

Photochemistry of alkyl ketones included within the zeolite cavities: The effect of ion-exchanged alkali metal cations and types of zeolites

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The relative yields of the Norrish Type I and Type II reactions in the photolysis of 2-pentanone included within various types of zeolites (Y, Mordenite, L, ZSM-5, FSM-16) changed depending on the size of the restricted void space of the zeolite cavities. The yields in the photolysis of 2-pentanone and 2-butanone included within the alkali metal cation-exchanged ZSM-5 zeolite increased by changing the cation from Li⁺ to Cs⁺. The IR and phosphorescence spectra of adsorbed ketones and ab initio molecular orbital calculations indicate that these alkyl ketones interact with two different adsorption sites, i.e., the surface OH groups and alkali metal cations. 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.

1. INTRODUCTION

Studies of the photophysics and photochemistry of molecules adsorbed on various adsorbents have recently attracted a great deal of attention in the field of heterogeneous photochemistry [1-3]. An interesting aim in this field is to define what the influences are to the photochemistry of the adsorbed molecules when the micro-environment of the adsorption sites are modified in their chemical and physical nature. Zeolites are considered to be one of the most suitable materials to investigate a variety of host-guest interactions and their role in the photochemical nature of the guest molecules [4-7]. In the present work, the effects of ion-exchanged alkali metal cations and type of zeolite on the photochemical properties of alkyl ketones (2-pentanone and 2-butanone) included within the zeolite cavities have been investigated. Special attention has been focused on the vital role the adsorption site-ketone

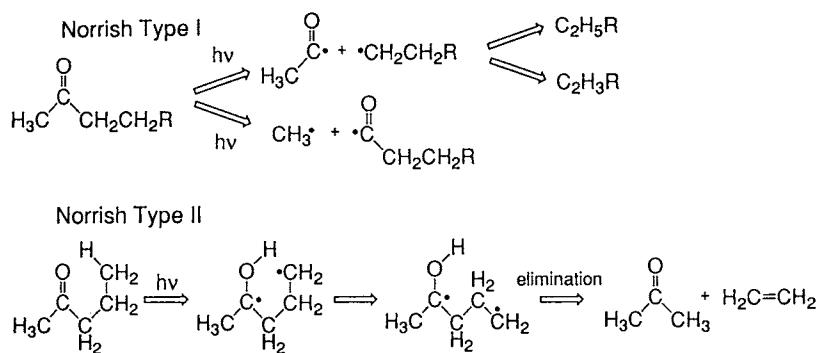
interaction plays in the photophysical and photochemical properties of the ketone molecules at the molecular level through investigations of the adsorption state of the molecules by spectroscopic measurements, ab initio molecular orbital calculations as well as an analysis of the photolysis of the ketone molecules included within the zeolite cavities.

2. EXPERIMENTAL

Various types of zeolites (ZSM-5 (Si/Al ratio = 23.3), Mordenite (Si/Al ratio = 14.9), L-zeolite (Si/Al ratio = 6.2), Y-zeolite (Si/Al ratio = 5.5), FSM-16) 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 an atomic absorption spectroscopy; 90 % for Li⁺, 80 % for K⁺, 70 % for Rb⁺, and 40 % for Cs⁺, respectively. Adsorption of alkyl ketones (2-pentanone and 2-butanone) 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 alkyl ketones introduced into the samples was about 8.4x10⁻⁵ mol·g⁻¹. The phosphorescence spectra and lifetimes of the alkyl ketones adsorbed on the zeolite samples were recorded at 77 K. The IR measurements were carried out at 295 K. The XPS spectra were measured at 295 K using VG ESCASCOPE with Mg radiation. Binding energies were corrected for samples charging by reference to carbon (C1s=285 eV) contaminated onto the samples. Photolysis of the alkyl ketones was carried out at 275 K using a high pressure mercury lamp ($\lambda > 290$ nm). The reaction products were analyzed by gas chromatography. The ab initio molecular orbital calculations for the interaction between the alkyl ketones and alkali metal cations were performed using a Gaussian 92 package. The equilibrium geometries and harmonic vibrational frequencies were computed at HF(SCF) levels. The basis sets were based on the 6-31G type for H, C, O, Li, Na and (8s6p)/[3s3p] for K, Rb, Cs. Wadt-Hay ECP was added to K, Rb, Cs.

3. RESULTS AND DISCUSSION

As shown in the following reaction scheme 1, alkyl ketones having γ -hydrogen atoms such as 2-pentanone undergo the Norrish Type I process (α -cleavage into radical pairs) and the Norrish Type II process (intramolecular elimination). 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



Scheme 1. The mechanism behind the photolysis of alkyl ketones (R=H, CH₃).

Table 1. Yield of the products in the photolysis of 2-pentanone included within various zeolites.

Samples	Pore size / nm	Yield of products / $\times 10^{-7}$ mol·g ⁻¹			Ratio of Type I/II
		Type II	Type I		
		ethylene	propylene	propane	
Na ⁺ -ZSM-5	0.56x0.53	0.51	0.00	1.47	2.87
K ⁺ -ZSM-5	0.51x0.55	1.15	0.75	2.15	2.51
Na ⁺ -Mordenite	0.67x0.70	0.28	0.10	0.36	1.64
K ⁺ -L-zeolite	0.71	9.40	7.40	10.90	1.94
Na ⁺ -Y-zeolite	0.74	9.04	1.43	8.50	1.10
FSM-16	2.0	15.10	0.81	2.17	0.19

Table 2. Yield of the products in the photolysis of 2-butanone included within alkali metal cation-exchanged ZSM-5.

Samples	Yield of products / $\times 10^{-7}$ mol·g ⁻¹		
	ethylene	ethane	ethylene /ethane
Li ⁺ -ZSM-5	0.00	0.63	0.00
Na ⁺ -ZSM-5	0.03	0.88	0.04
K ⁺ -ZSM-5	0.86	2.86	0.23
Rb ⁺ -ZSM-5	3.25	2.98	0.52
Cs ⁺ -ZSM-5	6.38	3.13	0.67

either by the insertion of a hydrogen atom into 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. On the other hand, in the photolysis of 2-butanone included within the zeolite cavities the major products were ethylene and ethane which are produced from ethyl radicals formed by the Norrish Type I cleavage. Therefore, from these results, the yields of the Norrish Type I and the Norrish Type II reactions can be determined from the total yield of these products. Table 1 shows the effect of the type of zeolite on the photolysis of 2-pentanone included within the alkali metal (Na^+ or K^+) cation-exchanged zeolites. The ratios of the Norrish Type I /Type II reaction in the photolysis of 2-pentanone are 2.9 ~ 0.2 and they are much larger than those obtained for the corresponding photolysis in the gas phase, i. e., the Norrish Type I /Type II = 0.1. It can clearly be seen in Table 1 that the relative yield of ethylene decreases and the ratio of the Norrish Type I /Type II increases with decreasing the pore size of the zeolites. As shown in reaction scheme 1, the Norrish type II reaction proceeds via the 1,4-biradical intermediate. A favorable conformation, i. e., a six-membered intermediate is required for a γ -hydrogen atom abstraction to take place. In the restricted zeolite cavities, the formation of such a six-membered transition state is considerably suppressed, its extent strongly depending on the pore size of the zeolites. Such steric hindrance seems to be more significant for the ZSM-5 zeolite than the mordenite and Y-zeolite. Thus, the results in Table 1 clearly indicate that steric hindrance due to the restricted void space of the zeolite cavities causes difficulty in the formation of a six-membered intermediate and restrains the Norrish Type II reaction.

In the cavities of the ZSM-5 zeolite, the Norrish Type II reaction is considerably difficult. However, it was found that the yield of the photolysis of 2-pentanone included within alkali metal cation-exchanged ZSM-5 increases by changing the cation from Li^+ to Cs^+ . As shown in Table 2, it was also found that the yield in the photolysis of 2-butanone included within alkali metal cation-exchanged ZSM-5 also increases by changing the cation from Li^+ to Cs^+ . These results clearly indicate that the photolysis of alkyl ketones included within zeolites is strongly affected by changing the micro-environment of the adsorption sites, specifically by exchanging the alkali metal from Li^+ to Cs^+ .

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 $1700\sim 1640\text{ cm}^{-1}$ and their intensities increased with increasing the amount of 2-pentanone added. The peak at around 1700 cm^{-1} scarcely varies

by changing the cation. Increasing the amount of adsorbed 2-pentanone led to a decrease in the intensity at around 3740 cm^{-1} which could be attributed to the surface OH groups and an increase in the intensity at around 3400 cm^{-1} attributed to the hydrogen bonding between the surface OH groups and 2-pentanone. Alkyl ketones adsorbed on the SiO_2 surfaces by hydrogen bonding exhibit only one IR absorption peak at around 1700 cm^{-1} [1,8]. These results clearly indicate that the peak at around 1700 cm^{-1} can be assigned to ketones which interact with the surface OH groups through hydrogen bonding. On the other hand, the peak at around 1660 cm^{-1} shifts from 1658 cm^{-1} to 1678 cm^{-1} by changing the cation from Li^+ to Cs^+ . Thus, the peak is sensitively affected by the cations, indicating that the peaks at around 1660 cm^{-1} can be assigned to the ketones which interact directly with the cation.

In order to clarify the adsorption state of these ketones, 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 temperature determined by monitoring the IR peak at around 1660 cm^{-1} decreases when the cation is changed from Li^+ to Cs^+ indicating that the magnitude of the interaction between the cation and ketone molecules decreases with the changing of the cation.

Ab initio molecular orbital calculations of such ketones which directly interact with the cation provide useful and important information on the

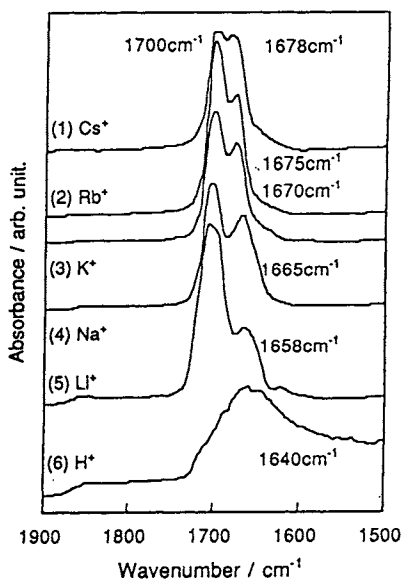


Fig. 1. The IR spectra of 2-pentanone included within alkali metal cation-exchanged ZSM-5.

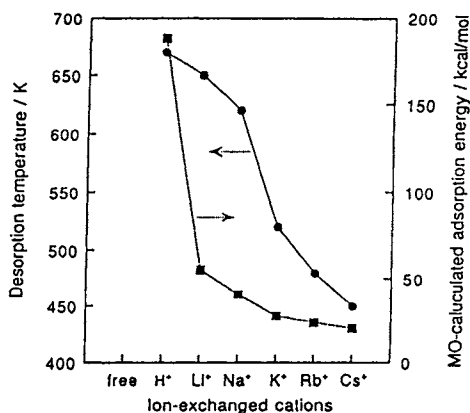


Fig. 2. The effects of the ion-exchanged alkali metal cations on the desorption temperature of 2-pentanone determined by IR measurements and the adsorption energy obtained by MO calculations.

geometry, heat of adsorption, and vibrational frequencies of the C=O groups of the ketones. Figures 2 and 3 show the results obtained from MO calculations. In the SCF optimized structures of the adsorption of the ketone, the alkali metal cation locates in the configuration which is linear to the C=O bond. The results of the ab initio calculations suggest not only that there is no significant overlap between the orbitals of alkyl ketones and cations but also that alkyl ketones are stabilized on the cations by an electrostatic interaction. As shown in Fig. 2, the heat of the adsorption of 2-pentanone calculated for the systems decreases with the changing of the cation, being in good agreement with the desorption temperature determined from the IR measurements. In the analysis of the vibrational mode of the C=O groups, as shown in Fig. 3, the theoretical harmonic vibrational frequencies of the C=O stretching mode can be seen to shift from 1830 cm^{-1} to 1865 cm^{-1} by changing the cation from Li^+ to Cs^+ , showing a good parallel to the results obtained by IR measurements. These results support our findings that not only do the alkyl ketones interact directly with the cations by an electrostatic interaction but also that the magnitude of the interaction decreases by changing the cation from Li^+ to Cs^+ .

2-pentanone included within alkali metal cation-exchanged ZSM-5 exhibits a phosphorescence spectrum at around 430 nm when excited at around 300 nm. The decay curves of the phosphorescence are well fitted with a double exponential decay mechanism indicating the presence of the two 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 alkyl ketones. Figure 4 shows the lifetimes of the

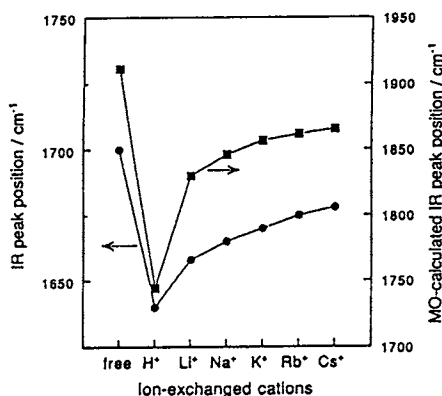


Fig. 3. A comparison between experimentally observed IR peak positions and IR peak positions obtained by MO calculations.

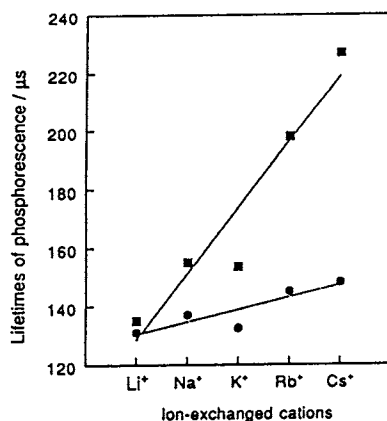


Fig. 4. Lifetimes of the phosphorescence of 2-pentanone included within alkali metal cation-exchanged ZSM-5.

phosphorescence of 2-pentanone included within ZSM-5. The lifetime values of the components with a longer lifetime strongly depends on the kind of cations exchanged, becoming longer by changing the cation from Li^+ to Cs^+ . The values of the component with the shorter lifetime scarcely changes and remains 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, 8]. 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 ketone interacting with the cation by weak electrostatic forces, its magnitude changing with the cation.

The lifetime of 2-pentanone interacting with the cation becomes longer when the cation is changed from Li^+ to Cs^+ which in turn indicates that the opportunity for the reaction of the excited state of 2-pentanone becomes greater as well. The desorption temperature of 2-pentanone from the system also becomes lower by changing the cation from Li^+ to Cs^+ suggesting that the interaction between 2-pentanone and the cation becomes weaker 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 Cs^+ to Li^+ in the order of the magnitude of the interaction between the ketone and the interactions.

Furthermore, it was found that the product ratio of propylene to propane in the photolysis of 2-pentanone increases by changing the cation from Li^+ to Cs^+ . As seen in Table. 2, it can also be seen that the product ratio of ethylene to ethane in the photolysis of 2-butanone increases by the change in the cation. As mentioned above, propylene and ethylene are produced by a hydrogen atom abstraction from their parent radicals which are produced by the Norrish Type I α -cleavage of 2-pentanone and 2-butanone. Figure 5 shows that the binding energy of the O_{1s} XPS peak of the alkali metal cation-exchanged zeolites decreases when the electronegativity of the ion-exchanged

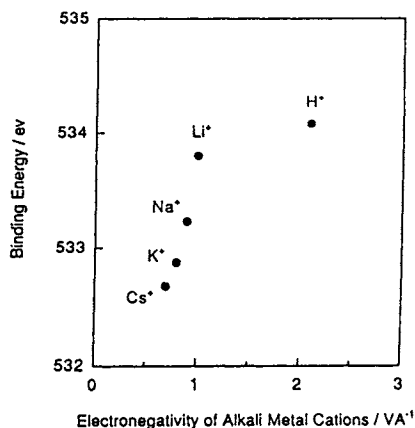


Fig. 5. The dependence of the binding energy of O_{1s} XPS peaks of ZSM-5 zeolites on the electronegativity of the exchanged alkali metal cations.

alkali metal cations are decreased in the order of $\text{Li}^+ > \text{Na}^+ > \text{Rb}^+ > \text{Cs}^+$. These results clearly indicate that the negative charge in the oxygen atoms of the zeolite increases by changing the cation from Li^+ to Cs^+ . Although such changes in the binding energy of O1s XPS peak of zeolites strongly depend on the types of zeolites [9], these investigations clearly show that the basicity of the lattice oxygen of the zeolites increases by changing the cation from Li^+ to Cs^+ which in turn results in the enhancement of the hydrogen atom abstraction from the parent radicals to form propylene and ethylene, respectively.

4. CONCLUSIONS

A modification of the micro-environment of the adsorption sites in the zeolite cavities by changing the types of zeolites and the ion-exchanged cations causes a significant perturbation in the geometrical conformation and electronic state of the ketone molecules included within the cavities. A comprehensive examination of the unique characteristics of the photolysis of alkyl ketones included within the zeolite cavities was clarified on the basis of these perturbations.

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