Photocatalytic reduction of nitrite and nitrate ions over TiO$_2$ semiconductors

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Photocatalysis has recently gained attention in the field of pollutant degradation [1–4]. Among the various semiconductors employed, anatase phase of TiO$_2$ appears to be a promising photocatalyst [5, 6]. TiO$_2$ has become a benchmark semiconductor, showing the best compromise between catalytic performance and stability at any pH value of aqueous dispersion.

It has been reported that for the same photoreaction, the preparation of TiO$_2$ and its thermal treatment significantly affect the activity of the semiconductors. Indeed, preparation parameters influence the photoactivity since the physico-chemical features are determined by the catalyst's origin and preparation.

The sol–gel method provides a convenient method for the preparation of several inorganic oxides with tailored physical and chemical properties. We report here the synthesis and photocatalytic performance of TiO$_2$ prepared by a sol–gel method and compare its activity with a commercial sample of TiO$_2$ (J. T. Baker, USA).

TiO$_2$ gels were prepared by the acid catalysed sol–gel method. The sol was prepared by mixing Ti(IV) isopropoxide with anhydrous 2-propanol, H$_2$O and HNO$_3$ at ambient temperature with stirring. A series of gels with varying ratio of alcohol, water content and different molar ratio between titanium (IV) isopropoxide and acid was prepared. The gels were dried at 383 K for 12 h. Crystallization to anatase was achieved in air by heating at 823 K for 24 h.

Titanium hydroxide was precipitated by reacting an aqueous solution of TiCl$_4$ with an aqueous ammonia solution (25 wt%). This was done by adding the latter drop-wise to the metal solution at room temperature, with vigorous stirring owing to the exothermicity of the reaction. After standing for 24 h at room temperature, the solid was filtered and repeatedly washed with double distilled water until free of chloride ions. The resulting solid was dried at 393 K for 24 h and then fired in air at 823 K for 24 h.

X-ray diffractograms were obtained for the powdered samples using a Philips diffractometer (Philips Generator, Holland; Model PW 1130) provided with an online recorder and dot-matrix printer (Tele type, USA). The diffraction patterns were recorded at room temperature using Ni-filtered CuK$_\alpha$ radiation ($\lambda = 0.154\,18$ nm) for all samples. A

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scanning speed of 3 deg/min and a chart speed of 5 mm/deg were generally employed. Line broadening was performed in accordance with the procedure suggested by Klug and Alexander [8] using the Scherrer formula $t = 0.89\,\lambda/\beta\cos\theta_B$.

A Hitachi spectrophotometer (Model 150-20) equipped with an integrating sphere was used to record the diffuse reflectance spectra of the samples. The base line correction was done using a calibrated sample of barium sulphate. The spectra were recorded at room temperature in air in the range 350–900 nm. The same spectrophotometer was used for recording the UV absorption spectra of solutions.

FT-IR absorption spectra of the samples were recorded using a Bruker FT-IR spectrometer (Model IFS 66v) at room temperature in the range 4000–400 cm^{-1}. The powdered samples were ground with KBr and pressed into pellets (5 ton/cm^2) for recording the spectra.

TG-DSC experiments of some of the catalysts were carried out in a Perkin-Elmer (TGA-DSC-7) instrument in the temperature range 322–873 K for TG studies and 323-773 K for DSC studies, under air. A flow rate of 20 ml/min and a heating rate of 20 °C/min was usually employed for all samples.

The surface area of the samples were measured by N$_2$ adsorption at 77 K using the dynamic BET method [10] using a Carlo Erba (Model 1800) sorptometer. The samples were outgassed in an evacuation chamber to a pressure of 10^{-3} atm at 393 K prior to adsorption.

The photocatalytic experiments were performed in an all-glass static system at ambient temperature and atmospheric pressure. In all the experiments, 100 mg of the freshly prepared catalyst and 20 ml of the appropriate solution (sodium nitrite and sodium nitrate of appropriate concentration for nitrite and nitrate reduction) was taken in a double walled cylindrical pyrex glass reactor. The reactor was equipped with water circulation in the outer jacket in order to maintain a constant temperature as well as for infrared filtering. The reaction mixture was stirred by a magnetic stirrer at a constant speed during illumination. The suspension was irradiated using a 450 W Xe lamp (Oriel corporation, USA). Argon gas was purged when nitrite (nitrate) solutions were illuminated. Before starting the illumination, the reaction mixture was stirred for half an hour in the dark. After irradiation the solution was centrifuged to remove essentially all the catalyst and the centrifugate was analysed for ammonia.

The extent of equilibrium adsorption of nitrite was evaluated from ΔC, the decrease in nitrite concentration in 20 ml aliquots of solution after equilibration under magnetic stirring for 4 h with 100 mg of the semiconductor. Longer tests under similar conditions confirmed that the equilibrium extent of adsorption was closely approached by 4 h equilibration. In order to express extents of adsorption in normalized form n_2^s, the number of moles of nitrite adsorbed per gram of catalyst, was calculated from $n_2^s = (\Delta C \cdot V)/10^3\ W$ where ΔC is the decrease in nitrite concentration, V is the volume of the solution and W is the weight of the catalyst.

Ammonia was estimated by indophenol method [10] and nitrite by modified Griess method [11].

The TiO_2 gels were prepared by an acid catalysed sol–gel method described earlier and designated as G-1, G-2 and G-3, respectively. A series of gels with varying molar ratio between titanium (IV) isopropoxide, nitric acid and different alcohol and water contents were prepared. The composition of the gels are shown in Table I.

From the values given in Table I it is clear that, in general, shorter gelation time is needed when a smaller water/Ti ratio is used. The gel process is acid catalysed and hence the rate of hydrolysis of metal alkoxide should increase with increase in acid content, but this has no direct effect on the gelation time as observed in Table I.

The BET surface area and the particle size calculated are given in Table II.

X-ray diffraction patterns of the three catalysts prepared shows only TiO_2 anatase phase. Fig. 1a shows the X-ray pattern of catalyst G-1. However G-3, shows an additional reflection (20% intense) with $d = 0.324\ 50$ nm, which can be attributed to TiO_2 rutile phase.

Differential scanning calorimetric studies showed an endotherm centred at 470 K for all the sol–gel derived catalysts.

The IR spectrum of sol–gel derived TiO_2 (G-2) recorded in the transmission mode on a Kbr pellet is shown in Fig. 2. In all three catalysts an asymmetric broad absorption is centred around 3450 ± 15 cm^{-1}, which is due to O–H stretching due to the presence of both hydroxyl groups of anatase TiO_2 and adsorbed water. The latter leads to adsorption at 1598 ± 2 cm^{-1} in all samples, while the bending of Ti–OH groups could give rise to the band observed around 1355 cm^{-1} in all samples. The typical strong absorption of Ti–O bonds in the range 400–700 cm^{-1} is observed for all samples.

TiO_2 was also prepared using another precursor, namely $TiCl_4$ (designated as home prepared 'HP') as described earlier. X-ray analysis revealed the forma-

TABLE II Surface area and particle size of TiO_2 prepared by the sol–gel method

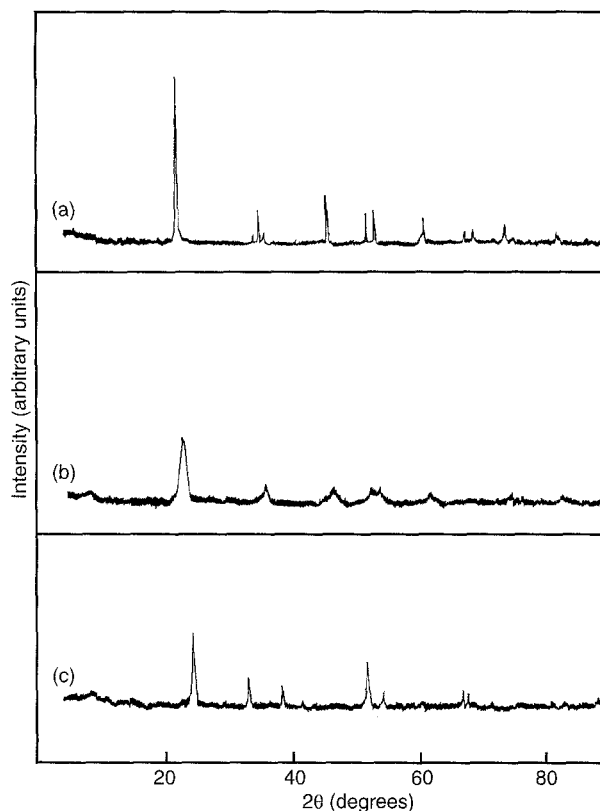| Gel	Surface area (m^2/g)	Particle size (nm)
G-1	28.6	21.2
G-2	23.7	25.7
G-3	31.2	19.0

Figure 1 X-ray diffraction patterns of TiO_2 catalysts prepared by (a) sol–gel derived catalysts; (b) hydrolysis of $TiCl_4$; (c) commercial sample (J. T. Baker, USA).
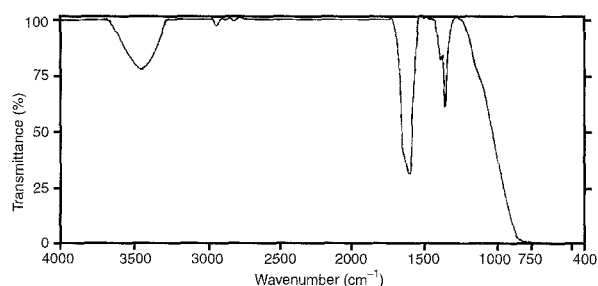

Figure 2 IR spectrum of sol–gel derived TiO_2 catalyst (G-2).

tion of anatase phase only, as shown in Fig. 1b. The IR spectrum showed an asymmetric broad absorption centred at 3422 cm^{-1} due to O–H stretching, attributed to both the presence of hydroxyl groups of anatase TiO_2 and adsorbed water. The latter leads

TABLE I Reactant compositions used, gelation time and features of the gels prepared

Gel	Temp (K)	H$_2$O/Ti	ROH/Ti	Ti:HNO$_3$	Gelation time (days)
G-1	308	25	41	0.61	2.5
G-2	308	8	20	0.40	2
G-3	333	6	38	0.16	1

R = 2-propanol

to absorption at 1633 cm^{-1}, while the bending of Ti–OH groups gives rise to two small bands at around 1397 and 1331 cm^{-1}. In addition, typical strong absorption of Ti–O bonds in the range 400–700 cm^{-1} is also observed. The specific surface area was found to be 84.4 m^2/g and the particle size around 9.5 nm.

Thermogravimetric analysis indicated the presence of two weight losses centred at 383 K and 463 K, both associated with endothermic processes.

The commercial sample (J. T. Baker) designated as (C) employed in the present study consists of anatase phase only with a specific surface area of 13.5 m^2/g (particle size 36.9 nm). The X-ray diffraction pattern is shown in Fig. 1c. The IR spectrum of this catalyst showed similar features to those exhibited by TiO$_2$ catalysts prepared in the present study.

The results obtained from the diffuse reflectance spectra are given in Table III. The onset of absorption was shifted marginally for all the TiO$_2$ prepared catalysts. However, the absorbance of the TiO$_2$ catalysts was found to be much lower in magnitude than for the commercial TiO$_2$ sample.

The equilibrium adsorption of nitrite was studied. It was observed that the amount of nitrite adsorbed increased with increase in concentration of nitrite, up to 10 ppm, and then remained constant. Thus, the adsorption of nitrite follows a Langmuir model. The data on the amount of nitrite adsorbed on TiO$_2$ catalysts are given in Table IV. It is clear from the data that adsorption of nitrite is higher on TiO$_2$ prepared by the sol–gel process when compared to the commercial sample.

The present authors have observed that the photocatalytic reduction of nitrite and nitrate ions to ammonia is dependent on various experimental parameters such as irradiation time, concentration of substrate, pH, precursor employed for preparation etc. The photocatalytic reduction of nitrite and nitrate ions was evaluated over TiO$_2$ catalysts and

TABLE III Diffuse reflectance spectra results for TiO$_2$ catalysts

Catalyst	Onset of absorption (nm)
G-1[a]	398
G-2[a]	402
G-3[a]	402
HP[b]	415
C[c]	391

[a]TiO$_2$ prepared by sol–gel process
[b]Home prepared TiO$_2$ (hydrolysis of TiCl$_4$)
[c]Commercial sample TiO$_2$ (J. T. Baker)

TABLE IV Equilibrium dark adsorption of nitrite on TiO$_2$ catalysts

Catalyst	Amount of nitrite adsorbed (μmol/g)
G-1[a]	12.0
G-2[a]	9.1
G-3[a]	4.5
C[b]	1.4

[a]TiO$_2$ prepared by sol–gel process
[b]Commercial sample TiO$_2$ (J. T. Baker)

TABLE V Photocatalytic reduction of nitrite and nitrate ions to ammonia on TiO$_2$ catalysts

Catalyst	Yield of ammonia (μmol)	
	$NO_2^- \rightarrow NH_3$	$NO_3^- \rightarrow NH_3$
G-1[a]	6.47	0.59
G-2[a]	2.49	0.81
G-3[a]	0.53	4.73
HP[b]	0.57	0.19
C[c]	N.D.	N.D.

N.D. not detected
[a]TiO$_2$ prepared by sol–gel process
[b]Home prepared TiO$_2$ (hydrolysis of TiCl$_4$)
[c]Commercial sample TiO$_2$ (J. T. Baker)
Reaction conditions: 20 ml of 10 ppm nitrite (nitrate), 2 h irradiation, 50 mg catalyst.

the results are given in Table V. From the values given in Table V it is clear that the sol–gel derived TiO$_2$ exhibits higher activity compared to other TiO$_2$ catalysts. It is reported in the literature [15–17] that with unsupported photocatalyst, the kinetics are limited by adsorption of the substrate, while for supported photocatalyst the kinetics are diffusion-limited. Thus, the sol–gel derived TiO$_2$ catalysts exhibit higher photocatalytic activity because of the greater adsorption of the substrates. The lower activity exhibited by home prepared catalyst (HP catalyst) may be attributed to the presence of chloride ions which is known [18] to decrease the activity.

Light absorption capacity is an important parameter which determines the activity of any photocatalyst. However, from the diffuse reflectance spectral studies one can conclude that other factors such as electron–hole recombination and acid–base properties of the surface affect the photocatalytic performance of TiO$_2$ catalyst to a greater extent. This study has also demonstrated that the adsorption properties of the semiconductor towards nitrite and nitrate determine the ultimate activity of the photocatalyst.

A sol–gel method can be successfully used for the preparation of TiO$_2$ (anatase) semiconductor photoactive for the degradation of nitrite and nitrate ions.

The adsorption property of the semiconductor determines the ultimate activity of the photocatalyst.

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