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# The effect of ion-exchanged alkali metal cations on the excited states of xanthone and the photolysis of 2-pentanone included within zeolite cavities

Hiroyasu Nishiguchi, Keishi Yukawa, Hiromi Yamashita, Masakazu Anpo *

*Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Gakuen-cho 1-1, Sakai, Osaka 593, Japan*

## Abstract

In order to clarify the effect of the microenvironment of the host adsorbents on the photophysical and photochemical properties of the guest molecules in restricted void spaces, the characteristic properties of the phosphorescence of xanthone and photolysis of 2-pentanone included within alkali metal cation-exchanged zeolites were investigated. An enhancement of the phosphorescence yield of xanthone included within the zeolite cavities and a reduction in the phosphorescence lifetime were observed on changing the exchangeable alkali metal cation from $Li^+$ to $Cs^+$. These results suggest an external heavy-atom effect derived from the alkali metal cation on the singlet–triplet transitions of xanthone molecules within the zeolite cavities.

During the photolysis of 2-pentanone included within the zeolite cavities, the selectivity of the Norrish type II reaction was found to decrease remarkably due to the steric hindrance caused by the restricted void space of the zeolite cavities. IR and photoluminescence investigations indicated that 2-pentanone consists of two different adsorption types: one is adsorbed on the surface OH group by hydrogen bonding and the other is directly adsorbed onto the alkali metal cations. On changing the cation from $Li^+$ to $Cs^+$, a decrease in the strength of the interaction between the alkali metal cation and 2-pentanone caused an increase in the yield of photolysis of 2-pentanone. Thus changes in the zeolite cavities, modified by the exchange of cations, have a significant effect on the excited states and chemical reactions of ketones.

*Keywords:* Alkali metal cation; Excited states; Photolysis; Xanthone; 2-Pentanone; Zeolite cavity

## 1. Introduction

Few investigations have been performed on the photophysical and photochemical properties of adsorbed molecules. Many studies on the photophysics of adsorbed molecules have attempted to discover the effect of the surface on the electronic behaviour of the adsorbed molecules and to examine the nature of the surface itself [1–5]. Moreover, recent studies on surface photochemistry have attracted considerable attention due to potential applications in the control of photochemical reaction pathways and the conversion of light energy to useful chemical energy. In order to obtain a detailed understanding of surface studies, the investigation of the photophysics and photochemistry of molecules included and/or adsorbed on well-defined and restricted reaction fields at the molecular level is vital.

One of the most interesting aims in this field involves the determination of the influence of the microenvironment of the adsorption sites (physical and/or chemical nature) on the photophysical and photochemical properties of adsorbed molecules [6–10]. Zeolites are interesting materials in this respect due to their well-defined structures, pores and cation-exchangeable sites. In this study, the phosphorescence properties of xanthone and the photolysis of 2-pentanone included within zeolite cavities were investigated; two different types of zeolite were used: Y-zeolite and ZSM-5 zeolite. We examined the relationship between the host–guest interactions and the photophysical and photochemical properties at the molecular level by continuously changing the cation-exchangeable sites in the cavities from $Li^+$ to $Cs^+$.

## 2. Experimental details

The alkali metal cation-exchanged Y-zeolites and ZSM-5 zeolites were prepared as follows. Y-zeolite (Brunauer–Emmett–Teller (BET) surface area, 710 $m^2\ g^{-1}$; Si/Al ratio, 5.5; pore size, 7.4 Å) and ZSM-5 zeolite (BET surface area, 267 $m^2\ g^{-1}$; Si/Al ratio, 23.3; pore size, 5.7 Å) samples, supplied by Toso-Chemical Co., were degassed at 295 K for

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* Corresponding author.

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Table 1
Characteristics of alkali metal cations included within the Y-zeolites

| | $Li^+$ | $Na^+$ | $K^+$ | $Rb^+$ | $Cs^+$ |
|---|---|---|---|---|---|
| Cation size (Å) | 0.68 | 0.97 | 1.33 | 1.55 | 1.70 |
| Electrostatic field (V $Å^{-1}$) | 2.1 | 1.3 | 1.0 | 0.8 | 0.6 |
| Electrostatic potential (e $r^{-1}$) | 1.67 | 1.05 | 0.75 | 0.67 | 0.59 |
| Magnitude of spin–orbit coupling ($cm^{-1}$) | – | 27 | 87 | 360 | 840 |
| Space volume of cavity 837 ($Å^3$) | 837 | 827 | 807 | 796 | 781 |

1 h, heated at 773 K under 20 Torr of $O_2$ for 1 h, and then degassed at 773 K. The exchange of the alkali metal cation was carried out using the nitrate aqueous solution of the cation. The ion-exchanged percentages of these cations were determined by atomic absorption spectroscopy (90% for $Li^+$, 80% for $K^+$, 70% for $Rb^+$ and 40% for $Cs^+$). The characteristics of the alkali metal cations included within Y-zeolites are shown in Table 1.

Prior to the adsorption of xanthone or 2-pentanone, the alkali metal cation-exchanged Y-zeolite and ZSM-5 samples were evacuated to about $10^{-6}$ Torr at 473 K. Adsorption of xanthone was carried out from *n*-hexane solution. The amount of xanthone included in the samples was about $2.5 \times 10^{-6}$ mol $g^{-1}$, which corresponds to a surface coverage of $\theta = 0.003$ for the Y-zeolite. The photoluminescence spectra and lifetimes of the ketone were recorded at 77 and 295 K with a Shimadzu RF-5000 spectrofluorophotometer and an apparatus for lifetime measurements respectively. The IR absorption spectra were recorded with a Shimadzu IR-460 spectrometer at 295 K. The adsorption of 2-pentanone onto alkali metal cation-exchanged ZSM-5 was carried out using a conventional vacuum system. After evacuation of the zeolite, ketone molecules were introduced into the system from the gas phase at 295 K. About $8.4 \times 10^{-5}$ mol $g^{-1}$ of 2-pentanone molecules were induced onto the zeolite samples. Photolysis of 2-pentanone included within the zeolite was carried out at 275 K using a high pressure mercury lamp ($\lambda > 290$ nm). The reaction products were analysed by gas chromatography.

## 3. Results and discussion

### *3.1. Effect of the alkali metal cations on the phosphorescence properties of xanthone*

The phosphorescence spectrum of xanthone in non-polar solvents is observed at 400–500 nm with a well-resolved vibrational fine structure due to the C=O bond. However, xanthone molecules in polar solvents exhibit a less well-resolved phosphorescence spectrum at longer wavelengths (red shift) [10]. The lifetime of the excited triplet state of xanthone at 77 K is 25 ms in non-polar solvents (hexane) and 125 ms in polar solvents (ethanol). These results indicate that the lowest excited triplet state of xanthone in polar solvents no longer has (n,π*) character, but exhibits (π,π*) character.

Fig. 1 shows the phosphorescence spectra of xanthone included within $Li^+$-Y-zeolite (a), $Na^+$-Y-zeolite (b), $K^+$-Y-zeolite (c), $Rb^+$-Y-zeolite (d) and $Cs^+$- Y-zeolite (e). These spectra remain almost constant with changing excitation wavelength, suggesting that the xanthone molecules included within the zeolite cavities are homogeneous. A large red shift is observed in the phosphorescence spectra compared with that in hexane. In addition, the vibrational fine structure disappears even at 77 K. These results suggest that the lowest excited triplet state of xanthone included within the alkali metal cation-exchanged Y-zeolites has (π,π*) character.

Only xanthone molecules included within $Li^+$-Y-zeolite (a) and $Na^+$-Y-zeolite (b) exhibit very weak fluorescence spectra with shoulders at around 370–400 nm. As shown in Fig. 1, the phosphorescence yields of xanthone increase in the order $Li^+$-Y-zeolite (a), $Na^+$-Y-zeolite (b), $K^+$-Y-zeolite (c), $Rb^+$-Y-zeolite (d) and $Cs^+$-Y-zeolite (e).

Fig. 2 shows the relative phosphorescence yields of xanthone molecules included within the alkali metal cation-exchanged Y-zeolites and ZSM-5 zeolites. The phosphorescence lifetimes are also shown. The phosphorescence yields increase in the order $Li^+$, $Na^+$, $K^+$, $Rb^+$ and $Cs^+$, while the lifetimes decrease in the same order. As shown in Fig. 2, the relative phosphorescence yields of xanthone included within ZSM-5 zeolites are lower than those included within Y-zeolites and their lifetimes are shorter than those in Y-zeolites.

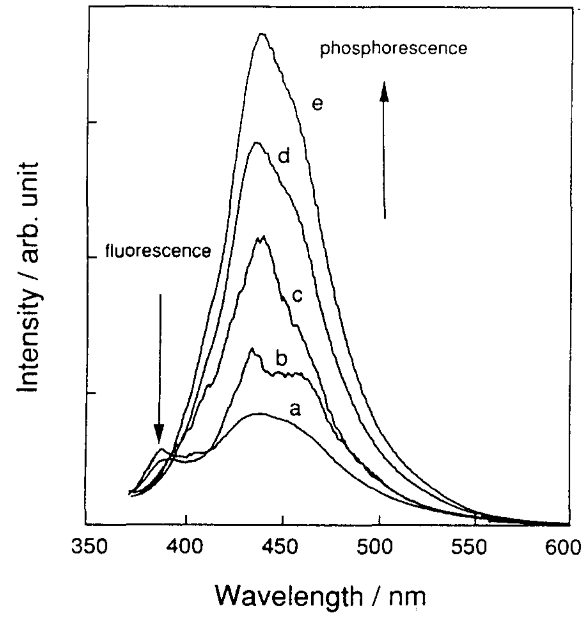


Fig. 1. Effect of the alkali metal cations on the phosphorescence spectrum at 77 K of xanthone included within the alkali metal cation-exchanged Y-zeolites (same amount of xanthone included; excitation at 340 nm): (a) $Li^+$; (b) $Na^+$; (c) $K^+$; (d) $Rb^+$; (e) $Cs^+$.

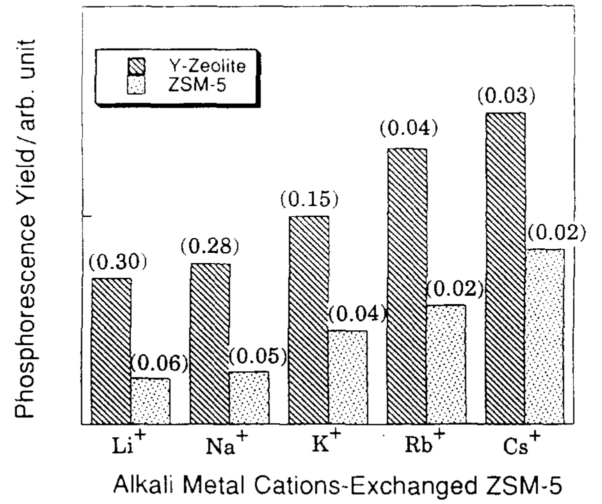


Fig. 2. Effect of the alkali metal cations on the phosphorescence yields and lifetimes of xanthone at 77 K included within the alkali metal cation-exchanged Y-zeolites and ZSM-5 zeolites (excitation at 340 nm): (a) $Li^+$; (b) $Na^+$; (c) $K^+$; (d) $Rb^+$; (e) $Cs^+$. Values in parentheses show the lifetimes of xanthone in seconds.

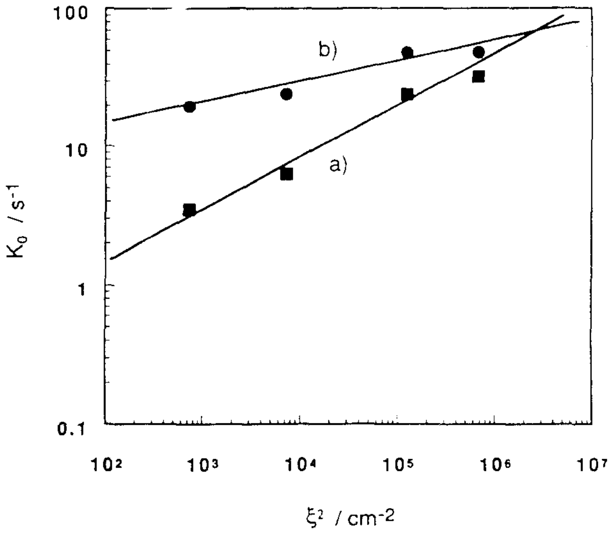


Fig. 3. Relationships between the decay rate of the excited triplet state of xanthone included within the alkali metal cation-exchanged zeolites and the spin–orbit coupling parameters of the cations: (a) xanthone included in Y-zeolites; (b) xanthone included in ZSM-5 zeolites.

A strong enhancement of the phosphorescence yield and a large decrease in the phosphorescence lifetime of the xanthone molecules included within the zeolite cavities are observed on changing the alkali metal cations in the cavities from $Li^+$ to $Cs^+$, i.e. changing the cations from light to heavy metals. Table 1 shows the magnitude of the spin–orbit coupling of these alkali metals. This increases with increasing mass number of the alkali metal cations. The spin–orbit coupling effect of the alkali metals promotes the singlet–triplet transition of the electrons, which becomes more probable in the presence of an external heavy-atom effect.

It is well known that the external heavy-atom effect changes with the square of the spin–orbit coupling constant $\xi^2$ and that a log–log plot of $(\text{lifetime})^{-1}$ vs. $\xi^2$ should be linear with a slope close to unity [11,12]. Ramamurthy et al. [13] found the expected dependence for the triplet decay of naphthalene included within alkali cation-exchanged zeolites. They attributed this result to the close approach between the naphthalene molecule and the heavy atom (alkali cation) and to the presence of more than one heavy-atom cation per supercage of zeolite. In this case, the alkali cation is rigidly held over the naphthalene $\pi$ face resulting in a slope close to unity.

In Fig. 3, log–log plots of $(\text{lifetime})^{-1}$ of the xanthone molecules vs. $\xi^2$ for the alkali metals included within the zeolite cavities are shown for the Y-zeolites and ZSM-5 zeolites. Linear relationships are observed for both systems with a slope smaller than unity. It is expected that the orientation of the heavy-atom cation with respect to the chromophore and symmetry restriction lead to a deviation from unit slope [11–15]. Slopes smaller than unity have been observed previously [13,14]. As shown in Fig. 3, the external heavy-atom effect on the excited states of xanthone molecules is larger for the Y-zeolite than the ZSM-5 zeolite. It is believed that these differences may be attributed to differences in the effective concentration of the heavy-atom cations in the vicinity of xanthone and/or differences in the orientation, atomic distance or symmetry restriction arising from differences in the void spaces or magnitudes of the supercages of the zeolites.

A large heavy-atom effect on singlet–triplet transitions can be observed only for molecules with $(\pi,\pi^*)$ character in their lowest triplet state [16,17]. Xanthone molecules often exhibit dual phosphorescence and the magnitude of the interchange between $(n,\pi^*)$ and $(\pi,\pi^*)$ character is significantly affected by the polarity of the solvent and/or the electronic state of the molecular environment. The external heavy-atom effect of the alkali metal cations on the excited states of xanthone suggests that the lowest excited state of xanthone included within the zeolites has $(\pi,\pi^*)$ character due to direct host–guest interactions.

### *3.2. Effect of the alkali metal cations on the photolysis of 2-pentanone*

In the photolysis of 2-pentanone included within alkali metal cation-exchanged zeolites, the major products are propane, propylene, ethylene, acetone and a small amount of methane. Fig. 4 shows the effect of the alkali metal cations on the product yields during the photolysis of 2-pentanone included within the ZSM-5 zeolite. The reaction yields and ratio of propylene to propane (the selectivity of propylene formation) increase on changing the alkali metal cation from $Li^+$ to $Cs^+$, indicating that the modification of the microenvironment of the reaction field by this exchange causes a change in the reaction efficiency and product distribution.

As shown in Scheme 1, the photolysis of alkyl ketones, such as 2-pentanone, containing $\gamma$-hydrogen atoms occurs via the Norrish type II (intramolecular elimination) and Norrish type I ($\alpha$-cleavage into radical pairs) processes [18,19].

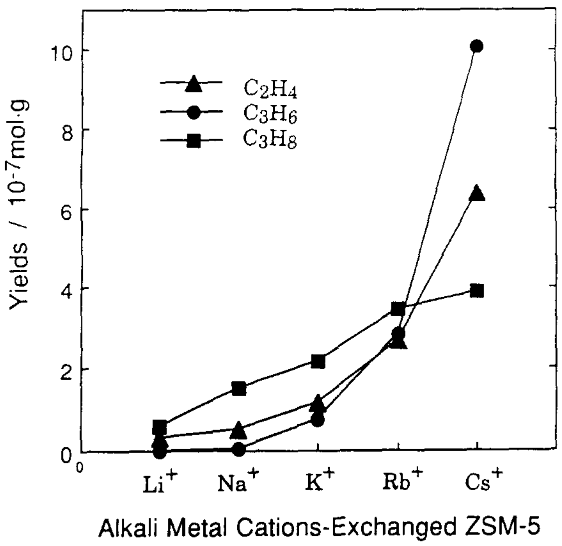
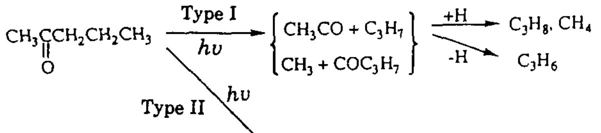


Fig. 4. Effect of the alkali metal cations on the yield of photolysis of 2-pentanone.



Scheme 1. Norrish type I and type II processes during the photolysis of 2-pentanone.

Table 2
Effect of the alkali metal cations on the relative yields of photolysis of 2-pentanone included within the zeolites

| | $Li^+$ | $Na^+$ | $K^+$ | $Rb^+$ | $Cs^+$ |
|---|---|---|---|---|---|
| Type I (%) | 3.1 | 9.2 | 16.3 | 35.2 | 30.1 |
| Type II (%) | 1.2 | 2.8 | 6.2 | 14.2 | 73.5 |
| Type II/type I | 0.39 | 0.30 | 0.38 | 0.40 | 0.41 |

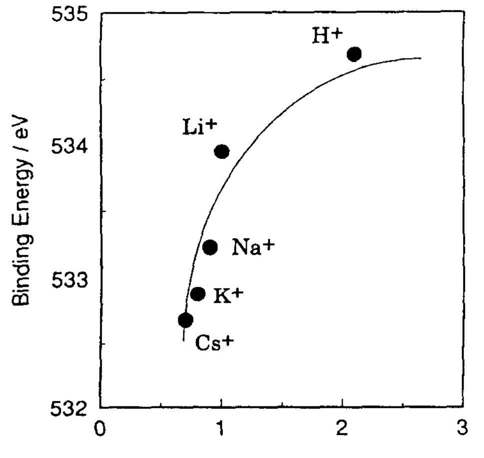


Fig. 5. Dependence of the binding energy of the $O_{1s}$ X-ray photoelectron spectral peaks of ZSM-5 zeolites on the electronegativity of the alkali metal cations.

Propane and propylene are formed by the insertion of a hydrogen atom into a propyl radical and the elimination of a hydrogen atom from a propyl radical formed during Norrish type I cleavage respectively. Ethylene and acetone are formed during the Norrish type II reaction. Thus the extent of participation of type I and type II reactions can be estimated from the yields of these products; the results are summarized in Table 2. The type II/type I ratio during the photolysis of 2-pentanone included within the zeolite cavities is 0.3–0.4, which is much smaller than that recorded during photolysis in the gas phase (type II/type I = 6.8) and in the large pores (40 Å) of Vycor glass (type II/type I = 1.3). Considering that the formation of a six-membered intermediate by interaction between a CO group and a $\gamma$-hydrogen is required for the type II reaction, the present results obtained within the microcavities of zeolites strongly indicate that steric hindrance due to the restricted void space of the zeolite cavities inhibits the formation of the six-membered intermediate and thus the type II reaction.

As shown in Fig. 4, the selectivity of propylene formation increases with a change in cation from $Li^+$ to $Cs^+$. In order to investigate the effect of the modification of the electronic structure of the zeolites on the selectivity of photolysis of 2-pentanone by changing the alkali metal cations, the X-ray photoelectron spectra of the alkali metal cation-exchanged zeolites were measured. Fig. 5 shows the effect of the electronegativity of the alkali metal cations on the chemical shift in the $O_{1s}$ spectra of the ZSM-5 zeolites. The binding energies of the $O_{1s}$ band increase with increasing electronegativity of the alkali metal cation in the order $H^+ < Li^+ < Na^+ < K^+ < Cs^+$ (Table 1), indicating that the negative charges on the oxygen atoms of the zeolite increase in the same order. These changes lead to an increase in the basicity of the lattice oxygen of the zeolite framework. As a result, it can be expected that this increase in basicity of the lattice oxygen of the zeolite will lead to an enhancement of the hydrogen atom abstraction from propyl radicals to form propylene, resulting in an increase in the selectivity of propylene formation as shown in Fig. 4.

Fig. 6 shows the IR absorption spectra of 2-pentanone included within the alkali metal cation-exchanged ZSM-5 zeolites. Two distinct absorption bands are observed, both being assigned to the C=O stretching mode of 2-pentanone. The peak at around 1660 $cm^{-1}$ shifts from 1658 $cm^{-1}$ to 1678 $cm^{-1}$ on changing the cation from $Li^+$ to $Cs^+$; however, the wavenumber of the peak at around 1700 $cm^{-1}$ remains almost constant on changing the cation. Increasing the amount of adsorbed 2-pentanone leads to a decrease in the intensity of the band at around 3740 $cm^{-1}$ due to the surface OH groups, and a broad band at around 3400 $cm^{-1}$, attributed to hydrogen bonding between the surface OH groups and 2-pentanone, appears. Alkyl ketones adsorbed on an $SiO_2$ surface by hydrogen bonding [1,20] exhibit only one absorption band at around 1700 $cm^{-1}$. These results clearly indicate that 2-pentanone interacts with two different adsorption sites on the alkali metal cation-exchanged ZSM-

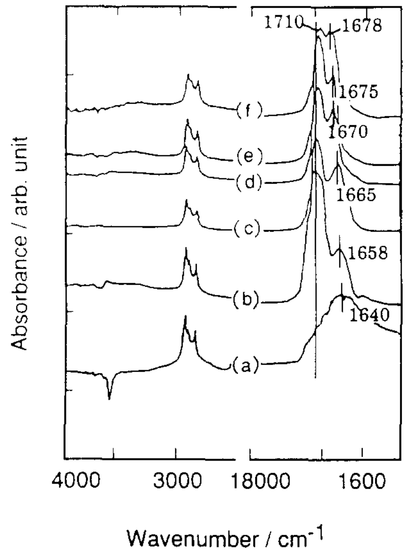


Fig. 6. IR spectra of 2-pentanone included within the alkali metal cation-exchanged ZSM-5 zeolites: (a) $H^+$; (b) $Li^+$; (c) $Na^+$; (d) $K^+$; (e) $Rb^+$; (f) $Cs^+$.

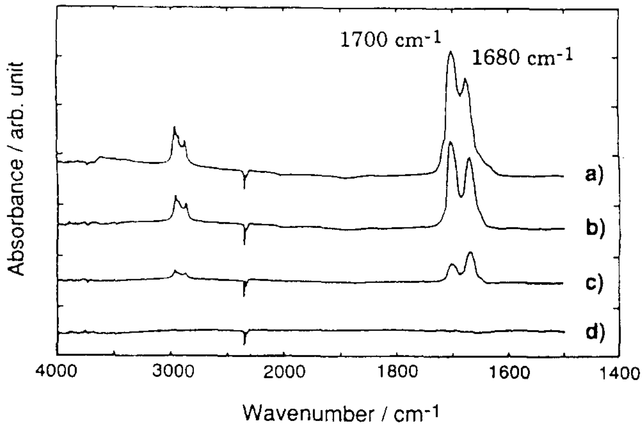


Fig. 7. Effect of the evacuation temperature on the IR spectra of 2-pentanone included within $K^+$-ZSM-5: (a) 295 K; (b) 423 K; (c) 475 K; (d) 523 K.

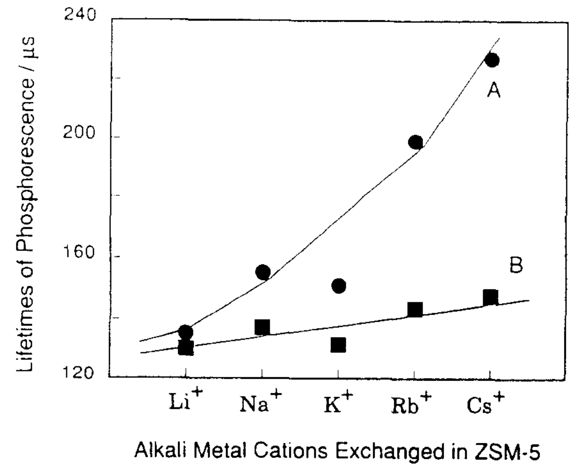


Fig. 8. Effect of the alkali metal cations on the phosphorescence lifetime of 2-pentanone included within the alkali metal cation-exchanged ZSM-5 zeolites at 77 K: (A) longer lived species; (B) shorter lived species.

5 zeolite: one generates hydrogen bonding between CO groups and surface OH groups, and the other is sensitively affected by the cations suggesting direct interaction of 2-pentanone with the cations.

Fig. 7 shows the effect of the evacuation temperature on the IR absorption spectra due to the C=O stretching of 2-pentanone included within $K^+$-ZSM-5. When the evacuation temperature is increased, the intensity of the two distinct absorption peaks attributed to the C=O stretching of 2-pentanone decrease with different desorption rates, leading to a remarkable increase in the ratio of the peak at 1670 $cm^{-1}$ to that at 1700 $cm^{-1}$. Similar results were observed when 2-pentanone was included within the other alkali metal cation-exchanged ZSM-5 zeolites. These results indicate that 2-pentanone molecules interact with two different adsorption sites having different adsorption strengths, and that 2-pentanone molecules adsorbed on the sites which are sensitively affected by the ion-exchanged cations are more stable than hydrogen-bonded 2-pentanone molecules.

The effect of the alkali metal cations on the desorption temperature of 2-pentanone included within the ZSM-5 zeolite was also investigated. The desorption temperature of 2-pentanone decreases when the cation is changed from $Li^+$ to $Cs^+$; the order is 648 K for $Li^+$, 623 K for $Na^+$, 523 K for $K^+$, 473 K for $Rb^+$ and 448 K for $Cs^+$. These results clearly indicate that the strength of the interaction between the ketone molecules and the cations weakens on going from $Li^+$ to $Cs^+$.

2-Pentanone included within the alkali metal cation-exchanged zeolites exhibits a phosphorescence spectrum at around 430 nm. The analysis of the phosphorescence decay curves reveals two different components. Fig. 8 shows the effect of the alkali cations on the lifetimes of 2-pentanone included within the cation-exchanged ZSM-5 zeolites. The lifetime of the longer lived component strongly depends on the cation, increasing on going from $Li^+$ to $Cs^+$. The lifetime of the second component is almost constant and independent of the cation. These results suggest that there are at least two different types of ketone with different lifetimes.

Alkyl ketones interacting with surface OH groups by hydrogen bonding show a very rapid deactivation process of the excited triplet state through a photoassisted hydrogen exchange reaction [1,20]. Therefore the shorter lived component of the phosphorescence spectrum can be attributed to the hydrogen-bonded species and the longer lived component, whose lifetime changes with the type of cation, can be attributed to the ketone interacting with the cations via weak electrostatic forces.

The lifetime of 2-pentanone interacting with the cation increases on going from $Li^+$ to $Cs^+$, which in turn indicates that the excited state of 2-pentanone becomes more stable on going from $Li^+$ to $Cs^+$. As described above, the desorption temperature of 2-pentanone decreases on going from $Li^+$ to $Cs^+$, suggesting that the interaction forces between the ketone and cations become weaker in this direction. These changes in interaction lead to an enhancement of the efficiency of photolysis of 2-pentanone included within the alkali cation-exchanged ZSM-5 zeolite.

## 4. Conclusions

The phosphorescence properties of xanthone and the photolysis of 2-pentanone included within alkali metal cation-exchanged zeolites were investigated to determine the effect of the microenvironment of the host adsorbents on the electronic excited states and reactivity of the guest molecules in the restricted void spaces. An enhancement of the phosphorescence yield of xanthone and a reduction in the lifetime were observed on changing the alkali cation from $Li^+$ to $Cs^+$, indicating that the external heavy-atom effect, derived from the alkali metal cations, on the excited states of xanthone enhances the singlet–triplet transitions in the order $Li^+$, $Na^+$, $K^+$, $Rb^+$ and $Cs^+$.

The yield of photolysis of 2-pentanone included within the alkali metal cation-exchanged ZSM-5 zeolites increases on changing the cation from $Li^+$ to $Cs^+$. 2-Pentanone interacts with two different adsorption sites; one species interacts with the surface OH groups through hydrogen bonding, while the other species interacts directly with the alkali metal cation. The strength of the interaction between the cation and 2-pentanone decreases on going from $Li^+$ to $Cs^+$.

These results indicate that variations in the microenvironment of the adsorption sites cause a significant perturbation of the electronic excited states of the adsorbed molecules, resulting in dramatic changes in the efficiency and selectivity of photolysis.

## Acknowledgements

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