CHEMISTRY LETTERS, pp. 629-630, 1982. © The Chemical Society of Japan 1982

MEASUREMENT OF INFRARED SPECTRA OF SURFACE SPECIES FOR NO_2-C_3H_6-ZnO SYSTEM UNDER PHOTOIRRADIATION

Takashi IBUSUKI*, Nobuyuki IZAWA, and Koji TAKEUCHI

National Research Institute for Pollution and Resources,
Yatabe, Tsukuba-gun, Ibaraki 305

A reaction cell for measurement of ir spectra of surface species on solid catalysts under photoirradiation is developed and is applied to NO_2-C_3H_6-ZnO system. A remarkable change in ir spectra of NO_2 adsorbed on ZnO with photoirradiation is satisfactorily observed and is briefly discussed.

Photocatalytic oxidation reactions over metal oxides such as zinc oxide(ZnO), TiO_2 and other n-type semiconductors have widely been studied.[1)] Spectroscopic studies on the surface species over the metal oxides especially under photoirradiation will be very valuable for understanding the reaction mechanisms and the photocatalytic action of the catalysts. We therefore designed and fabricated a new reaction cell capable of measuring ir spectra of adsorbed species under photoirradiation. We have examined its performance characteristics with respect to propylene(C_3H_6)-NO_2-ZnO reaction system, since it has been shown that ZnO catalyzed the formation of hydrogen cyanide, aldehydes, carbon dioxide and alkyl nitrates for this reaction system.[2)]

A high-purity powdered ZnO(Kadox-25, New Jersey Zinc Co.) was used, the BET surface area of which was determined as 8.3 $m^2 g^{-1}$. About 0.1 g of ZnO powder was pressed into a disk (20 mm diameter) at 600 kg cm^{-2}(1 kg cm^{-2}=9.807 x10^4 Pa). As shown in Fig. 1, the disk of ZnO was hung with a glass sample holder which formed an angle of 45 degree with respect to both the ir and uv light beam axes, and it was moved vertically in the ir cell (the ir pathlength of 10 cm) with a platinum wire. The cell was equipped with CaF_2 and optically flat quartz windows for ir and uv beams, respectively. The sample was preheated at 400 °C for one day under oxygen atmosphere, followed by evacuation for several hours. The adsorption of NO_2 was carried out at room temperature under the gas pressure of ca. 5 mmHg and the gas phase NO_2 was evacuated after the equilibrium was attained. The spectra of surface species on ZnO was measured at room temperature with a JASCO model IRA-3 infrared spectrophotometer under photoirradiation (Ushio Electric Inc., model USH-500 D superhigh-pressure mercury lamp, wavelength: 300-740 nm).

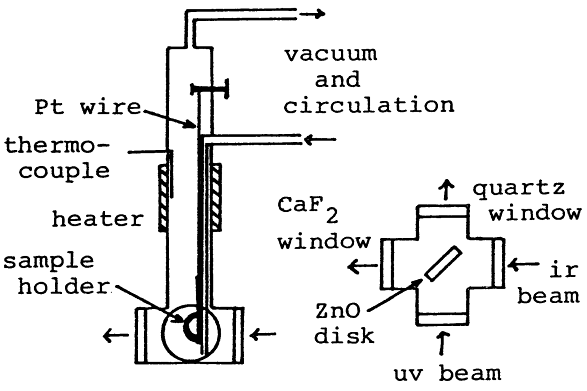

Fig. 1. Schematic diagram of the apparatus for measurement of ir spectra of surface species on ZnO under photoirradiation

Infrared spectra of ZnO only (A) and C_3H_6-ZnO (B) are shown in Fig. 2 to reveal the baseline. Very small broad peaks at near 1650 and 1480 cm^{-1} were observed in the

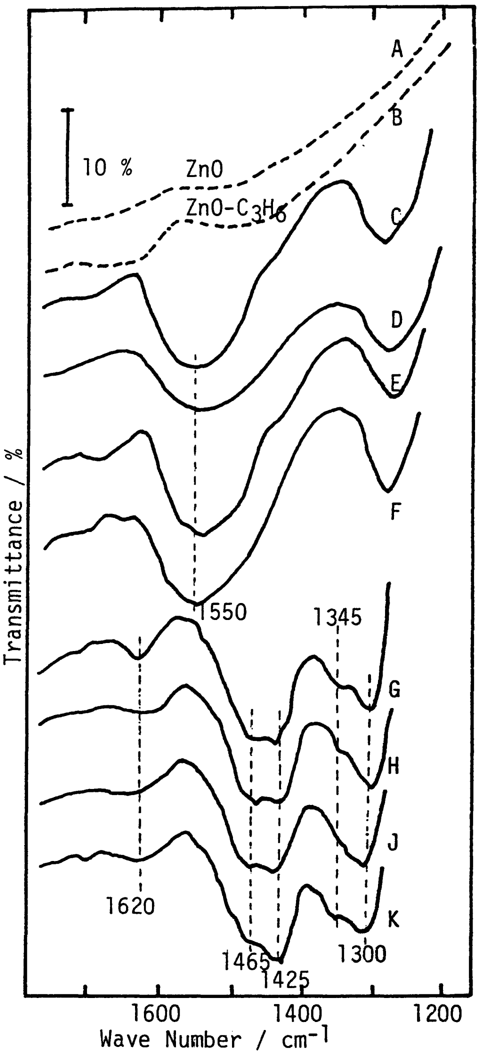

Fig. 2. Ir spectra of NO_2-C_3H_6-ZnO under dark(A,B,C,E,F & K) and photoirradiation(D,G,H & J)

FREQUENCIES OF ADSORBED NO_2 ON METAL OXIDES[3)]

STRUCTURE	Freq./CM^{-1}
$M\genfrac{}{}{0pt}{}{\diagup O \diagdown}{\diagdown O \diagup}N=O$ (I) bidentate nitrato	1500-1565 1290
$M-O-N\genfrac{}{}{0pt}{}{\diagup O}{\diagdown O}$ (II) monodentate nitrato	1490 ± 10 1280
M-O-N=O (III) nitrito	1465 ± 10
$M-N\genfrac{}{}{0pt}{}{\diagup O}{\diagdown O}$ (IV) nitro	1410 ± 10 1340 ± 10

spectrum(B). The spectra of adsorbed NO_2 on ZnO were measured under dark (C) and photoirradiated (D) conditions, respectively. The intensity of the observed two bands at 1550 and 1280 cm^{-1} decreased during photoirradiation, but was restored by stop of irradiation as shown in (E). Then about 5 mmHg of C_3H_6 was introduced to the cell and the total pressure of the reaction system was set at 1 atm by using helium. The circulation of the system may have been helpful in keeping the temperature of the ZnO disk constant under photoirradiation. Little effect of C_3H_6 introduction on ir spectra was observed from the comparison of (E) and (F). The spectrum of (G) measured during irradiation (12 min) seemed very different from the spectra of (C),(E) and (F). The band near 1550 cm^{-1} completely disappeared, while a small peak at 1620 cm^{-1}, a broad band having two peaks at 1465 and 1425 cm^{-1} and a broad band with a shoulder at 1345 cm^{-1} appeared. A longer irradiation resulted in a sight decrease in intensity of the peak at 1620 cm^{-1} (H: 38 min and J: 94 min). The stop of irradiation induced a very small change in intensity and shape of the ir spectrum as shown in (K).

By comparison to the Table where the ir bands concerning the surface species of NO_2 on metal oxides are summarized,[3)] the bands at 1550 and 1280 cm^{-1} can be reasonably assigned to the mixture of the bidentate nitrato(I) and the monodentate nitrato(II). The peaks at 1465 and 1425 cm^{-1} and a shoulder at 1345 cm^{-1} are considered as due to the species of (III) and (IV), respectively. The peak at 1620 cm^{-1} may be assigned to adsorbed water formed during reaction, since a broad band at 3450 cm^{-1} also appeared after irradiation. From the gas phase analysis by an FID gas chromatograph, trace quantities of acetaldehyde and acrolein have been detected.

In summary it is implied that 1) the photoirradiation of NO_2-ZnO induces the desorption of NO_2 from ZnO on account of photoexcitation of ZnO and/or NO_2 adsorbed, 2) the change in the adsorbed species from (I) and (II) to (III) and (IV) with irradiation for NO_2-C_3H_6-ZnO ascribes to the release of oxygen from (I) and (II) with assistance of C_3H_6, 3) C_3H_6 is partly converted to the aldehydes.

The authors acknowledge Dr. J.Take, University of Tokyo for his helpful suggestion about the design of the ir cell.

References: 1) P.Pichat et al., J. Phys. Chem., 83, 3122 (1979); S.oshida et al., Chem. Comm., (1981) 601; and the literatures cited therein. 2) T.Ibusuki, Chem. Letters, (1979), 913; K.Takeuchi et al., submitted for publication. 3) G. Blyholder et al., J. Phys. Chem., 70, 352 (1966).

(Received February 6, 1982)