

Aerogel processing of MTi_2O_5 ($\text{M} = \text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Zn}, \text{Sn}$) compositions using single source precursors: synthesis, characterization and photocatalytic behavior

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Abstract

Oxide semiconductor photocatalysts based on TiO_2 (band gap of 3.2 eV) are normally used to destroy organics under UV irradiation. Currently we have been focused on the aerogel synthesis of nanocrystalline photocatalysts that will destroy organic compounds such as acetaldehyde using visible and UV radiations. Herein we report the results of our attempts to synthesize mixed metal oxides of the type MTi_2O_5 ($\text{M} = \text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Zn}, \text{and Sn}$). The preparation method involves the formation of a single source precursor by the condensation reaction of $\text{Ti}(\text{OPr}^n)_4$ with $\text{M}(\text{OAc})_2$, followed by their $(\text{M}[\text{O}-\text{Ti}(\text{OPr}^n)_3]_2)$ hydrolysis and drying under supercritical conditions by a modified aerogel process. Product compositions, oxide structure types, and morphology were characterized by powder X-ray diffraction, scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDXA), and BET surface area measurements. Only for Mg, the stoichiometry MgTi_2O_5 with pseudo-brookite structure type was obtained, while the composites $\text{MTiO}_3/\text{TiO}_2$ were obtained for $\text{M} = \text{Fe}, \text{Co}$ and Zn . Photocatalytic behavior of these composite oxides were tested by the decomposition of gaseous acetaldehyde under UV light ($320 \text{ nm} < \lambda < 400 \text{ nm}$). Of these, $\text{CoTiO}_3/\text{TiO}_2$ showed an interesting catalytic behavior; it decomposed acetaldehyde in the dark, at room temperature. Other mixed metal oxides such as MgTi_2O_5 , and composites such as $\text{FeTiO}_3/\text{TiO}_2$ and $\text{ZnTiO}_3/\text{TiO}_2$ decomposed acetaldehyde only under UV light (not under visible light or in the dark). The photocatalytic activity was compared with the reference degussa P25 TiO_2 photocatalyst.

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1. Introduction

Titanium dioxide is the most widely used photocatalyst due to energy and environmental considerations [1]. However, titania can operate only under UV light irradiation, since the light energy must be higher than its band gap (3.2 eV). Currently many research efforts are aimed at the discovery of photocatalysts that work under visible light irradiation [1,2]. One such effort involves the usage of mixed metal oxides for the photodecomposition of volatile organics. In our laborato-

ries some of the mixed metal oxides with high surface areas ($>600 \text{ m}^2/\text{g}$), have been studied for the decomposition of acetaldehyde under visible and UV light irradiation. Cr, Co, Mn, V, Ni, and Fe incorporated titania-silica aerogels were effective for the photocatalytic decomposition of acetaldehyde under visible light irradiation ($\lambda > 420 \text{ nm}$) [3]. We further showed efficient visible and UV photocatalytic activities for acetaldehyde decomposition based on microporous titanium silicate [ETS-10, $(\text{Na,K})_2\text{TiSi}_5\text{O}_{13}$], and transition metal incorporated ETS-10 [4].

Composite semiconducting materials such as $\text{TiO}_2/\text{SnO}_2$ [5], TiO_2/WO_3 [6], ZnO/SnO_2 [7], have also been used as UV photocatalysts. These oxides with their different band

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positions provide wider charge separation, thereby preventing the recombination of holes and electrons. Coating a thin layer of MgO particles on TiO₂ particles was found to enhance the photocatalytic oxidation of 2-chlorophenol, 2,4-dichlorophenol and 4-aminobenzoic acid [8]. TiO₂/Fe₂O₃ binary mixed oxides (1:1 composition) prepared by sol–gel impregnation, exhibiting absorption in the visible spectral region (570–600 nm) showed photocatalytic activity for the aqueous degradation of *o*-cresol under UV light [9]. Nanocomposites of ZnFe₂O₄/TiO₂ (with a Zn/Ti molar ratio of 0.05) showed increased activity for the photodecomposition of phenol as compared to pure TiO₂ [10]. Increased photodecomposition of phenol by TiO₂/SiO₂ has also been noted and was attributed to the adsorption sites provided by SiO₂ [11]. Furthermore, intimately mixed metal oxides such as CaO–Al₂O₃ and MgO–Al₂O₃ were shown to have increased adsorption for paraoxon (diethyl-*p*-nitrophenyl phosphate) [12].

We wanted to investigate some of the titanium containing mixed metal oxides MTi₂O₅ (M = Mg, Mn, Fe, Co, Zn, and Sn) as photocatalysts. We preferred utilizing high surface area nanostructured mixed metal oxides in order to enhance surface adsorption and photocatalysis. While synthesizing mixed metal oxides by aerogel processing, single source precursors, which would possess both (Ti and M) the elements, are essential to control stoichiometry. Although a mixture of homometallic alkoxides could be used, single source precursors have the advantage of avoiding the mismatch between the hydrolysis rates of the different nonmetal precursors.

For example, homogeneous, high surface area nanocrystalline or amorphous forms of mixed metal spinel oxides MA₂O₄ (M = Mg, Ca, Mn, Co, Fe, and Zn) have been successfully synthesized [13] using a modified aerogel method, from bimetallic oxo-bridged alkoxides [(RO)₂Al–O–M–O–Al(OR)₂]. Final products MA₂O₄ were obtained by the thermal decomposition of the hydroxides [(HO)₂Al–O–M–O–Al(OH)₂]. Nanosized BaTiO₃, BaZrO₃, and BaTi_{0.5}Zr_{0.5}O₃ have been prepared by single-source alkoxide, semi-alkoxide routes [14]. Through sol–gel chemistry, NdAlO₃ embedded in an Al₂O₃ matrix was obtained [15], using a single source precursor [NdAl₃(OPr^{*i*})₁₂(Pr^{*i*}OH)]. Titanium iron isopropoxide [FeCl{Ti₂(OPr^{*i*})₉}] has been used as a single source precursor to prepare TiO₂/Fe₂TiO₅ composites by the sol–gel route [16].

In this article we discuss the results of our investigation on the synthesis and characterization of mixed metal oxides with stoichiometry, MTi₂O₅ (M = Mg, Mn, Fe, Co, Zn, and Sn) using an aerogel method from a single source precursor. Only for Mg, the stoichiometry MgTi₂O₅ with pseudobrookite structure type was obtained, while the composites MTiO₃/TiO₂ were obtained for M = Fe, Co and Zn. We tested the photocatalytic behavior of the products for the decomposition of gaseous acetaldehyde. Although our primary goal was to obtain photocatalysts, we surprisingly discovered a catalyst, CoTiO₃/TiO₂, that would decompose acetaldehyde in the dark at room temperature.

2. Experimental

2.1. Synthesis

Metal acetates, Co(OAc)₂, Mn(OAc)₂, Fe(OAc)₂, Zn(OAc)₂ were purchased from Aldrich and used as received. Samples of Mg(OAc)₂·4H₂O, also from Aldrich were refluxed overnight with excess acetic anhydride to remove water, and the insoluble Mg(OAc)₂ was collected by filtration, washed with dry toluene and dried at 50 °C under vacuum overnight. Ti(OPr^{*n*})₄ and decalin were purchased from Aldrich and used as received.

2.2. Synthesis and hydrolysis of Mg[O–Ti(OPr^{*n*})₃]₂

The starting materials, M[O–Ti(OPr^{*n*})₄]₂ (M = divalent metal), have been synthesized earlier by the thermal condensation of Ti alkoxide with metal (M) acetate [17]. A similar synthetic procedure has been followed. The Mg analog was prepared by refluxing two moles of Ti(OPr^{*n*})₄ (4.94 g, 0.0174 mol) and 1 mol of Mg(OAc)₂ (1.24 g, 0.0087 mol) in 50 ml decalin in a flask connected to a fractionating column. The solution was refluxed and *n*-propyl acetate was removed continuously from 90 to 100 °C (a sample of this *n*-propyl acetate was confirmed by GC–MS; total yield of ester is about 1.83 g). Eventually, the reflux temperature was raised to the boiling point of decalin (190 °C). The refluxing was continued for 5 h with the slow removal of decalin. The remaining decalin was removed by vacuum distillation and a pale yellow clear solution formed was dried under vacuum at 50 °C for overnight. Finally a pale yellow viscous paste of Mg[O–Ti(OPr^{*n*})₃]₂ was obtained (total yield 4.40 g).

2.3. Hydrolysis and supercritical drying of Mg[O–Ti(OPr^{*n*})₃]₂

The yellow paste from the above preparation was dissolved in 30 ml toluene and 30 ml of isopropanol. The clear pale yellow solution obtained was refluxed, cooled, and was added, with stirring, 3 ml of water in 10 ml of isopropanol. The white gel obtained was stirred continuously at 40 °C overnight. The gel was placed in a high-pressure autoclave, which was sealed, pressured to 100 psi with nitrogen, and heated with stirring at 265 °C for 4 h (the pressure rose to 900 psi). The solvent was vented over several minutes at this temperature. After cooling, a gray white fluffy solid (yield 1.83 g) was obtained. Calcinations of these powders were carried out at different temperatures depending upon the products obtained. Similar procedures were also used for preparation of other alkoxide precursors and they are summarized in Table 1.

2.4. Characterization

Textural characterization of the samples was performed on a Nova 1200 gas sorption analyzer (Quantachrome Corp.).

Table 1
Preparative conditions, product stoichiometry and surface areas of the materials

Starting materials stoichiometry	Surface area after supercritical drying (m ² /g)	Surface area after heat treatment in air (m ² /g) (heating conditions)	Product stoichiometry (from XRD and EDAX)
Two moles of Ti(OPr ^{<i>t</i>}) ₄ and 1 mol of magnesium acetate	78	51 (500 °C/4 h)	MgTi ₂ O ₅
Two moles of Ti(OPr ^{<i>t</i>}) ₄ and 1 mol of manganese(II) acetate	204	126 (500 °C/4 h)	Amorphous
Two moles of Ti(OPr ^{<i>t</i>}) ₄ and 1 mol of iron(II) acetate	297	25 (700 °C/4 h) 157 (500 °C/4 h)	Mn ₂ O ₃ and TiO ₂ (rutile) Amorphous
Two moles of Ti(OPr ^{<i>t</i>}) ₄ and 1 mol of cobalt(II) acetate	237	20 (500 °C/4 h)	Amorphous
Two moles of Ti(OPr ^{<i>t</i>}) ₄ and 1 mol of zinc acetate	320	16 (700 °C/4 h) 152 (500 °C/4 h)	CoTiO ₃ /TiO ₂ (rutile) Amorphous
Two moles of Ti(OPr ^{<i>t</i>}) ₄ and 1 mol of tin(II) acetate	146	27 (700 °C/4 h) 58 (500 °C/4 h) 43 (700 °C/4 h)	ZnTiO ₃ /TiO ₂ (anatase and rutile) Amorphous Unidentified by powder X-ray diffraction

The specific surface areas were calculated according to the Brunauer–Emmett–Teller (BET) method. X-ray powder diffraction experiments were conducted on a Scintag-XDS-2000 and Bruker D8 Advance powder X-ray diffractometers with Cu K α radiation. Scans were made in the 2θ range 5–60° with a step size of 0.025. The surface morphology of the calcined samples was visualized using a Hitachi S-3500N Scanning Electron Microscope. Visible absorption spectra of the samples were recorded on a Cary 500 Scan UV–vis NIR Spectrophotometer with an integrating sphere attachment for their diffuse reflectance in the range 200–800 nm.

2.5. Photocatalysis studies

The experimental set up for the photocatalytic oxidation of acetaldehyde includes a light source, a static reactor, and a circulating water bath. The static reactor is a 305 cm³ glass container with a quartz lid to access light radiation. A typical experiment was carried out as follows. The required amount of the powdered sample (about 60–80 mg) was uniformly spread over a quartz basket. The sample was later placed in the air filled reactor. The temperatures for all the experiments were carried out at 298 K. The reactor was closed and stirred continuously after the introduction of 100 μ l of liquid acetaldehyde. The samples were illuminated with a 1000 W high pressure Hg lamp. A combination of two filters, VIS-NIR long pass filter (400 nm) and a colored glass filter (>420 nm) was utilized for the purpose of allowing only visible radiation. For UV illumination (320 nm < λ < 400 nm), most of the IR and visible light was cut off. Gaseous samples (35 μ l) were extracted and analyzed by GC–MS (gas chromatograph equipped with a mass selective detector GCMS-QP5000 from Shimadzu) to follow the concen-

tration of the reactant acetaldehyde and the product carbon dioxide.

3. Results and discussion

3.1. Characterization

One of the important aspects of this work is the successful synthesis of MTi₂O₅ nanostructured materials by a modified aerogel procedure. This approach is concerned with hydrolysis, gel formation, supercritical drying, and vacuum or air dehydration. However, only in the case of Mg, the composition MgTi₂O₅ with a pseudo-brookite structure was obtained after calcinations at 500 °C in air (Fig. 1a). The powder diffrac-

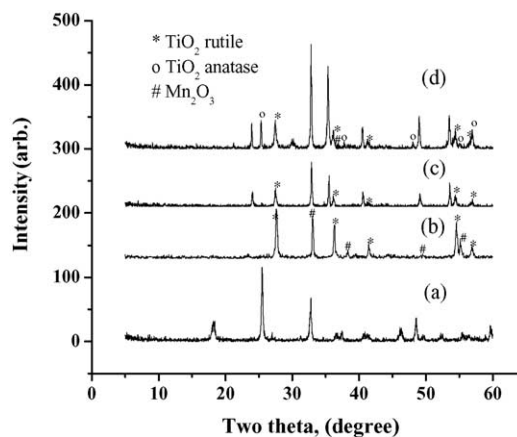


Fig. 1. Powder X-ray diffraction patterns of (a) MgTi₂O₅, (b) mixture of Mn₂O₃ and TiO₂, (c) CoTiO₃/TiO₂, and (d) ZnTiO₃/TiO₂ after calcinations (see Table 1).

tion pattern matched very well with that of the reported PDF (JCPDS Powder Diffraction File) number 35-0796. MgTi_2O_5 with a pseudo-brookite structure has so far been prepared only by high temperature quenching ($>700^\circ\text{C}$) [18,19]. In the case of Co, and Zn, the products obtained even after heating at 700°C was a mixture of MTiO_3 and TiO_2 (mostly rutile) (Fig. 1). For Mn, the powder X-ray pattern indicated the formation of Mn_2O_3 and TiO_2 (anatase and rutile) (Fig. 1b). The reason might be the instability of the compositions, CoTi_2O_5 , MnTi_2O_5 , and ZnTi_2O_5 in the pseudo-brookite structure. The formation of solid solutions between MnTi_2O_5 and CoTi_2O_5 were known without the formation of the end members [20]. It is important to mention that these earlier preparations were done by the traditional ceramic method. For Fe and Sn, calcinations of the hydroxylated products at 500°C in air resulted in amorphous powders as shown by the X-ray powder

diffraction patterns. Usually iron oxide in the presence of TiO_2 in air tends to stabilize in a 3+ state with a composition Fe_2TiO_5 , in the pseudo-brookite structure [8,20,21]. Preparation of FeTi_2O_5 normally requires much more stringent conditions, such as heating the mixture of Fe, Fe_2O_3 , and TiO_2 at 1170 – 1300°C in sealed quartz tubes containing 200 mbar of He [21]. Sn in a 4+ oxidation state has been substituted for Ti in the pseudo-brookite structure [22], and there are no known phases with Sn in a 2+ oxidation state with titanium. This probably explains the unidentified powder X-ray pattern obtained by us, while heating the precursor in vacuum. Product formation, calcinations conditions along with the surface areas obtained for the different samples are listed in Table 1.

Surface areas of the as prepared materials after supercritical extraction were 150 – $300\text{ m}^2/\text{g}$, except for the Mg compo-

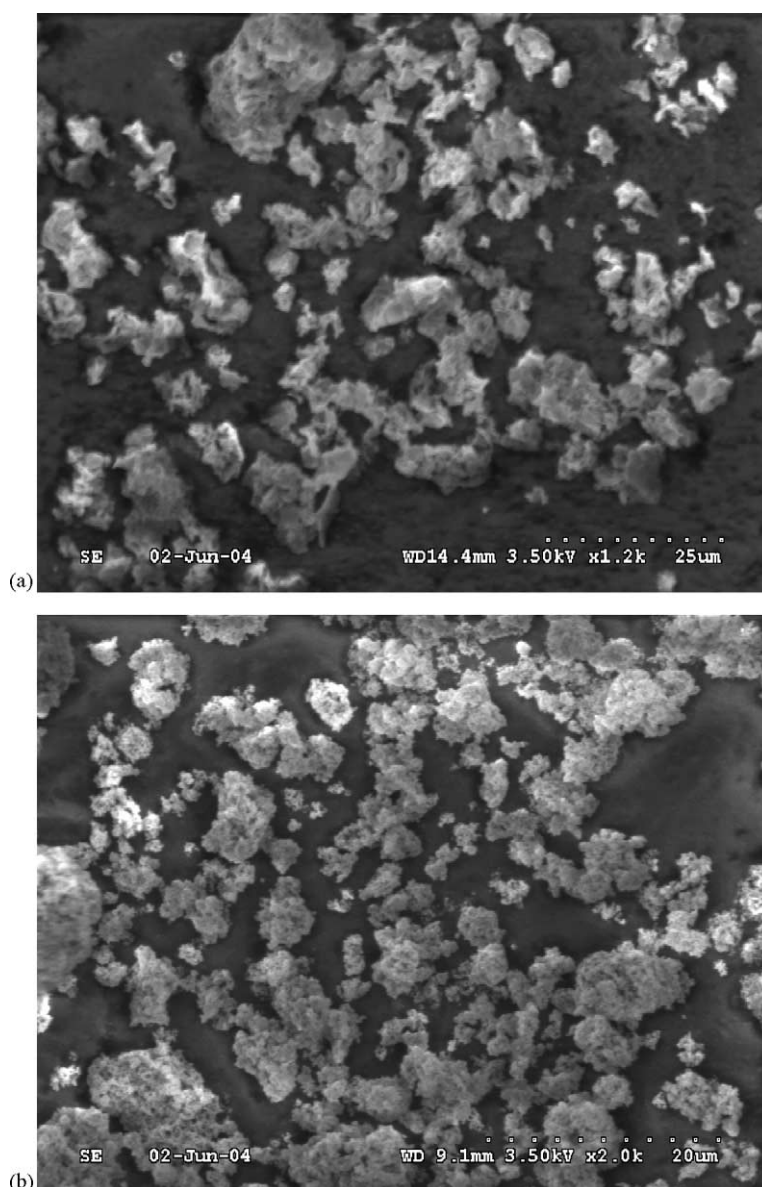


Fig. 2. Scanning electron micrographs of (a) $\text{CoTiO}_3/\text{TiO}_2$ and (b) $\text{ZnTiO}_3/\text{TiO}_2$.

sition for which the surface area was $78 \text{ m}^2/\text{g}$ (Table 1). The surface areas decrease after calcinations and also with increase in calcination temperatures. Even so, the surface area obtained for MgTi_2O_5 ($51 \text{ m}^2/\text{g}$) is notable, since a similar surface area cannot be achieved by the traditional ceramic method of preparing MgTi_2O_5 at temperatures $>700^\circ\text{C}$ [18].

The morphology as indicated by the SEM images (Fig. 2) for the $\text{MTiO}_3/\text{TiO}_2$ ($M = \text{Co}, \text{Zn}$) composites indicate uniform crystallites. The ratios of Co/Ti and Zn/Ti as indicated by the EDAX analyses were 0.51 and 0.52, respectively. This ratio matched very well the expected total composition of MTi_2O_5 . The Fe sample that was calcined at 500°C , which was amorphous, also exhibited a ratio of Fe/Ti , 0.45. The results from EDAX coupled with powder X-ray diffraction results clearly indicate that we have crystalline solid MgTi_2O_5 and the formation of $\text{MTiO}_3/\text{TiO}_2$ composites for $M = \text{Fe}, \text{Co},$ and Zn .

Inspection of the UV–vis spectra for the different products (Fig. 3), clearly indicate that the cobalt and iron composites have stronger visible absorption in the range of 450–650 nm. A similar visible absorption behavior has been observed for $\text{TiO}_2/\text{Fe}_2\text{O}_3$ mixed metal oxides and also for iron doped titania [8,23]. The broad peak between 500 and 700 nm observed for the cobalt sample is mainly due to the presence of CoTiO_3 [24]. Note that in the case of Zn and Mg, the absorption edge is moved below 350 nm as compared to that of degussa P25 TiO_2 .

3.2. Photocatalytic studies

We investigated the photocatalytic activities of MgTi_2O_5 and the $\text{MTiO}_3/\text{TiO}_2$ composites ($M = \text{Fe}, \text{Co},$ and Zn) for the gas phase decomposition of acetaldehyde. MgTi_2O_5 and the composites $\text{MTiO}_3/\text{TiO}_2$ ($M = \text{Fe}$ and Zn) decomposed acetaldehyde only under UV irradiation ($320 \text{ nm} < \lambda < 400 \text{ nm}$). The pseudo-first-order rate constants, calculated from the plots of $\ln(C_0/C)$ versus time (t), where C_0 and C denote the gas phase concentrations of acetaldehyde at $t=0$ and $t=t$, respectively, are listed in Table 2. In spite of the strong visible absorption shown by the Fe sample, it did not show

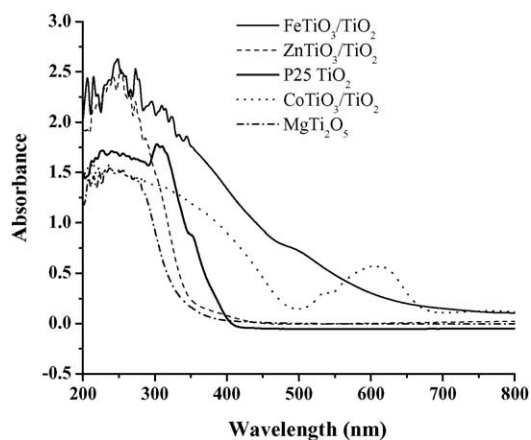


Fig. 3. UV–vis diffuse reflectance spectra of materials under study.

Table 2

Pseudo-first-order rate constants^a (k , min^{-1}) for the decrease of acetaldehyde by MgTi_2O_5 and the composites $\text{MTiO}_3/\text{TiO}_2$ ($M = \text{Fe}, \text{Zn}$) under UV irradiation ($320 \text{ nm} < \lambda < 400 \text{ nm}$)

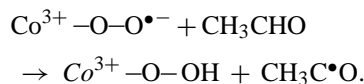
Sample	k (min^{-1})
Degussa P25 TiO_2	0.01(3)
MgTi_2O_5	0.004(5)
$\text{FeTiO}_3/\text{TiO}_2$	0.001(4)
$\text{ZnTiO}_3/\text{TiO}_2$	0.003(4)

^a Calculated from the plots of $\ln(C_0/C)$ vs. time (t), where C_0 and C denote the gas phase concentrations of acetaldehyde at $t=0$ and $t=t$, respectively.

any photocatalytic activity under visible light. Comparison of the pseudo-first-order rate constants under UV light for MgTi_2O_5 (0.004 min^{-1}) and the composites $\text{FeTiO}_3/\text{TiO}_2$ (0.001 min^{-1}) and $\text{ZnTiO}_3/\text{TiO}_2$ (0.003 min^{-1}) were found to be lower when compared to degussa P25 TiO_2 (0.01 min^{-1}) (Table 2).

However, we obtained interesting results for the cobalt sample. $\text{CoTiO}_3/\text{TiO}_2$ decomposed acetaldehyde at room temperature in the dark as indicated by the increase in CO_2 concentration and the decrease in acetaldehyde concentration with time (Fig. 4). The activity in the dark was higher than degussa TiO_2 which decomposes acetaldehyde only under UV light. A balance between the consumed acetaldehyde concentration and the amount of CO_2 formed was not achieved, since CO_2 was the only dominant gaseous product of the reaction of acetaldehyde oxidation. A trace amount of acetic acid was the only other product seen in the gaseous phase. The gas phase concentrations of other organic compounds were probably below GC–MS detection limits. The acetic acid, being less volatile (bp 118°C), probably was strongly adsorbed on the surface of the catalyst. The concentration of acetic acid observed in the gaseous phase, might not correspond to the total concentration of acetic acid produced in the reaction [25].

The catalytic activity in the absence of light is due to the presence of Co, and a similar behavior has previously been reported by us in the case of CoO_x loaded SiO_2 xerogels [25]. The mechanism was explained by the reaction of Co^{2+} to form superoxo complexes ($\text{L}_x\text{Co}^{3+} - \text{O} - \text{O}^{\bullet -}$) in the presence of oxygen. This complex formation is considered to be responsible for the chain initiation



Alternately, Co^{3+} can react with acetaldehyde to form an acetyl radical, which then proceeds to form the acetylperoxy radical with oxygen. This chain initiation was then explained as the reason for the activity of the cobalt catalyst.

In summary, we have attempted to prepare MTi_2O_5 ($M = \text{divalent metal}$) oxides by aerogel approach. We succeeded in preparing MgTi_2O_5 by this method at temperatures as low as 500°C , while the composites $\text{MTiO}_3/\text{TiO}_2$ have been found for $M = \text{Fe}, \text{Co},$ and Zn . Cobalt containing material showed an interesting catalytic activity, by decomposing

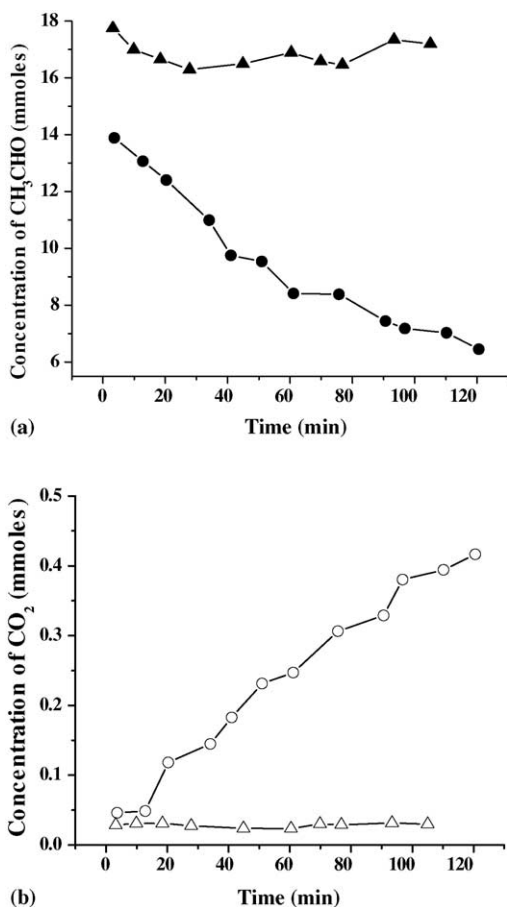


Fig. 4. (a) Rate of decomposition of acetaldehyde in the dark by $\text{CoTiO}_3/\text{TiO}_2$ (filled circles). Filled triangles represent the concentration of acetaldehyde in the absence of any catalyst. (b) Formation of CO_2 in the dark by $\text{CoTiO}_3/\text{TiO}_2$ (open circles). Open triangles show the concentration of CO_2 in the absence of any catalyst.

acetaldehyde in the dark at room temperature. The MgTi_2O_5 and the composites $\text{MTiO}_3/\text{TiO}_2$ ($M = \text{Fe}, \text{Zn}$) acted as regular UV photocatalysts under UV light.

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