In-Situ Diffuse Reflectance Infrared Spectroscopic Study of the Photodecomposition of Dibenzyl Ketone Adsorbed on Zeolites[†]

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The infrared spectra of 1,3-diphenyl-2-propanone (dibenzyl ketone, DBK) adsorbed on the hydrophobic zeolite Silicalite have been measured by diffuse reflectance techniques. These spectra are consistent with the existence of several classes of adsorption/inclusion sites in the Silicalite framework; in accord with previous studies, two main classes of sites are discernible. The photodecomposition of included dibenzyl ketone was followed directly by in-situ UV photolysis. The formation of products can be followed directly from the infrared spectra. The results demonstrate that the photodecomposition of included DBK proceeds preferentially in one class of sites which are tentatively assigned to channel inclusion as opposed to surface adsorption sites.

Introduction

The study of organic photoprocesses in nonhomogeneous media is a subject of current widespread interest.¹ Systems studied¹⁻⁴ include crystals, inclusion adducts, surfaces, emulsions, micelles, liquid crystals, and recently zeolites.⁵⁻⁷ In the latter, the effect of conformational restrictions have been explored in photophysical studies⁵ and cage effects have been found in the reaction of several ketones supported in different zeolites.⁶

Silicalite ($\geq 99\%$ SiO₂) belongs to a class of zeolites with a novel topologic type of tetrahedral framework.⁸ Its channel system consists of near-circular zig-zag channels $(5.4 \pm 0.2 \text{ Å diameter})$ cross-linked by elliptical straight channels ($5.75 \times 5.15 \text{ Å}^2$ free cross section). Molecules with kinetic diameter comparable to that of benzene (~ 5.8 Å) are capable of being included in the channels of Silicalite. It has been previously found that molecular geometry, size, and conformational flexibility play important roles in determining channel inclusion.5

Crystallographic,⁸ NMR,⁹ and photophysical⁵ studies have shown that Silicalite offers several sites (or classes of sites) for inclusion and/or surface adsorption. In the case of dibenzyl ketone (DBK) studied here there will be surface adsorption and channel inclusion. The adsorption isotherm for adsorption of DBK on Silicalite indicates that there is considerable channel inclusion.^{6a}

In this work we report infrared spectroscopic studies of DBK supported on Silicalite. The heterogeneity of adsorption/inclusion sites is clearly manifested in the infrared spectra of the guest DBK. At the same time, the photodecomposition of DBK was followed directly by in-situ UV photolysis. These experiments reveal that DBK photodecomposes faster or more efficiently when occupying one class of sites which are tentatively assigned to channel inclusion sites.

Experimental Section

Silicalite S-115 was obtained from Union-Carbide Canada; it had a particle size of $\sim 1-2 \ \mu m$ and was calcined at 500 °C for 24 h prior to use. 1,3-Diphenyl-2-propanone (DBK) was from Aldrich and was recrystallized. The samples were prepared following procedures described earlier⁵ using isooctane as solvent. The amounts of DBK were selected to yield various nominal occupancies which were 10, 20, 40, 60, 80, and 100% based on the void volume of Silicalite⁸ (0.19 mL/g). These values correspond to 1.5, 3.0, 6.0, 9.0, 12.0, and 15.0 wt % DBK to Silicalite, respectively.

Infrared spectra at 4-cm⁻¹ resolution were recorded wth a Digilab FTS-11 infrared spectrometer equipped with a HgCdTe detector. The diffuse reflectance accessory adapted for in-situ UV photolysis studies is described elsewhere.¹⁰ The diffuse reflectance infrared spectra were converted to Kubelka-Munk units by using a sample of KCl as reference.¹¹ For measuring relative

peak heights of DBK bands the spectra were deconvolved following the procedures described in ref 12 using a Lorentzian band of 10-cm⁻¹ full width at half-height and a resolution enhancement factor (K) of 1.7. These parameters were selected to avoid the appearance of negative side lobes in the spectra.¹³ For UV photolysis, unfiltered light from a high-pressure Xe lamp was used.

Results and Discussion

Studies as a Function of Loading. The carbonyl stretching vibrational mode ($\nu_{C=0}$) is the most characteristic in the infrared spectra of ketones. Figure 1 shows the 2000-1560-cm⁻¹ region of the spectra of Silicalite-supported DBK at several loadings; also shown in Figure 1A is the spectrum of Silicalite with no guests. The two bands observed at 1721 and 1697 cm⁻¹ can be assigned to the C=O stretching of DBK while the bands at $\sim 1600 \text{ cm}^{-1}$ are due to C=C stretching vibrations of the aromatic rings of DBK. The bands at 1874 and 1630 cm⁻¹ are due to Silicalite.

The C=O stretching of DBK supported on Silicalite gives rise to two bands whose relative peak heights vary with loading (see Figure 1). This indicates that there are at least two different environments for the DBK molecules. These two environments are sufficiently different from each other to induce very different frequencies for $\nu_{C=0}$.

In order to attempt identifying a given C=O stretch with the different classes of sites we recorded spectra of DBK adsorbed

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Figure 1. Diffuse reflectance infrared spectra of (A) Silicalite; (B) DBK-Silicalite at 1.5 wt % loading; (C) DBK-Silicalite at 6.0% loading; and (D) DBK-Silicalite at 15% loading.



Figure 2. Diffuse reflectance infrared spectra of (A) DBK adsorbed on silica gel and (B) DBK mixed with KCl.

on silica gel and supported on KCl and the spectra are shown in Figure 2. In both cases, silica gel and KCl, there is only one band due to C=O stretching; it is at 1701 cm⁻¹ when DBK is adsorbed on silica gel and at 1716 cm⁻¹ when supported on KCl. In the case of silica gel, surface adsorption is the only possible interaction of DBK while there should not be major conformational and/or adsorption effects due to mixing with KCl. These spectra suggest that a low value of $\nu_{C=O}$ is associated with surface adsorption while a higher $\nu_{C=O}$ frequency is associated with an environment not imposing conformational and/or electrostatic effects. On this basis we can associate the band at 1697 cm⁻¹ observed in the DBK-Silicalite spectrum to DBK molecules primarily associated with the Silicalite surface while the band at 1721 cm⁻¹ is associated



Figure 3. Loading dependence of the peak height ratio h_{1721}/h_{1697} obtained from the spectra of DBK supported on Silicalite; and adsorption isotherm for DBK on Silicalite taken from ref 6a.

with DBK molecules included in the channel system of Silicalite.

As seen in Figure 1 the peak height ratio h_{1721}/h_{1697} varies with loading. The values of h_{1721}/h_{1697} are plotted as a function of loading in Figure 3 where we have also included the adsorption isotherm for DBK on Silicalite determined by Turro and Wan.^{6a} The shape of this isotherm, compared to that obtained from DBK on Na-A zeolite, was interpreted as demonstrating that the DBK molecules are included in the Silicalite channels and not only surface adsorbed as with other zeolites. Thus, the variation of h_{1721}/h_{1697} with loading lends support to our tentative assignment of the band at 1721 cm⁻¹ as arising from DBK molecules included in the channels.

The intensity of the band at 1697 cm⁻¹ is constant with loading with respect to the Silicalite bands (e.g., the band at 1874 cm⁻¹) for all loadings studied which span from 1.5 to 15 wt % (or 10 to 100% of the Silicalite void volume). This means that the class of sites with DBK molecules giving the band at 1697 cm⁻¹ are occupied preferentially and also that these sites are fully occupied at very low loadings (<1.5 wt %). These sites show a high affinity for DBK since all are occupied even at low loading and for convenience we shall refer to them as class A sites. Thus, surface A sites are occupied at all loadings followed by adsorption of DBK in internal sites.

Photodecomposition of DBK Supported on Silicalite. The photodecomposition of DBK is a well-known reaction:



It yields primarily 1,2-diphenylethane as the major product and isomers of DBK as minor products.¹⁴ The reaction has been widely studied in several media including silica gel,¹⁵ Silicalite,⁶ and other zeolites.⁶ When the reaction is carried out with substituted derivatives it is possible to use the product distributions to characterize the media on the basis of cage effects. In the case

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Figure 4. Diffuse reflectance infrared spectra of DBK on Silicalite: (A) before irradiation; (B) after 1 h of irradiation; (C) after 3 h of irradiation.

of Silicalite a large cage effect has been found and interpreted as a consequence of the structure of Silicalite.⁶ The channel system, where most of the DBK molecules are found, imposes a drastic reduction of the mobility of the photogenerated benzyl radicals which cannot escape the geminate radical pair in Silicalite. On the other hand, on other zeolites (such as Na-A) no cage effect was found reflecting the high degree of mobility for surface adsorbed species.⁶

Figure 4 shows the 2000-1560-cm⁻¹ region of the infrared spectrum of DBK supported on Silicalite (60% nominal occupancy; 9 wt %) as a function of irradiation time. The UV photolysis was carried out in-situ maintaining the sample untouched in a nitrogen atmosphere thus eliminating possible artifacts associated with repositioning the samples after photolysis.

The effects of photodecomposition can be clearly seen from the spectra of Figure 4. DBK photolysis should reduce the intensity of the C=O stretching bands since decomposition implies disappearance of the carbonyl group. However, only the band at 1721 cm⁻¹ is reduced in intensity as photolysis proceeds. The h_{1721}/h_{1697} peak height ratio changes from 3.72 before irradiation to 0.89 after irradiation for 3 h. This change in peak height ratio is entirely due to the decrease in intensity of the band at 1721 cm⁻¹ since the intensity of the 1697-cm⁻¹ band remains constant (with respect to the 1874-cm⁻¹ band of Silicalite). As photolysis proceeds there are some slight frequency shifts of the two carbonyl bands such that after 3 h the bands appear at 1719 and 1692 cm⁻¹, respectively.

As the intensity of the 1721-cm⁻¹ band decreases there appears a band at ~1681 cm⁻¹ which is clearly visible in the spectrum after 2 and 3 h of irradiation. This band can be assigned to the minor products of reaction, the isomers of DBK. The infrared spectrum of the para isomer III shows a band due to carbonyl stretching at ~ 1683 cm⁻¹.

The fact that UV photolysis of DBK supported in Silicalite induces disappearance of only one band indicates a priori that the reaction is occurring in only one class of adsorption/inclusion sites. These are the sites occupied by DBK molecules giving rise to the band at 1721 cm^{-1} which were identified with channel inclusion sites (sites B). However, the sites A occupied by DBK molecules giving rise to the band at 1697 cm^{-1} have a high affinity for DBK. Thus, the disappearance of the 1721-cm^{-1} band could also be interpreted as indicating that as DBK decomposes in sites A; the products are displaced from sites A by DBK molecules diffusing from sites B.

The high value of the cage effect found for DBK supported in Silicalite^{6a} demonstrate very low mobility for the photogenerated benzyl radicals. If this low mobility implies slow diffusion of the parent DBK molecules, the constancy in intensity of the carbonyl band from sites A implies low reactivity for the molecules occupying sites A.

The parent DBK molecules are occupying at least two classes of sites in Silicalite; however, the products giving rise to the band at 1682 cm^{-1} seem to occupy only one class of sites since only one band is observed. This is an indication that DBK is reacting in only one class of sites in which the products remain.

The photolysis of DBK supported in silica gel and KCl was also followed by in-situ irradiation. In both cases, photolysis produced a steady decrease in the intensity of the C=O stretching bands. We note that in neither of these cases we observed bands at ~1682 cm⁻¹ which could be assigned to the isomeric products III or IV. This is in accord with previous studies which showed that the yield of III is larger in the case of DBK adsorbed in Silicalite^{6a} (~20%) compared to silica gel (~2%).¹⁵

Conclusions

Diffuse reflectance infrared spectra of DBK supported on Silicalite can be used to probe the nature of the inclusion/adsorption sites of this zeolite. The heterogeneity of the Silicalite sites is manifested in different carbonyl stretching bands for the different sites. On the basis of comparison with the spectra of DBK supported on silica gel and KCl the different signals from the guest DBK molecules were tentatively assigned. The good correspondence between the observed peak height ratio as a function of loading and the adsorption isotherm for DBK on Silicalite yields support for our assignment. The present infrared spectra are indicative of the existence of two major classes of sites for DBK adsorption and/or inclusion. However, it is quite possible that there are more classes of sites which may not be discernible in the present manner. NMR spectroscopic studies⁹ have found that silicalite contains 24 distinct tetrahedral locations.

The photodecomposition of DBK support on Silicalite occurs primarily in channel inclusion sites. This corresponds with the observation of high cage effects for decomposition of substituted DBK in Silicalite.

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