Characterization of Vanadium Oxide/ZSM-5 Zeolite Catalysts Prepared by the Solid-State Reaction and Their Photocatalytic Reactivity: In Situ Photoluminescence, XAFS, ESR, FT-IR, and UV−vis Investigations

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The solid-state reaction of the ZSM-5 zeolite with V_2O_5 has been investigated by means of photoluminescence spectroscopy in combination with other spectroscopic techniques such as XAFS (XANES and FT-EXAFS), UV−vis, ESR, and FT-IR. It has been found that this reaction leads to the formation of the VO^{2+} species as well as the vanadium oxide species, $(Si-O)_3V=O$, which has a C_{3v} symmetrical geometry and is located at two different sites, i.e., at positions accessible to small molecules as well as at inaccessible positions. These vanadium oxide species formed in the zeolite exhibits unique and specific photocatalytic reactivity toward the isomerization of *cis*-2-butene at 273 K.

Introduction

Zeolites encapsulated with transition metals have been the subject of many recent studies due to their significant role in various efficient and selective catalytic reactions such as the partial oxidation of hydrocarbons.[1−17] The transition-metal atoms can be introduced into the framework of the zeolites by a hydrothermal synthesis method[1−12] and postsynthesis method.[13−17] They can also be introduced onto the cation-exchangeable sites by a conventional ion-exchange method and a solid-state exchange method. It has been shown that the location of such transition metals in the zeolites remarkably modifies the catalytic and photocatalytic reactivities of the zeolites.[1−3,10,11]

The application of the solid-state reaction of zeolites with various inorganic salts or metal oxides in preparing zeolite catalysts involving transition metals has opened a new field in zeolite chemistry,[13−17] especially for zeolites involving transition-metal elements which are difficult to introduce into zeolite cavities by conventional ion-exchange methods.

The solid-state reaction of V_2O_5 with high silica zeolites has also been studied by ESR techniques.[14−17] Kucherov and Slinkin studied the reaction of V_2O_5 with the HZSM-5 zeolite using ESR techniques and observed the insertion of the VO^{2+} species at cationic sites in the zeolite.[14,15] Petras and Wichterlova also reported that the same reaction results in the insertion of the VO^{2+} species and that at least two different kinds of VO^{2+} species are located within the zeolite: one located at the cationic sites and the other connected to the surface Si−OH groups.[17]

Nevertheless, investigations employing ESR techniques have lacked information on the presence and characterization of ESR-inactive V^{5+} ions. For this purpose, a select combination of various techniques that are able to detect and monitor the various kinds of metal centers formed in the solid-state reaction is vital for a complete understanding of the local structures of vanadium ions and their role in the photocatalytic reactivity.

Photoluminescence techniques are known to be very sensitive and useful in detecting the presence of highly dispersed tetrahedrally coordinated V^{5+} species,[18−31] but there have been no photoluminescence studies on the solid-state reaction of V_2O_5 with zeolites. Thus, it is expected that detailed investigations on the V^{5+} species by photoluminescence spectroscopy methods will provide significant insight into the nature of solid-state reactions which in turn will lead to the design of useful and efficient catalytic and photocatalytic zeolite systems.

In the present study, we have carried out investigations on the solid-state reaction of the HZSM-5 zeolite with V_2O_5 by means of in situ photoluminescence in combination with other spectroscopic techniques such as XAFS (XANES and FT-EXAFS), ESR, UV−vis, and FT-IR. Special attention has been focused on the location, coordination, and photocatalytic reactivity of the vanadium oxide species incorporated within the zeolites.

Experimental Section

V_2O_5 (99.9%) was supplied by Kishida Chemicals, Japan, and used as received. The HZSM-5 zeolite was used as the parent zeolite. It was prepared by a conventional ion-exchange method with 5.0 g of NaZSM-5 (SiO_2/Al_2O_3 = 23.8:1) supplied by the Tosoh Co., with 500 mL of an aqueous solution of 0.1 M NH_4Cl at 300 K for 24 h. This procedure was then repeated three times. After filtering and washing with water at 353 K several times, the NH_4ZSM-5 sample was heated from 300 to 773 K (5 K/min) in air and kept at 773 K for 5 h. The solid-state reaction products of the HZSM-5 zeolite and V_2O_5 were prepared in accordance with procedures published in previous literature.[14−17] A 50.0 mg sample of V_2O_5 was mixed with 1.0 g of the HZSM-5 zeolite and stirred using a laboratory mill for 8 h and then calcined and dried in an oven under a dry flow of air at different temperatures for 5 h. The photoluminescence spectra were recorded with a Shimadzu RF-501 spectrofluorophotometer at 77 and 295 K. The FT-IR spectra were recorded at 295 K with a Shimadzu FTIR-8500 spectrophotometer using the sample wafers of mixture of the catalyst and KBr. The UV−

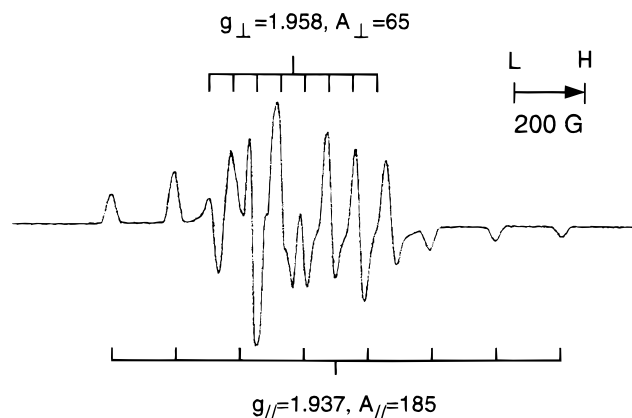* To whom correspondence should be addressed.

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Figure 1. ESR spectrum of the V oxide/ZSM-5 catalyst prepared by the solid-state reaction between HZSM-5 and V_2O_5 after reaction at 1073 K for 5 h. (Spectra were recorded at 77 K.)

Figure 2. Excitation (a−c) and photoluminescence (A−C) spectra of the V oxide/ZSM-5 catalyst prepared by the solid-state reaction between HZSM-5 and V_2O_5 at 1073 K for 5 h. (Spectra were recorded at 77 K. Excitation spectra were monitored at 500 nm, and photoluminescence spectra were observed at the excitation of 300 nm.) (a, A) After the solid-state reaction without pretreatment. (b, B) After degassing at room temperature for 1 h. (c, C) After further degassing of sample B at 473 K for 1 h. (D) The second-derivative spectrum of spectrum C.

vis absorption spectra were recorded in the diffuse reflectance mode at 295 K with a Shimadzu UV-2200A spectrophotometer equipped with the conventional component of a reflectance spectrometer. The XAFS spectra (XANES and FT-EXAFS) were obtained at the BL-7C facility of the Photon Factory at the National Laboratory for High Energy Physics (KEK-PF) in Tsukuba. A Si(111) double crystal was used to monochromatize the X-rays from the 2.5 GeV electron storage ring. The V K-edge absorption spectra were recorded in the fluorescence mode at 295 K. The normalized spectra were obtained by procedures described in previous papers,[11] and the Fourier transformation was performed on k^3-weighted EXAFS oscillations in the range 4−10 Å^{-1}. The curve fitting of the EXAFS data was carried out by employing the iterative nonlinear least-squares method and the empirical backscattering parameter sets extracted from the shell features of vanadium compounds. Photocatalytic reactions were carried out in a quartz reactor under UV irradiation (λ > 280 nm) at 275 K using a high-pressure mercury lamp (Toshiba SHL-100UVQ-2) through water and color filters. The reaction products were analyzed by on-line gas chromatography.

Results and Discussion

The samples were prepared by the solid-state reactions of HZSM-5 and V_2O_5 at various temperatures from 673 to 1073 K. From the XRD analysis, it was indicated that there is no damage in the MFI structure of HZSM-5 and that no crystalline vanadium species is formed after the reaction even at 1073 K. Furthermore, a strong ESR signal was observed with the products formed from the solid-state reaction, though neither HZSM-5 nor V_2O_5 exhibited any ESR signals before the reaction. Figure 1 shows the ESR spectrum at 77 K of the reaction product of HZSM-5 and V_2O_5 at 1073 K. The similarity of the ESR signal in its shape and g values with the signals reported in previous literature[14−17] indicated that the V_2O_5 composition decomposed and dispersed into the zeolite as isolated VO^{2+} species. From the relative ESR signal intensity referred to the standard $VOSO_4$ solution, the contribution of VO^{2+} species to the total vanadium species in the reaction product at 1073 K was roughly estimated to be about 7%.

Figure 2A shows the photoluminescence spectrum observed with the products of HZSM-5 and V_2O_5 at 1073 K, recorded at 77 K in air. At 295 K, no detectable photoluminescence spectrum could be observed, but at 77 K a photoluminescence spectrum with a strong intensity was detected at around 450−550 nm with a peak at 500 nm and an excitation spectrum at
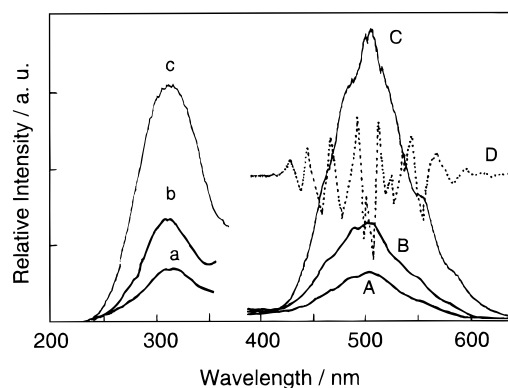
around 280−350 nm with a peak at around 315 nm. The photoluminescence observed at around 500 nm shows a vibrational fine structure which resembles that of the V^{5+} oxide species highly dispersed on SiO_2 and having a tetrahedral coordination with a VO_4 unit involving the V=O vanadyl group.[24] Highly dispersed V^{5+} oxide species were shown to exhibit photoluminescence spectra on porous Vycor glass (PVG), SiO_2, Al_2O_3, and MgO.[18−31] The shape and the vibrational fine structure of the photoluminescence spectrum were found to depend strongly on the support. On PVG or SiO_2, the highly dispersed V^{5+} oxide species exhibited a photoluminescence spectrum with a vibrational fine structure due to the V=O vanadyl group, while on Al_2O_3 and MgO only structureless photoluminescence spectra could be observed. Moreover, on semiconducting supports such as TiO_2 and ZnO, no spectrum could be observed at all due to the energy transfer from the excited state of the vanadium oxide species $(V^{4+}-O^-)^*$ to the semiconductors. Many studies of highly dispersed vanadium oxide catalysts supported on SiO_2 (V oxide/SiO_2) have shown that the vanadium oxide species has a $(Si-O)_3V=O$ unit structure in a well-separated and distorted 4-fold coordinated state.[18−24,28−31] Thus, the present photoluminescence studies indicate that the solid-state reaction between high-silica zeolites and V_2O_5 has resulted in the formation of highly dispersed V^{5+} oxide species in a distorted 4-fold coordinated state. The good coincidence of the photoluminescence spectrum with that of V oxide/SiO_2 suggested that the V^{5+} centers are connected to the framework Si atoms through a bridge O rather than to the framework Al atoms.

The appearance of a photoluminescence spectrum even in air suggests that the V^{5+} oxide species exists in positions inaccessible to O_2 and H_2O. This is quite different from other systems such as the V oxide/SiO_2 catalyst in which the photoluminescence is completely quenched, and no photoluminescence can be observed with detectable intensity in air.

When the sample was degassed at room temperature for 1 h, the intensity of the photoluminescence spectrum increased, and as shown in Figure 2B, its structure also became slightly well-resolved. This shows that some part of the photoluminescence is quenched by the presence of air, indicating that the V^{5+} oxide species also exists in positions accessible to small molecules as well as in inaccessible positions. It can be assumed that the former sites exist on the outside surface of the zeolites or on
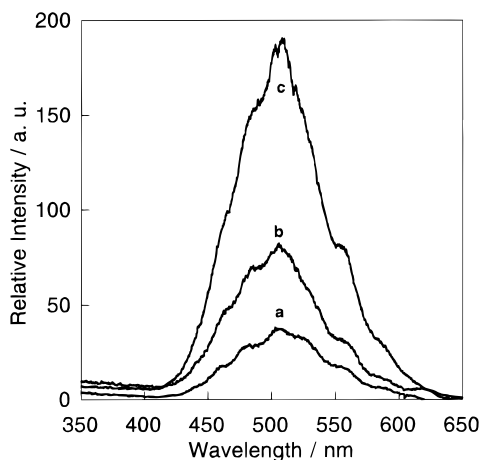
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Figure 3. Effect of the solid-state reaction temperatures on the photoluminescence spectra of the V oxide/ZSM-5 catalysts prepared by the solid-state reaction between HZSM-5 and V_2O_5. (Experimental conditions were the same as in Figure 2.) (a) 673, (b) 873, and (c) 1073 K.

the surface of the large cavities within the zeolites. As shown in Figure 2C, after the sample was further degassed at 473 K for 1 h, a remarkable increase in the photoluminescence intensity can be observed. The photoluminescence spectrum becomes about 6 times stronger than that observed in air without any pretreatment. The vibrational fine structure of the photoluminescence due to the V=O vanadyl group becomes much better resolved, and the corresponding second-derivative photoluminescence spectrum is shown in Figure 2D. These findings clearly demonstrate not only that the vanadium oxide species are present mainly as a 4-fold tetrahedrally coordinated V^{5+} species having a V=O vanadyl group but also that large amounts of the V^{5+} oxide species formed in the products of the solid-state reaction are accessible to small molecules which showed no photoluminescence spectrum before pretreatment in a vacuum due to the adsorption of quencher molecules such as H_2O and O_2 in air. Additionally, the observation of some perturbation in the vibrational fine structure of the photoluminescence at 77 K can be attributed to the presence of the neighboring surface OH groups in the electronic state of the V=O species. The presence of such weak interaction has already been reported by the analysis of the photoluminescence spectra of the V silicalite catalyst at 77 K in our previous paper.[11]

As shown in Figure 3, the temperature of the solid-state reaction of V_2O_5 with HZSM-5 has a significant effect on the intensity of the photoluminescence observed with the products, showing that a higher reaction temperature leads to a stronger photoluminescence intensity. This indicates that the solid-state reaction is already initiated at lower temperatures and proceeds further at higher temperatures. These findings also demonstrate that the formation of the V^{5+} oxide species may occur at the same time as that of the V^{4+} (VO^{2+}) species in the process of the reaction.

Figure 4 shows the FT-IR spectra of the solid-state reaction products in the wavenumber regions of 1400–400 cm^{-1}. The FT-IR spectra of the parent HZSM-5 zeolite and V_2O_5 were also measured for reference. It was found that after the solid-state reaction the characteristic bands of HZSM-5 at around 550 cm^{-1} were well retained. The crystallinity of zeolite can be estimated from the ratio of the intensity of the bands at 550 and 450 cm^{-1}. Considering value of 0.7 for well crystalline ZSM-5, the observed value of 0.65 for the products in the reaction of 1073 K clearly suggests that the framework of the zeolite remained intact even after reaction at 1073 K. A small
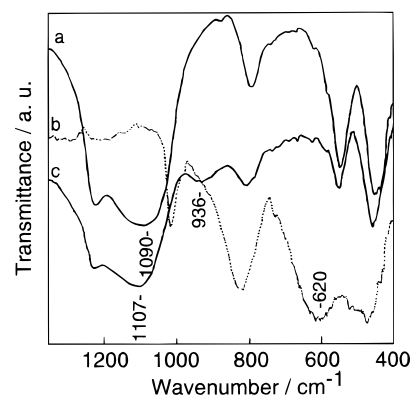

Figure 4. FT-IR spectra of the V oxide/ZSM-5 catalyst prepared by the solid-state reaction between HZSM-5 and V_2O_5 after reaction at 1073 K for 5 h and its parent materials. (Spectra were recorded at 295 K.) (a) Parent HZSM-5 zeolite. (b) Parent V_2O_5. (c) The V oxide/ZSM-5 catalyst prepared by the solid-state reaction at 1073 K for 5 h.
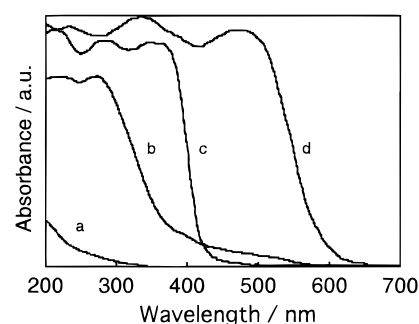

Figure 5. UV–vis absorption (diffuse reflectance) spectra of the V oxide/ZSM-5 catalyst prepared by the solid-state reaction between HZSM-5 and V_2O_5 at 1073 K for 5 h, the parent materials, and NH_4VO_3 used as reference. (Spectra were recorded at 295 K.) (a) Parent HZSM-5 zeolite. (b) NH_4VO_3. (c) The V oxide/ZSM-5 catalyst prepared by the solid-state reaction at 1073 K for 5 h. (d) Parent V_2O_5.

shift of the band at around 1090 cm^{-1} toward higher wavenumbers can be observed with the products of the solid-state reaction, indicating that the reaction has slightly influenced the bonding strength of the zeolite framework. The characteristic bands of V_2O_5 observed at around 620 cm^{-1} disappeared almost completely, revealing that V_2O_5 is decomposed and highly dispersed within the zeolite during the solid-state reaction.

With the products of the solid-state reaction, a new broad band appears at around 936 cm^{-1} which cannot be observed with the parent HZSM-5. For highly dispersed and dehydrated V_2O_5, a vibrational band due to the V=O vanadyl group can be observed at around 1035–1049 cm^{-1} while for hydrated V_2O_5 a band appeared in the vicinity of 900–1000 cm^{-1}.[28−31] On the other hand, when transition metals such as Ti or V are introduced into the framework of the zeolites by hydrothermal synthesis, an IR band at around 960–970 cm^{-1} can be observed, indicating that the appearance of this IR band is associated with the insertion of metals into the zeolite framework.[32,33] Since our FT-IR spectra were recorded in air, the sample may be hydrated. This IR band is, therefore, tentatively assigned to the hydrated vanadyl group existing in the solid-state reaction products. Another possibility that this band is due to the defect sites of Si−O$^-$ seems unlikely, since we have not observed any serious changes in the zeolite framework (see below).

Figure 5 shows the UV–vis spectra of the products generated by the solid-state reaction and their parent materials. The spectrum of NH_4VO_3 with a 4-fold coordinated VO_4 unit is also shown for comparison. With the solid-state reaction products, the characteristic absorption band due to V_2O_5 almost completely

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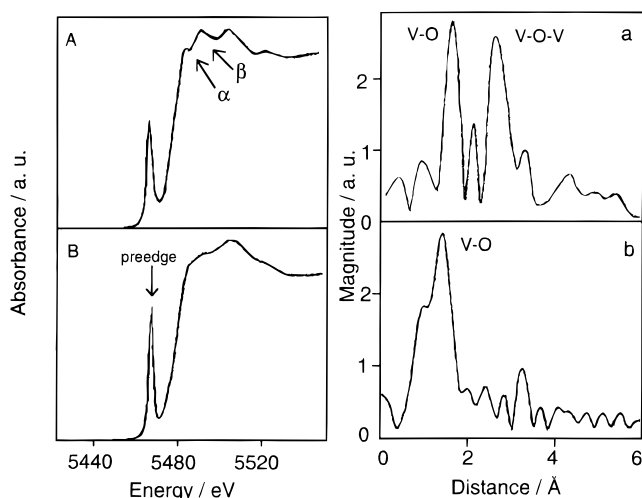*J. Phys. Chem. B, Vol. 102, No. 29, 1998* **5593**

Figure 6. Effect of the solid-state reaction temperature on the XANES (left) and FT-EXAFS spectra of the V oxide/ZSM-5 catalyst prepared by the solid-state reaction between HZSM-5 and V_2O_5. (Spectra were recorded at 295 K.) (a, A) 673 and (b, B) 1073 K.

disappears, while an intense absorption band appeared at around 200−400 nm. When compared with the spectrum of the NH_4-VO_3 reference compound, it is likely that the absorption band in this region may involve the presence of V oxide species having a 4-fold coordinated structure. These results indicate that the vanadium species having a lower coordination exist in great amounts in the solid-state reaction products. The weak absorption bands in the region beyond 450 nm can be attributed to the presence of 6-fold coordinated vanadium oxide species rather than the aggregated vanadium oxide species. Although the coexistence of the VO^{2+} and V^{5+} oxide species makes further analysis of the spectra difficult, the present results clearly show that the solid-state reaction of V_2O_5 with HZSM-5 has transformed V_2O_5 almost completely into a V oxide species highly dispersed within the zeolite.

Figure 6 shows the V K-edge XAFS (XANES and FT-EXAFS) spectra of the products generated by the solid-state reaction of the HZSM-5 zeolite with V_2O_5 at different temperatures. The product prepared at 673 K exhibits a XANES spectrum having characteristic bands (α and β in Figure 6A) at energy regions higher than the edge position. This spectrum is very similar to that of V_2O_5 having a square-pyramidal VO_5 unit. Increasing the temperature of the solid-state reaction caused the intensity of these characteristic bands (α and β) to become weaker. On the other hand, the preedge peak is very strong even after the reaction at 1073 K (Figure 6B). This preedge peak can be assigned to the so-called 1s−3d transition mainly caused by the mixing of 2p orbitals of the oxygen anions with 3dp orbitals of the vanadium atoms.[10,11,34] The spectrum of this product prepared at 1073 K and having an intense preedge peak without the characteristic bands (α and β) is similar to that of (iso-C_3H_7−O)$_3$V=O having a O_3V=O unit. These findings suggest the presence of a tetrahedrally coordinated V^{5+} oxide species having a terminal vanadyl group (V=O) in the product prepared at 1073 K.[10,11,34] Furthermore, as shown in the FT-EXAFS spectra, the peak due to the presence of the neighboring V atoms (V−O−V) can scarcely be observed in the solid-state reaction products, indicating that the reaction has occurred to a significant extent at 1073 K.[10,11,34] A curve-fitting analysis is actually difficult for a mixed system with both the VO^{2+} and V^{5+} oxide species, but the above results clearly indicate that the solid-state reaction proceeds mainly at higher temperatures while after the reaction at 1073 K for 5 h, most

TABLE 1: Curve Fitting of V K-Edge FT-EXAFS Data with the V Oxide/ZSM-5 Catalyst Prepared by the Solid-State Reaction at 1073 K

catalysts	shell	R^a (Å)	CN^b	σ^c (Å)
V oxide/ZSM-5	V−O	1.64	0.85	0.004
		1.81	2.82	0.006
		2.18	0.36	0.003
V_2O_5	V−O	1.59	1.0	
		1.78	1.0	
		1.88	2.0	
		2.02	1.0	

[a] Bond distance between V and O atoms. [b] Coordination number. [c] Debye−Waller factor.
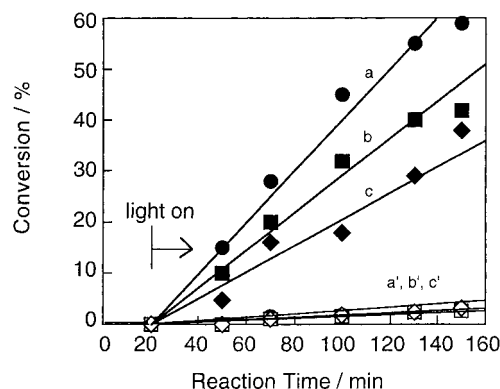

Figure 7. Time profile of the photocatalytic isomerization of *cis*-2-butene on V oxide/ZSM-5 catalysts prepared by the solid-state reaction between HZSM-5 and V_2O_5 at various temperatures. (a, a′) Prepared at 1073 K, (b, b′) 873 K, and (c, c′) 673 K. Black symbols, *trans*-2-butene; white symbols, 1-butene.

of the V_2O_5 is transformed into a dispersed state, in either the VO^{2+} or V^{5+} species. The best fitting was obtained with the parameters given in Table 1. The total coordination number is 4.3, revealing that the 4-fold coordinated vanadium centers (mainly V^{5+}) and 5- or 6-fold coordinated vanadium centers may coexist.

Since highly dispersed vanadium oxide species has been reported to exhibit photocatalytic reactivity,[18−24,28−31] V oxide/ZSM-5 catalysts prepared by the solid-state reaction of V_2O_5 and HZSM-5 at different temperatures were applied to examine their photocatalytic reactivity for the photocatalytic isomerization of *cis*-2-butene at 273 K. As can be seen in Figure 7, under dark conditions, the catalytic isomerization reaction of *cis*-2-butene on the V oxide/ZSM-5 zeolite proceeds slowly to form only *trans*-2-butene. The temperature of the solid-state reaction did not show any significant influence on this reaction under dark conditions, indicating that the reaction in the dark may originate from the characteristics of the parent HZSM-5 zeolite rather than from the product of the solid-state reactions. However, UV irradiation of the catalysts in the presence of *cis*-2-butene efficiently promoted the isomerization reaction of *cis*-2-butene to form *trans*-2-butene and 1-butene, indicating the efficient initiation of photocatalytic isomerization reactions.

As can be seen in Figure 8, the yields of the photocatalytic isomerization and the photoluminescence of the catalysts increase in parallel to the increase in the temperature of the reaction of V_2O_5 with the HZSM-5 zeolite. Such a good parallel relationship strongly suggests that the active sites for this reaction under UV irradiation are the emitting sites in the V oxide/ZSM-5 catalysts, i.e., the charge-transfer excited state of the C_{3v} vanadium oxide moieties formed in the product during the solid-state reaction. Furthermore, the formation of this species is greatly enhanced by carrying out the reactions at
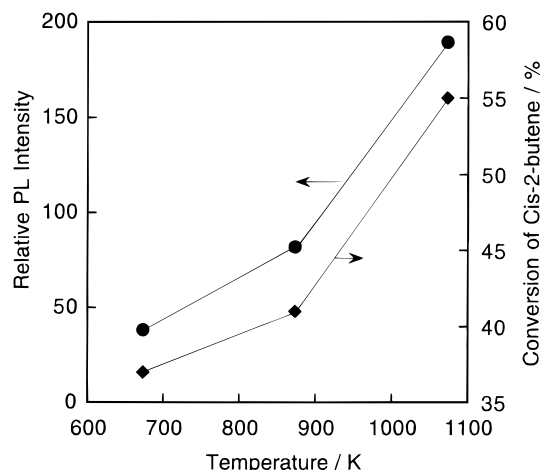
Figure 8. Effect of the solid-state reaction temperature on the photoluminescence yields and the photocatalytic reactivity of the V oxide/ZSM-5 catalyst prepared by the solid-state reaction between HZSM-5 and V_2O_5 at various temperatures.

higher temperatures. Thus, as can be seen with photocatalytic reactions involving the C_{3v} vanadium oxide species, V oxide/ZSM-5 catalysts can also be used as effective and efficient photocatalysts for various unique and significant reactions.

Conclusions

These studies on the solid-state reaction of HZSM-5 and V_2O_5 have provided strong evidence indicating the formation of a tetrahedrally coordinated V^{5+} oxide species. We have seen that the amount of the vanadium oxide species having a C_{3v} unit structure increased significantly when the solid-state reaction temperature was increased. It was also found that the V^{5+} oxide species formed in this way exists at two separate sites: most are sites within a large population accessible to small molecules such as O_2 and H_2O while the other sites are few and inaccessible to small molecules.

Moreover, we have demonstrated that the V oxide/ZSM-5 catalyst formed also acts as an efficient photocatalyst. The solid-state reaction of metal oxides with high silica zeolites has been shown to be a new and effective method to prepare photocatalysts which enable the use of a wide range of transition metals such as Mo, W, Cr, Nb, etc., all of which are difficult to be incorporated into the zeolite cavities by conventional ion-exchange methods.

References and Notes

(1) Notari, B. *Adv. Catal.* **1996**, 253.
(2) Corma, A. *Chem. Rev.* **1997**, *97*, 2373.
(3) Tatsumi, T.; Nakamura, M.; Negishi, S.; Tominaga, H. *J. Chem. Soc., Chem. Commun.* **1990**, 476.
(4) Bordiga, S.; Coluccia, S.; Lamberti, C.; Marchese, L.; Zecchina, A.; Boscherini, F.; Buffa, F.; Genoni, F.; Leofaniti, G.; Petrini, G.; Vlaic, G. *J. Phys. Chem.* **1994**, *98*, 4125.
(5) Ramasawamy, A. V.; Sivasanker, S.; Ratnasamy, P. *Microporous Mater.* **1994**, *2*, 451.
(6) Selvam, T.; Vinod, M. P. *Appl. Catal.* **1996**, *134*, 197.
(7) Whittington, B. I.; Anderson, J. R. *J. Phys. Chem.* **1991**, *95*, 3306.
(8) Sen, T.; Ramasawamy, A. V.; Rajamohanan, P. R.; Sivasanker, S. *J. Phys. Chem.* **1996**, *100*, 3809.
(9) Vayssilov, G. N. *Catal. Rev.* **1997**, *39*, 209.
(10) Anpo, M.; Yamashita, H.; Zhang, S. G. *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 630.
(11) Anpo, M.; Zhang, S. G.; Yamashita, H. *Stud. Surf. Sci. Catal.* **1996**, *101*, 941.
(12) Centi, G.; Perathoner, S.; Trifiró, F.; Aboukais, A.; Aïssi, C. F.; Guelton, M. *J. Phys. Chem.* **1992**, *96*, 2617.
(13) Karge, H. G. S*tud. Surf. Sci. Catal.* **1994**, *83*, 135.
(14) Kucherov, A. V.; Slinkin, A. A. *Zeolites* **1987**, *7*, 38.
(15) Kucherov, A. V.; Slinkin, A. A. *J. Mol. Catal.* **1994***, 90,* 323.
(16) Sass, C. E.; Chen, X.; Kevan, L. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 189.
(17) Petrás, M.; Wichterlová, B. *J. Phys. Chem.* **1992**, *96*, 1805.
(18) Anpo, M.; Kubokawa, Y. *Res. Chem. Intermed.* **1987**, *8*, 105.
(19) Anpo, M.; Tanahashi, I.; Kubokawa, Y. *J. Phys. Chem.* **1980**, *84*, 3340.
(20) Anpo, M.; Tanahashi, I.; Kubokawa, Y. *J. Phys. Chem.* **1982**, *86*, 1.
(21) Anpo, M.; Che, M. *Adv. Catal.*, in press.
(22) Anpo, M.; Sunamoto, M.; Fujii, T.; Patterson, H. H.; Che, M. *Res. Chem. Intermed.* **1989**, *11*, 245.
(23) Anpo, M. In *Handbook of Heterogenious Catalysis*; Ertl, G., Knözinger, H., Weitkamp, J., Eds.; Wiley-VCH: Weinheim, 1997; Vol. 2, p 664.
(24) Patterson, H. H.; Cheng, J.; Despres, S.; Sunamoto, M.; Anpo, M. *J. Phys. Chem.* **1991**, *95*, 8813.
(25) Hazenkamp, M. F.; Blasse, G. *J. Phys. Chem.* **1992**, *96*, 3442.
(26) Iwamoto, M.; Furukawa, H.; Matsukami, K.; Takenaka, T.; Kagawa, S. *J. Am. Chem. Soc.* **1983**, *105*, 3719.
(27) Kazansky, V. B. *Kinet. Katal.* **1983**, *24*, 1338.
(28) Anpo, M.; Sunamoto, M.; Che, M. *J. Phys. Chem.* **1989**, *93*, 1187.
(29) Anpo, M.; Sunamoto, M.; Fujii, T.; Che, M.; Patterson, H. H. *Res. Chem. Intermed.* **1989**, *11*, 320.
(30) Anpo, M.; Sunamoto, M.; Fujii, T.; Che, M.; Patterson, H. H. *Res. Chem. Intermed.* **1992**, *17,* 15.
(31) Anpo, M.; Yamashita, H. In *Surface Photochemistry*; Anpo, M., Ed.; Wiley: London, 1996; p 117.
(32) Tuel, A.; Taarit, Y. B. *Zeolites* **1994**, *14*, 18.
(33) Camblor, M. A.; Corma, A.; Pérez-Pariente, T. *J. Chem. Soc., Chem. Commun.* **1993**, 557.
(34) Tanaka, T.; Yamashita, H.; Tsuchitani, R.; Funabiki, T.; Yoshida, S. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 2987.