Vibrational Relaxation of Hydroxyls in Zeolite Y: H-Bonding, Dipole-Dipole Coupling and Accepting Modes


1POM-Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands
2Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Abstract. Excited vibrational population lifetimes of hydroxyls in zeolite Y are shown to provide insight in the (dynamic) coupling of the hydroxyls to the zeolitic lattice as well as to other O-H oscillators.

Time-resolved saturation spectroscopy on O-H in zeolites was performed to gain new information about the relaxation dynamics of the O-H stretch vibration in this crystalline solid and about the structural environment of the acid O-H groups. The presence of these acid sites in proton loaded zeolites is exploited widely in the petrochemical industry, where they are used as catalysts in the hydrocarbon cracking process. The dynamical chemical and physical interactions of the protons with the zeolitic lattice are of interest to understand the catalytic properties.

Zeolites Y with silicon to aluminum ratios Si/Al = 2.4 and 2.8 and different proton concentrations were studied. Conventional FTIR spectra show two resolved absorption bands that are attributed to O-H stretch vibrations of bridging oxygen atoms: a low frequency band (LF) near 3550 cm\(^{-1}\) and a HF band near 3640 cm\(^{-1}\).\(^{[2]}\)

We have measured O-H vibrational population relaxation times \(T_1\) for both LF and HF absorption bands, using intense (~220 \(\mu\)J) picosecond (20 ps) tunable infrared pulses (the experimental setup is described in ref.\(^{[3]}\)). After excitation by a strong pump pulse that bleaches the O-H absorption, the decay of the excited population difference between \(v = 1\) and \(v = 0\) is monitored by the transmission of a weak probe pulse, whose time-delay with respect to the pump pulse is varied. From this decay the energy relaxation time \(T_1\) can be deduced.

In Fig.1 results of typical pump-probe experiments are shown for both the LF and the HF absorption bands of zeolite Y with a proton to T (T = Si or Al) ratio of 0.22 and with Si/Al=2.4. Note that the population lifetime for the LF band is significantly smaller than \(T_1^{HF}\) (see also ref.\(^{[4]}\)). When the laser frequency is scanned through the LF absorption band, the relaxation lifetime increases from \(T_1^{LP} = 29 \pm 10\) ps at 3518 cm\(^{-1}\) to 83 \(\pm\) 14 ps at 3567 cm\(^{-1}\) for this particular zeolite. No frequency dependence of \(T_1^{HF}\) was observed. The same observations were made for zeolites with different proton concentrations, but both \(T_1^{LP}\) and \(T_1^{HF}\) decrease with increasing proton concentration.
Figure 1: Relative transmission of a probe pulse as function of the delay between pump and probe, for both the LF and the HF absorption bands of zeolite Y.

The smaller $T_1^{LF}$ compared to $T_1^{HF}$ and the dependence of $T_1^{LF}$ on the laser frequency are explained by hydrogen bonding of the protons in the LF band. Both LF and HF stretch vibrations relax to very similar accepting modes, but H-bonding of the protons in the LF band increases the coupling to the accepting modes.

To study the effect of proton concentration we decreased the proton concentration in a fully exchanged zeolite by partial deuteration. After correction for laser heating effects in the focus (temperature increases up to 250 K were estimated) we found that replacing 80% of O–H by O–D increases $T_1^{LF}$ and $T_1^{HF}$ for the O–H stretch vibration with a factor 1.5. This indicates that a (nearly) resonant deactivation mechanism like dipole-dipole coupling increases the relaxation rate at higher proton concentrations.

The relatively long O–D lifetimes (only a factor $\leq 3$ smaller than O–H lifetimes) indicate that the O–H bending vibrations are important accepting modes for O–H stretch relaxation. Both from this and from the temperature dependence of $T_1^{HF}$ for O–H the relaxation scheme for O–H stretch relaxation is concluded to be a five-mode process with at least three O–H bending vibrations.

References