measure zeolites at RT [5]. This new cell has operated for the first time at GILDA D8 beamline of ESRF during experiment CH- 107, where we have successfully observed Rb^+...CO and Rb^+...N_2 adducs on ZSM-5 and mordenite. A detailed description of the samples treatments procedure and all technical details on the cell are reported elsewhere [6].

XAFS experiments heve been carried out in transmission mode using a dynamical sagittal focused Si(3 11) monochromator; energy calibration has been performed with Kr gas. In the XANES part of the spectra, a detailed analysis of the white line area [7,8] assure that we are dealing, in vacuum conditions, with Rb^+ species, giving so a further proof of the quality of the prepared samples.

Moreover, being the edge position and the white line area nearly unaffected upon CO and N_2 dosages, XANES data strongly confirm that the charge of Rb still remains +1 and that both $Rb^+...CO$ and $Rb^+...N_2$ interactions are of electrostatic nature, in fully agreament with our previous findings [1-4]. EXAFS analysis is complex, because: **i)** Rb ions are surrounded (see Fig.2) by only two oxygens atoms, which have a weak backscattering power, so giving rise to a weak EXAFS signals; **ii)** Rb is affected by double electron excitation manifesting in a sharp peak at about 6. lA^{-1} [9- 10]; **iii)** the use of analyis program able to work in the framework of multiple scattering (MS) theory [11] is necessary for the spectra taken in presence of adsorbates, because for both $Rb^+...CO$ and $Rb^+...N_2$ adducts a linear adsorption geometry is expected [1-4], see Fig.2, so enhancing the MS contributions. EXAFS analysis is still in progress at the moment and, from a fully qualitative ground, we can now only state that an increment of the Rb coordination number has been observed after CO and N_2 dosage.

We have also obtained 6 shifts for performing powder X-ray diffraction measurement on the same samples at ESRF D 16 beamline: experiments will be performed in the next weeks. We are indebted with all the GILDA D8 staff and in particular with our local contact F. D'Acapito and with the ESRF chemical lab. staff which have enabled us to operate in ideal conditions.



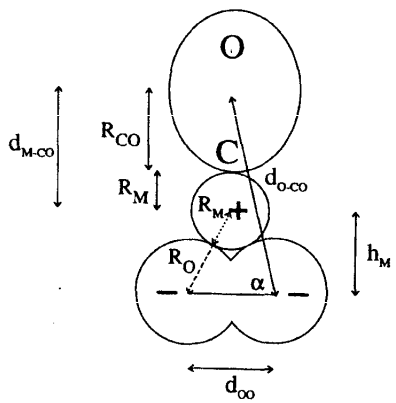


Fig. 2

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