

Photocatalytic Synthesis of Urea from *in situ* Generated Ammonia and Carbon Dioxide

Basavaraju Srinivas¹, Valluri Durga Kumari¹, Gullapelli Sadanandam¹, Chilumula Hymavathi¹, Machiraju Subrahmanyam¹ and Bhudev Ranjan De²

¹Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad, India

²Department of Chemistry and Chemical Technology, Vidyasagar University, Midnapur, West Bengal, India

Received 13 July 2011, accepted 6 November 2011, DOI: 10.1111/j.1751-1097.2011.01037.x

ABSTRACT

TiO₂ and Fe-titanate (different wt%) supported on zeolite were prepared by sol-gel and solid-state dispersion methods. The photocatalysts prepared were characterized by X-ray diffraction, scanning electron microscopy and ultraviolet (UV)–visible diffuse reflectance spectroscopy techniques. Photocatalytic reduction of nitrate in water and isopropanol/oxalic acid as hole scavengers are investigated in a batch reactor under UV illumination. The yield of urea increased notably when the catalysts were supported on zeolite. The Fe-titanate supported catalyst promotes the charge separation that contributes to an increase in selective formation of urea. The product formation is because of the high adsorption of *in situ* generated CO₂ and NH₃ over shape-selective property of the zeolite in the composite photocatalyst. The maximum yield of urea is found to be 18 ppm while 1% isopropanol containing solution over 10 wt% Fe-titanate/HZSM-5 photocatalyst was used.

INTRODUCTION

The major industrial source of nitrate and nitrite ions are in steel mill, fertilizer and explosives plants, mines, paper mills and food production. They are the common pollutants in water and remediation by photocatalytic mineralization using semiconductors is one of the possible methods (1–15). However, instead of mineralization, transforming into useful chemicals is a challenging task. In the present work, transformations of NO₃⁻, CO₂ and H₂O into urea using photocatalysis technique is explored.

Industrial production of ammonia is mainly based on the Haber process, which involves the heterogeneous reaction of nitrogen and hydrogen on an iron-based catalyst at high pressure (150–300 atm) and temperature (400°–500°C). The equilibrium conversion of hydrogen and nitrogen gas into ammonia in the process is only in the order of 10–15%. Such low conversion efficiencies in large-scale chemical plants warrant costly operating conditions required to commercially produce hundreds to thousands of tons per day of ammonia. Urea is commercially produced via the reaction of carbon dioxide and ammonia at high pressure (100–200 atm) and

temperature (180°–185°C) to form ammonium carbamate, which is dehydrated subsequently into urea and water.



Therefore, it is of high basic science interest to develop a simplified method for the production of nitrogen containing fertilizers, especially at a small to middle scale of operation. A single-step process that can convert CO₂, N₂ and H₂ sources to nitrogen fertilizers at decreased pressure and/or temperature has the potential for development. The report of Shibata *et al.* (16) is worth mentioning here where urea was synthesized by electrochemical reduction of CO₂ in the presence of NO₂⁻ using a Cu-loaded gas diffusion electrode. Furthermore, the photocatalytic synthesis process reported in the literature allows urea formation under room temperature and pressure (17–19). The photo-induced conversion of CO₂ and NO₃⁻ to urea was attempted under many permutations and combinations of photocatalysts and solvents. Here, we have investigated the photocatalytic reduction of CO₂ from CO₂-purged gas, or *in situ*-generated CO₂ through mineralization of isopropyl alcohol/oxalic acid in the presence of TiO₂-based semiconductor-supported zeolite systems in aqueous medium at room temperature under normal pressure conditions.

MATERIALS AND METHODS

Materials. TiO₂ P-25 (anatase-80%, rutile-20%, surface area 50 m² g⁻¹ and particle size 27 nm) from Degussa Corporation, Germany; Fe(NO₃)₂ is procured from Loba Chemie Pvt. Ltd., India. Titanium isopropoxide was from Fluka. Acetonitrile used was HPLC grade from Rankem, India. Zeolites are procured from SUD-CHIEMIE, India.

Techniques. 1 About 2, 5, 10 and 15 wt% of TiO₂ were loaded on HZSM-5 by solid-state dispersion method. Required amount of TiO₂ (P-25) was added to HZSM-5 (Si/Al = 30) powder and thoroughly mixed in a mortar and pestle. Minimum amount of ethanol was added to it and mixed thoroughly. The sample was evaporated to dryness at 110°C and calcined at 500°C for 5 h at the rate of 2°C min⁻¹.

2 Fe₂TiO₅ and Fe₂Ti₂O₇ were prepared by sol-gel method. Ferric nitrate and titanium-isopropoxide (Fe/Ti = 2:1 and 1:1) were dissolved in required quantity of isopropanol with constant stirring and dilute HNO₃ was added to form a sol and fine gel was obtained in two-and-a-half days. The gel thus obtained was dried at 110°C and calcined at 600–700°C for 5 h at the rate of 2°C min⁻¹. The surface ratio of Fe/Ti was estimated by scanning electron microscopy (SEM)-energy dispersive X-ray spectroscopy (EDAX) technique and the overall composition (bulk) was estimated by atomic absorption spectroscopy (AAS) technique.

*Corresponding author email: durgakumari@iict.res.in (Valluri Durga Kumari)
© 2011 Wiley Periodicals, Inc.
Photochemistry and Photobiology © 2011 The American Society of Photobiology 0031-8655/12

3 Fe₂TiO₅ and Fe₂Ti₂O₇/HZSM-5 were prepared by solid-state dispersion method. About 5, 10 and 15 wt% of Fe₂TiO₅ and Fe₂Ti₂O₇ systems were added to HZSM-5 (Si/Al = 30) powder and thoroughly mixed in a mortar and pestle. Minimum amount of ethanol was added and mixed thoroughly. The sample was evaporated at 110°C and calcined at 500°C for 5 h at the rate of 2°C min⁻¹.

Characterization. The X-ray diffraction (XRD) patterns of the TiO₂, Fe₂TiO₅ and Fe₂Ti₂O₇ and their respective samples loaded on HZSM-5 catalysts were recorded with Siemens D-5000 XRD using Ni-filtered Cu K α radiation ($\lambda = 1.5409 \text{ \AA}$) and 2θ range between 2° and 60°. The ultraviolet-visible (UV-Vis) diffuse reflectance spectra (DRS) were recorded on a GBC UV-Visible Cintra 10_e spectrometer in the wavelength range of 200–800 nm. The SEM analyses of the catalysts were performed on Hitachi S-520 SEM unit. Elemental analysis was carried out using Link, ISIS-300, Oxford, EDAX detector.

Analysis. Photocatalytic reactions were carried out in a closed and deaerated condition in a quartz reactor (250 mL capacity) under UV irradiation. The reaction was performed by taking known amount of KNO₃ as nitrogen source in 225 mL water containing 3 g L⁻¹ catalyst suspensions. The progress of the reaction was monitored by high-pressure liquid chromatography with Zorbax Rx-SIL column, UV-VIS detector, mobile phase (acetonitrile:water in the ratio 9:1), flow rate = 1 mL min⁻¹. HPLC (high pressure liquid chromatography) analysis was carried out for the analysis of NO₂⁻, NO₂⁻ ions present during the course of reaction using ion conductivity detector IC-A1 and with (Shim-pack) HPLC column, 2.5 mm phthalic acid (pH = 4.7) as mobile phase, flow rate = 1 mL min⁻¹. Urea was also detected by enzymatic method (blood urea nitrogen; BUN) using diagnostic kits. Ammonia liberated was cross-checked with indophenol blue; a popular method for the analysis of ammonia and the determination of NO₂⁻ was performed by diazotization method.

All the reactions were carried out at the original pH of the solution. Samples were collected at periodic intervals, filtered through millipore membrane filters and centrifuged to remove the catalyst particles. Control experiments were performed in the absence of respective catalysts and it revealed that no conversion to nitrate was observed.

RESULTS AND DISCUSSION

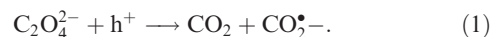
In the case of bulk semiconductor particles of high stability, such as TiO₂, several kinds of reduction products of carbon dioxide including formate and formaldehyde are obtained in aqueous solutions in the absence of hole scavenger. However, the amounts of the products are very small. To improve the yields, various scavengers were used along with photocatalysts to minimize the electron-hole recombination process (6). The present investigation was carried out with isopropanol/oxalic acid as a hole scavenger and also to act as a CO₂ source whereas the NO₃⁻ ion was used as the nitrogen source.

To begin with, all the experiments are carried out on bare TiO₂ and the results obtained are depicted in Table 1. From the data in Table 1, it is clearly seen that when no scavenger was used, the reduction of nitrate was minimal as the oxidation of water and hence it was difficult to generate hydrogen radicals that will be subsequently utilized in nitrate reduction. Therefore,

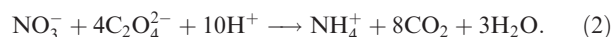
very low conversions of nitrate were observed with no scavenger. Moreover, the absence of carbon source was lacking in the electrolyte, consequently no urea formation was observed.

NO₃⁻ and oxalic acid in urea synthesis

In the case of oxalic acid as hole scavenger, the oxalate anion is oxidized by holes (h⁺) to produce two moles of carbon dioxide (CO₂) as expressed in Eq. (1).



The generated CO₂ dissolves in water and produces carbonic acid which will dissociate and release protons in the solution. The protons thus generated undergo reduction at the conduction band of TiO₂. In the present investigation, the formation of ammonia is attributed to the following steps. The NO₃⁻ ion adsorbed over the surface of TiO₂ is reduced by eight photogenerated electrons (e⁻) to give NH₃. In the overall reaction, one NO₃⁻ ion reacts with four oxalate anions to yield NH₃ and eight CO₂ molecules as shown in Eq. (2).



When TiO₂ bare was used as a photocatalyst, conversion of NO₃⁻ to traces of NO₂⁻ and 0.8 ppm of NH₃ was observed in pure water. When oxalic acid was used as a hole scavenger, about 2.0 ppm of ammonia generation was noted. It seemed that the reduction of NO₃⁻ was an indirect reaction path and probably initiated by the oxidation of oxalate ions to the species CO₂ and CO₂^{*-} at the expense of photogenerated holes. In the presence of oxalic acid, NO₃⁻ reduction follows as expressed in Eq. (2).

It is well established that CO₂^{*-} species are very active and have stronger reduction ability as E^0 of (CO₂/CO₂^{*-}) = -1.8 V as compared with NO₃⁻ and NO₂⁻ ions whose E^0 (NO₃⁻/NH₄⁺) = 1.203 V and E^0 of (NO₂⁻/NH₄⁺) = 0.897 V, respectively, for the formation of ammonia (4). The reaction was aimed and expected to utilize the *in situ*-generated ammonia for the formation of urea. When oxalic acid was used as hole scavenger, there was the possibility of formation of ammonium oxalate in a parallel reaction which was observed and confirmed by the mass spectral analysis. This might be expected during the course of NO₃⁻ reduction to ammonia. The ammonia formed reacts with oxalic acid and it may retard the rate of urea formation. To avoid the formation of unwanted ammonium oxalate under the set of experimental conditions, further experiments were conducted with propan-2-ol as hole scavenger and also as a source for CO₂.

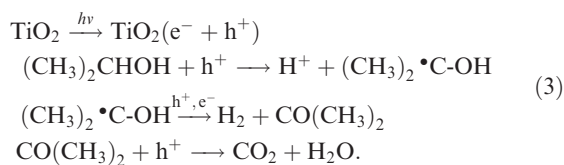
Table 1. Influence of hole scavenger on nitrate reduction for urea formation over TiO₂ catalyst.

S. no.	Scavenger	Percentage conversion of nitrate	Product distribution (ppm)		
			Nitrite	Ammonia	Urea
1	Oxalic acid	80	–	2.0	10.75
2	Isopropanol	60	–	2.5	12.2
3	–	5	Trace	0.8	–

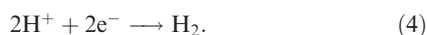
Reaction conditions: catalyst = 3 g L⁻¹, nitrogen source = KNO₃ (1.6 × 10⁻³ M), pH = original, batch capacity = 100 mL, illumination source = high-pressure Hg vapor lamp (Phillips 250 W), time = 6 h, pressure = 1 atmosphere, temperature = 40°C, CO₂ source = 1% oxalic acid (w/v), isopropanol (v/v) in water (s. nos. 1 and 2).

NO₃⁻ and propan-2-ol in urea synthesis

It is known that the recombination of photoexcited electron-hole pairs is the main energy wastage step of photocatalytic reaction. To inhibit the recombination, the reaction is conducted with different scavengers such as methanol, ethanol and isopropanol. It is reported that CH₃OH and (CH₃)₂CHOH are known to act as the best hole-capturing agents to accelerate various photocatalytic reactions. The holes in the valence band (h⁺_{vb}) are captured by isopropanol to yield (CH₃)₂•C-OH radicals and these further react with electron and holes generated releasing hydrogen and a ketone. The ketone thus formed undergoes further oxidation to carbon dioxide and water as shown in Eq. (3).



α-hydroxyl radicals are generated during the process of isopropanol oxidation with holes of TiO₂. These radicals have strong reducing power and can inject another electron into the conduction band of TiO₂ (as depicted in Scheme 1). This additional electron subsequently utilized to improve the rate of proton reduction as expressed in equation 4 (6).



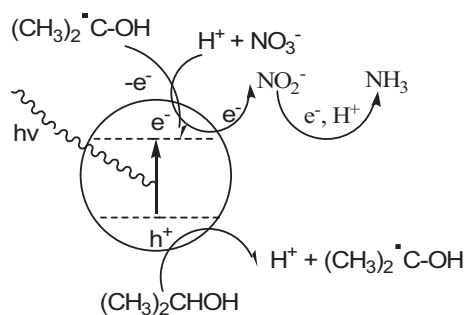
It is assumed that *in situ*-generated carbon dioxide and ammonia react to form ammonium carbamate, which on dehydration forms urea as shown in Eq. (5).



The course of the reduction reaction of nitrate and formation of ammonia over bare TiO₂ is illustrated in Fig. 1a,b. From the reported experiments, the optimized required concentration of the hole scavenger is arrived at and further experiments are conducted with the same.

Influence of TiO₂-zeolite on urea formation

Zeolites are widely used as desiccant and sorbent. Nevertheless, they are often used as catalysts possibly because of their



Scheme 1. Ammonia formation.

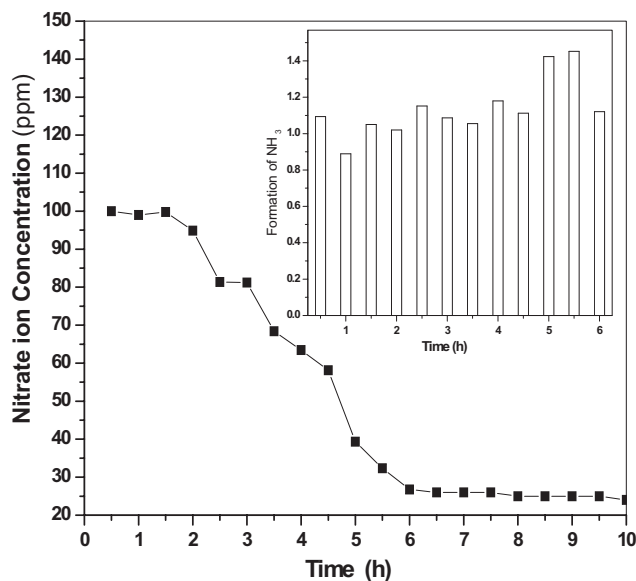


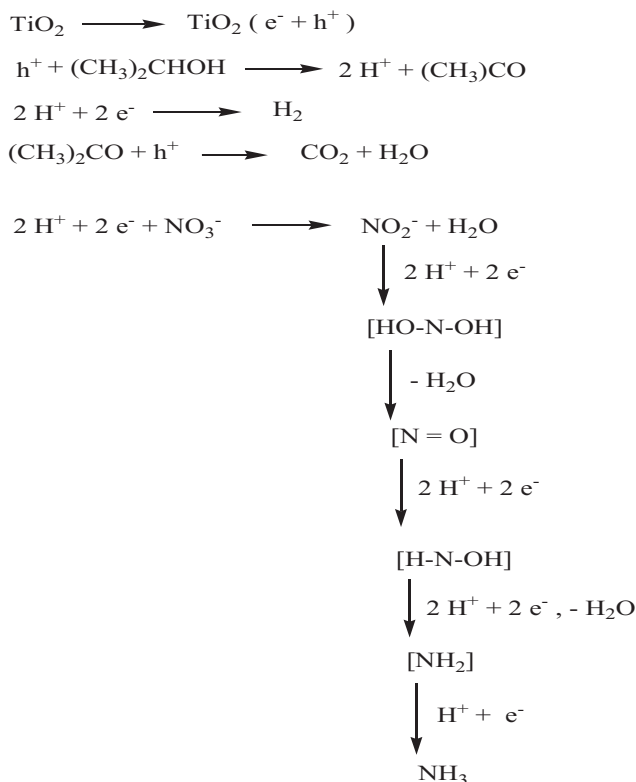
Figure 1. Photo catalytic nitrate reduction and (inset) ammonia formation with time over bare TiO₂ catalyst. Reaction conditions: catalyst = 3 g L⁻¹, nitrogen source = KNO₃ (1.6 × 10⁻³ M), pH = original, batch capacity = 100 mL, illumination source = high-pressure Hg vapor lamp (Phillips 250 W), time = 6 h, pressure = 1 atmosphere, temperature = 40°C. CO₂ sources = 1% oxalic acid (w/v) and isopropanol (v/v) in water (s. nos. 1 and 2).

thermal stability and resistance to acids and bases is fairly good. Zeolite can be used as support material for the semiconductors. TiO₂ supported on zeolite for various cyclization reactions, mineralization studies and also CO₂ reduction reaction was reported earlier from our group (20–24). In the present investigation, to improve the adsorption of nitrate and to prevent the oxidation of ammonia, which was formed during nitrate reduction, the immobilization of TiO₂ on zeolite was envisaged and a speculative mechanism is proposed (Scheme 2).

Different TiO₂ (wt%) supported on HZSM-5 zeolite are prepared by the solid-state dispersion method (25–27). The XRD patterns of the samples are shown in Fig. 2. The characteristic 101, 200 planes of TiO₂ anatase and 110 of rutile are identified from the XRD results. The reduction of nitrate is carried out in the presence of isopropanol as the hole scavenger. The results obtained are shown in Table 2.

SEM photographs of different TiO₂ (wt%) supported on HZSM-5 catalysts (prepared by solid-state dispersion) are provided in Fig. 3. It is observed that HZSM-5 morphology is not changed, wherein preformed TiO₂ was dispersed on the zeolite support.

It is seen clearly from the results that formation of nitrite and ammonia are very evident. Although the conversion of nitrate is less on TiO₂-supported zeolites compared with bare TiO₂, it is a noteworthy observation of stable ammonia being formed in the reaction and not undergoing oxidation. Further oxidation of ammonia is prevented; probably ammonia formed is adsorbed over the zeolite. The *in situ*-generated ammonia and CO₂ adsorbed are on the TiO₂-supported zeolite and further condensation reaction on the surface led to the formation of urea. The difference in the photocatalytic activity of bare titania and different TiO₂ (wt%) loaded on zeolite



Scheme 2. Schematic representation and stabilization of intermediate species during nitrate reduction and prevention of ammonia oxidation over TiO₂-zeolite.

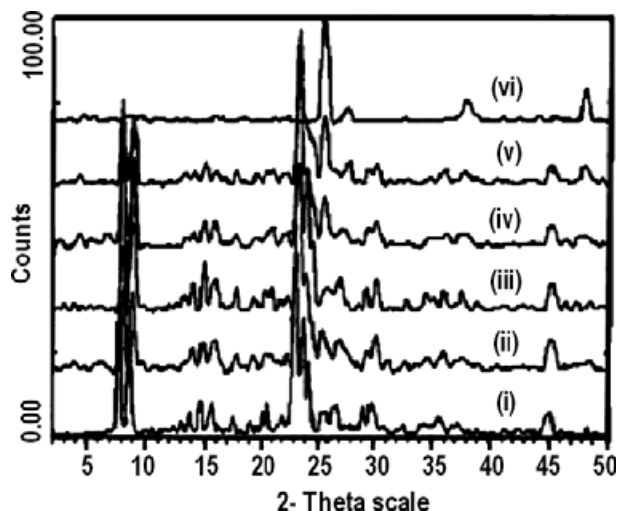


Figure 2. X-ray diffraction spectra of: (i) HZSM-5, TiO₂ (ii) 2 wt%, (iii) 5 wt%, (iv) 10 wt%, (v) 15 wt% supported over HZSM-5 and (vi) TiO₂.

catalysts may be attributed to the following reasons. It is known that the loading of TiO₂ on zeolite brings blue shift in the absorption thereby showing better photocatalytic activity than bare titania catalyst. This may be owing to the shift toward more energetic UV region. It is evident from the DRS spectra that TiO₂ loading resulted in a decrease in absorption and a blue shift in the absorption edge of the titania (Fig. 4).

Table 2. Effect of TiO₂-zeolite for urea formation.

S. no.	TiO ₂ (Wt %)	Percentage conversion of nitrate	Product distribution (ppm)		
			Nitrite	Ammonia	Urea
1	5	25	4.7	3.61	4
2	10	22	6.3	1.88	6
3	15	10	3.9	0.8	3

Reaction conditions: catalyst = 3 g L⁻¹, N₂ source = KNO₃ (1.6 × 10⁻³ M), CO₂ source = 1% (vol.) isopropanol, pH = original, batch capacity = 100 mL, illumination source = high-pressure Hg vapor lamp (Phillips 250 W), time = 6 h, pressure = 1 atmosphere, temperature = 40°C.

However, the higher loadings of TiO₂ over zeolite samples have shown decreasing trends in photocatalytic activity, as they show more red shifts in the absorption edge as seen from Fig. 4. It might be owing to the fact that the excess loading improves the electron-hole recombination centers resulting in lowering of the activity. Therefore, the photocatalytic activity is achieved by the dispersion of TiO₂ on zeolite to a certain extent. The high activity of the TiO₂ (10 wt%) supported over zeolite sample can be ascribed to the high dispersion of TiO₂ on the surface, strong adsorption of substrates and also because of lower recombination of electron-hole pairs generated.

The DRS of TiO₂/HZSM-5 photocatalysts are shown in Fig. 4. These spectra are examined to understand the size quantization effect and the TiO₂ interaction with the zeolite. The position of the absorption edge for anatase form of TiO₂ around 380 nm corresponds to band gap energy of 3.2 eV. A blue shift of about 40–50 nm at low loadings of TiO₂ was observed and the shift decreased with increasing TiO₂ loading.

Fe-titanates

In view of the aforesaid observations, it is inferred that bare TiO₂ shows better activity than when supported over zeolite. To improve the activity of TiO₂ further, iron titanates were made using sol-gel technique. The prepared catalysts are tested under similar conditions as with TiO₂. The reduction of nitrate was performed using isopropanol, which played a dual role: (1) as a hole scavenger and (2) in releasing CO₂ by undergoing oxidation. Thus, *in situ* formed ammonia and carbon dioxide react under illuminated conditions in the presence of photocatalyst to form an unstable C–N linkage and subsequent reaction with protons forms an amide. At this stage, there are two further courses of the reaction for the formation of urea: (1) oxidation to an amino acid and reaction with ammonia and subsequent dehydration; (2) amide undergoes hydroxylation by hydroxyl radical and amination leads to the formation of carbamate and subsequent dehydration to urea as shown in Scheme 3. All the catalyst systems are prepared by sol-gel method with varying iron to titanium ratios. These systems are supported on zeolites and their activities are evaluated under UV irradiation.

Fe₂TiO₅ prepared by sol-gel method was reported as an anode for photoelectrolysis of water and the quantum efficiency was 15% at 350 nm (28). The characteristics of Fe₂TiO₅ are identified from the XRD results (JCPDS 76-1158). This

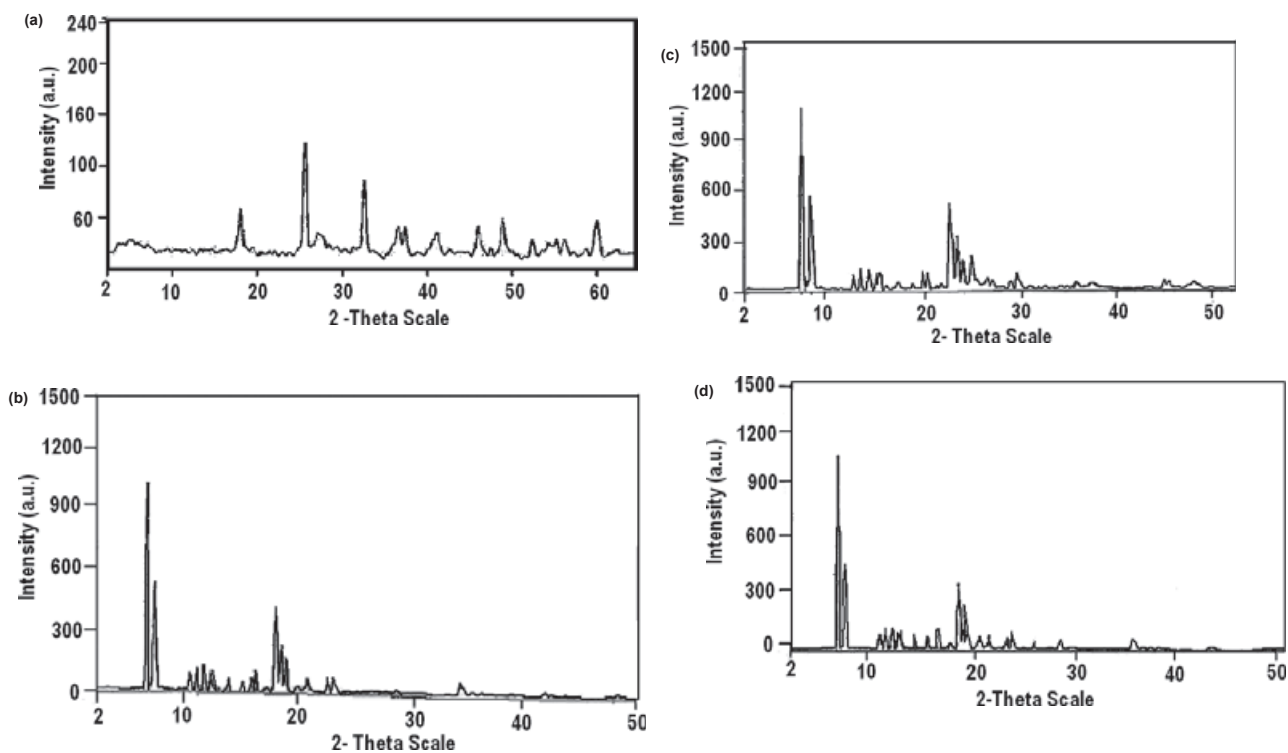


Figure 5. (a) X-ray diffraction spectra of: (a) Fe_2TiO_5 , (b) HZSM-5, (c) 5 wt% $\text{Fe}_2\text{TiO}_5/\text{HZSM-5}$ and (d) 10 wt% $\text{Fe}_2\text{TiO}_5/\text{HZSM-5}$.

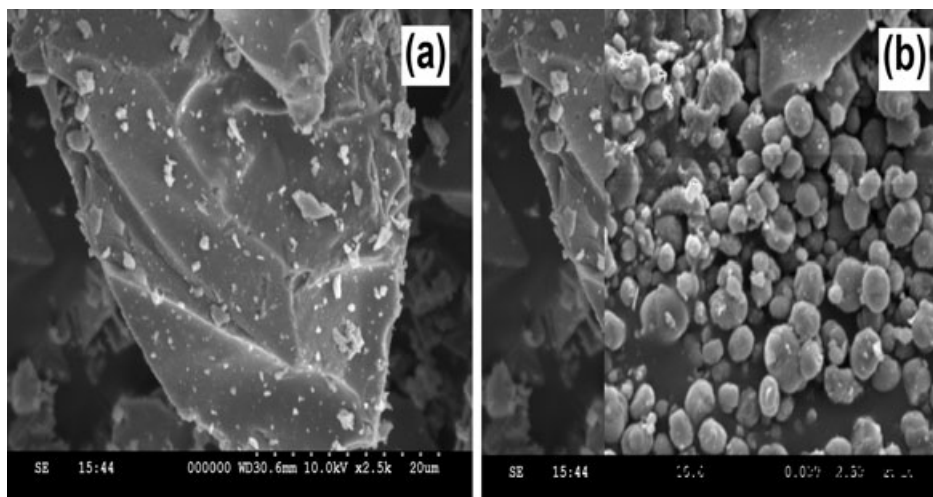


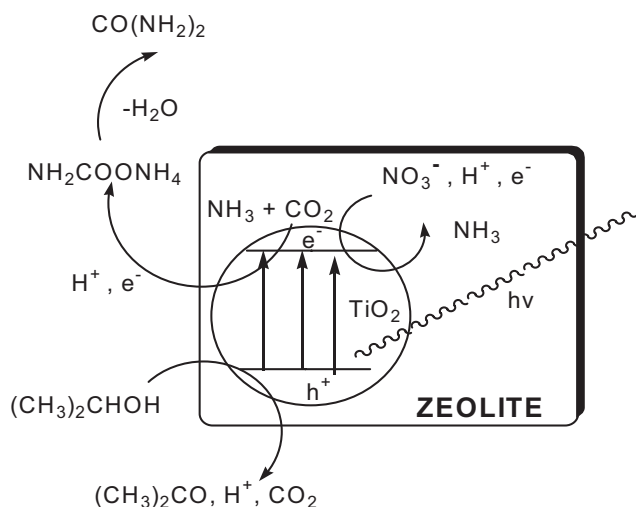
Figure 6. Scanning electron micrographic photographs of: (a) Fe_2TiO_5 and (b) 10 wt% $\text{Fe}_2\text{TiO}_5/\text{HZSM-5}$.

It is clear from the data that on bare Fe-titanates maximum conversion of nitrate observed was 35%. Furthermore, when the formation of urea content is taken into account, $\text{Fe}/\text{Ti} = 1:1$ shows better activity than $\text{Fe}/\text{Ti} = 2:1$. Fe-titanates show comparatively better activity than bare TiO_2 . However, the yield of urea was not appreciable. This may be attributed to the generated ammonia in the reaction undergoing further oxidation. In view of this, it is suggested to suppress the oxidation of ammonia with the modification of the catalyst. Thus, the reactions are performed with Fe-titanates supported over zeolites.

XRD patterns of bare Fe_2TiO_5 , HZSM-5 and 5 and 10 wt% Fe_2TiO_5 supported over HZSM-5, are shown in Fig. 5a–d.

Supported Fe-titanates

Keeping in view the aforesaid observations from the activity of TiO_2 for the formation of urea, the optimum loading of the TiO_2 on zeolite was 10 wt%. Furthermore, taking into account the observations made, Fe_2TiO_5 or $\text{Fe}_2\text{Ti}_2\text{O}_7$ (10 wt%) supported on HZSM-5 were investigated for the formation of urea during reduction of nitrate with isopropanol as hole scavenger. The SEM photographs of Fe_2TiO_5 and 10 wt% Fe_2TiO_5



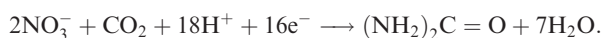
Scheme 4. Schematic representation of urea formation over TiO_2 supported on zeolite photo catalyst under ultraviolet illumination.

Table 4. Effect of Fe:Ti ratio on the formation of urea.

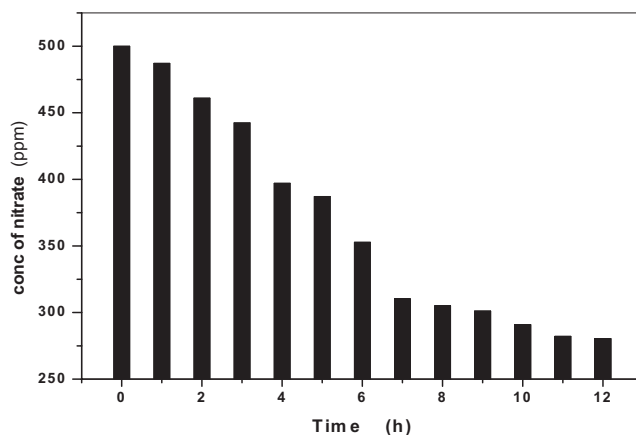
S. no.	Catalyst	Percentage conversion of nitrate	Product distribution (ppm)		
			Nitrite	Ammonia	Urea
1	10 wt% $\text{Fe}_2\text{TiO}_5/\text{HZSM-5}$	90	10	2.6	18.77
2	10 wt% $\text{Fe}_2\text{TiO}_5/\text{HZSM-5}$	88	9	1.5	9.26
3	10 wt% $\text{Fe}_2\text{Ti}_2\text{O}_7/\text{HZSM-5}$	30	1.2	0.2	7.0

Reaction conditions: catalyst = 3 g L^{-1} , N_2 source = KNO_3 ($1.6 \times 10^{-3} \text{ M}$), CO_2 source = 1% (vol.) isopropanol, pH = original, batch capacity = 100 mL, illumination source = high-pressure Hg vapor lamp (Phillips 250 W), time = 6 h, pressure = 1 atmosphere, temperature = 40°C ; hole scavenger: serial nos. 1, 3 = isopropanol; serial no. 2 = oxalic acid.

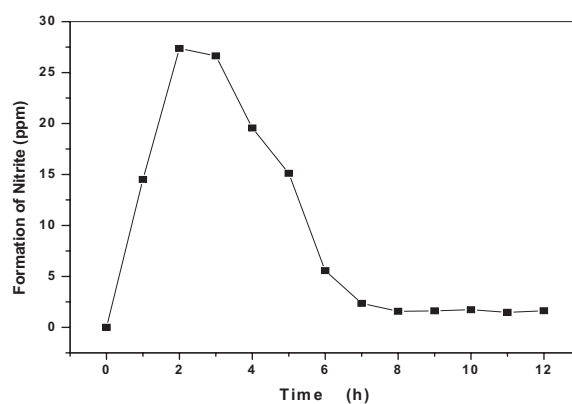
$\text{TiO}_5/\text{HZSM-5}$ are shown in Fig. 6 and the zeolite was found to play a dual role in the adsorption of both the reactants and products (Scheme 4) by virtue of uniform regular pore geometry of zeolites. The ammonia and urea (as evidenced from authentic sample and mass spectral analysis) formed in the reaction do not undergo further polymerization. The polymerization and condensation products of urea were observed under the experimental study whereas when the reaction was performed on bare TiO_2 , the urea yields are found to be decreased (evidenced from high pressure liquid chromatography analysis). The condensation of products was reduced on Fe-titanates supported on zeolites, which may be because of the virtue of shape-selectivity property of the zeolite. The results obtained are depicted in Table 4. The overall reaction is as follows:



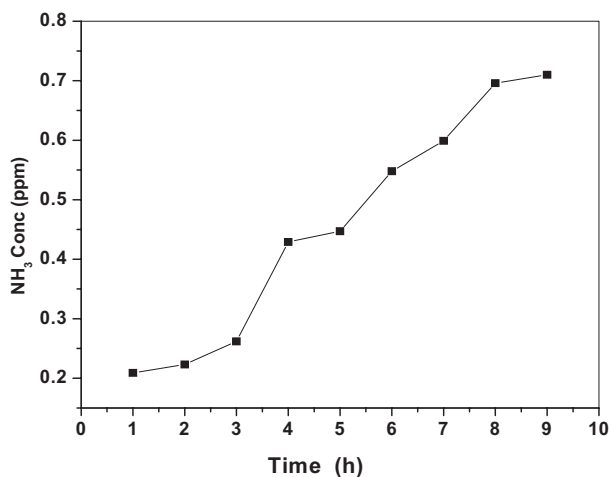
The optimized parameter of initial feasibility of the reaction at lab scale was scaled-up to five-fold. During the course of the reaction, nitrate reduction is depicted in Fig. 7a and the formation of nitrite over period of time is illustrated in Fig. 7b. The formation of ammonia is seen in Fig. 7c with time on



(a)



(b)



(c)

Figure 7. Scale-up experiment. (a) Nitrate reduction over time variable; (b) formation of nitrite over time variable; (c) NH_3 formation with time on illumination. Reaction conditions: catalyst = 3 g L^{-1} , N_2 source = KNO_3 ($8.3 \times 10^{-3} \text{ M}$), CO_2 source = 5% (vol.) isopropanol, pH = original, batch capacity = 500 mL, illumination source = high-pressure Hg vapor lamp (Phillips 250 W), time = 12 h, pressure = 1 atmosphere, temperature = 40°C .

stream. The maximum conversion of nitrate achieved was 90% and the urea yields are $\sim 18\%$ in scale-up experiments as shown in Table 5.

Table 5. The trend in formation of urea with time in a five-fold scale-up experiment.

S. no.	Time (h)	Urea (ppm)
1	0	–
2	1	5.2
3	2	9.41
4	3	3.85
5	4	18.92
6	5	1.92
8	8	3.0
10	10	3.5

Reaction conditions: catalyst = 3 g L⁻¹, N₂ source = KNO₃ (8.3 × 10⁻³ M), CO₂ source = 5% (vol.) isopropanol, pH = original, batch capacity = 500 mL, illumination source = high-pressure Hg vapor lamp (Phillips 250 W), time = 12 h, pressure = 1 atmosphere, temperature = 40°C.

CONCLUSIONS

Urea was synthesized using TiO₂ (P25) and Fe-titanate supported over zeolite photocatalysts under atmospheric pressure and ambient temperature in a batch reactor. The reactions are performed in aqueous medium containing NO₃⁻ ion and 2-propanol (acts as hole scavenger and source for CO₂) under UV light illumination. It is investigated that an optimum of TiO₂ or Fe-titanate (10 wt%) supported over zeolite is required to achieve 90% reduction of nitrate to ammonia. The photoactive component and zeolite combine to inhibit polymerization of the product and facilitates the condensation to form urea. A maximum of 18 ppm of urea was obtained at 90% conversion of nitrate. The reaction conducted under solar illumination was found to have lower rates of urea formation. The optimized parameter of initial feasibility of the reaction at lab scale was scaled-up to five-fold with a greater success by achieving the urea production in milder reaction conditions compared with the existing conditions for urea formation.

Acknowledgements—The authors thank MCF New Delhi for the project grant and MS thanks CSIR Emeritus Scientist Scheme.

REFERENCES

- Hamanoi, O. and A. Kudo (2002) Reduction of nitrate and nitrite ions over Ni-ZnS photocatalyst under visible light irradiation in the presence of a sacrificial reagent. *Chem. Lett.* **8**, 838–839.
- Tawkaew, S., S. Yin and T. Sato (2001) Photo reduction of nitrate ion and photo evolution of hydrogen on unsupported TiO₂ and TiO₂ pillared H₄Nb₆O₁₇ nano composites. *Int. J. Inorg. Mater.* **3**, 855–859.
- Mori, T., J. Suzuki, K. Fujimoto, M. Watanabe and Y. Hasegawa (1999) Reductive decomposition of nitrate ion to nitrogen in water on a unique hollandite photo catalyst. *Appl. Catal. B: Env.* **23**, 283–289.
- Li, Y. and F. Wasgestian (1998) Photo catalytic reduction of nitrate ions on TiO₂ by oxalic acid. *J. Photochem. Photobiol. A: Chem.* **112**, 255–259.
- Jin, R., W. Gao, J. Chen, H. Zeng, F. Zhang, Z. Liu and N. Guan (2004) Photocatalytic reduction of nitrate ion in drinking water by using metal-loaded MgTiO₃-TiO₂ composite semiconductor catalyst. *J. Photochem. Photobiol. A: Chem.* **162**, 585–590.
- Yamagata, S., S. Nakabayashi, K. M. Sancier and A. Fujishima (1998) Photo catalytic oxidation of alcohols on TiO₂. *Bull. Chem. Soc. Jpn.* **61**, 3429–3434.
- Liu, F. and H. He (2010) Structure–activity relationship of iron titanate catalysts in the selective catalytic reduction of NO_x with NH₃. *J. Phys. Chem. C*, **114**, 16929–16936.
- Constantinou, C. L., C. N. Costa and A. M. Efstathiou (2010) Catalytic removal of nitrates from waters. *Catal. Today* **151**, 190–194.
- Kominami, H., A. Furusho, S. Murakami, H. Inoue, Y. Kera and B. Ohtani (2001) Effective photocatalytic reduction of nitrate to ammonia in an aqueous suspension of metal-loaded titanium (IV) oxide particles in the presence of oxalic acid. *Catal. Lett.* **76**, 31–33.
- Gao, W., R. Jin, J. Chen, X. Guan, H. Zeng, F. Zhang and N. Guan (2004) Titania-supported bimetallic catalysts for photocatalytic reduction of nitrate. *Catal. Today* **90**, 331–336.
- Gao, W., J. Chen, X. Guan, R. Jin, F. Zhang and N. Guan (2004) Catalytic reduction of nitrite ions in drinking water over Pd-Cu/TiO₂ bimetallic catalyst. *Catal. Today* **93–95**, 333–339.
- Sa, J., T. Berger, K. Föttinger, A. Riss, J. A. Anderson and H. Vinek (2005) Can TiO₂ promote the reduction of nitrates in water? *J. Catal.* **234**, 282–291.
- Ranjit, K. T. and B. Viswanathan (1997) Photocatalytic reduction of nitrite and nitrate ions over doped TiO₂ catalysts. *J. Photochem. Photobiol. A: Chem.* **107**, 215–220.
- Ranjit, K. T. and B. Viswanathan (1997) Photocatalytic reduction of nitrite and nitrate ions to ammonia on M/TiO₂ catalysts. *J. Photochem. Photobiol. A: Chem.* **108**, 73–78.
- Ranjit, K. T., B. Viswanathan and T. K. Varadarajan (1996) Photo catalytic reduction of nitrite and nitrate ions over TiO₂ semiconductors. *J. Mater. Sci. Lett.* **15**, 874–877.
- Shibata, M., K. Yoshida and N. Furuya (1995) Electrochemical synthesis of urea on reduction of carbon dioxide with nitrate and nitrite ions using Cu-loaded gas-diffusion electrode. *J. Electroanal. Chem.* **387**, 143–145.
- Shchukin, D. G. and H. Mohwald (2005) Urea photosynthesis inside polyelectrolyte capsules: Effect of confined media. *Langmuir* **21**, 5582–5587.
- Kuwabata, S., H. Yamauchi and H. Yoneyama (1998) Urea photosynthesis from inorganic carbon and nitrogen compounds using TiO₂ as photo catalyst. *Langmuir* **14**, 1899–1904.
- Ustinovich, E. A., D. G. Shchukin and D. V. Sviridov (2005) Heterogeneous photocatalysis in titania-stabilized per fluorocarbon-in-water emulsions: Urea photosynthesis and chloroform photo degradation. *J. Photochem. Photobiol. A: Chem.* **175**, 249–252.
- Subba Rao, K. V., B. Srinivas and M. Subrahmanyam (2004) Photocatalytic reactions over semiconductor based zeolites for organic synthesis: A review. In *Photo/Electrochemistry & Photo Biology in the Environment, Energy and Fuel* (Edited by S. Kaneco, B. Viawanathan and K. Funasaka), pp. 31–89. Research Signpost, Trivandrum, Kerala, India.
- Subrahmanyam, M., S. Kaneco and N. A. Vante (1999) A screening for the photo reduction of carbon dioxide supported on metal oxide catalysts for C₁–C₃ selectivity. *Appl. Catal. B* **23**, 169–174.
- Srinivas, B., B. Shubhamangala, K. Lalitha, V. Durga Kumari, M. Subrahmanyam and B. R. De (2011) Photo catalytic reduction of CO₂ over Cu–TiO₂/molecular sieve-5A composite. *Photochem. Photobiol.* **87**, 995–1001.
- Sandhya, P., C. H. Hymavathi, V. Durga Kumari and M. Subrahmanyam (2006) *Photo Catalytic Urea Synthesis from Nitrate, CO₂ and Water*, 8th Asian Academic Network for Environmental Safety and Waste Management (AANESWM). Editors: V. Murugesan, R. Jayabalou, S. Nanjundan and M. Palanichamy, organized by the Department of Chemistry and Centre with Potential for Excellence in Environmental Science, Anna University, Chennai, India, December.
- Sangeetha Kumari, N., P. Saritha, V. Durga Kumari and M. Subrahmanyam (2006) *Photo Reduction of Nitrate Assisted by Photocatalytic Degradation of Organic Waste*. National Workshop on Catalysis for Energy at Banaras Hindu University, Varanasi, February.
- Zhang, S., N. Fujii and Y. Nosaka (1998) The dispersion effect of TiO₂ loaded over ZSM-5 zeolite. *J. Mol. Catal. A: Chem.* **129**, 219–224.

26. Panpa, W., P. Sujaridworakun and S. Jinawath (2008) Photocatalytic activity of TiO₂/ZSM-5 composites in the presence of SO₄²⁻ ion. *Appl. Catal. B: Env.* **80**, 271–276.
27. Durgakumari, V., M. Subrahmanyam, K. V. Subba Rao, A. Ratnamala, M. Noorjahan and K. Tanaka (2002) An easy and efficient use of TiO₂ supported HZSM-5 and TiO₂+HZSM-5 zeolite combinate in the photo degradation of aqueous phenol and *p*-chlorophenol. *Appl. Catal. A: Gen.* **234**, 155–165.
28. Rusina, O., W. Macyk and H. Kisch (2005) Photo electrochemical properties of a dinitrogen-fixing iron titanate thin film. *J. Phys. Chem. B.* **109**, 10858–10862.