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HETEROGENEOUS PHOTOCATALYTIC OXIDATION OF NO_2^- IN AQUEOUS SUSPENSION OF VARIOUS SEMICONDUCTOR POWDERS

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NO_2^- ion was shown to be oxidized to NO_3^- with or without O_2 under illumination in aqueous suspension of some semiconductor powders. Photoactive substances were Ag_2O, PbO, TiO_2(anatase), Si, ZnO, SnO_2, CdS, and Bi_2O_3. The reaction proceeded with band gap illumination of semiconductors.

Acid rain water contains nitric acid as well as sulfuric acid. The concentration of NO_3^- in rain water prevails over that of NO_2^-. Nitric acid may result from the gaseous oxidation of nitrogen oxides in the atmospheric air as discussed by Calvert and Stockwell.1) But NO_2^-, most probably stemming from dissolution of NO and NO_2 into water, may possibly be oxidized to NO_3^- in water droplets in the atmosphere. The rate of oxidation of NO_2^- by O_2 is very low without any catalyst at ambient temperature.

Heterogeneous photocatalytic reaction has been studied by numerous workers with particular emphasis on utilization of solar energy. Several papers reported photocatalytic reactions of air pollutants.2-9) However, heterogeneous photocatalytic reaction of nitrogen oxide species in aqueous media has not yet been published except the photocatalytic reduction of NO by Yoneyama et al.3) Airborne particulate substance, as is well known, contains semiconductor metal oxides. Thus, the photocatalytic process is interesting in cennection with oxidation of NO_2^- in water. This preliminary communication reports the oxidation of NO_2^- in water under illumination with various metal compounds.

Typical experiments consisted of illuminating 40 cm^3 of $NaNO_2$ aqueous solution (ca. 25 x 10^{-6} mol dm^{-3}) in a quartz tube (25 mm outer diameter) containing ca. 0.05 g of catalyst powder kept in suspension supersonically. The flow gas was bubbled (50 cm^3 min^{-1}) through the solution at 1 atm. The tube was positioned 9.5 cm apart from a 150 W xenon lamp. NO_2^- in the solution was determined by NEDA colorimetric analysis. The analysis of NO_3^- was conducted after decomposition of NO_2^- with sulfamic acid. NO_3^- was then reduced to NO_2^- by a cadmium-copper column, and analyzed by NEDA method.

Catalysts employed were reagent grade powder chemicals as presented below. The surface areas of some catalysts are indicated therewith. Ag_2O (Kanto Kagaku, 0.7 m^2 g^{-1}), Co_3O_4 (Merck, 34 m^2 g^{-1}), CuO (Kanto Kagaku, 0.7 m^2 g^{-1}), MnO_2 (Merck, 3.9 m^2 g^{-1}), NiO (Kanto Kagaku, 13 m^2 g^{-1}), PbO (Kanto Kagaku, 0.5 m^2 g^{-1}), PbO_2

(Kanto Kagaku, 0.6 $m^2\ g^{-1}$), TiO_2 anatase (Kanto Kagaku, 111 $m^2\ g^{-1}$), ZnO (Kanto Kagaku, 4.0 $m^2\ g^{-1}$), Cu_2O (Kanto Kagaku), Al_2O_3 (Junsei Kagaku), CdS, CuS, MoS_2, WO_3, SnO_2, SnO, TiO_2(rutile), Bi_2O_3, MoO_3 (Wako Junyaku), Si (99.99%, -300 mesh, Furuuchi Kagaku), SiC (99.5%, -300 mesh, Furuuchi Kagaku). All the catalyst powders were washed twice in doubly distilled water supersonically. The catalysts were centrifugally separated from aqueous suspensions. The flow gas was a mixture of N_2 and O_2 (1:1); N_2 was purified with an activated copper column and a silica-gel column; O_2 with a silica-gel column. The water was doubly distilled after deionization.

The fraction oxidized was defined as the increase of NO_3^- during the reaction time divided by the initial amount of NO_2^-. The fraction oxidized was below 0.03 under illumination for 1 h in the presence of the following substances; TiO_2 (rutile), Cu_2O, CuO, MoS_2, WO_3, MnO_2, Al_2O_3, NiO, Co_3O_4, and SiC.

Table 1 presents the fraction oxidized for active catalysts under irradiation for 1 h. NO_2^- decreased and NO_3^- increased during the reaction time. The sum of NO_2^- and NO_3^- agreed well within the experimental error before and after the reaction. pH values, approximately 6, remained constant within $\pm$ 0.5 during the reaction. Hence, we concluded that the principal reaction was oxidation of NO_2^- to NO_3^-. The active substances are divided into four groups as described below. (1) PbO and Ag_2O showed an appreciable photochemical activity under illumination with or without oxygen. They were not active in the dark. Analysis by atomic absorption revealed that Pb^{2+} and Ag^+ was dissolved into the solution after the reaction. (2) TiO_2 (anatase), ZnO, Si, and SnO_2 exhibited photocatalytic activity in the oxidation of NO_2^- by O_2. The fraction oxidized increased with time. The time course and its detailed features will be discussed eleswhere. The catalytic activity virtually disappeared when O_2 was not supplied to the aqueous suspension. (3) Bi_2O_3 and CdS are the intermediate between the two groups described above. These substances appreciably oxidized NO_2^- with oxygen under illumination. They still exhibited photocatalytic activity to a certain extent even in the absence of oxygen. The fraction oxidized increased with time. These substances were inactive in the dark. (4) PbO_2 and MoO_3 oxidized NO_2^- with or without oxygen and illumination. These substances appear to work simply as oxidants.

TiO_2(anatase), ZnO, CdS, and Bi_2O_3 showed little or no photocatalytic activity, when cut-off filters were placed in the beam to eliminate radiation of wave length shorter than the respective band gap energies (410, 410, 520, 480 nm). Hence, the reactions were obviously initiated by the electron-hole formation in semiconductors by illumination.

TiO_2, ZnO, Si, and SnO_2 allow NO_2^- to be photochemically oxidized in the presence of O_2. O_2 will react in the following two mechanisms. If the oxidation of NO_2^- proceeds in an electrochemical local cell mechanism, O_2 will scavenge electrons from the conduction band of the semiconductors; O_2 will simply be reduced to OH^- or H_2O (cathodic process). NO_2^- will in turn be oxidized by positive holes from the valence band in a reaction such as

$$NO_2^- + 2p^+ + H_2O \longrightarrow NO_3^- + 2H^+ \text{ (anodic process).}$$

Table 1. Oxidized fraction of NO_2^- to NO_3^- for 1 h.

	Band gap energy eV	Illuminated			Dark	Illuminated through cut-off filters
		with O_2	without O_2	with Cu^{2+}	with O_2	with O_2
Ag_2O		0.18	0.19	0.79	0.02	
PbO	2.8	0.30	0.25	0.00	0.01	
TiO_2(anatase)	3.2	0.96[a)]	0.02	0.04	0.01	0.01
ZnO	3.2	0.50[a)]	0.02	0.28	0.04	0.03
Si	1.1	0.12	0.02	0.03	0.00	
SnO_2	3.8	0.04	0.02	0.02	0.00	
CdS	2.5	0.28	0.17	0.02	0.01	0.01
Bi_2O_3	2.6	0.45	0.13	0.07	0.03	0.04
PbO_2		0.17	0.14		0.22	
MoO_3		0.17	0.18		0.14	

a) The reaction time 30 min.

If this is the case, anodic and cathodic processes proceed separately. NO_2^- will be oxidized to NO_3^- without O_2.

Alternatively, oxygen is known to be photoadsorbed on semiconductor surfaces as O_2^- and converted to $HO_2\cdot$ or HO_2^-. Several workers suggested that these intermediate species derived from O_2 are involved with various photocatalytic reactions.[4,10,11] These oxygen containing species have been confirmed by ESR in aqueous suspension systems.[12,13] These species would oxidize NO_2^- to NO_3^- in the present aqueous suspensions.

Cu^{2+} was added as an electron scavenger to aqueous suspensions(52×10^{-6} mol dm^{-3}) under purified N_2 atmosphere. The oxidation of NO_2^- took place in ZnO suspension, as presented in Table 1. Thus, the electrochemical local cell mechanism is likely to proceed in ZnO suspension to a great extent. However, Cu^{2+} does not appear to act as an electron scavenger in TiO_2(anatase), Si, and SnO_2 suspensions. The other mechanism via intermediate oxygen containing species will proceed in TiO_2(anatase), Si, and SnO_2 systems, although the details of the mechanism are not yet clarified.

The photochemical activity of Ag_2O was enhanced in the presence of Cu^{2+}, whereas that of PbO disappeared. The activity of CdS and Bi_2O_3 also dropped with Cu^{2+} in the aqueous suspensions. The electrochemical local cell mechanism will substantially proceed in Ag_2O suspension and partially in Bi_2O_3 suspension. The detailed reaction mechanisms for the individual catalyst powders are now under investigation in this laboratory.

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