

Electron Energy Loss Studies of Propylene Interactions in US-Y Faujasites

INTRODUCTION

There has been considerable interest in the interactions of hydrocarbons in the Y faujasites and the nature of the formation of "coke" (1-7). From the literature there is a question as to which site (Al or Si) is active in the formation of the residual carbonaceous material left in the molecular sieve after reaction with a hydrocarbon (7). In order to address this question, we have undertaken a study of the interaction of a simple probe molecule (propylene) with two series of ultrastable Y faujasite as a function of reaction temperature from 40-500°C. The techniques involved in the study are core electron energy loss spectroscopy (CEELS), X-ray photoelectron spectroscopy (XPS), and ¹³C nuclear magnetic resonance (NMR) using cross-polarization magic-angle spinning (CPMAS). In this note we will focus on the CEELS results and the new insight that it provides into this interaction in light of the information from the NMR and XPS data for this system.

Electron energy loss (EELS) in low resolution (1 eV) provides electronic interband and plasmon information in the low energy loss region just beneath the primary electron beam energy. When one analyzes above a core level of the system involved (e.g., Al and Si 2*p*, 74.5 and 103.5 eV, respectively) there is, in the near edge region, information about the density of states as well as the local structure (8). In the extended electron loss fine structure region (EXELFS) at higher loss energies from the core level, short range structural information is found very similar to that obtained in

extended X-ray absorption fine structure (EXAFS). These techniques have been applied with success to the study of carbonaceous deposits in catalytic systems (9-12) and amorphous carbon (13). We have looked in detail at the near-edge energy loss regions of the Al and Si 2*p* core loss as a function of reaction temperature for a series of US-Y samples reacted with propylene in a fixed bed reactor.

EXPERIMENTAL

High and low Na US-Y faujasites were prepared for these experiments. The US-Y with high Na content had 2.6 wt% Na and a unit cell dimension of 24.52 Å, while that with low Na had 0.5 wt% and a UCD of 24.52 Å. These fresh US-Y faujasites were reacted in a fixed bed reactor for several hours with flowing propylene at isothermal temperatures of 40-500°C. The samples were reacted until the propylene conversion, to either hydrocarbon products or coke, was less than 30%. The samples were then analyzed in a Perkin-Elmer scanning Auger microprobe 600 by pressing onto an indium foil to ensure electrical contact and minimize charging effects. The electron gun was operated at a primary energy of 750 eV and a beam current of 100-150 nA. The $\Delta E/E$ of the analyzer was set at 0.2% in order to ensure an analyzer resolution of 1 eV. The loss spectrum is acquired in a scanning mode with a magnification of $\times 120$ in order to minimize electron beam damage effects. Previous work has found that the upper limit of the electron dose for nondestructive analysis in SiO₂ and Al₂O₃ is of order 10²⁰ e⁻/cm² (14). We can estimate the electron irradiation doses received by these

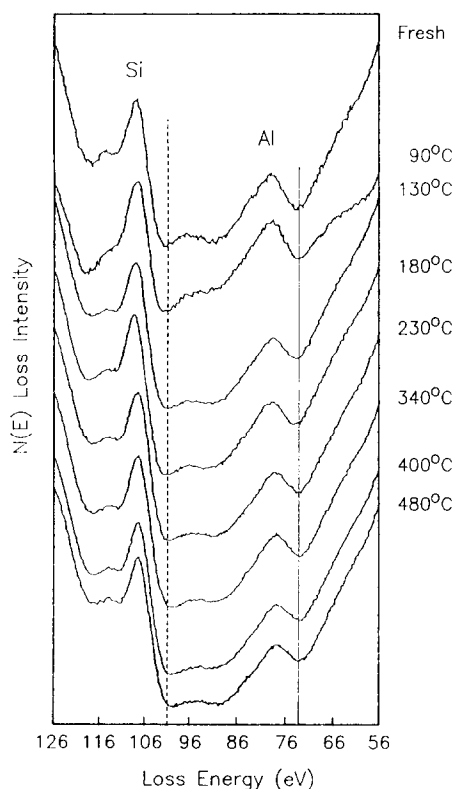


FIG. 1. Core electron energy loss near-edge intensity of Al and Si $2p$ as a function of propylene reaction temperature for low Na faujasite series.

samples taking into consideration the current (100–150 nA), spot size of the electron beam (0.5 μm), rastered area size (1000 μm), and irradiation time (10–15 hr). The dose is of order 10^{18} – 10^{19} e^-/cm^2 .

Electron beam damage appears to be negligible under these conditions as is evidenced by a lack of the reduced metallic Al or Si Auger peaks at 68 or 92 eV, respectively. The Al to Si $2p$ loss region is scanned for 70 eV from 10 eV below the onset of the Al $2p$ transition. This includes the Si $2p$ loss transition in this energy loss window. The analyzer is stepped by 0.1 eV through this window to ensure maximum resolution. A typical data acquisition time is 10 hr. XPS and CPMAS ^{13}C NMR measurements were additionally performed on these same sets of samples.

RESULTS

The results of the CEELS for the Al and Si $2p$ near-edge loss region for the low Na series, in the $N(E)$ mode, is shown in Fig. 1. The same trend is found in the high Na series with only minor differences. Quantitation can be performed by measuring the number of counts above a linear background subtraction from threshold to the end of the near-edge band. In the Al (Si) case, for example, this region extends from 74 to 90 eV (102 to 120 eV). The intensities that are quoted and ratioed are then the counts in the near-edge band above linear background subtraction. The intensity of the Si near-edge region (~ 15 eV) is constant across the series while the Al intensity for this same region decreases in strength by 50%. A plot of the ratio of the Al to Si intensity under the near-edge loss region (~ 15 eV) is shown in Fig. 2 along with the sp^2 carbon fraction of the carbon content as measured by CPMAS ^{13}C NMR. Note that the XPS measured carbon content across the series remains relatively invariant at ~ 7 – 10 wt% (see Table 1). Note that the semicontinuous decrease of the ratioed Al $2p$ near-edge loss intensity is paralleled by an increase in the sp^2 carbon fraction of the residual carbon content.

There are several implications from these results. The Si near-edge intensity and structure is little affected throughout the series. Therefore, the Si site in the faujasite is

TABLE I

Carbon Content of Coked Faujasites by Elemental Analysis (Low Na Series)

No.	Catalyst	Wt% C
1	US-Y fresh	0.28
2	Coked at 90°C	9.17
3	Coked at 180°C	7.76
4	Coked at 230°C	7.47
5	Coked at 340°C	6.07
6	Coked at 400°C	8.93
7	Coked at 480°C	9.95

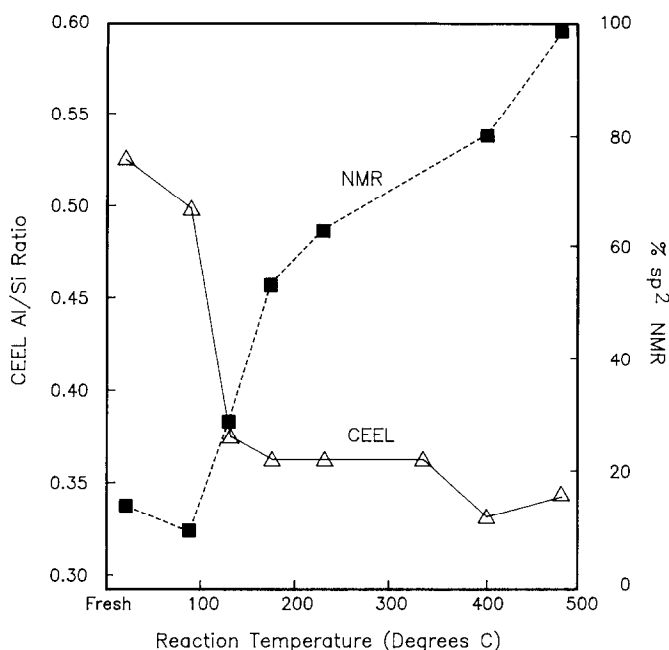


FIG. 2. Al/Si core electron energy loss near-edge intensity ratio plotted with the ^{13}C CPMAS NMR of the sp^2 carbon content as a function of propylene reaction temperature.

not implicated in the formation of π bonds in the residual carbonaceous material. Since the Si near-edge intensity is not attenuated by the increased carbon content, the carbon must be localized around the Al site. A physical blockage of the Al site by the carbonaceous network is one explanation for the electron energy loss signal attenuation. However, we have found attenuations of the near-edge intensity of the order of 50%, which are difficult to account for by a simple exponential attenuation due to increased carbonaceous material clustered about the Al site given the small weight percent of carbon found by XPS.

Notice from Table 1 that the total coke content also does not track the Al CEEL attenuation. While some Al attenuation undoubtedly results from the clustered coke deposition, another important factor appears to be an electronic interaction resulting in charge transfer from π bonds of the coke to the active Al site. Note from Fig. 2 that the Al CEEL signal inversely follows the sp^2 character of the carbon as measured by ^{13}C NMR. A charge transfer to the Al

site would result in a decrease in the matrix element and thus in a decrease in the transition strength of the Al $2p$ near-edge region. Direct evidence for C π states at the top of the valence band comes from XPS valence band analysis reported elsewhere (15).

Supporting evidence for a carbon-Al site interaction comes from NH_3 temperature-programmed desorption (TPD) studies. We found a decreasing NH_3 uptake and desorption with increasing reaction temperature of the propylene over the Y-Faujasite (15). The NH_3 uptake decreased appreciably across the series from lowest to highest reaction temperature correlating with the Al $2p$ near-edge intensity. The inverse correlation of decreasing NH_3 uptake with increasing sp^2 carbon percentage indicates an association of the sp^2 carbon species with the acid sites. Whether this is a physical site blockage or a more subtle electronic interaction is not clear from the NH_3 TPD alone.

Since dipole selection rules have been found not to strictly apply in electron loss core transitions (16) where high momentum transfer (as in reflection geometry) is in-

volved, we might expect a $2p-3p$ as well as the dipole allowed $2p-3s$ transition in the Al $2p$ core loss. Previous electron energy loss work on $\alpha\text{-Al}_2\text{O}_3$ (14) has identified states 1.0, 5.1, and 9.8 eV above the conduction band minimum. If one assigns the Fermi level at midgap (8.5 eV), then the main conduction band features would appear at 5.2, 9.3, and 14.0 eV. The measured separations of the Al loss peak from the threshold, which is the XPS measured binding energy, are 6.0 and 10.0 eV. This is within reasonable agreement considering that the Al site in the faujasite is tetrahedrally coordinated while that in $\alpha\text{-Al}_2\text{O}_3$ is octahedral. Recent calculations of $\alpha\text{-Al}_2\text{O}_3$ (17, 18) indicate that the Al $3s$ and $3p$ are predominantly antibonding in character, and hence readily available for the $2p$ loss transition. Additionally, the states nearest the conduction band edge are predominantly $3s$ in character. As a result the Al $2p$ loss near-edge would be a sensitive measure of the $3s^*$ density of states.

CONCLUSIONS

A model of the interaction of the catalyst with the coke formed at high temperature could be envisioned as follows. At high temperatures, the coke contains mainly sp^2 carbons, and we assume that the majority of these carbons are in polyaromatic structures. These polyaromatic clusters reside within the supercage of the faujasite. The aromatic basal plane would be lying on top and centered above a tetrahedral bare Al ion site. The π electrons of the polyaromatic sheet interact with the antibonding $3p-3s$ empty states of the Al site. There is π donation from the carbonaceous material to the antibonding $3p-3s$ states of the Al site giving rise to a decrease in the available states for the $2p$ transition. This model is consistent with the observed decrease in the Al $2p$ near-edge structure shown in Fig. 1. Although it cannot be directly shown at this time, this model directly implicates the bare Al ion site in the formation of coke in the faujasite pores.

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