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Photocatalysed Isomerization of Butenes on MgO Powders with Coordinatively Unsaturated Surface Ions

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The photocatalysed isomerization of but-2-enes has been studied on a standard MgO-I catalyst which exhibits photoluminescence at *ca.* 340–450 nm associated with coordinatively unsaturated surface ions with 4-coordination. A geometrical isomerization reaction, *i.e.* *trans* $\rightleftharpoons$ *cis* isomerization, occurs predominantly with high efficiency under u.v. irradiation of the MgO catalyst. The excitation wavelength that is effective on the rate of photocatalysed isomerization was found to be in accordance with the photoluminescence excitation spectrum. A complete parallel between the photoluminescence intensity and the rate of photocatalysed isomerization of but-2-enes was also observed. The addition of CO molecules led to the inhibition of the photocatalysed isomerization, its extent increasing with the CO pressure, as well as quenching of the photoluminescence. Stern–Volmer plots for the rate of the photocatalysed isomerization and for the yield of the photoluminescence showed complete agreement. These results clearly indicate that 4-coordinated surface ions play a significant role in the photocatalytic activity of degassed MgO powder catalysts.

Photocatalysis with powdered semiconductors such as TiO_2, Pt/TiO_2 and CdS *etc.* has received much attention from the standpoint of photochemistry of solid surfaces as well as potential utilization of solar energy.[1] Recent studies focus on problems with extremely small size colloidal semiconductors where size quantization effects are expected to be observable,[2] as well as on semiconductors supported on inert supports, where carrier effects are expected,[3] and on various binary metal oxides and sulphides, where complex effects are operating.[4] However, most studies of photocatalysis have mainly been undertaken with reactions associated with the photodecomposition of water over semiconductors in the solid–liquid reaction system, in which it is relatively easy to set up an experimental system and to achieve higher quantum yields compared with those in the solid–gas reaction systems. Consequently, very few studies have been concerned with surface-active sites, excited states of catalysts and primary processes in photocatalysis.[5]

On the other hand, it is well established that surface ions at the position of coordinative unsaturation play a significant role in heterogeneous catalysis.[6] Such coordinatively unsaturated surface ions are also well known to play a significant role in the appearance of abnormal absorption and photoluminescence in insulating materials with a high surface area, such as powdered MgO and SrO.[7] However, their role is still unclear in photocatalysis. To understand the true nature of photocatalysis, it is important to clarify the role of such surface ions in photocatalytic reactions, especially in primary processes.

Recently, Anpo *et al.*[8] have reinvestigated the photoluminescence spectrum of powdered MgO degassed at high temperatures using a standard JRC-MgO-I catalyst because the contribution of low-coordination surface sites to the observed photoluminescence of the degassed MgO samples has been questioned by Shvets *et al.*[9] Anpo *et al.*[8] have clarified that the observed short-lifetime (10^{-6}–10^{-3} s) photoluminescence spectra at *ca.* 340–450 nm are directly associated with the following charge-transfer process in reaction (I) (LC means low coordination) on the 4-coordinated ions located on the surfaces of the well degassed MgO powders, reconfirming the charge-transfer mechanism proposed by Tench and Pott,[10] Stone[11] and Cunningham *et al*:[12]

$$(\mathrm{Mg^{2+}_{LC}}\text{—}\mathrm{O^{2-}_{LC}}) \underset{h\nu'}{\overset{h\nu}{\rightleftharpoons}} (\mathrm{Mg^{+}_{LC}}\text{—}\mathrm{O^{-}_{LC}})^{*}. \qquad \text{(I)}$$

Although little attention was paid on the photocatalysed isomerization reactions, recently, various photocatalysed isomerization reactions have been studied by a number of workers.[13-16] More recently, Anpo *et al.* have reported that the double-bond shift isomerization as well as *cis*$\rightleftharpoons$*trans* isomerization of but-2-ene is markedly enhanced on metal oxides, such as TiO_2,[17] binary oxides, such as Ti–Si[18] or Ti–Al,[19] and the highly dispersed supported metal oxides such as V_2O_5,[20] under u.v. irradiation. For these photocatalysed isomerization reactions, it has been suggested that the pair state of photoproduced electron and hole, $(M^{(n-1)+}\text{—}O^-)^*$, plays a significant role in weakening the C═C double bond of butene molecules to result in their isomerization. It has been also found that such a *cis*$\rightleftharpoons$*trans* isomerization of but-2-ene is photocatalysed on degassed MgO powders.[21,22]

Therefore, it is of particular interest to investigate the isomerization of but-2-ene on a standard JRC-MgO-I catalyst under u.v. irradiation in order to clarify the role of coordinately unsaturated surface ions in the photocatalysed isomerization reaction, studying the relationship between the intensity of photoluminescence and the rate of photocatalysed isomerization.

Experimental

Samples of MgO microcrystals (JRC-MgO-I) were supplied from the Catalysis Society of Japan as a standard catalyst (MgO purity, 99.02%; major impurities, Ca, Si and Fe; B.E.T. surface area, *ca.* 40 $m^2\,g^{-1}$; bulk specific density 0.42 $g\,cm^{-3}$).[8,21,22] Detailed information about this standard MgO-I catalyst is available from the Catalysis Society of Japan.[23] MgO catalysts were degassed for 2 h at the desired temperature. The rate of increase of the degassing temperature was *ca.* 1 K min^{-1} and ultimate pressures of *ca.* 10^{-6} Torr (10^{-4} Nm^{-2}) were attainable. The photoluminescence spectra were recorded at 77 K or at 295–298 K using a Shimadzu RF-501 spectrofluorophotometer (equipped with 500 W Xe lamp as an excitation source) with a resolution of 0.3 nm, equipped with colour filters to eliminate scattered light.

The quartz cell with window and furnace sections, having a volume of *ca.* 50 cm^3, was connected to a vacuum system. A 0.05–0.1 g sample was degassed for 2 h at the desired temperature. The rate of increase of the degassing temperature was also *ca.* 1 K min^{-1}. Then the MgO powder was spread on the quartz window, having a surface area of *ca.* 20 cm^2. The reactant butene was introduced onto the catalyst, its temperature being adjusted to 273 K. Then, u.v. irradiation of the catalyst in the presence of *trans*-but-2-ene (6 Torr) was also carried out at 273 K, to minimize the dark reaction, using a high-pressure mercury lamp (Toshiba, SHL-100UV) through various colour filters and a water filter. The reaction products were collected at 273–293 K at definite time intervals, and analysed by a gas chromatography using a 2,4-dimethylsulpholane column. In

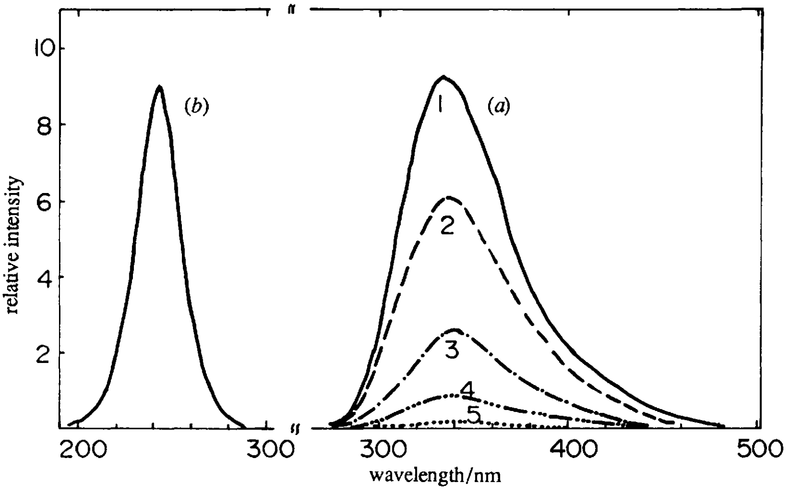


Fig. 1. (*a*) Photoluminescence spectrum and (*b*) its corresponding excitation spectrum at 298 K of MgO sample degassed at 1073 K for 2 h and effect of the addition of *trans*-but-2-ene of the photoluminescence spectrum. Excitation, 240 ± 10 nm; *trans*-but-2-ene added at 298 K; amount of *trans*-but-2-ene, 10^{-6} mol g^{-1}, (1) under vacuum, (2) 1.16, (3) 2.32, (4) 7.87, (5) 22.2.

addition to the photoformed *cis*-but-2-ene and but-1-ene, small amounts of CH_4, C_2H_4 and C_2H_6 were also observed as minor products. At 273 K, thermal isomerization (dark reaction) was negligible. Experimental details were described elsewhere.[8, 17-22]

Results and Discussion

Quenching of the Photoluminescence with Added But-2-ene

As shown in fig. 1, the degassed MgO sample exhibits a photoluminescence spectrum at *ca.* 340–450 nm when it is excited with u.v. light with 240–280 nm wavelength, owing to the charge-transfer process described in reaction (I).[8] Fig. 1 also shows that the addition of *trans*-but-2-ene at 293 K onto the MgO sample that had been degassed at 1073 K leads to efficient quenching of the photoluminescence intensity without any change of shape, its extent increasing with the pressure of *trans*-but-2-ene. For example, the addition of only 1.16×10^{-6} mol g^{-1} *trans*-but-2-ene quenches the photoluminescence by *ca.* 66%, the addition of *ca.* 7.9×10^{-6} mol g^{-1} of *trans*-but-2-ene leading to 92% quenching of the emission. As shown in fig. 1, the evacuation of *trans*-but-2-ene at 298 K for 30 min, after complete quenching of the emission, leads to a recovery of most of the emission.

As described previously,[8, 22] such quenching behaviour suggests that dynamic quenching, whereby quencher molecules interact with the emitting sites in their metastable excited state to give a non-radiative deactivation pathway, mainly operates for quenching with butenes. Therefore, the quenching efficiency is dependent on the amount of quencher adsorbed on the surfaces, and in turn the equilibrium pressure of the added butene molecules.

Photocatalysed Isomerization of *trans*-But-2-ene

As shown in fig. 2 and 3, the u.v. irradiation of a degassed MgO sample in the presence of *trans*-but-2-enes at 273 K is found to lead to a remarkable enhancement of the formation of *cis*-but-2-enes, as well as the formation of a small amount of but-1-enes.

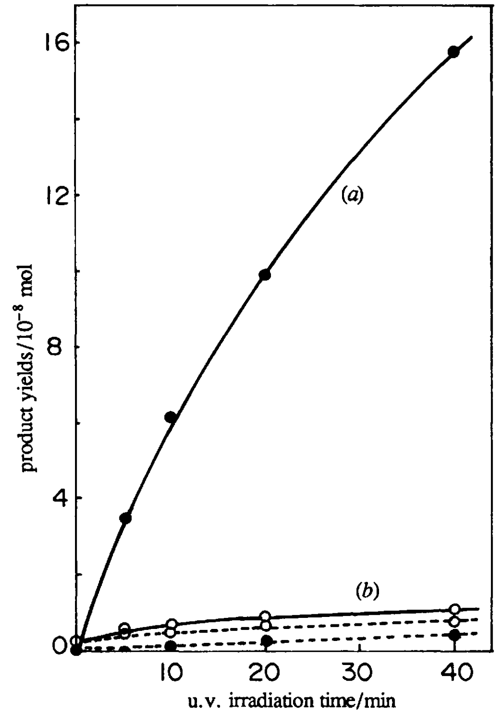


Fig. 2. Photocatalytic (solid lines) and thermal (dotted lines) isomerization of *trans*-but-2-enes on MgO catalyst degassed at 1173 K for 2 h. (*a*) *cis*-But-2-ene, (*b*) but-1-ene. MgO used, 0.05 g; initial pressure of *trans*-but-2-enes, 6.0 Torr; reaction temperature, 273 K.

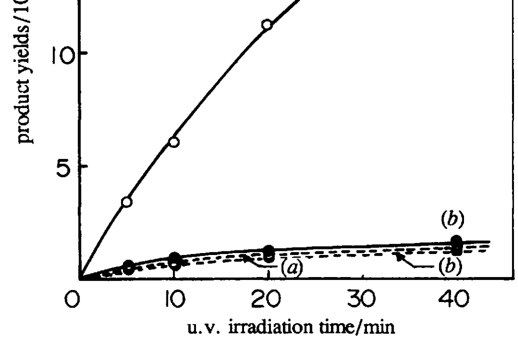


Fig. 3. Photocatalytic (solid lines) and thermal (dotted lines) isomerization of *trans*-but-2-enes on an MgO catalyst degassed at 1273 K for 2 h. (*a*) *cis*-But-2-ene; (*b*) but-1-ene. MgO used, 0.05 g; initial pressure of *trans*-but-2-enes, 6.0 Torr; reaction temperature, 273 K.

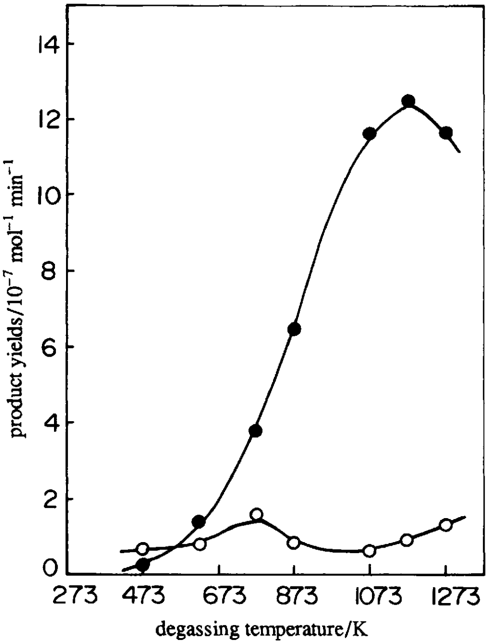


Fig. 4. Effect of degassing temperature of MgO catalysts upon the initial rate of photocatalysed isomerization of *trans*-but-2-enes at 273 K. ●, *cis*-But-2-ene; ○, but-1-ene.

It was found that the extent of enhancement is strongly dependent on the degassing temperature of the MgO samples. The yields of photoisomerization products increase with u.v. irradiation time. With the MgO samples degassed at higher temperatures, the yields of photoisomerization products increase linearly with u.v. irradiation time, indicating that the reactions proceed catalytically under u.v. irradiation at 273 K.

Fig. 2 and 3 also show that at this temperature, with these MgO samples degassed at higher temperatures, thermal isomerization (dotted line) is very small, and is negligible in comparison with photoisomerization, especially for geometrical isomerization.[21] Thus the major photocatalysed isomerization product is the geometrical isomer, *cis*-but-2-ene. The formation of but-1-ene, *i.e.* double-bond shift isomerization, is a minor reaction. CH_4 and C_2H_6 were also observed as minor products. Small amounts of but-2-enes were irreversibly adsorbed onto the catalyst, which may correspond to the unrecovered fraction of the photoluminescence measured after the evacuation of added but-2-ene molecules, as described above. These features were common for all MgO samples which were degassed at various temperatures.

Relationship between Photocatalysed Isomerization and Photoluminescence

The initial rates of the photocatalysed isomerization determined from the slopes of the plots of the yields of products *vs.* u.v. irradiation time are markedly dependent on the degassing temperature of the MgO samples. The results are shown in fig. 4. The initial rate of geometrical isomerization increases, passing through a maximum at 1173 K, and then decreases on increasing the degassing temperature. On the other hand, the rate of double-bond shift isomerization increases, passing through a maximum at 773 K, and then decreases on increasing the degassing temperature up to 1073 K, again increasing a little at the highest degassing temperature.

As described in a previous paper (fig. 5),[8] the trend of the effects of the degassing

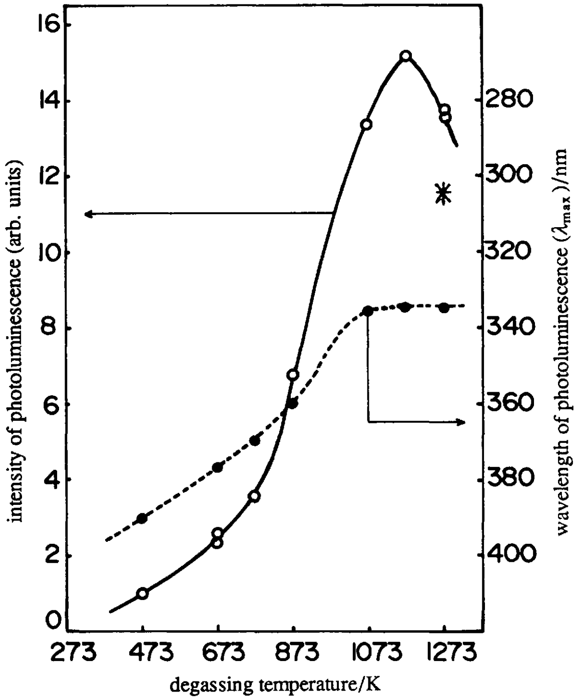


Fig. 5. Effect of degassing temperature on the photoluminescence spectrum of MgO.[8] *, MgO was degassed for 3 h rather than 2 h.

temperature upon the intensity and wavelength of the photoluminescence of the MgO samples is very similar to that seen in fig. 4. From fig. 4 and 5 it is clear that a good parallel exists between the initial rate of photocatalysed geometrical isomerization and the photoluminescence intensity. Although details have been described in the previous paper,[8] the results in fig. 6 show that the concentration of the low-coordinated surface ions produced increases with increasing degassing temperature up to 1173 K, and then decreases with increasing temperature. Simultaneously, with increasing degassing temperature the emitting environment associated with the 4-coordinated surface sites becomes more uniform, the uniformity changes being complete at *ca.* 1073 K. Therefore, it is indicated that the isomerization of butenes proceed catalytically on the low coordinated surface sites with uniform environment, under u.v. irradiation at 273 K.

On the other hand, it is also seen that a good agreement between (i) the photoluminescence intensity at *ca.* 420 nm, having its excitation spectrum at *ca.* 280 nm (linked with the existence of surface OH^- ions, which was shown in fig. 6 of our previous paper)[8] and (ii) the rate of photocatalysed double-bond shift isomerization was also observed (*vide infra*).

Active Sites for Photocatalysed Isomerization

The effect of excitation wavelength upon the rate of the photocatalysed isomerization reactions was investigated by using various colour filters. Fig. 6 shows the effect of excitation wavelength upon the rate of the major photocatalysed isomerization, *i.e.* geometrical isomerization, taking place on an MgO catalyst which had been degassed at 1173 K, by using various colour filters. The spectroscopic features of the colour filters used, together with the excitation spectrum (*i.e.* the absorption spectrum) of the MgO

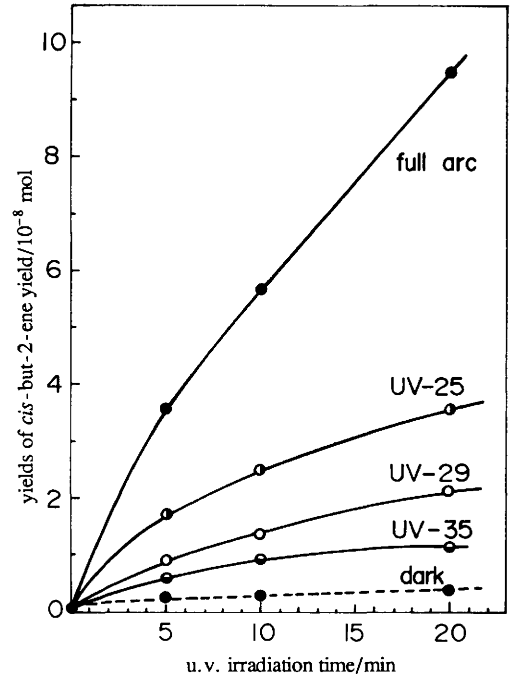


Fig. 6. Effect of excitation wavelength on the rate of photocatalysed isomerization of *trans*-but-2-enes on an MgO catalyst degassed at 1173 K for 2 h. High-pressure mercury lamp omitting light with $\lambda > 237$ nm; reaction temperature, 273 K; filters, UV-25 with 50% cut-off at 250 nm wavelength, UV-29 with 50% cut-off at 290 nm wavelength, UV-35 with 50% cut-off at 350 nm wavelength.

samples degassed at higher temperatures clearly showed that the excitation wavelength that is effective on the photocatalysed isomerization is < 270 nm, in accordance with the excitation spectrum (fig. 1) for the photoluminescence of the samples due to charge-transfer processes on the 4-coordinated surface sites [reaction (I)].

As described in our previous paper,[8] the addition of O_2 or CO molecules led to the quenching of the photoluminescence of MgO samples. Therefore, the effects of adding CO molecules upon the photocatalysed isomerization reaction were investigated. Fig. 7 shows the effect of the addition of CO upon the photocatalysed geometrical isomerization on the MgO sample which had been degassed at 1073 and 1173 K. The rates of the photocatalysed isomerization reaction to produce *cis*-but-2-ene from *trans*-but-2-ene are easily inhibited by the addition of CO molecules, the extent increasing with CO pressure. The addition of CO molecules was also found to inhibit the minor photocatalysed isomerization to produce but-1-ene, although in this case a quantitative analysis was difficult owing to lower yields of but-1-enes.

These results suggest that photocatalysed isomerization reactions on the MgO catalyst proceed *via* the same excited state as with photoluminescence. Thus the photophysical processes on MgO surfaces in the presence of but-2-ene and CO molecules can be described as follows to extend the processes reported in our previous paper:[8]

$$\begin{tikzcd}[row sep=small] & & \text{photocatalysed reaction } (k_p) \\ (Mg^{2+}\text{—}O^{2-}) \arrow[r, "h\nu"] & (Mg^{+}\text{—}O^{-})^{*} \arrow[ur] \arrow[r] \arrow[dr] & \text{radiationless decay } (k_d) \\ & & \text{deactivation by added CO } (k_q). \end{tikzcd}$$

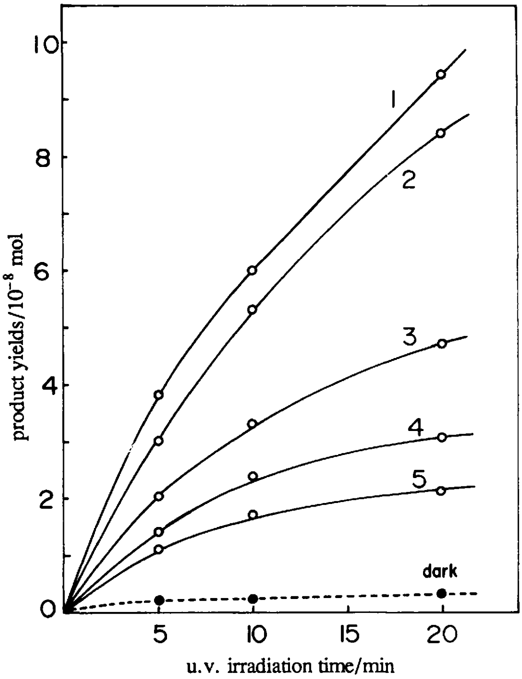


Fig. 7. Effect of the addition of CO molecules on the photocatalysed isomerization of *trans*-but-2-enes on an MgO catalyst degassed at 1173 K. Reaction temperature, 273 K; initial pressure of *trans*-but-2-ene, 6.0 Torr; pressure of added CO molecules (Torr): (1) 0.0, (2) 0.041, (3) 0.105, (4) 0.636, (5) 3.81.

As a result, the following Stern–Volmer equation is obtained for the rates of photocatalysed isomerization on the MgO sample using the steady-state treatment:[23]

$$Q_0/Q = 1 + tk_qC \qquad \text{(II)}$$

where Q_0 and Q are the yield of the photocatalysed isomerization of but-2-ene on the MgO in the absence and presence of CO molecules, respectively, and t, k_q and C are lifetime of the excited active sites on the MgO surface, the quenching rate constant and concentration of added CO molecules on the surface, respectively. In fact, as shown in fig. 10, Q_0/Q in the presence of CO molecules is a linear function of CO pressure in the low-pressure region, although there is some deviation from linearity at higher pressure. In other words, in the low-pressure region, dynamic quenching of the excited active sites by CO molecules mainly operates, in which the quenching efficiency is dependent on the amount of CO molecules on the surface and in turn the equilibrium pressure of the added CO molecules.[8] Deviation from linearity in the Stern–Volmer plots in the higher-pressure region might be attributed to the fact that the number of CO molecules on the surface did not increase linearly with the CO pressure in the pressure range 1–3 Torr.

The addition of CO at a pressure of 150 Torr onto thermally activated MgO which had been washed with boiling water prior to activation, leads to a change in the colour of the MgO sample from white to peach and/or yellow, and even to a very slow growth of radical species, although this takes a long time.[24, 25] Recently, Garrone and Stone[26] have studied the u.v. – visible spectra developed after adsorption of H_2 and/or CO and showed that the adsorption of H_2 occurs on the MgO sample, on which the adsorption of CO proceeds to yield coloured products, and suggested that 3-coordinated oxygen ions (O^{2-}_{3C}) are involved in this adsorption. As described in our previous paper,[8] with the

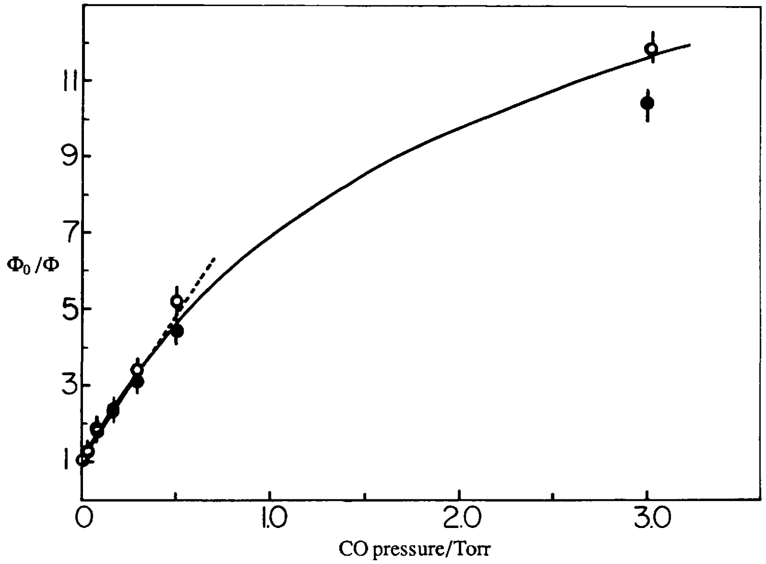


Fig. 8. Experimental Stern–Volmer plots, Q_0/Q *vs.* pressure of CO for the rate of photocatalysed isomerization of *trans*-but-2-enes and the photoluminescence yield of an MgO catalyst degassed at 1173 K for 2 h. Experimental conditions as for fig. 1, 2 and 7. ○, Photoluminescence; ●, photoreaction.

present JRC-MgO-I sample, such 3-coordinated surface sites are not involved, and in fact no effect of the addition of H_2 upon the photoluminescence due to the presence of 4-coordinated surface sites was observed. In agreement with the previous results, after the addition of CO at a pressure of 1–3 Torr onto the degassed standard MgO-I sample, no change in the colour of the white sample was observed.

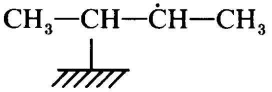
Fig. 8 also shows Stern–Volmer plots for the quenching of the photoluminescence intensity. Good agreement is seen between the Stern–Volmer plots for the photoluminescence intensity and those of the yields of the photocatalysed isomerization reactions. This agreement supports the assumption mentioned above, *i.e.* both the photocatalysed isomerization reaction and the photoluminescence observed at *ca.* 340–450 nm might proceed through the same excited state of the MgO catalyst. Taking into account the fact that added CO molecules easily interact with the charge-transfer excited state of the 4-coordinated surface sites to give a non-radiative deactivation pathway,[8] the results obtained in the present work clearly show that the photocatalysed isomerization reactions proceed through the charge-transfer excited state on the 4-coordinated surface sites, *i.e.* $(\mathrm{Mg}_{4C}^{+}\text{—}\mathrm{O}_{4C}^{-})^*$ complexes.

Characteristics of the Photocatalysed Isomerization on MgO

It has been reported by a number of workers that on an MgO catalyst degassed at *ca.* 573–873 K, the thermal isomerization of butene proceeds *via* π-allyl carbanion intermediates.[27,28] In this mechanism the key step is abstraction of hydrogen from butene molecules, which is easier with but-1-ene than with but-2-ene. This feature has been established as the characteristic of the thermal isomerization on oxide catalysts such as MgO. As described previously,[17,18,29] however, in the photocatalysed isomerization of butenes the reactivity of but-2-enes is much higher than that of but-1-enes. This was also confirmed in the present work with the MgO catalyst.

These results clearly indicate that the active species associated with photocatalysed isomerization is quite different from that in the thermal isomerization reactions.

Recently, Anpo *et al.* reported that the charge-transfer excited complex, $(M^{(n-1)+}—O^-)^*$,[17, 29, 30] on various metal oxides easily reacts with butene molecule to produce a radical intermediate species (A) resulting from the opening of the C=C double bond of the butene molecule. It is likely that the photocatalytic isomerization of *trans*-but-2-ene to *cis*-but-2-ene on an MgO catalyst proceeds *via* a mechanism similar to that proposed for metal oxides such as TiO_2[17] and supported V_2O_5.[20, 30] *trans*-But-2-ene interacts with the charge-transfer excited complex, $(Mg_{4C}^{4+}—O_{4C}^-)^*$, resulting in the opening of the C=C double bond to produce species (A), which participates in geometrical isomerization to *cis*-but-2-ene. The adsorption site is not specified at the present time between Mg^{2+} or O^{2-} ions. In this mechanism, therefore, if added quencher molecules such as CO interacted with the charge-transfer excited complex to give a deactivation pathway, the photocatalysed isomerization would be suppressed as a result, its extent increasing with the pressure of CO molecules.



$CH_3—CH—\dot{C}H—CH_3$ (A)

As described previously,[20, 29, 30] on the other hand, the presence of H atoms appears to be a prerequisite for the occurrence of the double-bond shift isomerization. Although the details of the mechanism are not clear, this requirement is intuitively linked with surface OH^- groups with a high acidity. Accordingly, the small increase in the rate of photocatalysed double-bond shift isomerization observed on the MgO sample degassed at *ca.* 773 K, as seen in fig. 4, suggests the existence and contribution of the acidic surface OH^- groups on the MgO surfaces. Taking into account the previous results of the photoluminescence due to surface OH^- ions obtained with an MgO sample,[8] it is likely that surface OH^- ions in specific low-coordination sites act as acidic groups which contribute to the photocatalytic double-bond shift isomerization of but-2-enes.

The selectivity of the photocatalysed double-bond shift isomerization to the photocatalysed geometrical isomerization on MgO catalysts was much lower than that of photocatalytic isomerization on a TiO_2 catalyst, although such selectivity more or less depends on the catalyst pretreatment.[17] This feature seems to reflect the lower acidity of the OH^- groups on an MgO catalyst as compared with that on a TiO_2 catalyst,[31] supporting the concept mentioned above.

Conclusions

The present results clearly indicate not only that degassed MgO powders exhibit photocatalytic activity for the isomerization of but-2-ene molecules, but also that the rate of photocatalysed isomerization and the intensity of the observed photoluminescence of the catalyst are closely associated with each other. The yield of the observed photoluminescence at *ca.* 340–450 nm, which is due to radiative decay from the charge-transfer excited state in reaction (I), scarcely changed in intensity whether it was recorded at 77 or 298 K. This suggests that the non-radiative pathway is a minor process; otherwise the photoluminescence yield would drastically change, because non-radiative pathways are temperature-sensitive processes.[23, 32] Consequently, with the present JRC-MgO-I sample, non-radiative decay processes do not appear to play a significant role in the deactivation of the photon energy absorbed by the MgO catalyst. In other words, a radiative decay process might be a major deactivation pathway to control the fate of the photon energy injected into the present MgO catalyst.

From these results, together with the result obtained by Coluccia[33] with degassed MgO, CaO and SrO, the following generalization concerning the fate of the photon energies absorbed by the alkaline-earth oxide catalysts emerges. Ions in a high coordination have a larger number of bonds to the oxide and couple more strongly with the phonon transitions of the lattice, providing a high probability of non-radiative decay, while on the lower-coordinated surface ions non-radiative decay is less efficient and the radiative-decay pathway is more predominant.

Therefore, on an oxide catalyst with lower-coordinated surface sites it is expected that higher yields for photocatalytic reactions are achieved, if reactants are present on them, as well as photoluminescence. The photoluminescence associated with the charge-transfer process, like those expressed in reaction (I), is also easily observed with highly dispersed supported metal oxides in which ions are expected to be located in coordinatively unsaturated surface sites but not in the bulk oxides.[3,34] Taking into account these facts, a proposed generalization concerning the fate of the photon energies absorbed by the oxides would be more widely applicable for various types of oxides.[12,20] Thus the present work provides useful information not only concerning the role of low-coordination unsaturated surface ions in photocatalytic reactions on oxide catalysts, but also concerning the fate of the photon energy absorbed by the oxides.

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