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# Mechanism for Promoting the Evolution of Lattice Oxygen by the Interaction between $V_2O_5$ and $TiO_2$

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The interaction of $V_2O_5$ with $TiO_2$ and the evolution of lattice oxygen in $V_2O_5/TiO_2$ catalysts have been studied by X-ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy, and thermal gravimetric analysis. The defect surface state associated with oxygen vacancies and the work function of $V_2O_5$ and $TiO_2$ are also measured by ultraviolet photoelectron spectroscopy. The results show that the evolution of lattice oxygen takes place mainly near the $V_2O_5/TiO_2$ interfacial region, and depends strongly on $V_2O_5$ content and the atmosphere in which the thermal gravimetric analysis is carried out. The defect surface state associated with oxygen vacancies is about 1 and 2.7 eV above the top edge of the valence band for $V_2O_5$ and $TiO_2$, respectively. A model for promoting the evolution of lattice oxygen is proposed on the basis of the energy band structure at the interface of $V_2O_5$ and $TiO_2$. The promotive action is probably due to the bending of the energy band at the interface of $V_2O_5$ and $TiO_2$, which draws the defect surface state of $V_2O_5$ closer to the valence band of $V_2O_5$. As a result, the probability of electron exchange between the defect surface state and the valence band of $V_2O_5$ increases, and the negative charges on the lattice oxygen ions become easy to remove, thus promoting the evolution of lattice oxygen. In addition, the impurity energy levels arising from vanadium ions in $TiO_2$ at the interface probably also exchange electrons with the valence band of $V_2O_5$, resulting in promotion of the evolution of lattice oxygen.

## INTRODUCTION

It is generally agreed that the activity of molecular oxygen in oxidation reactions is rather low, and in almost all good selective oxidation catalysts the lattice oxygen is given up to the reactant, to be replaced in another step of the reaction by adsorption of oxygen from the gas phase (*1–6*). Participation of the lattice oxygen in the oxidation reaction has been proved by isotopic exchange experiments (*5*) and by oxidation of anthracene to anthraquinone by vanadium oxide in the absence of gaseous oxygen (*6*). Obviously, knowledge of mechanism of lattice oxygen evolution is very helpful in gaining an understanding of the catalytic oxidation mechanism.

The evolution of lattice oxygen in metal oxide catalysts is usually promoted by the interaction between metal oxides. For instance, it has been found that both the reduction of $V_2O_5$, or the evolution of lattice oxygen, and the transformation of anatase $TiO_2$ into rutile are promoted by the interaction between $V_2O_5$ and $TiO_2$ (*7–11*).

Many studies have been devoted to investigation of the mechanism by which $TiO_2$ modifies the properties of supported $V_2O_5$, but the mechanism is still not yet well understood (*12, 13*). Inomata *et al.* (*7*) attribute this phenomenon to the selective exposure of the (010) planes of $V_2O_5$, in agreement with Vejux and Courtine (*10*), who suggested that the special properties of $V_2O_5/TiO_2$ catalysts arise from the close match in crystallographic pattern between the (010) planes of $V_2O_5$ and the (001) or (010) planes of the $TiO_2$ anatase. Kozlowski *et al.* (*13*) attribute this behavior to the intrinsic disorder of surface vanadia species on the $TiO_2$ surface. Several other authors proposed that the $TiO_2$ anatase modifies the properties of the supported vanadia phase

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by forming a complete monolayer of surface vanadia species coordinated to the $TiO_2$ support (*9, 11, 13–15*). However, some researchers (*16, 17*) have directly observed the high-resolution lattice image obtained by electron microscopy, and have not found a monolayer of vanadia species cordinated to the titania support.

Obviously, there are several points of view of the mechanism by which $TiO_2$ modifies the properties of supported $V_2O_5$. Furthermore, almost all the above mechanisms are based on structural considerations.

The present paper reports the studies of the interaction between $V_2O_5$ and $TiO_2$ and the evolution of lattice oxygen by means of X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and thermal gravimetric analysis (TGA). More attention is paid to the electronic interaction. A mechanism for promoting the evolution of lattice oxygen is proposed on the basis of the interfacial energy band structure and defect surface states associated with oxygen vacancies at the interface of $V_2O_5$ and $TiO_2$.

## EXPERIMENTAL

Sample preparation has been described in a previous paper (*17*). Thermal gravimetric analysis was carried out on a Perkin–Elmer TGS-2 thermobalance under a flowing atmosphere of $He : O_2 = 1 : 1$ and He, respectively. The sample loading is 20 mg. After purging with a He stream for 1 h at 400°C, the temperature was raised to 750°C at the rate of 5°C/min.

XPS and UPS were performed on a VGESCAlab-5 photoelectron spectrometer, with a vacuum of $10^{-9}$–$10^{-10}$ Torr. Al $K\alpha$ line and HeI were used as the exciting source for XPS and UPS, respectively. The powder samples were pressed into wafer form.

The $V_2O_5$ and $TiO_2$ samples were bombarded slightly with an $Ar^+$ ion beam (1 kV, 5 $\mu$A, 2 min) to remove surface contamination, and then annealed at 400°C for 10 min. The UPS spectra were taken at 400°C which is closer to the catalytic reaction temperature. Ion bombardment on a metal oxide surface usually removes oxygen preferentially resulting in a reduced metal-rich surface. The annealing at several hundred degrees centigrade after ion bombardment would help to restore the surface to bulk stoichiometry by diffusion of oxygen ions from the bulk (*19*). After annealing, a certain amount of oxygen vacancies still exist on the surface; these are needed to measure the defect surface state. The sample was isolated from ground and biased by a negative voltage of −3.0 V for work function measurement by UPS.

The surface oxygen concentration has been calculated by using $C_x = (A_xR_x/S_x)/\Sigma(A_xR_x/S_x)$, where $A_x$ is the area under the XPS peak for the element $x$, $R_x$ is the count rate setting, $S_x$ is the sensitivity factor for the specific photoelectron of element $x$, $\Sigma$ denotes the summation for all elements included in samples.

Relative sensitivity factors for V2$p$, Ti2$p$, and O1$s$ photoelectrons of 3.15, 1.9, and 1, respectively, have been obtained in our experiment.

## RESULTS AND DISCUSSION

Figure 1 shows the surface atom percentage concentration of oxygen calculated from quantitative XPS analysis as a function of $V_2O_5$ content for a series of catalytic

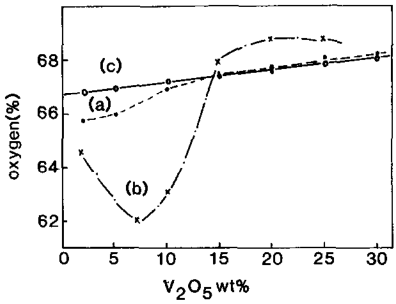

FIG. 1. Surface oxygen percentage concentration obtained from quantitative XPS analysis as a function of $V_2O_5$ content. (a) Catalytic samples. (b) After TGA experiment in $He : O_2 = 1 : 1$ atmosphere. (c) Calculated from a $V_2O_5 + TiO_2$ mixture.

samples before (a) and after (b) TGA experiments, which were carried out in a He : $O_2$ = 1 : 1 atmosphere. For comparison, the surface oxygen concentrations calculated for a $V_2O_5$ + $TiO_2$ mixture are also shown in Fig. 1c. In Fig. 1 it should be noted that the surface oxygen concentration depends strongly on $V_2O_5$ content and the sample processing conditions such as temperature and atmosphere. For low $V_2O_5$ content, the surface oxygen concentration of the catalytic sample is lower than that calculated from the mixture. After the TGA experiment, the surface oxygen concentration drops much lower, reaching a minimum at about 7 wt% $V_2O_5$ content. For $V_2O_5$ content above 15 wt%, the surface oxygen concentration of catalytic samples before TGA is basically the same as that of the mixture; it is even higher after TGA experiments. The results indicate that the $V_2O_5$ near the interface is slightly reduced during sample preparation (450°C, 4 h in air) and further reduced during the TGA experiment. However, away from the interface, the $V_2O_5$ is not reduced, and even absorbs gas-phase oxygen during TGA experiments. The same phenomenon has been observed for pure $V_2O_5$, which increases in weight during TGA experiments in a He : $O_2$ = 1 : 1 atmosphere.

Figures 2a and b show the weight loss for each gram of $V_2O_5$ in $V_2O_5/TiO_2$ catalysts as a function of $V_2O_5$ content for TGA experiments in He : $O_2$ = 1 : 1 and He atmospheres, respectively. It can be seen that the weight loss is strongly dependent on $V_2O_5$ content and the partial pressure of oxygen in the atmosphere in which the TGA experiments are carried out. The weight loss initially increases with $V_2O_5$ content, passes through a maximum, then decreases rapidly with increasing $V_2O_5$ content. The maximum weight loss is at about 7–10 wt% for TGA experiments in He : $O_2$ = 1 : 1 and at much higher $V_2O_5$ content for TGA experiments in He atmosphere.

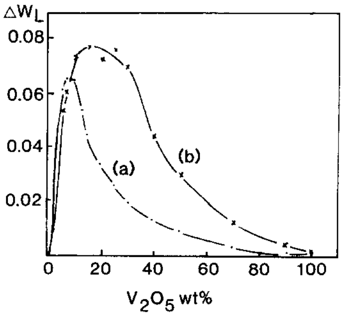

FIG. 2. Weight loss $\Delta W_L$ (in percent) per gram of $V_2O_5$ in catalysts in TGA experiments as a function of $V_2O_5$ content. (a) In He : $O_2$ = 1 : 1 atmosphere. (b) In He atmosphere.

The above results may be explained as follows: Both the reduction in surface oxygen concentration and the weight loss of catalytic samples in TGA experiments arise from the evolution of lattice oxygen, which is promoted by the interfacial interaction between $V_2O_5$ and $TiO_2$. At low $V_2O_5$ content, vanadia species are well dispersed on the $TiO_2$ surface, the coverage and thickness of vanadium oxide increase with $V_2O_5$ content up to 7–10 wt%, the surface $V_2O_5$ is therefore effectively reduced due to the interfacial interaction, and so the surface oxygen concentration decreases with increasing $V_2O_5$ content up to 7–10 wt%. Thereafter, any further increase in $V_2O_5$ content leads mainly to accumulation and thickening of vanadium oxide, which lead to interfacial interaction between surface $V_2O_5$ and $TiO_2$; therefore, the promotion for evolving lattice oxygen becomes weaker and weaker with increasing $V_2O_5$ content (*17, 18*). As a result, the surface oxygen concentration begins to increase, and the weight loss in TGA experiments begins to decrease, with increasing $V_2O_5$ content. When the thickness of vanadium oxide extends beyond the interaction range of $V_2O_5$ and $TiO_2$, which probably occurs above 15 wt% $V_2O_5$ content, the promotion for the evolution of lattice oxygen basically disappears, the surface $V_2O_5$ in catalysts behaves like pure $V_2O_5$, so the surface oxygen concentration even increases in TGA experiments for $V_2O_5$ content above

15 wt%, as mentioned above. The detailed calculation of the dispersion, coverage, and thickness of vanadia species in $V_2O_5/TiO_2$ catalysts has already been given (*17*).

According to the preceding analysis, the curve of weight loss in Fig. 2a should be basically flat for $V_2O_5$ content below 7–10 wt%. However, the experimental result is different from that expected, probably because some lattice oxygen evolved during the sample preparation, as has been discussed.

In all metal oxides, lattice oxygen ions are negatively charged, and form strong bonds with metal cations. The process of evolution of lattice oxygen must involve removal of valence electrons from lattice oxygen ions. From the energy band view point, which involves injecting holes from appropriate energy levels to the valence band which is derived predominantly from $O_L^{2-}$ ions. This process can be represented as $2h^+ + O_L^{2-} \rightarrow \frac{1}{2}O_2$, where $O_L^{2-}$ is a lattice oxygen ion of a solid oxide, and $h^+$ is the hole.

The results of both XPS and TGA experiments show that the evolution of lattice oxygen takes place mainly in a vanadia layer of certain thickness near the interface of $V_2O_5$ and $TiO_2$, beyond which the $V_2O_5$ has no activity for the evolution of lattice oxygen. $V_2O_5$ and $TiO_2$ are transition metal oxide semiconductors, and belong to nonstoichiometric compounds, their surface composition and oxygen vacancies depending on the equilibrium between the lattice and the gas-phase constituent or the partial pressure of oxygen. The oxygen vacancies in the lattice play an important role in electron exchange. Therefore, it seems reasonable to explain the evolution of lattice oxygen in terms of the interfacial energy band structure and defect surface state associated with oxygen vacancies.

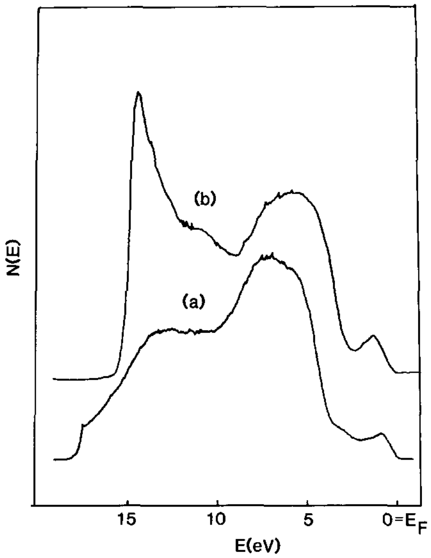

FIG. 3. UPS spectra for (a) $TiO_2$ and (b) $V_2O_5$ taken at 400°C. Samples were bombarded for 2 min with 1 kV of a 5-μA $Ar^+$ ion beam, and then annealed at 400°C for 10 min. The curves are aligned at $E_F$.

The defect surface state and work function of $V_2O_5$ and $TiO_2$ can be measured by using UPS. Figure 3 shows the UPS spectra of $V_2O_5$ and $TiO_2$. From Fig. 3, it is known that the work function of $V_2O_5$ (6 eV) is greater than that of $TiO_2$ (4.6 eV) as calculated with the formula of Jacobi *et al.* (*20*). The UPS spectra contain a small peak with a maximum at an energy about 1 and 2.7 eV above the top edge of the valence for $V_2O_5$ and $TiO_2$, respectively, which possibly is ascribed to the defect surface state associated with oxygen vacancies. Much work on defect surface state of $TiO_2$ and $SrTiO_3$ has been done by Henrich (*19*).

At the interface of $V_2O_5$ and $TiO_2$ the oxygen vacancies and defect surface state should exist, especially at high temperature. Figure 4 shows the UPS spectra of $V_2O_5$ and a 10 wt% $V_2O_5/TiO_2$ catalyst sample. The UPS peak due to the defect surface state can also be clearly seen for the unbombarded samples at 400°C. At room temperature, this peak is not obvious, probably because of the low density of oxygen vacancies and surface contamination.

Owing to the fact that the work function of $V_2O_5$ is greater than that of $TiO_2$, according to the semiconductor interfacial theory, the energy band of $V_2O_5$ will bend down at the interface of $V_2O_5$ and $TiO_2$. Figure 5

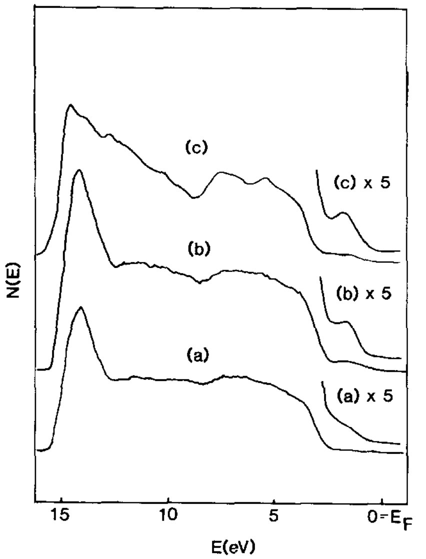

FIG. 4. UPS spectra for (a) $V_2O_5$ at room temperature, (b) $V_2O_5$ at 400°C, and (c) 10 wt% $V_2O_5/TiO_2$ catalyst at 400°C.

shows a schematic diagram of the interfacial energy band structure of $V_2O_5$ and $TiO_2$ and the defect surface states, which are about 1 and 2.7 eV above the top of the valence band for $V_2O_5$ and $TiO_2$, respectively. In addition, the densities and energy of the defect surface state strongly affect the interfacial energy band structure: if the densities of the defect surface states of $V_2O_5$ and $TiO_2$ are high enough, the Fermi energy level might be pinned at their own defect surface state. In this case, the Fermi energy level of $TiO_2$ is much higher than that of $V_2O_5$. However, at the interface of $V_2O_5$ and $TiO_2$ they should have the same Fermi energy level; thus the energy band of $V_2O_5$ should also bend down. The bending of the $V_2O_5$ energy band brings the energy levels of the defect surface states of $V_2O_5$ near the interface close to the valence band of bulk $V_2O_5$ as shown in Fig. 5. As a result, the probabilities of electron exchange between the defect surface state of $V_2O_5$ and the valence band of bulk $V_2O_5$ increase, or the probabilities of injecting holes from the defect surface state to the valence band of $V_2O_5$ increase; thus the negative charges on lattice oxygen ions become easily removable, and the evolution of lattice oxygen is promoted.

In addition, Sakata (*21*) reported that in $V_xTi_{1-x}O_2$ ($x = 2.5 \times 10^{-3}$), the excess 3*d* electrons of vanadium ions form impurity levels just above the top of the valence band is about 0.6 eV. It has also been reported that after a 650°C calcination treatment of the $V_2O_5/TiO_2$ catalyst, approximately 6% of the titania is present as solid solution $V_xTi_{1-x}O_2$ (rutile) at the interface of $V_2O_5$ and $TiO_2$ (*11*), and the maximum molar fraction of $V^{4+}$ ions able to be dissolved is about 0.04 (*22*). These V ions can be considered an impurity. Therefore, the impurity energy level mentioned above exists at the interface of $V_2O_5$ and $TiO_2$, especially at high temperature. It can probably also exchange electrons with the valence band of $V_2O_5$, leading to increased evolution of lattice oxygen.

From the preceding model, it can be expected that any change in the state of the $TiO_2$ surface before sample preparation or during formation of the $V_2O_5/TiO_2$ interface probably brings about changes in the interfacial energy band structure, and therefore

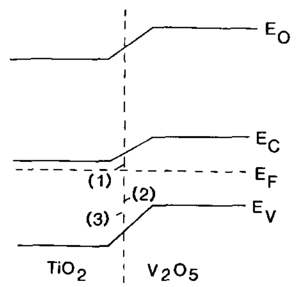

FIG. 5. Scheme of the energy band structure at the $V_2O_5/TiO_2$ interface. The bulk bandgaps are 2.5 and 3.05 eV for $V_2O_5$ and $TiO_2$, respectively. (1) and (2) represent the defect surface states associated with oxygen vacancies for $TiO_2$ and $V_2O_5$, respectively. (3) represents impurity energy levels induced by vanadia ions in $TiO_2$ at the interface. $E_0$, $E_c$, $E_v$, and $E_F$ represent the vacuum energy level, conduction band edge, valence band edge, and Fermi energy level, respectively.

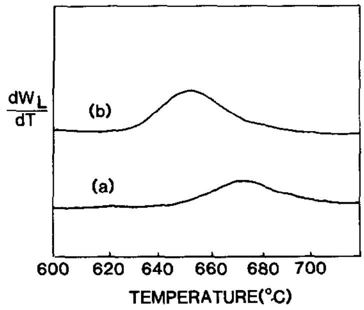

FIG. 6. Derivative curve of weight loss for 7 wt% $V_2O_5/TiO_2$ catalysts in the TGA experiments carried out in He atmosphere. (a) $TiO_2$ was not pretreated. (b) $TiO_2$ was pretreated by impregnation with 1 *N* $NH_4OH$ aqueous solution.

in the evolution of lattice oxygen. We changed the state of the $TiO_2$ surface by impregnating $TiO_2$ powder with 1 *N* $NH_4OH$ aqueous solution before sample preparation and have observed its effect on the evolution of lattice oxygen. Figure 6 shows the derivative curve of weight loss in TGA experiments for pretreated and unpretreated 7 wt% $V_2O_5/TiO_2$ catalytic samples. It can be seen that pretreatment of $TiO_2$ with $NH_4OH$ aqueous solution decreases the temperature of evolving lattice oxygen about 20°C. This is probably due to the fact that the pretreatment of $TiO_2$ decreases its work function, thus increasing the probability of electron exchange between the defect surface state and the valence band of $V_2O_5$.

The densities of the defect surface state can be changed by heating the metal oxide samples in a different atmosphere. Therefore, the evolution of lattice oxygen should be affected by the atmosphere in which the TGA experiment is carried out. Figure 2 shows that the maximum weight loss occurs at different $V_2O_5$ contents for TGA experiments in $He:O_2 = 1:1$ and in He atmosphere. This phenomenon can also be explained on the basis of the above model. The melting point of $V_2O_5$ is about 690°C and the temperature range of the TGA experiment 500–750°C. It can be imagined that during the TGA experiments a new interface forms in addition to the original ones, as shown in Fig. 7, which also promotes the evolution of lattice oxygen in TGA experiments. However, we should remember that the condition for the formation of a new interface is different for TGA experiments in $He:O_2 = 1:1$ and He atmospheres, which is also different from that of the original interface. The partial pressure of oxygen in a $He:O_2 = 1:1$ atmosphere is much higher than in air (the original interface is formed in air) and approach zero in a He atmosphere. Clearly, the number of oxygen vacancies and the densities of defect surface states associated with oxygen vacancies at the new interface of $V_2O_5$ and $TiO_2$ are much higher for the new interface formed in He than in $He:O_2 = 1:1$ atmosphere. For the TGA experiments in $He:O_2 = 1:1$ atmosphere the densities of defect surface states are very low due to the high partial pressure of oxygen. The promotive action for evolution of lattice oxygen is caused mainly by the original interface, so the maximum weight loss is at about 10 wt% $V_2O_5$ content, as has been discussed. However, for the TGA experiments in He atmosphere, the densities of defect surface states at the new $V_2O_5/TiO_2$ interface are high due to the very low

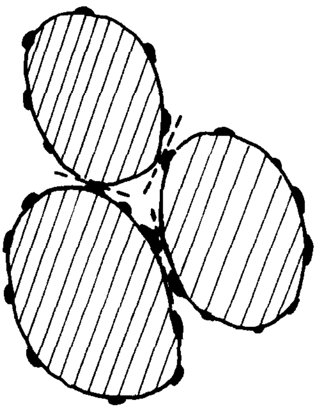

FIG. 7. Schematic diagram for the formation of new $V_2O_5/TiO_2$ interfaces between different catalytic particles during TGA experiments. ▨, $TiO_2$ particles; ●, $V_2O_5$ supported on $TiO_2$ surface; ---, new interfaces.

partial pressure of oxygen during formation of the new interface. The high densities of defect surface states at the new interface will affect the evolution of lattice oxygen in two aspects: (1) The increase in density of defect surface states directly increases the probability of electron exchange between the defect surface state and the valence band of $V_2O_5$. (2) The Fermi energy levels of $V_2O_5$ and $TiO_2$ are probably pinned at their own defect surface states, which makes the energy band of $V_2O_5$ near the interface bend down more, and brings the defect surface state of $V_2O_5$ closer to its bulk valence band at the interface, thus leading to increased electron exchange probabilities between the defect surface state and the valence band of bulk $V_2O_5$. The new interface therefore plays an even more important role in the evolution of lattice oxygen than the original interface. The new and original interfaces together make the maximum weight loss shift to high $V_2O_5$ content for TGA experiments in He atmosphere. These two results provide evidence for our model.

In summary, the evolution of lattice oxygen of $V_2O_5/TiO_2$ catalysts is strongly dependent on $V_2O_5$ content and on the atmosphere in which the TGA experiments are carried out, and is promoted by interfacial interaction between $V_2O_5$ and $TiO_2$. The defect surface states associated with oxygen vacancies play a very important role in promoting the evolution of lattice oxygen. The interfacial interaction of $V_2O_5$ with $TiO_2$ brings the defect surface state of $V_2O_5$ near the interface closer to the valence band of bulk $V_2O_5$, which results in an increase in the probability of electron exchange between the defect surface state of $V_2O_5$ and the valence band of bulk $V_2O_5$. The negative charges in lattice oxygen ions thus become easily removable, leading finally to promotion of the evolution of lattice oxygen. Work is now in progress to seek more proof for this model.

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## REFERENCES

1. Fuller, M. J., and Warwick, M. E., *J. Chem. Soc. Chem. Commun.*, 210 (1973).
2. Sachtler, W. M. H., *Catal. Rev.* **4,** 27 (1970).
3. Boreskov, G. K., *Adv. Catal.* **15,** 285 (1964).
4. Viswanathan, B., Ramalingam, V., and Sastri, M. V. C., *Ind. J. Chem.* **12,** 205 (1974).
5. Winter, E. R. S., *Adv. Catal.* **10,** 196 (1958).
6. Senseman, C. E., and Nelson, O., *Ind. Eng. Chem.* **15,** 521 (1923).
7. Inomata, M., Miyamoto, A., and Murakami, Y., *J. Phys. Chem.* **85,** 2372 (1981).
8. Nag, N. K., Chary, K. V. R., Mahipal Reddy, B., Ramarao, B., and Subrahmanyam, V. S., *Appl. Catal.* **9,** 225 (1984).
9. Kerkhof, F. D. J. M., and Moulijn, J. A., *J. Phys. Chem.* **83,** 1612 (1979).
10. Vejux, A., and Courtine, P., *J. Solid State Chem.* **23,** 93 (1978).
11. Saleh, R. Y., Wachs, I. E., Chan, S. S., *J. Catal.* **98,** 102 (1986).
12. Wainwright, M. S., and Foster, N. R., *Catal. Rev. Sci. Eng.* **19,** 211 (1979).
13. Kozlowski, R., Pettifer, R. F., and Thomas, J. M., *J. Phys. Chem.* **87,** 5176 (1983).
14. Bond, G. C., Zurita, J. P., and Flamerz, S., *Appl. Catal.* **27,** 353 (1986).
15. Gasior, M., Gasior, I., and Grzybowska, B., *Appl. Catal.* **10,** 87 (1984).
16. Kang, Z. C., and Bao, Q. X., *Appl. Catal.* **26,** 251 (1986).
17. Liu, Z. X., Lin, Z. D., Fan, H. J., Li, F. H., Bao, Q. X., and Zhang, S. G., *Appl. Phys. A* **45,** 159 (1988).
18. Bao, Q. X., Zhang, S. G., Li, Y. Q., Rao, G. Y., Liang, Y. D., and Liu, Z. X., *J. Catal.* **8,** 34 (1987) [in Chinese].
19. Henrich, V. E., *Prog. Surf. Sci.* **9,** 143 (1979).
20. Jacobi, K., Zwicker, G., and Gutmann, A., *Surf. Sci.* **141,** 109 (1984).
21. Sakata, K., *Phys. Status Solidi B* **116,** 145 (1983).
22. Bond, G. C., and Sarkany, A. J., *J. Catal.* **57,** 476 (1979)