

## Effect of ion-exchanged alkali metal cations on the photolysis of 2-pentanone included within ZSM-5 zeolite cavities: a study of ab initio molecular orbital calculations

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**Abstract**—The Norrish Type I and Type II reactions in the photolysis of 2-pentanone included within the alkali metal cation-exchanged ZSM-5 zeolite have been investigated by experimental and theoretical approaches. Changes in the molecular environment of the zeolite cavities by exchanging the cations had significant effects not only on the adsorption state but also on the photochemical reactions of the ketones included within the zeolite cavities. The yields of the photolysis decreased and the ratio of the Type I/Type II reactions increased, respectively, by changing the ion-exchanged cations from Cs<sup>+</sup> to Li<sup>+</sup>. The observed IR and phosphorescence spectra of the adsorbed ketones and the ab initio molecular orbital calculations of this host-guest system indicate that the ketones interact with two different adsorption sites, i.e. the surface OH groups and alkali metal cations, while the interaction between the ketones and cations increased by changing the cations from Cs<sup>+</sup> to Li<sup>+</sup>. Molecular orbital calculations were also carried out and indicated that the zeolite framework promotes the delocalization of the charge density of the alkali metal cations which can modify the interaction between the adsorbed ketones and cations, resulting in significant changes in the photolysis of these ketones.

## INTRODUCTION

A comprehensive understanding of the fundamental mechanisms and processes behind the photochemical reactions of molecules adsorbed on solid surfaces is

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important for the developments in the field of heterogeneous photochemistry and the photochemistry of molecular assembly systems [1–5]. One of the most interesting aims in these fields is to determine what the influences are to the photophysical and photochemical properties of the adsorbed molecules when the micro-environment of the adsorption sites is modified and changed in its physical and/or chemical nature. Zeolites are considered to be one of the most suitable materials in investigating a variety of host-guest interactions and their role in the photochemical nature of the guest molecules [6–13]. Since the pioneering works of Turro and Ramamurthy *et al.* [14–18], studies of the photophysics and photochemistry of molecules included within the restricted cavities of zeolites have been the focus of many studies relating to the effects of the micro-environment. These effects originate from the host-guest interaction on the electronic excited states and reactivities of the guest molecules adsorbed on the inner surfaces of the zeolites.

Charge-compensating cations are exchangeable and bring about variations in the physical characteristics of the micro-environment of the adsorption sites of zeolites such as the electrostatic potential and electric field within the cage, the spin-orbit coupling parameters, and the vacant spaces available for the guests within the supercage [6–16]. It has been reported that the presence of light-atom cations such as  $\text{Li}^+$  and  $\text{Na}^+$  can modify the photochemical behavior of the guest molecules through their high positive charge density and electrostatic potentials, while the heavy-atom cations can influence the behavior of the guests through the high spin-orbit coupling parameters [14–18]. The micropolarity of the zeolite cavities increases ( $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ ) with a decrease in the size of the alkali metal cation and a high polarity can be observed with  $\text{Li}^+$  and  $\text{Na}^+$  exchanged zeolites [8, 9, 13, 14]. The strength of the interaction between the cation and the guest molecules depend on the charge density and electrostatic potential of the cation. This cation-induced effect can be expected to modify the photochemical properties of the guest molecules [6–11].

In the present work, the effects of ion-exchanged alkali metal cations on the photochemical properties of alkyl ketones (2-pentanone) included within the zeolite cavities have been investigated. Special attention has been focused on a clarification of the vital role that the interaction between the adsorption sites and the ketones plays in the photophysical and photochemical properties of the ketone molecules at the molecular level. Investigations of the adsorption state of the ketone molecules were carried out by spectroscopic measurements, *ab initio* molecular orbital calculations as well as analysis of the photolysis of ketone molecules included within the zeolite cavities.

## EXPERIMENTAL

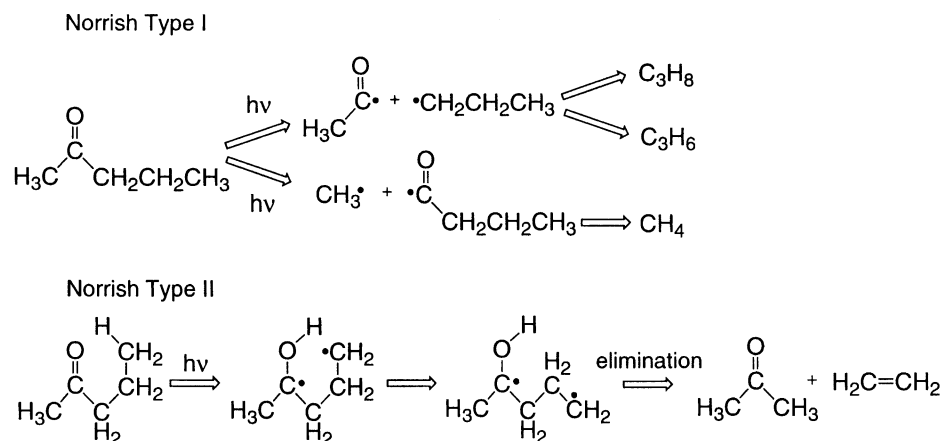
ZSM-5 zeolites (Si/Al ratio = 110) calcinated at 773 K for 7 h were used as adsorbents. Alkali metal cation-exchanged zeolites were prepared by an ion-exchange method using the nitrate aqueous solution of the cation. The ion-

exchanged percentages of these cations on ZSM-5 were determined by atomic absorption spectroscopy: 83% for  $\text{Li}^+$ ; 83% for  $\text{Na}^+$ ; 82% for  $\text{K}^+$ ; and 75% for  $\text{Cs}^+$ , respectively. Adsorption of 2-pentanone from the gas-phase into the zeolite cavities was carried out using a conventional vacuum system after the evacuation of the zeolite samples to  $10^{-6}$  torr at 295 K. The amount of 2-pentanone introduced into the samples was about  $2.2 \times 10^{-4}$  mol.g $^{-1}$ . IR measurements were carried out at 295 K using a JASCO FT-IR 7600 spectrometer with the ZSM-5 zeolite (Si/Al ratio = 11) [8–10]. The desorption temperatures of the pre-adsorbed 2-pentanone on various cation-exchanged zeolites were determined from IR measurements carried out after the evacuation of the samples at various temperatures. The temperatures at which the IR band due to the C=O stretching mode of the adsorbed 2-pentanone disappeared were adapted as the desorption temperatures. The photoluminescence spectra of ketones and their lifetimes were recorded at 77 K with a Shimadzu RF-5000 spectrofluorophotometer and an apparatus for lifetime measurements, respectively. Photolysis of the 2-pentanone was carried out at 275 K using a high pressure mercury lamp ( $\lambda > 290$  nm) in a quartz cell (50 cm $^3$ ) connected to a closed evacuation system. The reaction products in the gas phase which were trapped after evacuation, such as propane, propylene, ethylene, methane and acetone, were analyzed by gas chromatography. The products strongly adsorbed on the samples were extracted using diethyl ether and analyzed by GC-Mass. The ab initio molecular orbital calculations for the interaction between the alkyl ketones and alkali metal cations were performed using a Gaussian 94 package. The equilibrium geometries and harmonic vibrational frequencies were computed at HF(SCF) levels. The basis sets were: the 6-31G\* type for H, C, O of the ketone; (8s6p)/[3s3p] for K, Rb, Cs; and 6-31G for H, Si, Al, O, Li, Na of the zeolite framework and the alkali metal. Wadt-Hay ECP was added to K, Rb, Cs [10].

## RESULTS AND DISCUSSION

### *Photolysis of 2-pentanone and IR measurements for the 2-pentanone-zeolite interactions*

As shown in reaction Scheme 1, alkyl ketones having  $\gamma$ -hydrogen atoms such as 2-pentanone undergo the Norrish Type I process ( $\alpha$ -cleavage into radical pairs) and the Norrish Type II process (intramolecular elimination) [8–10]. In the photolysis of 2-pentanone included within the zeolite cavities, the major products were propane, propylene, ethylene and acetone involving a small amount of methane. Propane and propylene are formed either by a hydrogen atom abstraction by a propyl radical or a hydrogen atom elimination from a propyl radical formed in the Norrish Type I cleavage, respectively. Ethylene and acetone are formed in the Norrish Type II reaction. Therefore, from these results, the yields of the Norrish Type I and Type II reactions can be determined from the total yield of these products. The



**Scheme 1.** The reaction scheme for the Norrish Type I and Type II reactions in the photolysis of 2-pentanone.

**Table 1.**

The yields and the selectivities on Norrish Type I and Type II reactions on the photolysis of 2-pentanone included within alkali metal cation-exchanged ZSM-5 zeolite<sup>a,b</sup>

Cations	Yields of products/ $\times 10^{-7}$ mol				Selectivity	
	Type I			Type II	Type I + II	Type I/II
	CH <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>2</sub> H <sub>4</sub>		
Li <sup>+</sup>	0.1		0.4	0.5	1.0	1.00
Na <sup>+</sup>	0.2		2.8	5.1	8.1	0.59
K <sup>+</sup>	0.1	0.6	2.6	10.0	13.3	0.33
Cs <sup>+</sup>	0.1	1.3	4.4	18.8	24.6	0.31
SiO <sub>2</sub> <sup>c</sup>	0.1	0.1	0.9	4.7	5.9	0.23

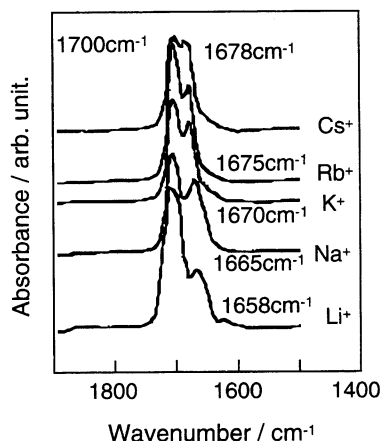
<sup>a</sup> Amount of 2-pentanone:  $2.2 \times 10^{-4}$  mol/g.

<sup>b</sup> Experimental conditions:  $\lambda > 290$  nm, 273 K, 4 h.

<sup>c</sup> Aerosil 300.

cyclobutanol produced from the Norrish Type II process could not be detected in the present reaction.

Table 1 shows the effect of the kind of cations on the photolysis of 2-pentanone included within the alkali metal cation-exchanged ZSM-5 zeolites. The ratios of the Norrish Type I/Type II reactions in the photolysis of 2-pentanone are 1.0–0.3, being much larger than those obtained for the corresponding photolysis in the gas phase, i.e. the Norrish Type I/Type II = 0.13. In the cavities of the ZSM-5 zeolite, the Norrish Type II reaction is considerably more difficult due to the formation of bulky intermediate species [14–18]. It can also be clearly seen in Table 1 that the yield decreases and the ratios of the Norrish Type I/Type II increase when the cations are changed from Cs<sup>+</sup> to Li<sup>+</sup>. These results clearly indicate that the photolysis of 2-pentanone included within the zeolite cavities is strongly affected by the change

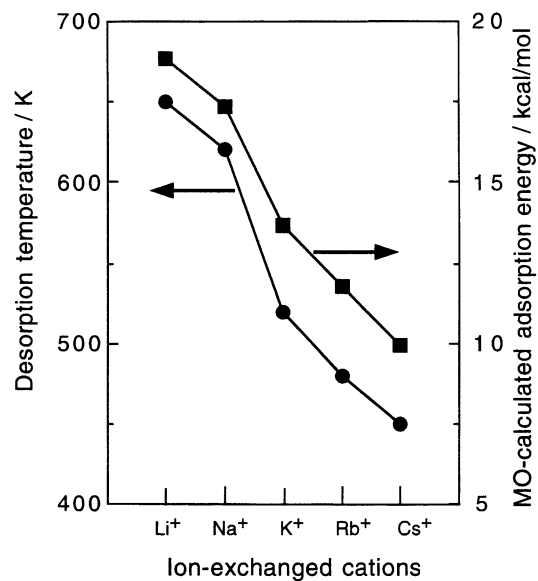


**Figure 1.** The IR spectra of 2-pentanone included within alkali metal cation-exchanged ZSM-5.

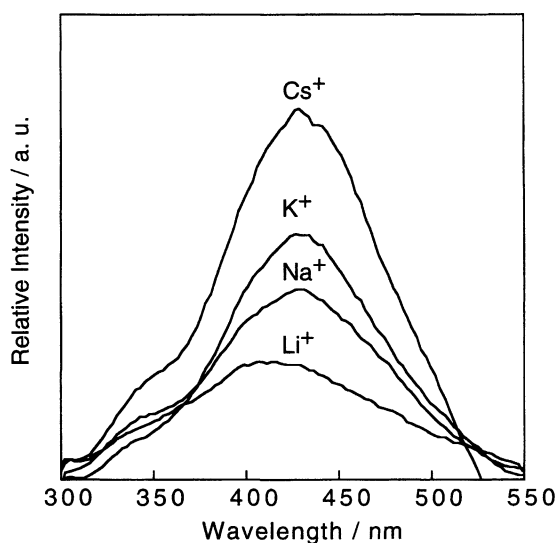
in the chemical nature of the micro-environment of the adsorption sites, specifically by exchanging the cations from Cs<sup>+</sup> to Li<sup>+</sup>.

Figure 1 shows the IR spectra of 2-pentanone included within alkali metal cation-exchanged ZSM-5. By the introduction of 2-pentanone onto the zeolite, two distinct IR absorption bands which are assigned to the C=O stretching mode of 2-pentanone included within ZSM-5 can be observed at around 1700–1640 cm<sup>-1</sup> and their intensities increased when the amount of 2-pentanone was increased. The peak at around 1700 cm<sup>-1</sup> scarcely changed by the change in the cations. Increasing the amount of adsorbed 2-pentanone led to a decrease in the intensity at around 3740 cm<sup>-1</sup> which could be attributed to the surface OH groups as well as an increase in the intensity at around 3400 cm<sup>-1</sup> attributed to the hydrogen bonding between the surface OH groups and 2-pentanone. Alkyl ketones adsorbed on the SiO<sub>2</sub> surfaces by hydrogen bonding exhibit only one IR absorption peak at around 1700 cm<sup>-1</sup> [1, 19]. These results clearly indicate that the peak at around 1700 cm<sup>-1</sup> can be assigned to 2-pentanone molecules which interact with the surface OH groups through hydrogen bonding. On the other hand, the peak at around 1670 cm<sup>-1</sup> shifts from 1678 cm<sup>-1</sup> to 1658 cm<sup>-1</sup> by changing the cation from Cs<sup>+</sup> to Li<sup>+</sup>. Thus, the peak is sensitively affected by the cations, indicating that the peaks at around 1670 cm<sup>-1</sup> can be assigned to 2-pentanone molecules which interact directly with the cations.

In order to clarify the adsorption state of 2-pentanone molecules, the effect of the ion-exchanged alkali metal cations on the desorption temperature of 2-pentanone included within ZSM-5 has been investigated. As shown in Fig. 2, the desorption temperatures determined by monitoring the IR peak at around 1670 cm<sup>-1</sup>, increases when the cations are changed from Cs<sup>+</sup> to Li<sup>+</sup>, indicating that the magnitude of the interaction between the cations and 2-pentanone molecules increases with the changing of the cations.

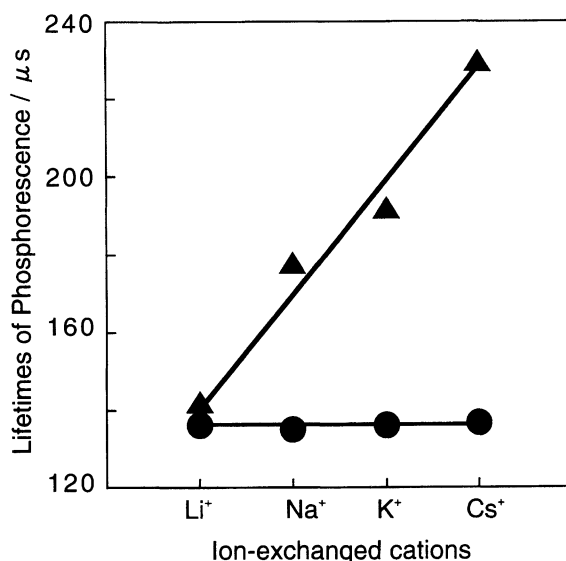


**Figure 2.** The effects of the ion-exchanged alkali metal cations on the desorption temperature of 2-pentanone determined by IR measurements and the adsorption energy obtained by MO calculations with the (ketone-M<sup>+</sup>-frame) system.



**Figure 3.** The phosphorescence spectra of 2-pentanone included within alkali metal cation-exchanged ZSM-5 at 77 K with the excitation at 290 nm.

As shown in Fig. 3, 2-pentanone included within alkali metal cation-exchanged ZSM-5 exhibits a phosphorescence spectrum at around 430 nm when excited at around 290 nm. The decay curves of the phosphorescence corresponded well with the double exponential decay mechanism, indicating the presence of two



**Figure 4.** Lifetimes of the phosphorescence of 2-pentanone included within alkali metal cation-exchanged ZSM-5 at 77 K with the excitation at 290 nm.

different lifetime components. These results are in agreement with the results of IR investigations and suggest that there are at least two different adsorption sites for the 2-pentanone molecules. Figure 4 shows the lifetimes of the phosphorescence of 2-pentanone included within the cation-exchanged zeolite. The lifetime values of the components with a longer lifetime strongly depend on the kind of cations exchanged, becoming shorter by changing the cation from  $\text{Cs}^+$  to  $\text{Li}^+$ . The values of the component with the shorter lifetime scarcely changed and remained almost constant, being independent of the kind of the cations exchanged. It is known that the alkyl ketones interacting with the surface OH groups by hydrogen bonding deactivate rapidly through a photo-assisted hydrogen exchange reaction [1, 19]. Therefore, the shorter lifetime component of the excited state of 2-pentanone can be attributed to the hydrogen bonded species. On the other hand, the component with a longer lifetime can be attributed to the 2-pentanone molecules interacting with the cation by weak electrostatic forces, its magnitude changing with the cation.

The lifetime of 2-pentanone interacting with the cation becomes shorter when the cation is changed from  $\text{Cs}^+$  to  $\text{Li}^+$ , which in turn indicates that the opportunity for reactions in the excited state of 2-pentanone becomes smaller as well. The desorption temperature of 2-pentanone from the system also becomes higher by changing the cation from  $\text{Cs}^+$  to  $\text{Li}^+$ , suggesting that the interaction between 2-pentanone molecules and the cations becomes stronger by this exchange. From these findings, it can be observed that the efficiency of the photolysis of 2-pentanone included within the alkali metal cation-exchanged zeolites changes with the cation, its extent decreasing by changing the cation from  $\text{Cs}^+$  to  $\text{Li}^+$  in the order of the magnitude of the interaction between the 2-pentanone molecules and the cations.

As shown in reaction Scheme 1, the Norrish type II reaction proceeds through the formation of a 1,4-biradical intermediate. A favorable conformation, i.e. a six-membered intermediate, is required for a  $\gamma$ -hydrogen atom abstraction to take place. In the strong interaction between the 2-pentanone molecules and cations within the zeolite cavities, the formation of such a six-membered transition state is considerably suppressed, its extent strongly depending on the kind of metal cation. Thus, the results in Table 1 and Figs 1, 2, 3 and 4 clearly indicate that the strong interaction between 2-pentanone molecules and the light atom cations such as  $\text{Li}^+$  and  $\text{Na}^+$  causes difficulty in the formation of a six-membered intermediate and restrains the Norrish Type II reaction in the photolysis of 2-pentanone.

#### *Molecular orbital calculation for the 2-pentanone-zeolite interaction*

In order to understand the nature of the interaction between the ketones and the cations, MO calculations have been carried out to clarify the electronic state of the ketones adsorbed on the cations. The isolated 2-pentanone molecule can have two types of stable conformation, a staggered conformation and an eclipsed conformation, as shown in Fig. 5. Tables 2 and 3 show the optimized geometry of 2-pentanone having these two conformation types. The geometry of the zeolite framework model used in the present study was obtained by the optimization of the geometry of the model representing the  $\text{T}_{12}\text{-O}_{24}\text{-T}_{12}\text{-O}_7\text{-T}_3$  site of ZSM-5 which is a part of the framework at the cross section with the straight channel and the sinusoidal channel of the ZSM-5 zeolite [20–22]. Figure 6 shows the model of the metal cation-exchanged zeolite framework ( $\text{M}^+$ -frame). The charge population and bond length between cations and the framework oxygen ( $\text{O}_z$ ) in the optimized geometry of these ( $\text{M}^+$ -frame) models are shown in Table 4. It can clearly be seen that the population charge of the cations is delocalized into the zeolite framework, especially with systems having light-atom cations such as  $\text{Li}^+$  and  $\text{Na}^+$ .

Ab initio molecular orbital calculations of such 2-pentanone molecules which directly interact with the cation-exchanged zeolite framework (2-pentane- $\text{M}^+$ -frame) provide useful and important information on the geometry, charge population, heat of adsorption, and vibrational frequencies of the  $\text{C}=\text{O}$  groups of the 2-pentanone molecules. In the SCF optimized structures of the adsorption of 2-pentanone, the alkali metal cation locates in the configuration which is linear to the  $\text{C}=\text{O}$  bond. The results of ab initio calculations suggest not only that there is no significant overlap between the orbitals of the 2-pentanone molecules and cations but also that they are stabilized on the cations by electrostatic interactions. Tables 5 and 6 show the calculated total energy of the supermolecular systems composed of the 2-pentanone molecules (in staggered and eclipsed conformations) and the cation-exchanged zeolite framework. The interaction energy (adsorption energy) between 2-pentanone and the cation-exchanged zeolite framework ( $\text{M}^+$ -frame) is also shown in Tables 4 and 5. The obtained values indicate that supermolecular systems (2-pentanone- $\text{M}^+$ -frame) with a staggered conformation are more stable than corresponding systems



**Table 2.**

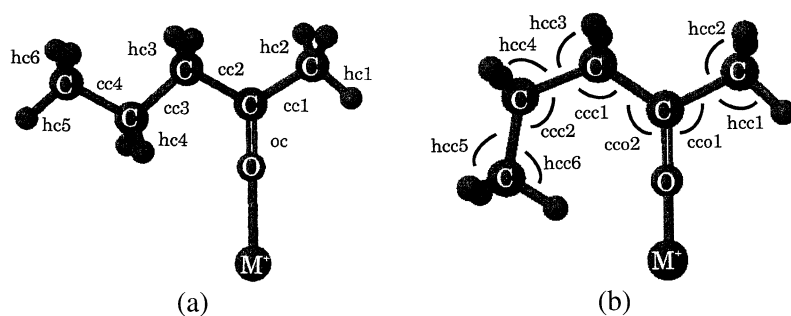
Optimized geometry of 2-pentanone (staggered conformation) in an isolated system

Bond length/Å		Bond angle/degree	
oc	1.2192	cco1	121.0320
cc1	1.5061	hcc1	109.7955
hc1	1.0796	hcc2	110.5882
hc2	1.0848	cco2	121.8810
cc2	1.5105	ccc1	114.2810
cc3	1.5283	ccc2	112.1420
cc4	1.5306	hcc3	108.0265
hc3	1.0886	hcc4	109.2451
hc4	1.0838	hcc5	110.8924
hc5	1.0840	hcc6	111.3520
hc6	1.0855		

**Table 3.**

Optimized geometry of 2-pentanone (eclipsed conformation) in an isolated system

Bond length/Å		Bond angle/degree	
oc	1.1285	cco1	119.6995
cc1	1.5114	hcc1	109.3184
hc1	1.0794	hcc2	110.7948
hc2	1.0844	cco2	125.6616
cc2	1.5143	ccc1	123.6096
cc3	1.5572	ccc2	121.1098
cc4	1.5494	hcc3	105.0886
hc3	1.0879	hcc4	106.6523
hc4	1.0840	hcc5	112.9559
hc5	1.0744	hcc6	110.4130
hc6	1.0840		

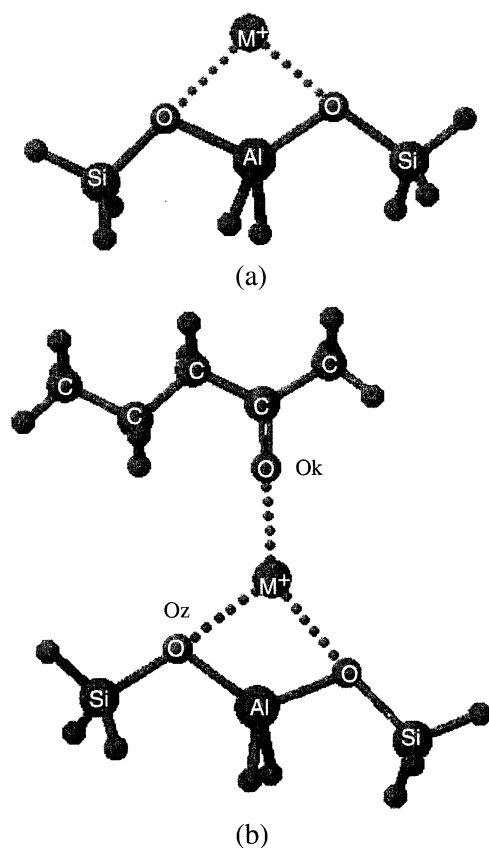


**Figure 5.** Calculation models of the system composed of 2-pentanone molecules and cations (2-pentanone- $M^+$ ). Conformation of a 2-pentanone molecule: (a) staggered conformation, (b) eclipsed conformation.

**Table 4.**

Charge populations and bond lengths of the equilibrium geometries of cation-exchanged zeolite framework ( $M^+$ -frame) models

Cations	Charge population on cation	$M^+ \cdots Oz$ bond lengths/ $\text{\AA}$
$Li^+$	0.5852	1.7332
$Na^+$	0.7367	2.0486
$K^+$	0.8624	2.4146
$Rb^+$	0.8826	2.6110
$Cs^+$	0.9018	2.8113



**Figure 6.** Calculation models of (a) the cation-exchanged zeolite framework ( $M^+$ -frame) system and (b) the system composed of 2-pentanone molecules (staggered conformation) and the cation-exchanged framework (2-pentanone- $M^+$ -frame).

with an eclipsed conformation, and the staggered model systems show stronger interactions between the 2-pentanone and the cation-exchanged zeolite framework. This interaction becomes stronger when the cations are changed from  $Cs^+$  to  $Li^+$ .

**Table 5.**

The total energy and interaction energy of 2-pentanone (staggered conformation) and cation-exchanged zeolite framework (ketone-M<sup>+</sup>-frame) system model

Cations	Total energy/a.u. <sup>a</sup>			Interaction energy between ketone and (M <sup>+</sup> -frame)/a.u. <sup>a</sup>
	Isolated system		Supermolecule (ketone-M <sup>+</sup> -frame)	
	ketone	(M <sup>+</sup> -frame)		
Li <sup>+</sup>	−270.0327	−981.6468	−1251.6874	−0.03009
Na <sup>+</sup>	−270.0327	−1135.9953	−1406.0557	−0.02765
K <sup>+</sup>	−270.0327	−1001.9956	−1272.0501	−0.02181
Rb <sup>+</sup>	−270.0327	−997.7185	−1267.7700	−0.01877
Cs <sup>+</sup>	−270.0327	−993.7399	−1263.7884	−0.01584

<sup>a</sup> 1 a.u. = 6.27510 × 10<sup>2</sup> kcal/mol.

**Table 6.**

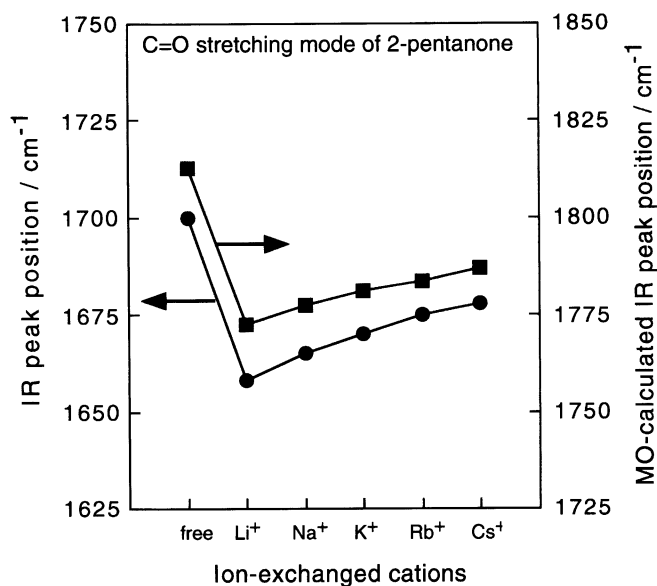
The total energy and interaction energy of 2-pentanone (eclipsed conformation) and cation-exchanged zeolite framework (ketone-M<sup>+</sup>-frame) system model

Cations	Total energy/a.u. <sup>a</sup>			Interaction energy between ketone and (M <sup>+</sup> -frame)/a.u. <sup>a</sup>
	Isolated system		Supermolecule (ketone-M <sup>+</sup> -frame)	
	ketone	(M <sup>+</sup> -frame)		
Li <sup>+</sup>	−270.0112	−981.6468	−1251.6610	−0.02515
Na <sup>+</sup>	−270.0327	−1135.9953	−1406.0321	−0.02563
K <sup>+</sup>	−270.0327	−1001.9956	−1272.0270	−0.02019
Rb <sup>+</sup>	−270.0327	−997.7185	−1267.7470	−0.01701
Cs <sup>+</sup>	−270.0327	−993.7399	−1263.7656	−0.01459

<sup>a</sup> 1 a.u. = 6.27510 × 10<sup>2</sup> kcal/mol.

As shown in Fig. 2, the heat of the adsorption of 2-pentanone calculated with the (2-pentanone-M<sup>+</sup>-frame) systems increases with the changing of the cations from Cs<sup>+</sup> to Li<sup>+</sup>, being in good agreement with the desorption temperature determined from IR measurements. In the analysis of the vibrational mode of the C=O groups, as shown in Fig. 7, the theoretical harmonic vibrational frequencies of the C=O stretching mode can be seen to shift to lower values by changing the cation from Cs<sup>+</sup> to Li<sup>+</sup>, also showing a good parallel with the results obtained by IR measurements. These results support our findings showing not only that 2-pentanone molecules interact directly with the cations by an electrostatic interaction but also that the magnitude of the interaction increases by changing the cations from Cs<sup>+</sup> to Li<sup>+</sup>.

Table 7 shows the optimized C=O bond length and the distance between the cations and oxygen atoms of 2-pentanone (M⋯Ok). By changing the cations from Cs<sup>+</sup> to Li<sup>+</sup>, these distances decrease, indicating that the interaction between the cations and 2-pentanone molecules has become stronger. Furthermore, the C=O bond length in the system with the zeolite framework (2-pentanone-M<sup>+</sup>-



**Figure 7.** The wavenumbers of the IR band measured with 2-pentanone adsorbed on the alkali metal cation-exchanged ZSM-5 zeolite and the wavenumbers and intensities of the IR band obtained by MO calculations with the (2-pentanone- $M^+$ -frame) system.

**Table 7.**

Bond lengths of the equilibrium geometries of system models with the 2-pentanone and cation-exchanged zeolite framework (ketone- $M^+$ -frame) and system models with the 2-pentanone and isolated cation (ketone- $M^+$ )

Cations	Bond lengths/Å				
	(ketone- $M^+$ -frame) model			(ketone- $M^+$ ) model	
	$M^+ \cdots Oz$	$M^+ \cdots Ok$	C=O	$M^+ \cdots Ok$	C=O
Li <sup>+</sup>	1.7601	1.9423	1.2032	1.7352	1.2435
Na <sup>+</sup>	2.0704	2.2483	1.2021	2.0844	1.2384
K <sup>+</sup>	2.4433	2.6930	1.2009	2.5085	1.2344
Rb <sup>+</sup>	2.6424	2.9174	1.2002	2.7170	1.2329
Cs <sup>+</sup>	2.8466	3.1767	1.1993	2.9437	1.2315
isolated 2-pentanone			1.1927		1.1927

frame) is shorter than the system without the zeolite framework (2-pentanone- $M^+$ ). The delocalization of the charge population of the cations induced by the zeolite framework which was estimated from calculations of the charge population on the framework ( $M^+$ -frame) cations can modify the interaction between the cations and 2-pentanone molecules. The zeolite framework was found to act as a buffer for the electronic charge of the ion-exchanged cations and produced unique electrostatic forces in the zeolite cavities.

## CONCLUSIONS

The efficiency of the photolysis of 2-pentanone included within alkali metal cation-exchanged zeolites changes with the cation, its extent decreasing by changing the cation from  $\text{Cs}^+$  to  $\text{Li}^+$  in the order of the magnitude of the interaction between the ketone and the cations. A modification of the chemical nature of the micro-environment of the adsorption sites in the zeolite cavities by changing the cations causes a significant perturbation in the geometrical conformation and electronic state of the 2-pentanone molecules included within the cavities. The 2-pentanone molecules interact with the cations by weak electrostatic forces in the zeolite cavities, its magnitude changing with the cation and being modified by the zeolite framework. A comprehensive examination of the unique characteristics of the photolysis of the alkyl ketones included within the zeolite cavities was clarified on the basis of these perturbations.

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## REFERENCES

1. M. Anpo and T. Matsuura (Eds), *Photochemistry on Solid Surfaces*. Elsevier, Amsterdam (1989).
2. M. Anpo (Ed.), *Surface Photochemistry*. John Wiley & Sons, London (1996).
3. M. Anpo and M. Che, *Adv. Catal.* **44**, 119 (1999).
4. J. K. Thomas, *Chem. Rev.* **93**, 301 (1993).
5. P. V. Kamat, *Chem. Rev.* **93**, 267 (1993).
6. S. Okamoto, H. Nishiguchi and M. Anpo, *Chem. Lett.* 1009 (1992).
7. H. Nishiguchi and M. Anpo, *J. Photochem. Photobiol. A: Chem.* **77**, 183 (1994).
8. H. Nishiguchi, K. Yukawa, H. Yamashita and M. Anpo, *Res. Chem. Intermed.* **21**, 885 (1995).
9. H. Nishiguchi, K. Yukawa, H. Yamashita and M. Anpo, *J. Photochem. Photobiol. A: Chem.* **99**, 1 (1995).
10. H. Yamashita, N. Sato, M. Anpo, T. Nakajima, M. Hada and H. Nakatsuji, *Stud. Surf. Sci. Catal.* **105**, 1141 (1997).
11. H. Nishiguchi, S. Okamoto, M. Nishimura, H. Yamashita and M. Anpo, *Res. Chem. Intermed.* **24**, 849 (1998).
12. H. Yamashita, A. Tanaka, M. Nishimura and M. Anpo, *Stud. Surf. Sci. Catal.* **117**, 651 (1998).
13. M. Anpo (Ed.), *Photofunctional Zeolites*. Nova Sci. Pub. Inc., New York (2000).
14. N. J. Turro, *Pure Appl. Chem.* **58**, 1219 (1986).
15. V. Ramamurthy, *Photochemistry in Organized and Constrained Media*. VCH, New York (1991).
16. V. Ramamurthy, D. F. Eaton and J. V. Caspar, *Acc. Chem. Res.* **25**, 299 (1992).
17. V. Ramamurthy, D. R. Corbin and L. J. Johnston, *J. Am. Chem. Soc.* **114**, 3870 (1992).
18. V. Ramamurthy, J. V. Caspar, D. F. Eaton, E. W. Kuo and D. R. Corbin, *J. Am. Chem. Soc.* **114**, 3882 (1992).

19. M. Anpo, *Chem. Lett.* 1221 (1987).
20. A. Redondo and P. J. Hay, *J. Phys. Chem.* **97**, 11754 (1993).
21. H. van Koningsveld, H. van Bekkum and J. C. Jansen, *Acta. Crystallog.* **B43**, 127 (1987).
22. H. van Koningsveld, H. van Bekkum and J. C. Jansen, *Zeolites* **10**, 235 (1990).