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A sol–gel route to synthesize vanadium doped silica through ionic liquid control and methylene blue degradation

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ABSTRACT

Silica and vanadium doped silica nanoparticles were obtained by sol–gel technique using ionic liquid (IL) 1-ethyl-3-methylimidazolium trifluoromethane sulfonate, [EMIM][TfO]. In order to understand characteristics of the nanoparticles without IL, we synthesized silica and vanadium doped silica nanoparticles without IL. Synthesis was also conducted without IL to interpret the nanoparticles characteristics in absence of IL. As-synthesized, as well as calcined (400 °C/4 h) nanoparticles were evaluated by HR-SEM, XRD, FTIR and TGA characterization. Morphology and size of the nanoparticles were found to be influenced due to the presence of IL during the synthesis. The EDX showed 8–10 wt% presence of vanadium on silica surface validating the formation of vanadium doped silica nanoparticles. Photodegradation efficiency of doped nanoparticles were assessed for methylene blue. Among different nanoparticles synthesized, vanadium doped and IL assisted silica nanoparticles showed higher photodegradation due to the reduced band gap energy substantiated by measurement of bandgap by UV-DRS.

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1. Introduction

Silicon dioxide or silica is one of the widely available oxides in the nature as mineral, which is also synthetically produced in the industry. Silica exists in different forms; such as fused quartz, crystal, fumed silica, silica gel, and aerogels; having applications in structural materials, microelectronics and food industry. Synthetic silica can be produced by sol–gel method using a variety of silicon precursors, out of which tetraalkyl silicate is widely used (Stöber et al., 1968). Silica is widely used to support transition metals in order to improve dispersion of transition metal leading to enhanced chemical reaction. Noguchi et al. (2011) synthesized copper nanoparticles on silica gel doped with flavins by sol–gel method. Cozzolino et al. (2006) produced vanadium on silica and titanium on silica by chemisorption of a reactive vanadium oxytrisopropoxide onto hydroxyl of silica to use for oxidative dehydrogenation.

Mendez et al. (2006) synthesized silica supported niobium, vanadium and titanium on silica and is used for oxidation of 1-hexene,

cyclohexene and cyclohexane. Krawiec and Kaskel (2009) carried out nitration and carbonization of vanadium oxide obtained by sol–gel synthesis of vanadium acetyl acetonate to synthesize silica supported vanadium nitride and carbide catalyst for propane dehydrogenation. Shin et al. (2014) synthesized 30–40 nm silver-doped silica nanoparticles which exhibited excellent antibacterial activity. Other reported studies include Pd–Ni doped silica nanoparticles synthesis for oxidation reaction (Saha et al., 2014), tungsten doped vanadium silica nanoparticles synthesis by chemical deposition method (Miyazaki et al., 2009), copper oxide doped silica nanoparticles (Huang et al., 2013), BiFeO₃ dispersed on mesoporous silica for photocatalytic activity (Bhunia et al., 2013) and CuO doped SiO₂ for methylene blue photodegradation (Batista et al., 2010), copper and vanadium anchored on 8.4 nm silica nanoparticles for cyclohexane oxidation (Kelly et al., 2015).

Recently, there have been efforts to focus on modification as well as doping on silica or doping on silica using ionic liquids (IL) to increase its performance efficiency. An IL has better thermal stability, better heat capacity, wide window of electrochemical potential, acidic or basic

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Nomenclature

Sample and description

SD	Silica nanoparticles synthesized in absence of IL
SDV	Vanadium doped silica nanoparticles synthesized in absence of IL
SDT	Silica nanoparticles synthesized using [EMIM][TfO]
SDVT	Vanadium doped silica nanoparticles synthesized using [EMIM][TfO]
SDC	Silica nanoparticles synthesized in absence of IL and heated for 4 h at 400 °C
SDVC	Vanadium doped Silica nanoparticles synthesized in absence of IL and heated for 4 h at 400 °C
SDTC	Silica nanoparticles synthesized using [EMIM][TfO] and heated for 4 h at 400 °C
SDVTC	Vanadium doped silica nanoparticles synthesized using [EMIM][TfO] and heated for 4 h at 400 °C

nature as well as solubility/selectivity for gases. Use of ionic liquid during nanoparticles formation can be an alternative for use of surfactant or ligand. Use of ligand or surfactant influences surface properties due to coordination on surface, while surface properties change slightly due to weak bonding of nanoparticles with IL. The ILs also work as structure directing template during sol-gel process to influence properties of the nanoparticles such as morphology, crystallinity, band gap, etc., and stabilize nanoparticles depending on polarity, ionic nature and dielectric constant of IL (Vollmer and Janiak, 2011; Zhang et al., 2015). The IL also keeps nanoparticles non-agglomerated. The IL can be possibly recovered from sol-gel synthesis process and can be recycled when it is in larger scale production without much vaporization losses due to its high boiling point. This way IL can provide cost effective process due to its recycling even though cost of IL is comparatively higher than normal solvent.

Valizadeh et al. (2013) synthesized silica nanoparticles based on organosilane based nitrite ionic liquid 1-(3-trimethoxysilylpropyl)-3-methylimidazolium nitrite, and 1-butyl-3-methylimidazolium nitrite-immobilized on silica and were used as effective reagents for synthesizing derivatives of benzotriazole. Gopala et al. (2013) used imidazole type ionic liquid, namely 1-hexadecyl-3-methylimidazolium chloride, to design higher surface area silica having mesoporous properties under acidic conditions and crystallize titanium dioxide (TiO₂)/tungsten on silica for oxidation of *n*-hexadecane under aerobic conditions. Zhu et al. (2006) used imidazole type ionic liquids, namely 1-hexadecyl-3-methylimidazolium and 1-hexadecyl-3-methylimidazolium chloride, to fabricate well-ordered hexagonal mesoporous SiO₂ as well as Ru-SiO₂ under acidic and basic conditions. It was observed that mesoporous structure of Ru-SiO₂ is preserved even after calcination. Kris et al. (2003) prepared aerogels containing palladium metal nanoparticles by mixing palladium acetate in 1-butyl-3-methylimidazolium bis(trifluorosulfonylimide) ionic liquid as solvent followed by incubation with (EtO)₄Si and formic acid to obtain the Pd loaded silica monolith. The Pd-silica was then used for hydrogenation of cinnamaldehyde to hydrocinnamaldehyde and Heck coupling of Bu acrylate and iodobenzene.

Most of the studies reported in literature have been conducted for TiO₂ or other transition metal doped silica nanoparticles using ionic liquid. Apart from several advantages, TiO₂ has also some disadvantages such as high electron-hole recombination rate and weak absorption in visible region due to large (3.2 eV) bandgap (Kahaththa et al., 2013). Hence, there is a need for exploring newer doping metals with silica. Although vanadium and titanium have close ionic radius, many of vanadium pentoxide/oxide studies focus either on chemical

conversion or on electrical/battery applications. To the best of our knowledge, no reported work is found in literature focusing on photocatalytic degradation of vanadium doped silica nanoparticles using ionic liquid. Vanadium has relatively lower band gap (2.0–2.6 eV) compared to TiO₂. Further, vanadium has multiple oxidation states of +3 to +5, hence we have chosen IL assisted vanadium doped silica for photocatalytic degradation. Literature on vanadium doped silica for photodegradation is feeble. Lee et al. (2009) synthesized vanadium-doped silica-titania photocatalysts with high surface area for photooxidation of styrene under UV- and visible light. Vanadium doped silica-titania nanoparticles showed higher photodegradation of styrene compared to silica-titania due to the presence of tetrahedrally coordinated vanadia species in the form of Ti—O—V bonding and reduced band gap due to vanadium doping.

In the present work, we have synthesized silica and vanadium-doped silica nanoparticles using [EMIM][TfO] ionic liquid to assess how the use of IL affects photodegradation efficiency. Synthesized nanoparticles were characterized by high-resolution scanning electron microscope (HR-SEM), X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR) and energy dispersive X-ray spectroscopy (EDX). Further, nanoparticles were assessed for their photodegradation efficiency of methylene blue (MB) in tailor made reactor under UV-light. This is, perhaps, first of its kind investigation on IL assisted vanadium doped silica nanoparticles and its application for photodegradation. Reasons for achieving better morphology, higher surface area and enhanced photodegradation with IL assisted nanoparticles are explained. Further, bandgap energy of IL assisted and non-IL assisted vanadium doped nanoparticles are examined to know the influence of IL on photodegradation. Schematic representation is also provided for explaining uniform and controlled morphology of synthesized nanoparticles under the influence of ionic liquid.

2. Experimental

2.1. Chemicals

Vanadium oxytripropoxide (98% VO(OiPr)₃), 99% ethanol, 99% tetraethyl silicate, 98% 1-ethyl-3-methylimidazolium trifluoromethane sulfonate [EMIM][TfO] (Sigma-Aldrich, Mumbai) were used for synthesis experiments. Demineralized (DM) water is used for sol-gel experiments. A 20% ammonia (commercially available) and LR (laboratory reagent) acetonitrile (Sigma-Aldrich, Mumbai) were utilized to bring pH to neutral range and for washing of the reaction products. Commercial grade methylene blue (MB) was used for photodegradation study.

2.2. Synthesis of silica or vanadium doped silica

Ethanol and tetraethyl orthosilicate (TEOS) were added in 250 mL round bottom flask (RBF) having condenser and temperature control oil bath. The RBF was stirred for 30 min at 500 RPM for proper mixing. Calculated amount of 25% ammonia (in water) was pipetted to RBF to start hydrolysis. Addition of ammonia solution was done at very slow rate by drop wise. Reaction was conducted at 50 °C for 5 h for completion of hydrolysis and kept overnight (~16 h) to complete gelation/condensation process. Reaction mass was converted to white colloidal solution which was centrifuged for the separation of silica nanoparticles (SD) followed by calcination at 400 °C for 4 h to get dehydrated silica nanoparticles (SDC). Calculated amount of vanadium oxytriisopropoxide was added along with ethanol and tetraethyl orthosilicate for vanadium doped silica nanoparticles (SDV) followed by calcination to get vanadium doped silica (SDVC) nanoparticles. Solids were

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