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An XPS Study of Coke Distribution on ZSM-5

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Two ZSM-5 catalysts were prepared with bulk Si/Al ratios of 39 and 74. After conversion to the hydrogen form they were partially deactivated at 370°C in a methanol/nitrogen stream. Coke contents were determined by combustion in a microbalance. Measurement of the surface and near-surface C/Si ratio by X-ray photoelectron spectroscopy showed internal and external coke formation. Internal coke formation predominated during methanol conversion over ZSM-5 until the catalyst was essentially deactivated. External coke was then formed, probably by the thermal cracking of methanol.

INTRODUCTION

The zeolite ZSM-5 used in the conversion of methanol to gasoline shows a remarkably low rate of coke formation and resultant deactivation. This property has been attributed (*1–7*) in part to the relatively low density of acid sites and in part to the dimensions of the channels, which are small enough to inhibit the formation of reaction complexes, or intermediates, which lead to the production of coke.

The site of coke formation and the nature of the coke formed on ZSM-5 have received relatively little consideration. It has been suggested (*6*) that coke forms on the external surfaces of the ZSM-5 crystals, causing pore mouth blocking and deactivation. An alternative view (*7*) is that while coke initially forms on the external surface, an internal coke later forms by the polymerisation of small olefins. The suggestion (*8*) that the coke is monoaromatic and forms within the pores has also been made. Previous work (*9*), based on void volume measurements and selective coke removal, implied that several weight percent of coke can be present in the channels of highly coked ZSM-5. Solid-state ^{13}C NMR (*10*) has shown that the coke is indeed highly aromatic, and when high levels of coke are present (>10%), an apparently graphitic coke forms. Because of the two-dimensional nature of graphite, the formation in the channels of a graphitic coke is not possible, so at high coke levels surface coke must be present. Studies based on X-ray diffraction show (*11*) that the structure of ZSM-5 distorts with the sorption of organic molecules. Similar changes also occur on deactivation of ZSM-5 (*12, 13*), suggesting that some coke must form in the channel system.

Currently available evidence is insufficient to determine the site of coke formation on ZSM-5 with certainty. In an attempt to determine more clearly the site of coke formation on ZSM-5 during methanol conversion we have used the technique of X-ray photoelectron spectroscopy (XPS) to analyse the surface of used catalysts. Surface analysis by XPS is limited to the first few atomic layers and has proved here to be useful in distinguishing internally and externally formed coke.

EXPERIMENTAL

Samples

The ZSM-5 catalysts of the present study comprised 29 samples prepared from two zeolites used in previous work (*9, 10, 20*):

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ZSM-5#2 with a Si/Al ratio of 74 and ZSM-5#3 with a Si/Al ratio of 39. These zeolites were prepared by hydrothermal crystallization of an aluminosilicate gel in the presence of tetrapropylammonium hydroxide (14). The external surface area of the precursors was 6 and 2 m^2/g for ZSM-5#2 and ZSM-5#3, respectively (9). After calcination of the precursor at 500°C in air, the zeolites were converted to the H-form by ammonium ion exchange and calcination at 450°C.

Formation of Coke

The ZSM-5 catalysts were used for methanol conversion in a tumbling bed reactor (*10*). A stream of methanol vapour in nitrogen was passed over the ZSM-5 at 370°C. After a preselected time the methanol feed was stopped and the ZSM-5 was held for 20 min at 370°C in flowing nitrogen to remove volatiles before being cooled to room temperature.

Coke Determination

The amount of coke formed on the ZSM-5 catalyst was determined by combustion in oxygen in a microbalance (*9*). The amount of coke present was expressed as a percentage of the weight of ZSM-5 at 600°C after combustion in oxygen.

Chemical analysis of the hydrogen and carbon content of the coke showed that the C/H ratio fell from ca. 2 at coke contents of 1% to less than 0.5 at coke contents above 17%. More details of the variation in hydrogen content will be presented elsewhere (*10*).

Surface Analysis

XPS measurements were conducted in a Vacuum Generators Escalab I instrument at a working pressure of approximately 10^{-9} Torr. All spectra were taken with Al K_α excitation, 35 eV pass energy with 4 mm slits, and were accumulated via pulse counting. Survey scans were recorded between 0 and 1250 eV, with peak areas determined by individual scans over a 12.5-eV range from 73 eV (Al), 102 eV (Si), and 282 eV (C). Si/Al and C/Si ratios were measured from electronically integrated peak areas, assuming a linear background. Atomic ratios were calculated from the integrated intensities and the Scofield cross sections (*15*). For example, the C/Si atomic ratio was calculated from

$$\frac{\mathrm{C}}{\mathrm{Si}} = \frac{I(\mathrm{C}\ 1s)}{I(\mathrm{Si}\ 2p)} \cdot \frac{\sigma(\mathrm{Si}\ 2p)}{\sigma(\mathrm{C}\ 1s)},$$

where $\sigma(\mathrm{C}\ 1s) = 1.0$ and $\sigma(\mathrm{Si}\ 2p) = 0.817$ (*15*). This equation assumes that the instrument transmission function ($\alpha E_k^{-0.5}$) and the mean free path ($\alpha E_k^{+0.5}$) terms cancel.

Samples were prepared by mounting the powders directly as a thin layer on stainless steel stubs. This method minimized contamination, since dispersion of the specimens with organic solvents increased the C/Si ratios noticeably on the low-coke specimens. Storing the ZSM-5 samples in polythene bottles also increased the amount of surface carbon; the use of glass vials was found to be suitable. There was no appreciable buildup of carbon during the XPS analysis.

RESULTS

Full scans of all catalysts showed only the presence of Al, Si, C and O. Results for the C/Si surface ratios as a function of coke loading are shown graphically in Figs. 1 and 2. In the ZSM-5#3 series which had been stored in plastic bottles, two samples of coke-free zeolite showed small residual surface C/Si ratios of 0.06 and 0.2; a mean value has therefore been subtracted from each result. The ZSM-5#2 series, stored in glass, had negligible levels of surface carbon contamination and the values given here are as measured. In Fig. 1 is shown a solid line calculated on the assumption that the carbon (coke) distributes itself throughout the channels (see Appendix). Because of the high BET surface area of the ZSM-5 samples (ca. 400 $m^2\ g^{-1}$), the bulk dispersion line in Fig. 1 is identical to a case

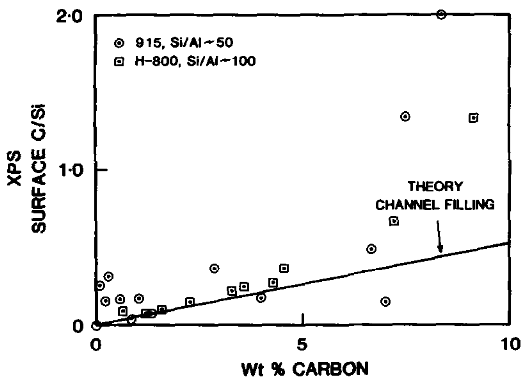

FIG. 1. Measured C/Si ratio versus the weight percent coke. The solid line is the C/Si function calculated assuming internal coke filling the zeolite channels. This function is identical to that expected from a solid solution of carbon in SiO_2 because of the high (ca. 400 m^2/g) surface area of ZSM-5.

in which carbon is uniformly distributed throughout the zeolite structure. The results lie very close to this line in Fig. 1 up to approximately 8 wt% coke, above which the points deviate from the line, indicating that some excess surface carbon is present.

A more dramatic plot can be seen in Fig. 2, where results from 8 to 17.2 wt% coke are included. From 8 to 13 wt% coke there is a slight excess of surface carbon over that expected from channel filling only. Above 14 wt% coke, the C/Si ratio increases dramatically, rising to a value of 31.2 at 17.2 wt% coke. The curved vertical line in Fig. 2 is the theoretical C/Si ratio calculated by assuming that carbon is now depositing uniformly on a 5-m^2/g external surface of the zeolite crystals (see Appendix). We have fitted the curve to pass through the 17.2 wt% coke point. On the basis of the calculation, the point at which no further channel filling occurs is about 15 ± 0.5 wt% coke.

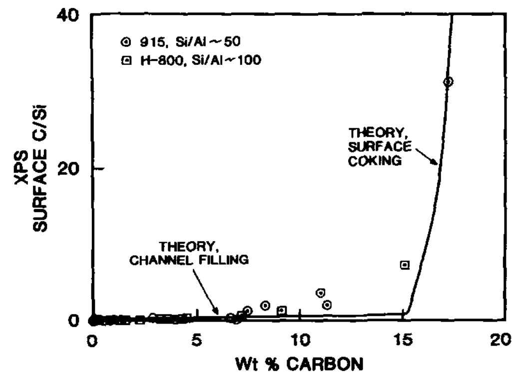

FIG. 2. Measured C/Si ratios by XPS versus weight percent coke. The exponential function ("external coking") is calculated assuming uniform deposition of carbon on the external surfaces of the zeolite (5 m^2/g) and has been fitted to pass through the last data point.

DISCUSSION

At low coke levels, ≤8 wt%, the data points lie close to the predicted line for a model which assumes channel filling, i.e., internal coking. At levels from 8 to about 14 wt% coke, some excess carbon is observed relative to this predicted line, showing that some external coke is being formed. Above 13–14 wt% coke there is a rapid deposition of carbon on the external surface, as indicated by the steep increase in the C/Si ratio. Extrapolation of the data back from the highest loading (17.2 wt% coke) gives an approximate channel filling point of 15 ± 0.5 wt%. The extra carbon signal observed between 8 and 14 wt% coke must be a consequence of some extra external coking occurring in parallel with channel filling. This is deduced from the slow rate of increase in the C/Si ratio over the range measured. Since approximately 0.2 wt% carbon corresponds to one monolayer of carbon (graphite) for a 5-m^2/g area, and only 2–3 monolayers of carbon have been deposited on the external surface at the 12 wt% coke level, the majority of the coke formed must be internal up to about 14 wt% coke. Alternatively, it is possible that a relatively small fraction of the ZSM-5 crystals have a composition such that a heavy layer of external coke forms from the 8% coke level. The majority of the ZSM-5 crystals could thus still be essentially free of external coke and the majority of the coke would be internal. Above 14 wt% the external coking predominates. At 17.2 wt% coke, the highest level studied here, we estimate from the C/Si ratio that an average of 10 monolayers of carbon has been deposited on the external zeolite surface. It was not possible to study samples with higher coke levels as the Si signal was undetectable.

To a degree the Si/Al ratio of the ZSM-5 does not seem to be an important parameter since these results suggest that the channel filling point is approximately the same for both catalysts. For the two catalysts studied, the average surface Si/Al ratio for the ZSM-5#2 was ca. 100, compared with the bulk value of 74. For the ZSM-5#3, the surface Si/Al ratio was ca. 17, compared to the bulk value of 39. Such differences between surface and bulk Si/Al ratios are not uncommon and have been reported by a number of investigators (*18, 19*).

It has been suggested (*10*) that at high coke levels the external coke becomes graphitic. Unfortunately, there is little difference in the C 1*s* binding energy levels of graphite and of $(CH_2)_n$ hydrocarbons (*17*). However, the C 1*s* binding energy from low-coke samples, where internal coke dominates, was 284.5 to 284.7 eV relative to a Si 2*p* level of 103.4 eV (*16*). The value from samples with high external coke contents was 284.3 eV. While these values are all within the range given for both hydrocarbons and graphite, the systematic decrease of 0.2 to 0.4 eV in the C 1*s* binding energies provides some support for an overall chemical difference between internal and external coke.

Our value, of about 15% carbon, for the beginning of dominant surface coking is consistent with the coke levels at which these zeolites ceased conversion of methanol to hydrocarbons (ca. 18 and ca. 14 wt% coke, respectively, for ZSM-5#2 and ZSM-5#3). It is also consistent with the level of coke at which NH_3 chemisorption becomes essentially zero (*20*). Internal coke formation dominates until the majority of the catalytic sites are blocked and methanol conversion falls to a low level. From this point external coking predominates.

This concept is supported by previous work (*9*) where it was found that the void volume of these zeolites fell linearly with coke content to a point when the void volume became constant, although coke formation continued. The linear fall in void volume would result mainly from channel filling by internal coke until the volume containing catalytic sites was occupied. From this point external coke formation would dominate and would have little or no effect on the remaining void volume. Since external coke formation continues when the catalytic activity of the zeolites has fallen to essentially zero, external coke cannot be formed from the hydrocarbon products of methanol conversion. After ZSM-5 deactivation the most likely source of external coke is thermal cracking of methanol. The external coke formed between 8 and 14 wt% may also arise from the thermal cracking of methanol although it is probable that the small, but increasing, amounts of polyaromatics produced as the ZSM-5 approaches deactivation may play an important role in the early stages of external coke formation.

CONCLUSION

Coke formation on the external and internal surfaces of ZSM-5 can be readily distinguished by using XPS to follow the C/Si ratio. This ratio increases linearly at a low rate with internal coke formation, and exponentially when external coke forms.

The present study of coke distribution on ZSM-5 provides strong evidence that coke fills the channel system initially before any significant amount of surface coke is formed. Up to 8 wt% coke there is no evidence for external coke formation. From 8 to 12 wt% coke one or two monolayers of external carbon are deposited as internal coking continues. Above about 15 wt% coke the channels are filled and the external surfaces accumulate coke. It is significant that hydrocarbon formation ceases and chemisorption of NH_3 falls to a very low level at about the same coke content. Since methanol conversion falls to essentially zero, external coke probably arises from thermal cracking of methanol.

APPENDIX

1. Calculation of the "Solid Solution" or "Channel Filling" Line

We assume that for surface areas in excess of 200 m^2/g, the surface C/Si ratios measured by XPS reflect the bulk loading without any enhancement effects (*21*). For 1% carbon-12 dispersed in 99% zeolite (assumed to be pure SiO_2, with a molecular weight of 60),

$$\mathrm{C:Si} = \frac{1}{12}:\frac{99}{60} = 0.051:1$$

Therefore a surface C/Si ratio of 0.051 would be expected for each weight percent of carbon added (at low carbon loadings), based on dispersion throughout the zeolite channels.

2. Calculation of the "Surface Coking Curve"

The silicon XPS signal will be attenuated by an amount

$$\frac{I(\mathrm{Si})}{I_\infty(\mathrm{Si})} = \exp(-d/\lambda(\mathrm{Si})), \qquad (1)$$

where $I(\mathrm{Si})$ = measured silicon intensity, $I_\infty(\mathrm{Si})$ = measured silicon intensity before coking, d = carbon overlayer thickness, and $\lambda(\mathrm{Si})$ = the mean free path of Si electrons in the carbon overlayer. The carbon overlayer signal will increase in intensity at the rate of

$$\frac{I(\mathrm{C})}{I_\infty(\mathrm{C})} = 1 - \exp(-d/\lambda(\mathrm{C})), \qquad (2)$$

where $I(\mathrm{C})$ = measured carbon intensity, $I_\infty(\mathrm{C})$ = intensity from an "infinitely" thick carbon layer, d = carbon overlayer thickness, and $\lambda(\mathrm{C})$ = mean free path of carbon electrons in carbon. We therefore calculate,

$$\frac{\mathrm{C}}{\mathrm{Si}} \cong \frac{N_\infty(\mathrm{C})}{N_\infty(\mathrm{Si})} \cdot \frac{(1 - \exp(-d/\lambda(\mathrm{C})))}{\exp(-d/\lambda(\mathrm{Si}))}, \qquad (3)$$

where N_∞ = the atomic density. This relationship assumes that the mean free path, λ, and spectrometer transmission function terms cancel, and is similar to the relationship derived by Carlson (*22*) for growth of tungsten oxide on tungsten. The theoretical ratio of atomic densities $N_\infty(\mathrm{C})/N_\infty(\mathrm{Si})$ is approximately 5.0, based on equal densities (2.25 g/cm^3 for graphite and SiO_2). Assuming a surface area of 5 m^2/g for the ZSM-5 samples and a density of 2.25 g/cm^3 for carbon, one monolayer corresponds to ca. 0.2 wt% carbon with an overlayer thickness of 2.2 Å. If we estimate the C 1*s* and Si 2*p* photoelectrons to have mean free paths of 10 ± 3 Å (*23*), then the final relationship simplifies to

$$\frac{\mathrm{C}}{\mathrm{Si}} \cong 5.0\,\frac{(1 - \exp(-1.0w))}{\exp(-1.0w)}, \qquad (4)$$

where w = carbon loading in weight percent. The carbon loading in weight percent in Eq. (4) is not the actual loading of the zeolite but the external carbon present in the surface region sampled by the photoelectrons. In order to fit the data we have shifted the calculated curve to pass through the final data point at 17.2 wt% loading (see Fig. 2). The calculated curve intercepts the coke axis at about 15 wt%, suggesting that external coke formation predominates from this point.

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