Catalysis Letters 4 (1990) 113–122

PHOTO-ENHANCED CATALYTIC DECOMPOSITION OF ISOPROPANOL ON V_2O_5

A.Z. MOSHFEGH and A. IGNATIEV

Department of Physics, University of Houston, Houston, TX 77204-5504, U.S.A.

Received 8 February 1989; accepted 28 November 1989

Photochemical isopropanol decomposition; vanadium oxide photocatalysis.

The effect of UV-visible photo irradiation has been investigated on the decomposition of isopropanol over V_2O_5. A ~ 2.5-fold photo-enhancement in the rate of the dehydration ($-H_2O$) reaction was observed under UV-visible photo irradiation compared to thermal heating of the catalyst. The increase in propene yield under photo irradiation is believed to be initiated from photo excitation (photo-reduction) of the V_2O_5 complex to $[-V^{4+}-O^{-}]^{*}$ thus, increasing surface concentration of V^{4+} species. The V^{4+} active surface species is assumed to serve as the center for adsorption of isopropanol. The observed increase in water formation along with the formation of propene suggests that the rate determining step for the dehydration reaction is desorption of water. Selectivity toward the dehydrogenation ($-H_2$) reaction has also been measured to be ~ 1% under UV-visible photo irradiation as compared to ~ 15% under thermal heating of the catalyst.

1. Introduction

The transition metal oxides have been widely used as catalysts for decomposition of aliphatic alcohols, especially isopropanol [1–3]. Generally, catalytic activity and selectivity depend on the type of catalyst (n-type, p-type), catalyst petreatment and reaction conditions. Attempts have been made to correlate the catalytic activity of the various transition metal oxides with their semiconducting properties [4], and within studies of the catalytic decomposition of isopropanol it has been shown that the reaction proceeds mainly in two directions: (i) dehydration which leads to propene formation (eq. (1)) and (ii) dehydrogenation that produces acetone (eq. (2)).

$$CH_3{-}CHOH{-}CH_3 \longrightarrow \begin{cases} \rightarrow CH_3{-}CH{=}CH_2 + H_2O & (1) \\ \rightarrow CH_3{-}CO{-}CH_3 + H_2 & (2) \end{cases}$$

© J.C. Baltzer A.G. Scientific Publishing Company

The competition between these two reaction pathways is strongly dependent on the type of catalyst.

Cunningham et al. [3] have examined the decomposition of isopropanol on different unsupported high surface area (2–170 m^2g^{-1}) metal oxide catalysts under thermal conditions and found the rate of dehydration on a V_2O_5 catalyst to be about 5 orders of magnitude higher as compared to the other metal oxides. For V_2O_5, it is well established in the literature [5–8] that the V^{4+} active species and the lower oxides of V_2O_5 probably V_6O_{13} and/or V_4O_9 play an important role in the catalytic oxidation and decomposition of many organic molecules.

Considering practical utilization of solar energy in the field of catalysis (photo-catalysis), recently Moshfegh and Ignatiev [9,10] have investigated the mechanism of the influence of photo-irradiation on a low surface area ($\simeq 1$ cm^2) nickel catalyst in the heterogeneous catalytic methanation reaction and observed significant enhancement of the rate of reaction. This communication focuses on the effect of both UV-visible photo-irradiation and thermal heating of a pure V_2O_5 catalyst ($\simeq 1$ cm^2) in studying the heterogeneous catalytic decomposition of isopropanol.

2. Experimental

A stainless steel bakable photo-catalytic reactor (fig. 1) has been utilized under static condition to investigate catalytic decomposition of isopropanol. The reactor is isolated by two ultra high vacuum (UHV) gate valves from a sample transfer device and an UHV surface analysis chamber. Gas sampling product analysis was obtained downstream of the reactor through a variable leak valve by quadrupole mass spectrometry (QMS). A chromel-alumel thermocouple (TC) was attached to the edge of the catalyst for monitoring the reaction temperature. A 5000 W xenon discharge lamp was utilized as a source of UV-visible photo-irradiation of the V_2O_5 catalyst through a focusing lens and a sapphire viewport. Thermal heating of the catalyst was achieved by a heating coil located inside a gold electroplated catalyst holder. To control the temperature of the catalyst, H_2O or LN_2 was used as a coolant in the cooling system. The reactor's wall was kept at room temperature during the reaction. The isopropanol partial pressure inside the reactor was measured by two MKS baratron gauges (in a range from 10^{-4} to 10^{+4} Torr). A detailed description of the operation of the combined system has been discussed elsewhere [11].

The vanadium pentoxide, V_2O_5, catalyst ($\simeq 1$ cm^2) with ~ 1 mm thickness, was prepared by oxidation of pure metallic vanadium (polished by Al_2O_3 polishing paste down to 0.05 μm size grit) in a continuous flow of ultra high purity oxygen at $T = 600\,°C$, $t = 3$ hr, $P_{O_2} = 1$ atm and $F = 1.5$ l/min. A relatively thick oxide layer (1–3 μm) of orange-yellow color was formed on the vanadium substrate under these conditions. Both Auger electron spectroscopy (AES) as well

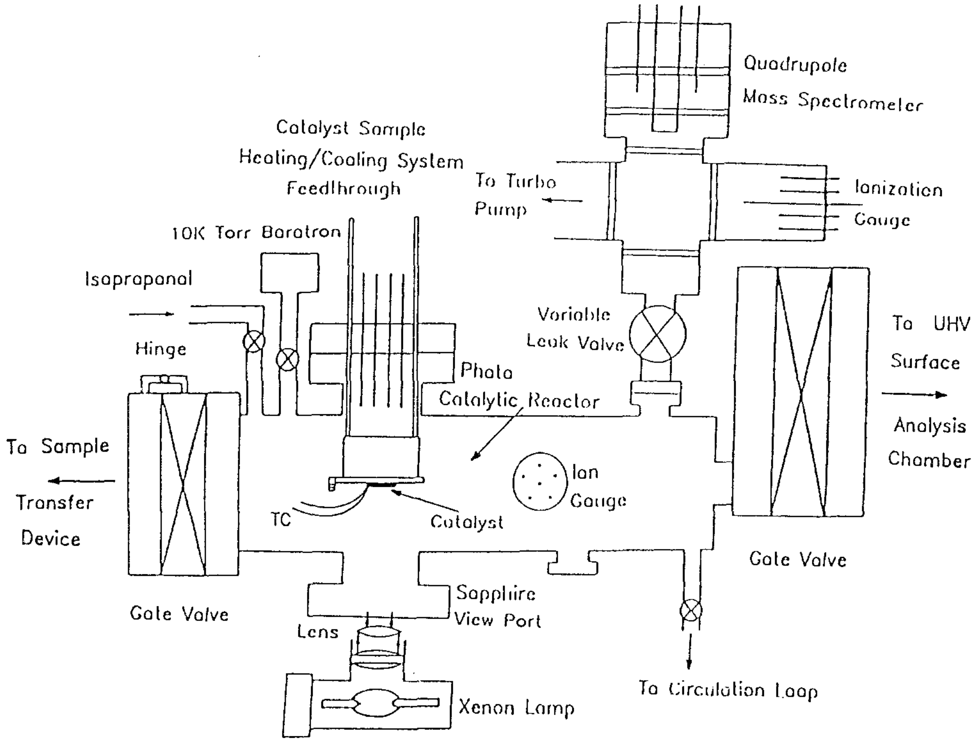


Fig. 1. A stainless steel bakable photo-catalytic reactor with a gas product detection system. The reactor is isolated from the sample transfer device and UHV surface analysis chamber by two UHV gate valves. A xenon discharge lamp is utilized as a source of UV-visible photo-irradiation on the V_2O_5 catalyst.

as X-ray photoelectron spectroscopy (XPS) analyses confirm formation of V_2O_5 composition. The high purity isopropanol was transferred to a chamber-mounted glass container through a series of freeze-evacuation cycles. The connecting gas line was evacuated to $\leqslant 1 \times 10^{-3}$ Torr prior to filling the reactor. Before adsorption of isopropanol, the V_2O_5 catalyst was heat treated in vacuum, $\leqslant 1 \times 10^{-7}$ Torr, in the temperature range 350–450 °C for 45 minutes.

3. Results and discussion

X-ray photoelectron spectroscopy (XPS) (using monochromatized MgK_α (1253.6 eV) radiation as the excitation source) was employed to characterize the oxidation state of vanadium. The prepared V_2O_5 samples were mounted on the carousel of the manipulator in the surface analysis chamber for the XPS measurement. During the measurements, samples were maintained at a temperature of 300 K and a pressure of $\sim 5 \times 10^{-10}$ Torr. All measured binding energies are given relative to the position of the C(1s) core level at 285.0 eV. Charging effects were minimal and could be controlled by flooding the sample surface with low energy electrons during the analysis. The $V(2p_{3/2})$ core level binding energy (BE) and its corresponding full width at half maximum (FWHM) were monitored in order to determine the change in surface chemical composition of the V_2O_5 catalyst. Under the oxidation conditions outlined above for metallic vanadium, a chemical shift of the $V\ (2p_{3/2})$ level was noted after oxidation. The 4.4 eV shift to higher binding energy (from 512.4 eV for metallic V to 516.8 eV for the oxide) is attributed to the formation of V_2O_5. This is in good agreement with previous studies [12,13].

It has been suggested [5,14,6,15] that V_2O_5 has to be reduced to a lower oxide (between V^{5+} and V^{4+}) in order to exhibit its catalytic performance. Therefore, UHV heat treatment (before adsorption of isopropanol) of V_2O_5 was used here for formation of a lower oxide on the surface. XPS analysis of the V_2O_5 catalyst before adsorption of isopropanol showed that upon heat treatment of the catalyst under the following conditions, $\leqslant 1 \times 10^{-7}$ Torr, at a temperature of 410 °C for 45 minutes, the $V\ (2p_{3/2})$ peak shifted ~ 0.6 eV to a lower binding energy and the FWHM broadened ~ 0.8 eV relative to the preheating condition. The observed shift and broadening of $V\ (2p_{3/2})$ as well as thermodynamic considerations suggest that the vanadium atoms are not in the single highest (V^{5+}) oxidation state, but are in mixed oxidation state of vanadium (V^{5+}–V^{4+}) that probably result in formation of lower oxide(s) V_4O_9 and/or V_6O_{13} on V_2O_5. A very slight color change has also been noticed after treatment of the catalyst. A chemical shift of 3.8 eV after the heat treatment is in agreement with Larrson et al. [12] who found a shift of 3–4 eV for a range of (V^{5+}–V^{4+}) compounds. A phase identified as "Q" with composition of V_4O_9 or $V_6O_{13.5}$ as a result of UHV thermal decomposition of an air-cleaved V_2O_5 (010) single crystal has been reported previously [14] which is consistent with our results. It is worth noting that V_2O_5 with the highest vanadium oxidation state has a great tendency to lose oxygen easily resulting in the formation of oxygen vacancies in the lattice. A possible reduction mechanism could be due to interaction of surface oxygen with surface carbon present either from residual gas or from carbon impurities present in the lattice leading to CO and/or CO_2 production. Mass spectrometric investigation by Colpaert et al. [14] supports this possible mechanism. The formation as well as the structure of V_4O_9 and V_6O_{13} from the parent V_2O_5 has been explained previously by several investigators [16–20].

Table 1 shows the binding energy (BE) and FWHM of C (1s) $V\ (2p_{3/2})$ and O (1s) core levels before heating and after heating of the V_2O_5 catalyst. These results indicate that the reduction of the V_2O_5 catalyst took place to a V^{4+} and/or the mixed oxidation state of vanadium V^{4+} and V^{5+} under vacuum heat treatment. Therefore upon reduction of V_2O_5, formation of V^{4+} is believed to occur. The V^{4+} centers are assumed to form adjacent to surface vacancies. It has been proposed [14,15,21,22] that the presence of V^{4+} ions and lower oxides at a V_2O_5 surface (V_4O_9 and/or V_6O_{13}) enhances catalytic activity and affects selectivity of

Table 1
Comparison of XPS analysis of the V_2O_5 catalyst before and after heating in vacuum $P \leqslant 1 \times 10^{-7}$ Torr, $T = 410\,^\circ C$ and $t = 45$ minutes.

	C(1s)		$V(2p_{3/2})$		O(1s)	
	BE(eV)	FWHM(eV)	BE(eV)	FWHM(eV)	BE(eV)	FWHM(eV)
Before heating	285.0	3.9	516.8	2.2	529.7	2.2
After heating	285.0	4.1	516.2	3.0	529.5	2.4

the catalyst. Therefore, the degree of non-stoichiometric character of V_2O_5 and formation of the V^{4+} ions as a consequence of the existence of oxygen vacancies are believed to play an important role in chemisorption and in heterogeneous catalytic reactions [15]. In this investigation, an increase in the concentration of these catalytic centers under photo-irradiation has been considered as a method to enhance the catalytic activity of V_2O_5, since it is assumed and has been reported [23,24] that light may influence the catalytic action of V_2O_5.

The catalytic properties of V_2O_5 (visible band gap $E_g \simeq 2.35$ eV) have been utilized to study heterogeneous catalytic decomposition of isopropanol under UV-visible photo-irradiation. The rate of dehydration ($-H_2O$) as well as dehydrogenation ($-H_2$) of the alcohol on V_2O_5 were measured under both the condition of thermal heating of the catalyst to the reaction temperature and UV-visible photo-irradiation of the catalyst to a similar reaction temperature with continuous irradiation after the reaction temperature was reached. Figure 2 shows clear photo-enhancement of dehydration of isopropanol (propene formation) at low flux (~ 5 W/cm^2) and high flux (~ 22 W/cm^2) under UV-visible photo-irradiation as compared to thermal heating of the V_2O_5 catalyst at the alcohol partial pressure of $P_{alc} = 0.1$ Torr and at a temperature of $T = 210\,^\circ C$. At constant pressure, increasing the temperature of the catalyst to as high as $\sim 350\,^\circ C$ under thermal conditions resulted in a substantial decrease in rate of propene formation. Based on this data, an enhancement of $\sim$ 2.5-fold in the rate of propene formation is observed (fig. 2) with high flux photo-irradiation over thermal heating of the V_2O_5 catalyst.

It may be argued that the observed enhanced dehydration ($-H_2O$) reaction is a thermal effect since photo absorption under UV-irradiation takes place over a shallower depth from the surface than under infrared irradiation due to skin depth considerations, and therefore, causes higher surface temperatures. Recently, an estimate of the surface temperature under UV-visible photo irradiation at different fluxes was reported [25] for the Ni(100) system using low energy electron diffraction (LEED). It is shown that even at fluxes as high as ~ 200 W/cm^2, the surface temperature differential was only $\Delta T = 63\,^\circ C$ at $\sim 550\,^\circ C$.

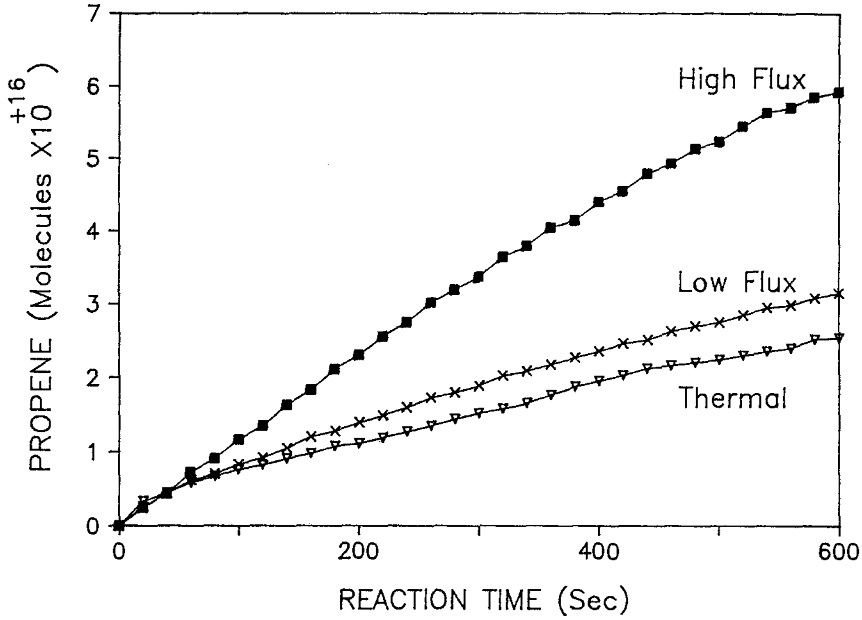


Fig. 2. The rate of propene formation under thermal, low flux (~ 5 W/cm^2) and high flux (~ 22 W/cm^2) conditions at P_{alc} = 0.1 Torr, T = 210 ° C.

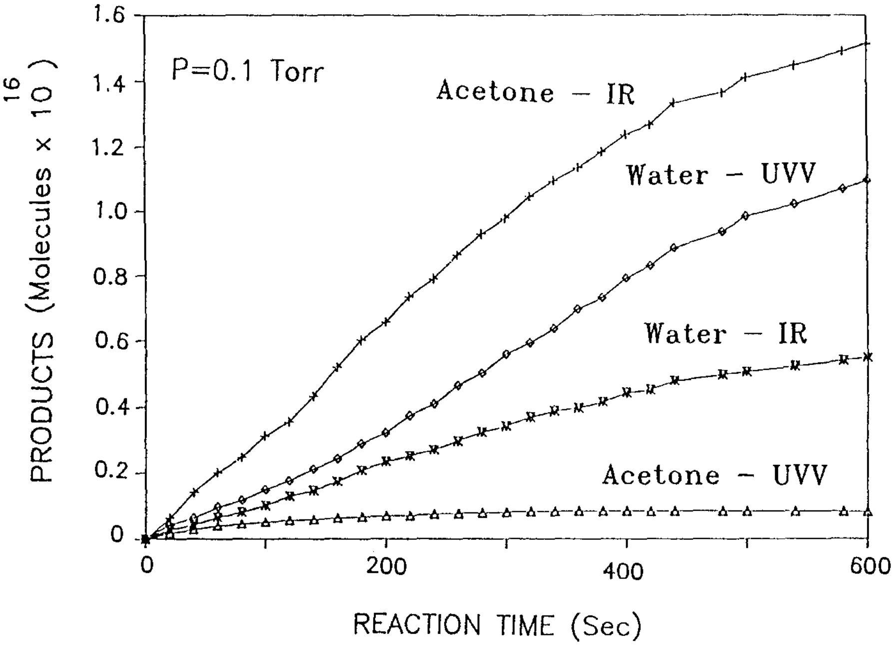


Fig. 3. The rate of acetone and water formation under both infrared (IR) and thermal heating and UV-visible (UVV) photo irradiation (flux ~ 15 W/cm^2) conditions at P_{alc} = 0.1 Torr, T = 210 ° C.

Considering the fact that the thermal conductivity of V_2O_5 is 2–3 orders of magnitude lower than Ni, the absorption coefficient of nickel in the visible range is ~ 15%, whereas that of V_2O_5 it is ~ 50%, and the electrical conductivity of Ni is ~ 7–8 orders of magnitude greater than that of V_2O_5, it can be estimated that for V_2O_5 under our reaction conditions (Flux ~ 22 W/cm^2, W/cm^2, $T = 210\,^\circ$C, $P = 0.1$ Torr) a temperature gradient of at most ~ $\pm 15\,^\circ$C may exist between the surface and bulk of the sample. This small temperature change cannot account for the observed photo enhancement, hence, we believe a different mechanism is involved in the dehydration ($-H_2O$) reaction of isopropanol over V_2O_5 under UV-visible photo irradiation than under infrared thermal heating of the catalyst (see section 4).

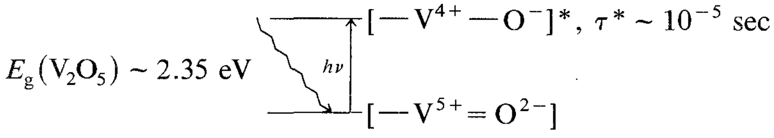
The dehydrogenation ($-H_2$) reaction (eq. (2)) also was observed on the catalyst; the selectivity of this decomposition path has been found to be ~ 15% under infrared (IR) thermal heating and only ~ 1% under UV-visible (UVV) photo-irradiation of the V_2O_5 catalyst as shown in fig. 3. Lower water formation under IR thermal heating compared to UVV photo-irradiation of the catalyst clearly shows that V_2O_5 has higher selectivity toward dehydration ($-H_2O$) under UV-visible photo-irradiation of the catalyst. This pattern is always observed under UVV regardless of input flux density. This is in agreement with Kazansky's investigation [26] that suggests excitation of the oxide lattice oxygen by light proceeds selectively.

4. Mechanism

It is widely believed [27,28,23,29,30] that the excited states of metal oxides (V_2O_5, MoO_3, WO_3, and CrO_3) by light are characterized by the charge transfer state, $[M^{(n-1)+}\text{–}O^-]^*$, which plays a significant role in the photocatalysis. Therefore, the primary step of the mechanism of the catalytic dehydration ($-H_2O$) of isopropanol under UV-visible photo-irradiation is proposed to be due to photo excitation (photo reduction) of the V_2O_5 complex

$$[-V^{5+}{=}O^{2-}] \xrightarrow{h\nu \geq E_g} [-V^{4+}-O^-]^*. \tag{4}$$

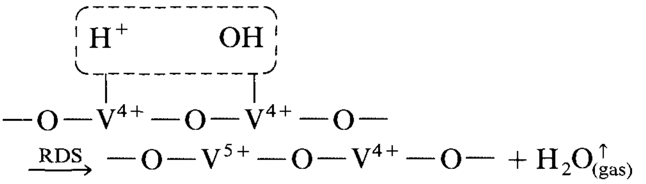
This photo process involves charge transfer from double bonded oxygen O^{2-} to vanadium V^{5+}. Photo-excitation of complex $[-V^{4+}\text{–}O^-]^*$ is shown schematically below



According to Kazansky [29,31], this electronic excited state has a sufficient life time ~ 10^{-5} seconds to react with surface adsorbed species. As a result of the photo reduction, the ions that are formed are usually all in a single specific valence state, whereas in thermal reduction they are in a set of different valence states [26]. Therefore, it is more convincing that under our thermal reduction of V_2O_5, a mixed oxidation state of vanadium (V^{5+}-V^{4+} as has been found, see section 3) is probably right.

There exist enough evidence [27,28,23,29,30] that absorption of UV-visible photons with energy $h\nu \geqslant E_g$ on V_2O_5 will create V^{4+} ions in the lattice. The nature and reactivity of V^{4+} ions in vanadium pentoxide catalyst is well known [6,22,32,33]. It is believed that increasing the V^{4+} surface concentration under UV visible photo irradiation (eq. (4)) increases the rate of propene formation ($^{4+}$ serves as the center for adsorption for isopropanol). This is consistent with the optical study by Kenny et al. [34] who found that the absorption coefficient of V_2O_5 increases when the concentration of oxygen is reduced.

The enhancement in rate of propene formation is under UV-visible (UVV) photo-irradiation of the V_2O_5 catalyst is in good agreement with the increase in the rate of water production under UVV compared to infrared (IR) thermal heating as is shown in fig. 3. Since the rate of formation of water increases proportionally with the rate of propene formation, the rate determining step (RDS) for the dehydration of isopropanol on the V_2O_5 catalyst could be the desorption of water as suggested earlier by Chakrabarty et al. [33]. To verify this, temperature programmed desorption (TPD) has been undertaken to investigate the temperature at which water is desorbed from the surface of vanadium pentoxide. For the H_2O/V_2O_5system, it has been found that water is desorbed from the V_2O_5 surface at $T_M \sim 125\,^{\circ}C$ for exposure of ~ 200 L, indicating that propene is not formed as long as water is present on the surface according to the following mechanism.



$$\overset{\boxed{H^+ \qquad OH}}{-O-\overset{|}{V^{4+}}-O-\overset{|}{V^{4+}}-O-} \xrightarrow{RDS} -O-V^{5+}-O-V^{4+}-O- + H_2O^{\uparrow}_{(gas)} \qquad (5)$$

The observation of photo-enhancement in the dehydration reaction certainly depends on the opto-catalytic properties of V_2O_5 with visible band gap of ~ 2.35 eV. Therefore, the rate enhancement in the $(-H_2O)$ reaction is not just due to simple heating effect, but involves a quantum effect which is associated with photo-excitation of V_2O_5 complex (eq. (4)]. Thus, two different mechanisms must be invoked for under infrared thermal heating as well as under UV-visible photo-irradiation. A detailed mechanistic study of the catalytic decomposition of isopropanol on V_2O_5 (n-type semiconductor) and CuO (p-type semiconductor) catalyst under both thermal and UV-visible photo-irradiation is in progress [35].

5. Conclusion

An ~ 2.5-fold photo-enhancement of the catalytic dehydration ($-H_2O$) of isopropanol on V_2O_5 was observed under UV-visible photo-irradiation compared to thermal heating of the catalyst. The enhancement stems from the opto-catalytic properties of V_2O_5 with visible band gap of ~ 2.35 eV. The increase of propene formation under photo-irradiation is initiated from photo excitation of the V_2O_5 complex. The electronic excited states $[-V^{4+}-O^{-}]^*$ will increase the formation of the surface concentration of the V^{4+}species. The V^{4+} ion has been identified as the basis for V_2O_5 catalytic activity. Therefore, the role of V^{4+} active surface species is of primary importance in the photo-enhancement of the dehydration of isopropanol. An increase in water formation along with the formation of propene indicates that the rate determining step for the ($-H_2O$) dehydration process could be the desorption of water. A much lower selectivity ~ 1% toward dehydrogenation ($-H_2$) reaction has been measured on V_2O_5 under UV-visible photo-irradiation compared to ~ 15% under thermal heating of the catalyst.

Acknowledgement

The authors would like to thank H. Nedhif for his assistance with the experimental set-up, and the U.S. Department of Energy–SERI and the R.A. Welch Foundation for their financial support.

References

[1] I. Carrizosa and G. Munera, J. Catal. 49 (1977) 174.
[2] D.V. Fikis, W.J. Murphy and R.A. Ross, Can. J. Chem. 56 (1978) 2530.
[3] J. Cunningham, B.K. Hodnett, M. Ilyas, J. Tobin, E.L. Heahy and J.L.G. Fierro, J. Chem. Soc. Faraday Trans. 1, 77 (1981) 283.
[4] O.V. Krylov, *Catalysis by Nonmetals* (Academic Press, London, 1970) p. 115.
[5] G.L. Simard, J.F. Steger, R.J. Arnott and L.A. Siegel, Ind. Eng. Chem. 47 (1955) 1424.
[6] M. Akimoto, M. Usami and E. Echigoya, Bull. Chem. Soc. Japan 51 (1978) 2195.
[7] D.V. Fikis, W.J. Murphy and R.A. Ross, Can J. Chem. 57 (1979) 2464.
[8] L.F. Fiermans, P. Clauws, W. Lambrecht, L. Vandenbroucke and J. Vennik, Phys. Stat. Sol. (a) 59 (1980) 485.
[9] A.Z. Moshfegh and A. Ignatiev, J. Vac. Sci. Technol. A 5 (1987) 820.
[10] A.Z. Moshfegh and A. Ignatiev, Energy 12 (1987) 277.
[11] A.Z. Moshfegh and A. Ignatiev, Rev. Sci. Instru. 59 (1988) 2202.
[12] R. Larrson, B. Folkesson and G. Schön, Chemica Scripta 3 (1973) 88.
[13] G.A. Sawatzky and D. Post, Phys. Rev. B. 20 (1979) 1546.
[14] M.N. Colpaert, P. Clauws, L. Fiermans and J. Vennik, Sur. Sci. 36 (1973) 513.
[15] L. Fiermans, L. Vandenbroucke, R.V. Berghe and J. Vennik, J. Microsc. Spectrosc. Electron 4 (1979) 543.

[16] E. Gillis, Compt. Rend. Acad. Sci. (Paris) 258 (1964) 4765.
[17] L. Fiermans and J. Vennik, Surface Sci. 9 (1968) 187.
[18] K.A. Wilhelmi, K. Waltersson and L. Kihlborg, Acta. Chem. Scand. 25 (1971) 2675.
[19] G. Grymonprez, L. Fiermans and J. Vennik, Acta. Cryst. A33 (1977) 834.
[20] R. Dziembaj, J. Sol. Stat. Chem. 26 (1978) 167.
[21] D.K. Chakrabarty and D. Guha, React. Kinet. Catal. Lett. 6 (1977) 307.
[22] D.K. Chakrabarty, M.R. Lakshmi and D. Guha, *Proc. Symp. on Science of Catalysis and Its Application in Industry*, p. 309, FPDIL, Sindri, (1979).
[23] S. Yoshida, Y. Matsumura, S. Noda and T. Funabiki, J. Chem. Soc. Faraday Trans 1, 77 (1981) 2237.
[24] W.E. Wentworth, C.F. Batten and G. Wei, Solar Energy (1990) accepted for publication.
[25] A. Mesarwi, Ph.D. Dissertation, University of Houston, 1989.
[26] V.B. Kazansky, Kinet. Katal. 24 (1983) 1338.
[27] A.M. Gritscov, V.A. Shvets and V.B. Kazansky, Chem. Phys. Lett. 35 (1975) 511.
[28] V.B. Kazansky, *Proc. 6th International Congress on Catalysis*, Vol. 1 (London, 1976). p. 50.
[29] M. Anpo, I. Tanahashi and Y. Kubokawa, J. Phys. Chem. 86 (1982) 1.
[30] Y. Kubokawa and M. Anpo, in: *Adsorption and Catalysis on Oxide Surfaces*, eds: M. Che and G.C. Bond (Elsevier Science Pub., Amsterdam, 1985). p. 127.
[31] V.B. Kazansky, Kinet. Katal. 19 (1978) 219.
[32] E.I. Andreikov, V.V. Shorokhod and N.D. Rus'yanova, Kinet. Katal. 14 (1973) 1189.
[33] D.K. Chakrabarty, M. Rajyalakshmi and A.B. Biswas, Proc. Indian. Acad. Sci. (Chem. Sci.) 89 (1980) 131.
[34] N. Kenny, C.R. Kannewurf and D.H. Whitmore, J. Phys. Chem. Solids 27 (1966) 1237.
[35] A.Z. Moshfegh and A. Ignatiev (to be published).