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FLUORESCENCE YIELD NEAR EDGE SPECTROSCOPY (FYNES) OF BENZENE ADSORBED IN Na-Y ZEOLITE

D.A. FISCHER [1], J.L. GLAND *, and S.M. DAVIS [2],**

[1] *Exxon PRT, Brookhaven National Laboratory, Bldg. 510E, Upton, NY 11973, U.S.A.*
[2] *Exxon Research and Development Laboratories, Baton Rouge, LA 70821, U.S.A.*

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Benzene adsorbed in sodium-Y zeolite has been investigated using Fluorescence Yield Near Edge Spectroscopy (FYNES). These studies demonstrate that FYNES measurements are feasible as a direct probe of the local electronic structure of hydrocarbons adsorbed in and on insulating, microporous practical catalysts. The distribution of π^* energy levels for adsorbed benzene was not significantly altered as compared to the condensed phase.

Fluorescence yield near edge (X-ray absorption) spectroscopy (FYNES) has emerged as a powerful tool for in situ studies of the structure and reorientation dynamics of chemisorbed species as well as bulk materials characterization [1]. This X-ray absorption technique uses tunable monochromatic synchrotron radiation in the soft X-ray region to create K shell core holes in the atoms of interest; the decay of these core holes is then detected by characteristic X-ray fluorescence during the deexcitation process. Thus, FYNES is a photon-in, photon-out spectroscopy which can be used in vacuum or in the presence of reactive gases. In situ experiments have been performed involving chemisorption, displacement, and dehydrogenation of organic molecules on surfaces [2–5]. Fluorescence yield measurements with energy dispersive detection afford high bulk sensitivity to low-Z elements, or mixtures thereof, and preclude limitations associated with differential charging of insulating materials rendering this technique especially suitable for hydrocarbon adsorption studies using microporous, high area practical catalysts.

In this communication, we report recent FYNES investigations of benzene adsorbed at room temperature in Na-Y zeolite. To our knowledge, this work

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* Present address: University of Michigan, Ann Arbor, MI, U.S.A.
** Author to whom correspondence should be addressed.

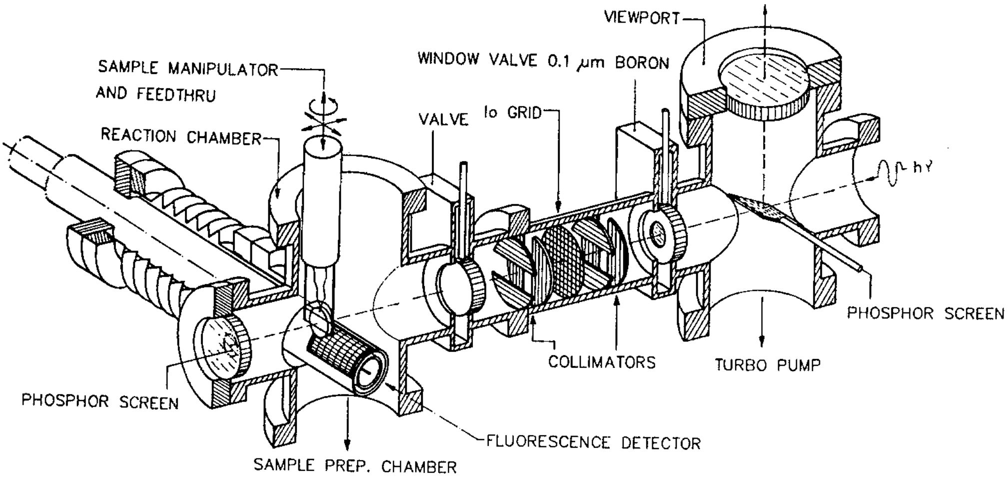

Fig. 1. Apparatus for ultra soft fluorescence X-ray absorption measurements in vacuum or a reactive atmosphere.

represents the first application of FYNES in studies of molecular adsorption on an insulating surface. Benzene in Na-Y was chosen for investigation because the adsorbate atomic structure and adsorption site were previously established using neutron diffraction [6] and infrared spectroscopy [7]. These studies indicated that at room temperature benzene is mostly located on top of sodium cation sites in S_{II}-supercage positions. At high loadings, a small fraction ($\leqslant 20\%$) of the adsorbed benzene is also localized in 12-ring window sites [6,7].

The vacuum carbon K edge X-ray absorption experiments described were performed on Beamline U1 of the National Synchrotron Light Source (NSLS) equipped with an extended range grasshopper (ERG) monochromator. The ultra soft X-ray absorption measurements were made using the fluorescence yield system shown in fig. 1 which consists of a ballast region, window valve, soft X-ray proportional counter (PC) and a sample chamber of small volume. The soft X-ray entrance window was 0.1 micron thick boron (about 40% transmitting above the carbon K edge) and was used to isolate the ultra high vacuum synchrotron environment from the high vacuum sample chamber for these experiments. This system allowed rapid sample exchange which typically took five minutes.

The proportional counter shown in the figure incorporates cylindrical electrode symmetry with a curved side window providing the ideal PC geometry for optimum energy resolution [8]. The side window consists of two cylindrical concentric one micron polypropylene windows with a differentially pumped region in between supported by 90% transmitting electroformed stainless steel mesh. The window collects nearly 10% of the available solid angle. In addition the side window geometry enables the PC to face the sample looking up, i.e., orthogonal to the plane of incidence away from the specular scattering peak. The energy dispersive characteristics of the proportional counter proved useful in

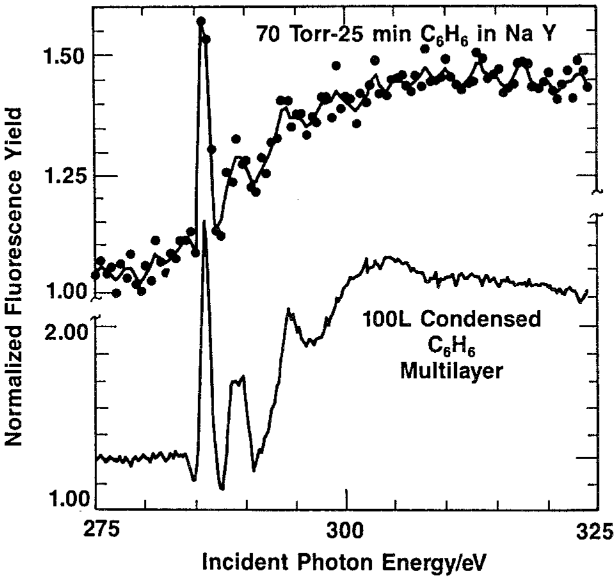

Fig. 2. Fluorescence yield near edge spectroscopy (FYNES) above the carbon K edge for benzene in a NaY zeolite and a condensed multilayer.

separating the carbon K_α fluorescence of interest from the background oxygen K_α (excited in 2nd order) using standard pulse height analysis techniques.

The sample chamber was equipped with a rotatable manipulator upon which thin pressed wafer samples (ca. 2 cm 2 × 1 mm) could be conveniently mounted and heated or cooled over the temperature range from -150 to 450 °C. In these experiments, fresh Na-Y (Linde, lot 80ME-2501) was dehydrated prior to benzene adsorption by heating to 350 °C for 30 minutes at 10^{-8} Torr. Subsequently, benzene was adsorbed by exposure to 70 Torr of benzene vapor at 35 °C for 20 minutes followed by evacuation to high vacuum at room temperature. Benzene (MCB, thiophene free) was filtered over activated alumina and freeze pumped repeatedly prior to use. Condensed benzene was examined by exposure of a clean holder to 100 Langmuirs of benzene vapor at -150 °C.

Fluorescence yield X-ray absorption spectra recorded above the carbon K-edge for condensed benzene and benzene adsorbed in Na-Y are compared in fig. 2. Within the 1 eV monochromator resolution and modest signal-to-noise recognized with adsorbed benzene, the spectra were indistinguishable and dominated by bound state $1s \rightarrow \pi^*$ resonances for photon energies near 285 and 289 eV, along with a σ^* resonance near 294 eV. A second σ^* shape resonance observed near 304 eV with condensed benzene could not be resolved for the adsorbed phase. The fluorescence yield spectrum for condensed benzene agrees closely with that reported and assigned by Stohr et al. [9] using partial electron yield detection combined with electronic structure calculations.

By comparison to the X-ray absorption behavior of zeolite/carbon mixtures with known carbon concentrations, we estimate that the benzene loading corresponding to fig. 2 is 2.5–3.5 wt% which corresponds to less than one benzene per supercage.

The similar nature of the spectra displayed in fig. 2 clearly suggests that the electronic structure of adsorbed benzene is not significantly altered by coordination at sodium cation sites. This finding is not too surprising in view of earlier studies of the benzene adsorption energetics [10,11]. While the enthalpy of benzene adsorption is in the range of 17 to 19 kcal/mole, the difference in adsorption energies between benzene and cyclohexane that appears to reflect the specific interaction of benzene π orbitals with Na-cation sites is only about 5 kcal/mole [10]. This behavior contrasts sharply with that for benzene chemisorbed on Pt(111) where significant alteration of the π^* resonances was detected [9]. Earlier work by Stohr et al. indicated that the energy of σ^* shape resonances is very sensitive to changes in C-C bond length [12]. While the σ^* resonances for benzene in Na-Y are not sufficiently resolved for an unambiguous conclusion, there is no evidence for changes in C-C bond length.

These results demonstrate that FYNES measurements are feasible for molecules adsorbed in or on insulating, microporous solids. We believe that these types of studies offer considerable potential for investigating changes in atomic and electronic structure for hydrocarbons adsorbed in zeolites. Extension of this work to other adsorbates and metal containing zeolites is planned.

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