PHOTOREDUCTION OF NITRATE IONS OVER Ag/TiO_2 SYSTEM

MIKHAIL SYCHEV[1*], ALEXANDR LOZOVSKI[1],
ROMAN PRIHOD'KO[1], KRZYSZTOF ERDMANN[2],
VLADISLAV GONCHARUK[1]
[1]*Dumanski Institute of Colloid and Water Chemistry, National Academy of Sciences of Ukraine, Vernadski blv. 42, Kiev 03142, Ukraine*
[2]*Faculty of Chemistry, Nicolaus Copernicus University, Gagarin Str. 7, 87-100 Torun, Poland*

Abstract. The Ag/TiO_2 materials synthesised by a pH-controlled photocatalytic process and triblock copolymer-induced reduction of the $[Ag(NH_3)_2]^+$ ions under ambient light illumination appeared to be active and selective catalysts for the photocatalytic reduction of the nitrate ions in water. High efficiency of such Ag/TiO_2 catalysts was attributed to the presence of both the highly dispersed silver nanoclusters on the surface of titania and the hetero-junctions in the TiO_2 support. The influence of the structural features and the phase composition of the titania support on catalytic properties of the Ag/TiO_2 materials is discussed.

Keywords: Photocatalysis, titania, silver, photoreduction, nitrate ions.

1. Introduction

Abundance of nitrate ions in ground water, which is the main source for drinking water, has strongly increased during the last years throughout the world as a result of intensive agricultural activities, mainly due to the overuse of man-made fertilisers. In some regions, the nitrate concentration in the ground water can be as high as 50 mg/l (calculated by the nitrogen weight).[1] Too high concentration of the NO_3^- ions may be fatal to infants in the bodies of whom they are reduced to nitrites that combine with hae-moglobin to form methaemoglobin. This results in methaemo-globinemia, commonly known as "blue baby syndrome". Moreover, the nitrate ions can be converted into nitrosoamine causing hypertension or cancer. Thus, to reduce the nitrate content in water is presently an imperative task.

---

[*] To whom correspondence should be addressed: Dr. M.V. Sychev, Leading researcher of Dumanski Institute of Colloid and Water Chemistry, National Academy of Sciences of Ukraine, Vernadski blv. 42, Kiev Ukraine; e-mail: m.v.sychev@icccw.kiev.ua

P. Innocenzi, Y. L. Zub and V. G. Kessler (eds.), *Sol-Gel Methods for Materials Processing.*

Direct conversion of the nitrate ions into nitrogen via their liquid-phase hydrogenation is an interesting and challenging subject, which is expected to be more economical and to have ecological advantages.

During the last two decades, the photocatalytic water denitrification over metal-loaded semiconductors was also extensively investigated.[1,2] Titania was considered to be the carrier material with a great potential for this purpose, due to its unique optical and electronic properties, chemical stability, and non-toxicity.[1,2] The nature of metal, its loading, and presence in the reacting medium of hole scavengers play a key role in the efficient photo-reduction of the NO_3^- ions. Recently, the Ag/TiO_2 catalysts synthesised by a pH-controlled photocatalytic process[3] were used in the photocatalytic nitrate reduction. It was reported that their performance was better than that of the Pd/Cu-based hydrogenation systems. It was suggested that silver nanoparticles enhanced the photocatalytic activity of TiO_2 while stimulating formation of the Schottky barrier at every Ag/TiO_2 contact surface.[1] Thus, they promote the charge separation and inhibition of the electron-hole pairs recombination, whereas the hole scavengers are essential for the reduction of the target ions.

In this study, we evaluated the significance of both the preparation procedure and the potentially controlling photocatalytic behaviour of the Ag/TiO_2 system towards its performance in the water denitrification. The influence of the structural features and phase composition of a titania support on the catalytic properties of the Ag/TiO_2 materials was investigated as well.

2. Experimental

Nanocrystalline TiO_2 anatase (NTi) has been prepared by the sol-gel method described by Gnanasekar et al.[4] Ordered macroporous titania (OMT) was synthesised, in accordance with the method reported in the literature,[5] by the dropwise addition of the above-mentioned titanium alkoxide to ammonia.

The Ag/TiO_2 catalysts, denoted as AT, were synthesised by a pH-controlled photocatalytic process[3] with $AgNO_3$ as the source of silver, whereas the materials designated as PAT were prepared by reduction of $[Ag(NH_3)_2]^+$ in ethanol, induced by the P123 triblock copolymer ($PEO_{20}PPO_{70}PEO_{20}$).[6,7] All the catalysts were characterised by means of the UV-Vis and IR spectroscopies, transmission electron microscopy (TEM), N_2 adsorption, and X-ray photoelectron spectroscopy (XPS). The photocatalytic reaction was carried out in a double-walled quartz cell cooled with water, using a 125-W high pressure Hg lamp (main wavelength around 365 nm) as a light source. The initial concentration of the nitrate anions was 100 mgN/l (calculated by the nitrogen weight). No treatment was performed to remove the dissolved oxygen. The residual concentrations of the nitrate, nitrite, and ammonium ions in supernatant were determined with the ion-exchange chromatography.

3. Results and Discussions

As reported by Gnanasekar et al.,[4] the TiO_2 sol obtained by hydrolysis of titanium isopropoxide in excess of 2-propanol and subsequently heated in water at 85°C exhibits, indeed, the anatase structure. This points to an important role of the 2-propanol excess in the hindering of an agglomeration process, which promotes the titania sol transformation directly to the nanocrystalline TiO_2 particles affected by the heat treatment of the reacting mixture. The heating of the material obtained in the presence of the 2-propanol excess at 400–410°C could not significantly affect the width of the XRD peaks, which points to the absence of the intense growth of the anatase grains. Similarly to the reported results,[4] our TiO_2 material contains a small fraction of the brookite phase. The BET surface area of the titania precipitate obtained in excess of isopropanol and then dried at 85°C is about 240 m^2/g, being much larger than that of the P-25 titania. As expected, the drop-wise addition of titanium isopropoxide to a 5-wt% ammonia solution leads to formation of the ordered macroporous titania (OMT). This material is arranged by millimetre-sized, irregularly shaped TiO_2 grains that are fragments of larger particles with heterogeneous channel dimensions (5–8 mm, SEM). Under heating, the air-dried precipitates transform to a mixture of crystalline anatase and rutile, with a complete or partial retention of the macroporous architecture. The ratio between those two phases depends on the calcination temperature. The BET surface area of the air-dried precipitates was as high as 350 m^2/g. After calcination, this value decreased to 80–90 m^2/g, most likely due to sintering of the titania particles in the channel walls.[5]

The AT catalysts synthesised by a pH-controlled photocatalytic process contain silver particles with diameter of ca. 2 nm (TEM), homogeneously dispersed on the surface of TiO_2. Based on the binding energy of silver in the XPS spectra (around 367.0 eV), the coated silver on those catalysts is expected to be in the metal state. All these data agree very well with those previously published by Zhang et al.[3] Upon preparation of the PAT catalysts, the reduction of $[Ag(NH_3)_2]^+$ under ambient light in the P123-ethanol solution led to the formation of highly dispersed silver nanoclusters (the average size of ca. 2 nm) on the surface of titania (TEM and HRTEM). Most likely, the surfactant micelles and TiO_2 nanoparticles prevent aggregation of the silver clusters, as suggested by Zhang and Yu.[6] The silver in the silver-coated TiO_2 is of a metallic nature, as evidenced by the presence of the UV-Vis absorption band at 480 nm, attributed to the surface plasmon resonance of metallic silver. However, the atomic ratios of Ag/Ti in the PAT catalysts noticeably differ in relation to the amount of the $[Ag(NH_3)_2]^+$ solution used for their preparation. One of possible reasons for that could be incomplete reduction of the $[Ag(NH_3)_2]^+$ ions during 1-h ambient light illumination.[6]

In order to enable comparison with the literature data,[1] the catalytic experiments were performed using formic acid as the hole scavenger in the amount of 0.04 mol/l. It was found that, when the P-25 titania was utilised as a carrier for silver nanoparticles, the Ag/TiO_2 catalysts prepared by the two applied methods exhibited a similar denitrification efficiency. Hence, further study was conducted while applying the P123 triblock copolymer for inducing the reduction of $[Ag(NH_3)_2]^+$ in ethanol. The dependence of catalytic activity on the silver content in the synthesised catalysts is of a volcano-type shape (Figure 1) that has commonly been detected for a number of photocatalytic systems.

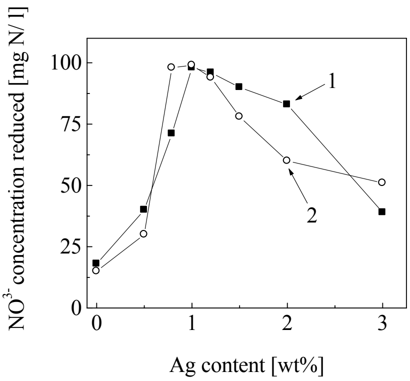

Figure 1. Influence of Ag loading on activity of differently prepared Ag/TiO_2(P-25) catalysts: (1) pH-controlled route, (2) ambient light reduction.

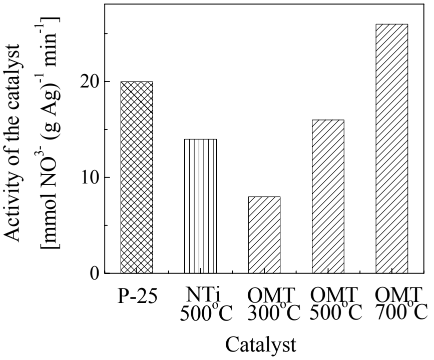

Figure 2. Influence of the TiO_2 origination on photocatalytic activity of Ag/TiO_2 catalysts.

To explain this feature, we have considered some optional hypotheses. It is well known that noble metal clusters can efficiently trap the photoinduced electrons.[1] At the same time, metal coating can reduce the photocatalytic ability due to the decreasing photoinduction efficiency of the semiconductor or because of formation of new recombination centres of photogenerated electrons and holes, when metal particles are too large. In the catalysts containing ca. 1% of silver, dispersion and/or size of coated Ag nanoparticles, most likely, provide in an optimum way prolongation of the lifetime of photogenerated electrons responsible for reduction of the nitrate ions, as manifested by the highest activity of these samples. Preliminary calcination of the NTi titania significantly improves activity of the Ag/TiO_2 catalyst prepared on its basis (Figure 2). Although the anatase structure of this material was already formed at 85°C, such a result indicates importance of the TiO_2 crystallinity, which increased upon heating, in the creation of a phocatalytic function of the Ag/TiO_2 system. The NTi-based catalyst exhibits a significantly larger surface area as compared to that of the P-25 titania; however, it shows somewhat lower activity. One option explaining this finding is that this material contains a noticeable amount of micropores (as reflected in the shape of the N_2 adsorption isotherm) in which transfer of the formic acid molecules and/or nitrate ions to the active sites can be hindered. It cannot be excluded that the presence of the rutile phase in the P-25 titania can also favourably affect the photocatalytic activity of the resulting Ag/TiO_2 catalyst. This suggestion is supported by the results obtained using the catalysts prepared from the ordered macroporous titania, OMT (Figure 2). Under heating, OMT transforms to a mixture of crystalline anatase and rutile, the ratio of which depends on the temperature. Since such TiO_2, pre-calcined at 700°C, contains about 15–19% of the rutile phase (XRD), its photocatalytic behaviour can be compared with that of P-25.

It is interesting that the denitrification activity of the catalysts prepared using OMT pre-calcined at 700°C is higher than that of the materials synthesised from the P-25 titania. This can be attributed to the fact that hetero-junctions, such as anatase/rutile, Ag/anatase, and Ag/rutile, existing in the Ag/TiO2 multiphase, can promote activity of those composite catalysts towards deni-trification. Also the macroporous architecture of the Ag/TiO_2 catalyst based on OMT could provide better mass transfer of the reacting hole scavenger molecules and nitrate ions and, thus, enhancement of the activity of the resulting catalysts. The preparation mode and origin of the titania support do not influence selectivity towards nitrogen formation of all the Ag/TiO_2 catalysts containing ca. 1 wt% of silver. Using the materials prepared from P-25 and OMT, it was possible to achieve the denitrification activity of about 20 and 25-26 mmol NO_3^- (g Ag)$^{-1}$ min^{-1}, respectively, with the selectivity to N_2 of ca. 100% after a 30-min illumination with UV.

4. Conclusions

The Ag/TiO_2 catalysts synthesised by both the pH-controlled photocatalytic process and the triblock copolymer-induced reduction of the $[Ag(NH_3)_2]^+$ ions under ambient light illumination are active and selective catalysts for the photocatalytic reduction of the nitrate ions in water. These differently prepared materials exhibit comparable catalytic behaviour although the same titania support was used. Nevertheless, the latter method is more preferable since it does not require use of the UV irradiation nor an energy-consuming thermal treatment process. The presence of hetero-junctions in the TiO_2 support enhances catalytic activity of the resulting Ag/TiO_2 catalysts. The ordered macroporous titania prepared by the drop-wise addition of titanium isopropoxide to ammonia seems to be a promising material for the synthesis of advanced photocatalysts for reduction of the nitrate ions in a water medium.

References

1. F. Zhang, R. Jin, J. Chen, C. Shao, W. Gao, L. Li, N. Guan, High photocatalytic activity and selectivity for nitrogen in nitrate reduction on Ag/TiO_2 catalyst with fine silver clusters, *J. Catal*. 232, 424–431(2005).
2. W. Gao, R. Jin., X. Guan, H. Zeng, F. Zhang, N. Guan, Titania-supported bimitallic catalysts for photocatalytic reduction of nitrate, *Catal. Today* 90, 331–336 (2004).
3. F. Zhang, N. Guan, Y. Li, X. Zhang, J. Chen, H. Zeng, Control of morphology of silver clusters coated on titanium dioxide during photocatalysis, *Langmuir* 19, 8230–8234 (2003).
4. K.I. Gnanasekar, V. Subramanian, J. Robinson, Direct conversion of TiO_2 sol to nano-crystalline anatase at 85°C, *J. Mater. Res.* 17(6), 1507–1512 (2002).
5. A. Collins, D. Carriazo, S.A. Davis, S. Mann, Spontaneous template-free assembly of ordered macroporous titania, *Chem. Commun.* 568–569 (2004).
6. L. Zhang, J.C. Yu, H.Y. Yip, Q. Li, K.W. Kwong, A.-W. Xu, P.K. Wong, Ambient light reduction strategy to synthesize silver nanoparticles and silver-coated TiO2 with enhanced photocatalytic and bactericidal activities, *Langmuir 19*, 10372–10380 (2003).
7. L. Zhang, J.C. Yu, A simple approach to reactivate silver-coated titanium dioxide photocatalyst, *Catal. Commun.* 6, 684–687 (2005).