CHEMISTRY LETTERS, pp. 1009-1012, 1992.

# Phosphorescence and Photochemical Properties of Benzophenone Adsorbed on Alkali Cations-Exchanged Zeolite

Seiji OKAMOTO, Hiroyasu NISHIGUCHI, and Masakazu ANPO*
Department of Applied Chemistry, Colledge of Engineering,
University of Osaka Prefecture, Sakai, Osaka 593

Benzophenone adsorbed on the cation-exchanged ZSM-5 zeolite was found to exist as a protonated form and a hydrogen-bonded form. The exchanged cations had a serious effect on the ratio of those concentrations. Both Benzhydrol and benzpinacol were observed as the major products of the photolysis of the system, their yields strongly depending on the kind of the exchanged cations. The protonated species play a significant role on the photoreactions of benzophenone adsorbed on the zeolite.

Studies of the photophysics and photochemistry of molecules adsorbed on solid surfaces such as $SiO_2$ and zeolites have been given a great deal of attention as heterogeneous photochemistry or surface photochemistry.1) An interesting aim in this field is what the influences are to the photophysics and photochemistry of the adsorbed molecules when the micro-environment of the adsorption sites is changed in the chemical and/or physical natures.2) In other words, photoluminescence measurements in these systems would give useful informations about the nature of the adsorption sites.3) Along these lines, the effects of alkali metal cation-exchange on the phosphorescence and photolysis of benzophenone adsorbed on ZSM-5 have been investigated in the present work.

ZSM-5 zeolite (supplied from Toso-Chemical Co.) was used as an adsorbent. Alkali metal cation-exchanged zeolites, for example, $Na^+$-ZSM-5 was prepared as follows; The zeolite sample was degassed at 290 K for 1 h, heated at 773 K under 20 Torr $O_2$ for 1 h, and then degassed at about 773 K before cooling down to 290 K. The exchange of alkali metal cations was performed from the nitrate aqueous solutions of the cations. The exchanged percentages of these cations were to be 90% for $Li^+$, 80% for $K^+$, 70% for $Rb^+$, and 40% for $Cs^+$, respectively. Prior to the adsorption of benzophenone (BP), the sample was evacuated to about $10^{-6}$ Torr at 473 K.

Adsorption of BP was carried out both from the $CCl_4$ solution of BP and BP vapor. There was no remarkable difference in these methods. The amount of BP adsorbed was about 1 X $10^{-7}$ mol/g. The phosphorescence spectra of BP and their lifetimes were recorded at 77 and 290 K with a Shimadzu RF-501 spectrofluoro-photometer and an apparatus for the lifetime measurements, respectively. Photolysis of BP adsorbed on the zeolites was carried out at 275 K using a high pressure mercury lamp ($\lambda > 300$ nm). Reaction products were analyzed by a GC-MS (Finnigan MAT TSQ-70).

It is known that on the excitation of BP in the n-$\pi^*$ band a phosphorescence spectrum due to a radiative transition from the excited triplet state to the ground state is observed at around 400-500 nm.[4,5] When BP molecules are adsorbed onto the surface of the oxides without strong acid sites such as $SiO_2$ and Vycor glass (PVG, major composition; $SiO_2 \fallingdotseq 97\%$ and $B_2O_3 \fallingdotseq 3\%$) they adsorb on the surface OH groups only via the hydrogen-bonding (BPH species) and their phosphorescence peaks are observed at around 430 nm with its excitation peak at around 330 nm. Figure 1b shows a typical phosphorescence spectrum of BP adsorbed on $Na^+$-ZSM-5 and the effect of desorption temperature on the spectrum. The phosphorescence spectrum exhibits a vibrational fine structure due to a C=O bond of BP. However, as shown in Fig. 1, the phosphorescence (1b) and its excitation spectrum (1a) of BP adsorbed on $Na^+$-ZSM-5 are changed in their shapes by increasing the desorption temperature of the system. When the desorption temperature rises from 323 to 383 K, the intensity of the phosphorescence becomes weaker and its fine structure disappears, and

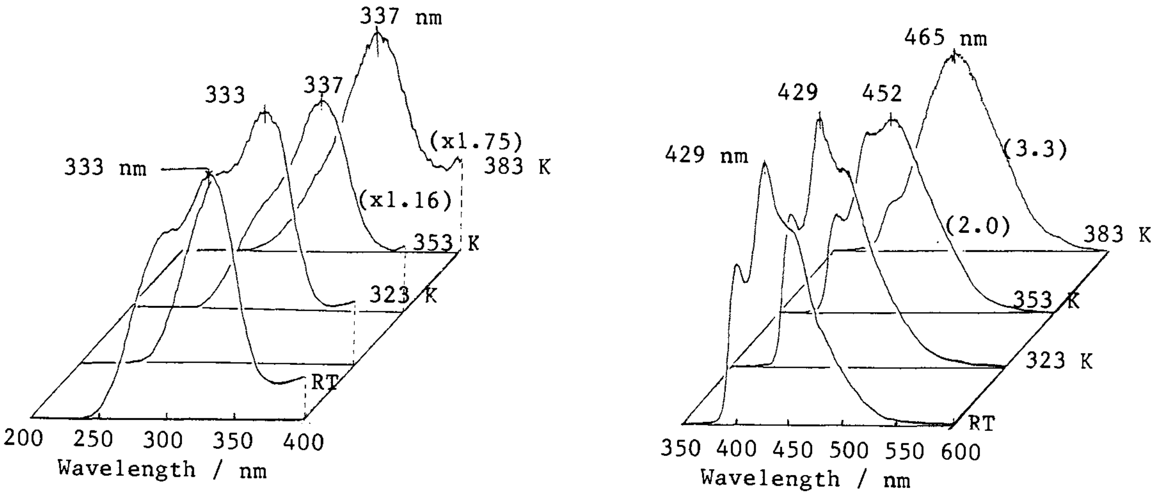

Fig. 1-a.

Fig. 1-b.

Fig. 1. The effect of desorption temperature on the excitation (a) and phosphorescence spectra (b) at 77 K of BP adsorbed on $Na^+$-ZSM-5 zeolite. (phosphorescence spectra were excited at 300 nm; excitation spectra were monitored at 450 nm beam.)

the peak at around 465 nm in the phosphorescence (peak at around 337 nm in the excitation spectrum) is remained. The results indicate that the remaining species are more stable with stronger adsorption bonding than the species which were desorbed below 383 K. From these results, it is clear that there are at least two different BP species on the $Na^+$-ZSM-5 with a different adsorption strength.

Figure 2 shows the effect of the exchanged alkali metal cations on the phosphorescence of BP adsorbed on zeolites. As shown in Fig. 2b, it is clear that the phosphorescence spectrum of benzophenone is shifted to a shorter wavelength regions from $H^+$- to $Cs^+$-ZSM-5, its shift becoming larger as the radius of the cations increases. It is known that the smaller the radius of the exchanged cations, the more the cation withdraws electrons from the surface OH groups which present near the exchanged cations. In other words, the cation on the surface drastically changes the surface acidity, the acidity depending on the exchanged-cation. Therefore, it is expected that the protonated benzophenone species ($BPH^+$) are easily formed on the cation-exchanged zeolites such as $H^+$- and $Na^+$-ZSM-5. On the other hand, the larger the radius of the exchanged cation, the less predominant the $BPH^+$ species become and the more predominant the BPH species become on the surface. According to the literatures, the $BPH^+$

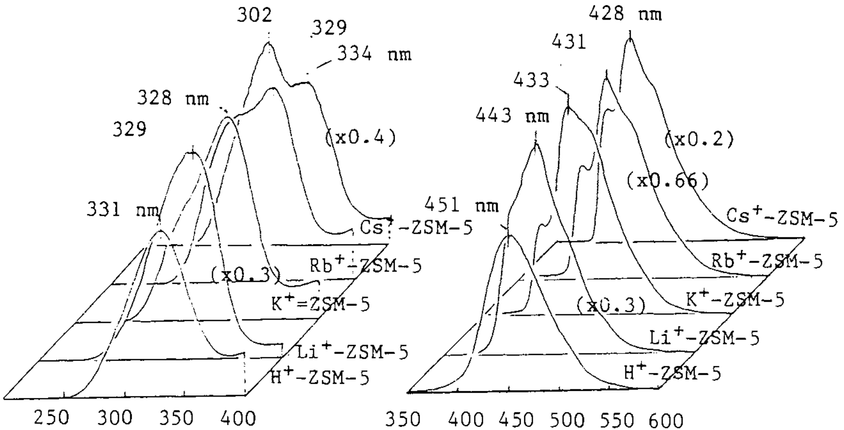

Fig. 2-a. Fig. 2-b.

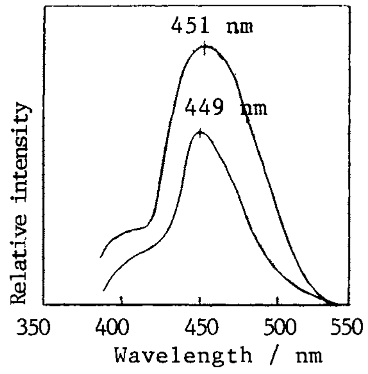

Fig. 3.

Fig. 2. The effect of the exchanged-cations on the excitation (a) and phosphorescence spectra at 77 K of BP adsorbed on ion-exchanged ZSM-5 zeolites (b).(phosphorescence spectra were excited at 300 nm; excitation spectra were monitored at 450 nm beam.)

Fig. 3. The effect of UV-irradiation on the phosphorescence spectrum at 77 K of BP adsorbed on $Na^+$-ZSM-5 zeolite.
(UV-irradiation time was 10 m at 275 K; phosphorescence spectra were excited at 300 nm; excitation spectra were monitored at 450 nm beam.)

species exhibit much longer life-times than that of the BPH species and BP molecule (the lifetime of $BPH^+$ species in $H_3PO_4$; 0.66 s, the lifetime of BPH in EPA; 0.006 s).6) The $BPH^+$ species on the zeolites showed quite long lifetimes (the lifetimes of $BPH^+$ on $H^+$-ZSM-5; 0.41 s, on $Na^+$-ZSM-5; 0.28 s, the lifetimes of BPH on $Na^+$-ZSM-5; 0.021 s, on Cs-ZSM-5; 0.017 s).

After the adsorption of BP on the $H^+$-ZSM-5 and cation exchanged-ZSM-5, these systems were UV-irradiated. Benzhydrol and benzpinacol were detected as major photolysis products of BP adsorbed on $H^+$- and $Na^+$-ZSM-5. Their yields increased with UV-irradiation time accompanied by a decrease in the intensity of the phosphorescence of BP and its excitation spectrum. Especially, as shown in Fig. 3, the intensity of the phosphorescence spectrum due to the $BPH^+$ species adsorbed on $Na^+$-ZSM-5 decreases with UV-irradiation, indicating that the $BPH^+$ species contribute to the photolysis to form those products. These facts suggest that the observed photo-products are mainly produced from the $BPH^+$ species, i. e., these species play a significant role in the photolysis of BP on zeolites. Taking account of the fact that the transient absorption due to the ketyl radicals has been detected by a laser flash photolysis in the similar systems, these products might be formed via the ketyl radicals from the $BPH^+$ species. On the other hand, only a small amount of benzhydrol was observed in the photolysis of BP adsorbed on $Cs^+$-ZSM-5, where only the BPH species exist and contribute to the photolysis to form benzhydrol.

Thus, it is likely that the smaller the exchanged cations become, the more predominant the $BPH^+$ species on the surface are. Accordingly, the number of the $BPH^+$ on the $Cs^+$-ZSM-5 zeolite is much smaller than that on the other samples, which results in the formation of benzhydrol alone.

## References

1) For example, "Photochemistry on Solid Surfaces," ed by M. Anpo and T. Matsuura, Elsevier, Amsterdam (1989).
2) M. Anpo, H. Nishiguchi, and T. Fujii, Res. Chem. Intermedi., **13**, 73 (1990) and references therein.
3) V. A. Fenin, V. A. Shvets, and V. B. Kazanskii, Kinet. Katal., **19**, 1041 (1979).
4) T. Nakayama, K. Sakurai, and K. Hamanoue, J. Chem. Soc., Faraday Trans., **87**, 1509 (1991).
5) W. L. Hsu and C. T. Lin, J. Phys. Chem., **94**, 3780 (1990).
6) R. Rusakowicz, G. Byers, and P. Leermakers, J. Am. Chem. Soc., **93**, 3263 (1971).

(Received February 26, 1992)