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Effect of Doping of Transition Metals Over Titania Based Nanocatalysts on the Degradation of Harmful Insecticides†

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Insecticides, pesticides and herbicides pollute the ground water to the larger extent. Their degradation by conventional methods do not lead to complete mineralization. Photodegradation using semi conductor oxides to remove these pollutants completely from water. TiO_2, $SrTiO_3$, Ni/Ru-TiO_2 and Ni/Ru-$SrTiO_3$ were prepared by sol-gel method and characterized by XRD, UV-DRS and BET surface area measurements. In the photodegradation of two important widely used insecticides such as thiamethoxam and acetamiprid has been studied using bare and metal supported TiO_2 and $SrTiO_3$ photocatalysts. It was observed that doping of transition metals Ni and Ru over TiO_2 and $SrTiO_3$ increased the degradation efficiency. All the catalysts degraded both but to different extents. Among them Ru doped catalysts degraded the insecticides in a very short time when compared to the time taken by other catalysts. Total organic carbon analysis was also carried out to study the extent of mineralization and the results showed that all the catalysts mineralized both the insecticides significantly.

Key Words: Photodegradation, Insecticides, Titania, Doping, Strontium titanate.

INTRODUCTION

The applications of semiconductor heterogeneous photocatalyst in the photodegradation of toxic organic pollutants has been extensively investigated in the past three decades[1-3]. Among the various water pollutants, pesticides, herbicides and insecticides contaminate both underground and surface waters to a larger extent[4,5]. Continuous consumption of this type of water containing these pollutants may cause some genetic disorders to the human[6,7]. Hence there is an urgent need of environmentally benign treatment method. Advanced oxidation processes (AOP) are the best treatment methods to detoxify harmful substances present in water. Among advanced oxidation processes, photocatalytic degradation (PCD) technique over semiconductors has been shown to be one of the most promising processes for the waste water treatment[8-10]. In the photocatalytic process, the photon is absorbed by a semiconductor exciting electron from valence band to conduction band and leaving holes in the valence band. The generation of electron and hole pairs in the photocatalytic reaction initiates the reactions at the active sites. The photocatalytic activities of several semiconductor oxides have been well documented[11,12]. Among them TiO_2 has gained much attention because of its advantages such as non-toxic, inexpensive and more stable than other photocatalyst[13]. Since both titania and strontium titanate have similar band gap of 3.2 eV, number of photocatalytic studies have been carried out using these two catalysts. However the main drawback of TiO_2 and $SrTiO_3$ is the recombination of electron hole pairs thus reducing the photocatalytic efficiency. The recombination of electron hole pairs can be prevented by several methods[14]. Doping of metal and nonmetal over semiconducting photocatalysts has proven to be one of the best methods to improve the photocatalytic efficiency[15-17]. The aim of the present study is to enhance the photodegradation efficiency of titania and strontium titanate catalysts by doping small amounts of transition metals such as nickel and ruthenium over them.

Herein, we report the synthesis of TiO_2, $SrTiO_3$, Ni (or) Ru/TiO_2 and Ni (or) Ru/$SrTiO_3$ catalysts, characterization by XRD, UV-DRS and BET surface area and the catalytic activity towards the degradation of carcinogenic chlorine containing insecticides such as thiamethoxam (TXM) and acetamiprid (ATP) (Fig. 1). Thiamethoxam and acetamiprid come under the group of neonicotinoids which are one of the newer classes

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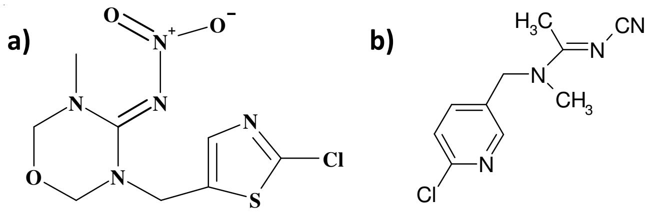

Fig. 1. Structures of (a) thiamethoxam and (b) acetamiprid

of synthetic system insecticides and they are used widely in the agricultural sector. Thiamethoxam is active for the control of aphids, wireworms, thrips and ricehoppers whereas acetamiprid controls sucking type insects on leafy vegetables, fruity vegetables and crops. Because of their wide usage, they are present in larger quantities in the environment. These insecticides are harmful to both aquatic and soil organisms. Hence, the destruction of these type of harmful pollutants through the greener technique is the need of the hour.

EXPERIMENTAL

Isopropanol, acetic acid from Sisco Research Laboratories Pvt. Ltd, India, titanium(IV) iso propoxide from Spectrochem Pvt. Ltd., India, strontium chloride hexa hydrate, citric acid, nickel nitrate from central drug house, Delhi were procured. Ruthenium acetyl acetonate obtained from Aldrich was used as such.

Synthesis of TiO_2 and M/TiO_2 catalysts: TiO_2 powder was prepared by sol-gel process by mixing titanium isopropoxide, isopropanol, water and acetic acid at room temperature. Solution A was prepared by adding 17 mL of titanium isopropoxide to 40 mL of isopropanol. Solution B was prepared by mixing 60 mL of isopropanol, 15 mL of acetic acid and 5 mL of water. Then solution A was mixed to solution B with vigorous stirring for 2 h. After the formation of sol, it was aged and the gel of TiO_2 was formed. TiO_2 powder was obtained after drying, grinding and sintering the gel at 500 ºC for 3 h[18].

For metal doped titania, 10 g of as synthesized TiO_2 catalyst was added to aqueous solution of nickel nitrate, stirred over night, dried and calcined at 500 ºC for 3 h to get 1 % Ni/TiO_2. Similarly Ru/TiO_2 catalysts were prepared by the addition of ruthenium(III) acetyl acetonate solution to 10 g of TiO_2, stirred well, dried and calcined at 400 ºC for 2 h to get 1 % Ru/TiO_2.

Synthesis of $SrTiO_3$ and metal doped $SrTiO_3$ catalysts: 30 mL water was added dropwise to the mixture containing 18.6 mL of titanium iso propoxide and 30 mL of glacial acetic acid till clear solution was obtained. To this mixture 30 mL of water containing stoichiometric quantity of strontium chloride hexa hydrate and Ni/Ru precursors were added. pH was adjusted with 4 M citric acid and the resulting solution was stirred overnight, heated at 65 ºC for 5 h in waterbath, dried at 110 ºC for 12 h and again at 180 ºC for 12 h. The dry mass obtained was ground, calcined at 400 ºC for 12 h and again at 650 ºC for another 12 h to get Ni/Ru/$SrTiO_3$. Without adding the metal precursors, the same procedure was followed for the synthesis of bare $SrTiO_3$[19].

X-ray diffraction patterns were recorded on a Rigaku diffractometer using CuK_α (Lambda = 0.154 nm) radiation in 2θ range of 0.6 to 10º with a step of 0.01º and integration time of 1 s. The UV-VIS diffuse reflectance spectra were taken at room temperature with a JASCO V-650 spectrophotometer in the wavelength range 200-800 nm. The surface area measurements of all the catalysts were carried out using nitrogen as probe molecule at liquid nitrogen temperature (-190 ºC) using BET surface area analyser [Micromeritics Pulse Chemisorb 2700]. Prior to surface area analysis, all samples were degassed at 200 ºC for 2 h using degassing unit [Micrometrics Pulse Desorb 2300 A].

Photodegradation studies: The photocatalytic degradation of thiamethoxam and acetamiprid was carried out using multilamp photoreactor [Heber HMLCOMPACT-SW-LW-44] fitted with 4 nos. of 8-W fluorescent black light. In each experiment, the optimized catalyst weight of 0.1 g (or) 0.05 g of photocatalyst was added to 100 mL of thiamethoxam (3×10^{-4} M) and acetamiprid (2×10^{-4} M) respectively. Before irradiation, the suspensions were aerated in the dark for 0.5 h to ensure the adsorption- desorption equilibrium. 2 mL of the reaction mixture was withdrawn at regular intervals and centrifuged to remove the dispersed photocatalyst particles. The catalyst free samples were analyzed using Shimadzu spectrophotometer [AU 2701- Bluestar UV visible spectrophotometer]. Total organic carbon analyses were carried out for the samples at which it showed maximum degradation using total organic carbon analyser [Shimadzu TOC-5000].

RESULTS AND DISCUSSION

X-Ray diffraction studies: XRD patterns of bare TiO_2, $SrTiO_3$ and their metal doped catalysts are shown in Fig. 2. The major peaks at $2\rho = 25.3$ º and the reflections of (1 0 1), (0 0 4), (2 0 0) and (2 0 4) confirmed the phase formation of titania. Similarly the phase formation of strontium titanate was confirmed by the major peak at $2\rho = 32.6$ º and the reflections of (1 1 0), (2 0 0), (1 1 1), (2 1 1) and (2 2 0)[20]. These XRD patterns clearly show that the crystallinity of parent compound has not been altered due to the doping of Ni and Ru. No observable peaks obtained for the addition of transition metals Ni and Ru in both TiO_2 and $SrTiO_3$ catalysts may be due to the less amount of loading of the metal. The crystallite size was calculated by Scherrer's equation, $D = K\lambda/\beta \cos\theta$ and listed in Table-1 where, β is the full width at half-height, K = 0.89, θ is the diffraction angle and λ is the X-ray wavelength corresponding to the CuK_α radiation.

UV-diffuse reflectance spectroscopic studies: UV-visible diffuse reflectance spectra of bare TiO_2, Ni/Ru-TiO_2, $SrTiO_3$ and Ni/Ru- $SrTiO_3$ are given in Fig. 3. The bandgap values are measured using the following formula and tabulated in Table-1.

TABLE-1
CRYSTALLITE SIZE, BANDGAP AND SURFACE AREA VALUES OF TiO_2, $SrTiO_3$ AND METAL DOPED CATALYSTS

Catalysts	Crystallite size (nm)	Bandgap (eV)	Surface area (m^2/g)
TiO_2	19	3.2	93
Ni/TiO_2	21	2.95	51
Ru/TiO_2	23	2.8	70
$SrTiO_3$	45	3.2	11
Ni/$SrTiO_3$	40	2.85	16
Ru/$SrTiO_3$	36	3.02	19

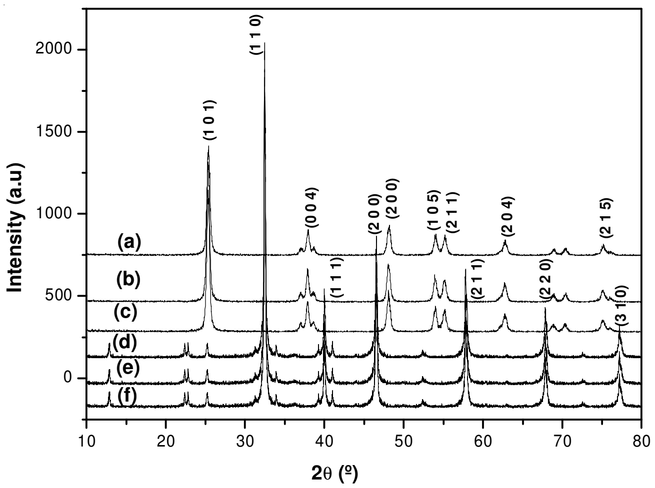

Fig. 2. XRD patterns of a) TiO_2; b) Ni/TiO_2; c) Ru/TiO_2; d) $SrTiO_3$; e) $Ni/SrTiO_3$ and f) $Ru/SrTiO_3$ catalysts

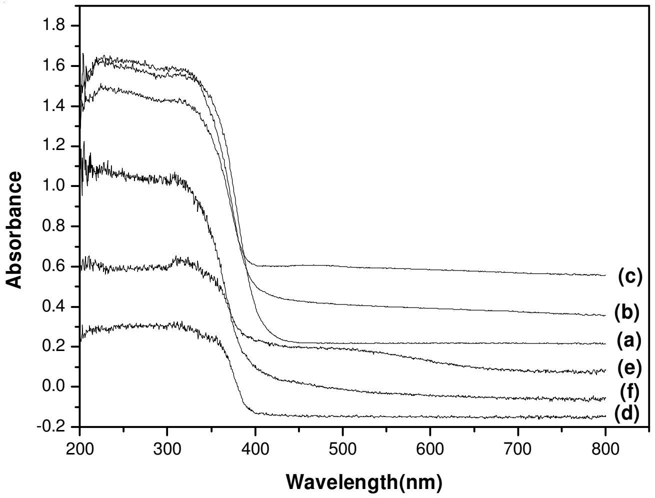

Fig. 3. UV-DRS spectra of a) TiO_2; b) Ni/TiO_2; c) Ru/TiO_2; d) $SrTiO_3$; e) $Ni/SrTiO_3$ and f) $Ru/SrTiO_3$ catalysts

$$E_g = 1240/\lambda$$

It can be seen from the table that doping of metals either on titania or on $SrTiO_3$ decreases the bandgap which clearly shows the shifting of optical response of the doped catalysts. The UV DRS spectra of Ni doped $SrTiO_3$ showed an absorption band in the visible region centred around 520 nm in addition to intrinsic adsorption band due to bandgap transition. Nickel on doping over $SrTiO_3$ exists in both Ni^{2+} and Ni^{3+} states. Ni^{2+} and Ni^{3+} occupies the acceptor and donar level in the forbidden band gap. This may be the reason for the appearance of new absorption band around 520 nm[21].

BET Surface area analyzer: The surface area values of synthesized TiO_2, $Ni/Ru-TiO_2$ and $Ni/Ru-SrTiO_3$ are given in Table-1. The surface area values decreased on doping Ni and Ru over titania and no observable change in the surface area was observed when the same metals were doped over strontium titanate. This difference in surface area values of titania and strontium titanate catalysts may be due to large difference in the initial surface areas of bare materials. The decrease in surface area of TiO_2 on doping either with nickel or ruthenium may be due to the blocking of fine capillaries of parent TiO_2 surface by metal which prevents the entry of nitrogen gas into the pores[22].

Photodegradation of insecticides over different catalysts: The results obtained in the degradation of TMX and acetamiprid over TiO_2, $SrTiO_3$ and their doped catalysts are shown in Figs. 4 and 5 respectively. The solid symbols represent catalytic activities of TiO_2 based catalysts and the hollow symbols represent the activities of $SrTiO_3$ based catalysts.

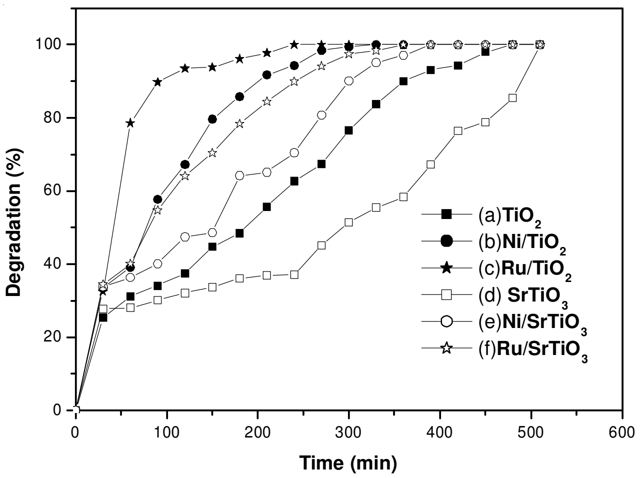

Fig. 4. Photocatalytic activities of TiO_2, $Ni/Ru-TiO_2$ and $Ni/Ru-SrTiO_3$ towards the degradation of thiamethoxam

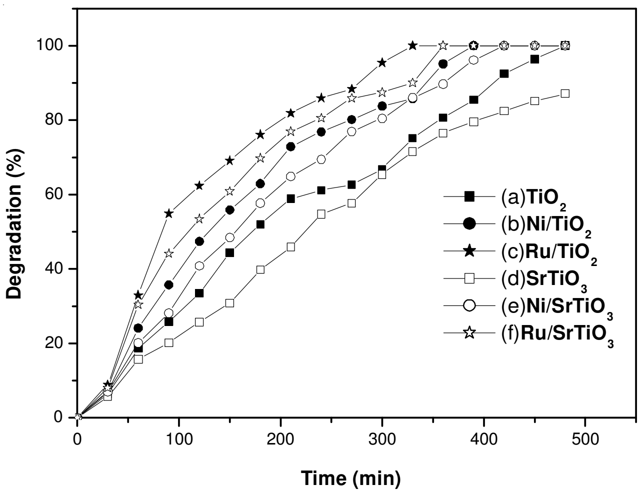

Fig. 5. Photocatalytic activities of TiO_2, $Ni/Ru-TiO_2$ and $Ni/Ru-SrTiO_3$ towards the degradation of acetamiprid

Although all the catalysts showed 100 % degradation towards the degradation of TMX, the time at which complete degradation took place was different for different catalysts. Ni and Ru doped catalysts degraded in 5.5 and 4 h, respectively. Time taken for 100 % degradation of TMX and acetamiprid over different catalysts are given in Table-2. Both titania and strontium titanate degraded TMX completely in 8-8 ½ h whereas their doped counterparts took less time than bare catalysts. Among all the catalysts Ru doped TiO_2 took only 4 h for complete degradation of TMX.

Another remarkable observation made in the degradation of TMX over Ru/TiO_2 catalyst is that it degraded 80 % of insecticide within 60 min of the reaction time. No other catalyst showed degradation to this extent. The second highest degradation (40 %) of TMX was observed over $Ru/SrTiO_3$ in the same reaction time of 60 min.

TABLE-2
TIME TAKEN FOR 100% DEGRADATION OF INSECTICIDES OVER DIFFERENT CATALYSTS

Catalysts	Thiamethoxam (h)	Acetamiprid (h)
TiO_2	8	8
Ni/TiO_2	5 ½	6 ½
Ru/TiO_2	4	5 ½
$SrTiO_3$	8 ½	8 ½*
$Ni/SrTiO_3$	6 ½	7
$Ru/SrTiO_3$	6	6

*only 89 % degradation even after 8 ½ h

As far as the degradation of acetamiprid is concerned all the catalysts except $SrTiO_3$ showed 100 % degradation but at various reaction times. $SrTiO_3$ degraded only 89 % even after conducting the reaction for 8 h. In the degradations of both TMX and acetamiprid, doped catalysts performed well than their bare counterparts. Among the doped catalysts the catalytic activities of Ru doped catalysts were found to be better than Ni doped catalysts. Ru/TiO_2 and $Ru/SrTiO_3$ catalysts degraded acetamiprid completely in 5 ½ h and 6 h respectively whereas other catalysts took longer time for complete degradation.

Large difference in the catalytic activities of various catalysts was observed in the degradation of TMX, whereas small difference in the catalytic activities of various catalysts was observed in the degradation of acetamiprid. It was also observed in the degradations of TMX and acetamiprid that most of the TMX has been degraded in a shorter time than acetamiprid. The degradation of TMX and acetamiprid obtained in the optimized reaction times of 60 min and 5 ½ h respectively are given in Table-3.

TABLE-3
DEGRADATION (%) OF THIAMETHOXAM AND ACETAMIPRID OVER DIFFERENT CATALYSTS AT THE OPTIMIZED REACTION TIMES

Catalysts	Thiamethoxam (%)	Acetamiprid (%)
TiO_2	31.2	75
Ni/TiO_2	39.9	85.7
Ru/TiO_2	80	100
$SrTiO_3$	28	71.5
$Ni/SrTiO_3$	36.3	86
$Ru/SrTiO_3$	40	90

Optimized Reaction time: 60 min for TMX and 5 ½ h for ATP

The enhanced activity of Ru and Ni doped titania based catalysts may be attributed to the electronic interaction occurring at the contact region between the metal deposits and the semiconductor surface. This may cause the removal of electrons from TiO_2 into the vicinity of the metal particle resulting in the formation of Schottky barriers leading to charge separation. The doped Ni and Ru act as electron traps immobilizing the photogenerated electrons in the traps and shortly transferring them to oxygen to form highly oxidative species such as O_2^-. Similar type of electron scavenging by different metals such as Pt, Ag and Au and enhancement of catalytic activities have already been reported[23]. Since the excited electrons from titania are trapped by Ru and Ni metals the recombination of e^-/h^+ pairs is prevented which enhanced the degradation of insecticides.

Total organic carbon analyses: Total organic carbon analyses were also carried out to study the extent of mineralization. Samples degraded at different interval over various catalysts are subjected to Total organic carbon analysis and the values are given in Table-4.

TABLE-4
TOTAL ORGANIC CARBON VALUES OBTAINED IN THE DEGRADATIONS OF TMX AND ATP

Catalysts	Thiamethoxam (%)	Acetamiprid (%)
TiO_2	34	64
Ni/TiO_2	64	39
Ru/TiO_2	70	35
$SrTiO_3$	32	55
$Ni/SrTiO_3$	54	46
$Ru/SrTiO_3$	59	36

All the catalysts mineralized both the insecticides but to different extent. Among them Ru/TiO_2 and $Ru/SrTiO_3$ showed the best efficiency towards the mineralization of both insecticides. The following trend was observed with regard to the % efficiency of the catalysts towards mineralization:

$Ru/TiO_2 > Ru/SrTiO_3 > Ni/TiO_2 > Ni/SrTiO_3 > TiO_2 > SrTiO_3$

Conclusion

Titania based catalysts were successfully synthesized by sol-gel method and characterized by XRD, UV-DRS and BET surface area analysis. XRD confirmed the phase formation. UV-DRS study showed reduction in the bandgap and BET surface area measurements revealed the change in surface area due to doping. Doping of nickel and ruthenium over both titania and strontium titanate increased the efficiency of catalysts. Between Ni and Ru doped catalysts Ru doped catalysts performed well in the degradation of TMX and acetamiprid. Total organic carbon studies confirmed the mineralization of insecticides.

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