SYNTHESIS AND APPLICATIONS OF METAL OXIDE PHOTOCATALYSTS BY USING SOL-GEL METHOD

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ABSTRACT

Colloidal suspension of 500 nm and below, containing solid particles on which Van der Waals forces are effective is the called sol. The formation of three-dimensional solid inorganic network structures in solution as a result of a series of the reactions, in other words, when the solids reach macro size is the called gel. The chemical reactant containing the M cation in the sol or gel is called the chemical starting material. In the production of metallic salts with the sol-gel method, alkoxides are preferred as the starting material since the reaction control is the difficult. The different chemical structures of the starting materials determine the type of solvent to be used in the sol-gel process. These solvents can be water, alcohol or alkyl halides. In the production of ceramics and some oxides, water are used as solvents, metal alkoxides are alcohols used as solvents.

An advantage of the sol-gel method is that the process can be carried out under room conditions, there by allowing materials with different functional properties to be synthesized. This technique is applied in the many fields and especially from the solution until the final solid product is the formed, control over the process parameters can be done very well. Therefore, the sol-gel method has an important place in the field of nanotechnology. The formation of the gel by alkoxide precursor undergoing a series of hydrolysis and condensation reactions forms the basis of the chemistry of the sol-gel process. After sol-gel formation, ripening, removing solution and drying processes are applied. This process can be catalyzed with acid or base catalysts so that hydrolysis kinetics are changed to be produce products with different physical properties. Sol-gel method is a method applied in the synthesis of many different photocatalysts. Well-controlled pore size distribution, high purity and homogeneity, high porosity and surface area are among in the important advantages of the sol-gel method. With the sol-gel method, proper metal distribution and thermal resistance are provided in the synthesis of photocatalysts containing active metals.

In theory, almost all of the porous metal oxides used in the heterogeneous photocatalysis such as SiO_2, Al_2O_3, TiO_2, ZrO_2, ZnO can be prepared by sol-gel process. The precursor salts commonly used in the preparation of the metal oxides by the sol-gel method are metal-organic compounds known as the metal alkoxide. The general formula of the all metal alkoxide compounds is $M(OR)_X$. Metal oxides such as SiO_2, Al_2O_3, TiO_2, ZrO_2, SnO_2, ZnO and Nb_2O_5 have the semiconductor properties. These semiconductor metal oxide materials can be prepared by a non-hydrolytic sol-gel process. In the Many metal oxides are known to be semiconductors. Numerous substances for the photocatalytic degradation process so far, such as Fe_2O_3, $SrTiO_3$, In_2O_3, WO_3, V_2O_5, TiO_2, MoO_3, MoS_2, SiC and $ZnFe_2O_4$; used as a photocatalyst in decomposition of a large number of organic pollutants such as aliphatic aromatics, dyes, pesticides and herbicides.

Keywords: Metal Oxides, Sol-Gel Method, Photocatalyst, Metal-Organic Compounds, Semiconductors.

1. INTRODUCTION

In it is simplest definition, the sol-gel method is the synthesis of an inorganic network with a chemical reaction at a low temperature, such as room temperature, in a suitable solvent medium. The inorganic network can also be formed by high temperature processes such as vapor phase or melting (Schmidt, 1988). The sol-gel process also means the formation of an amorphous network, in contrast to the crystallization process from a solution. In this method, there are all methods that involve gelation of the colloidal solutions and obtaining a solid phase. In the sol-gel reaction, the conversion to the two-phase "gel" position often takes place over the colloidal solution ("sol") (Schmidt, 1988).

The dispersion state in a liquid consisting of the solid particles with a diameter of 1-100 nm of colloidal particles is called the "sol" phase. Substances of the sub-micron size pores in the same the solution and having a average length greater than 1 µm are called the "gel" phase (Pierre, 1988). The molecules that make up the gel connect to each other the with weak or strong bonds and form network-like tissues that contain fluid between the cavities. Thus, a non-fluid phase is the formed by the combination of molecules in the liquid medium (Livage and Sanchez, 1992). Sol-gel chemistry takes place with nucleophilic reactions. Metal alkoxides are mostly used as the initiator (Livage and Sanchez, 1992). The chemical activity of metal alkoxides used as initiators against sol-gel reactions such as hydrolysis, condensation and complexation generally depends on the electro negativity of the metal atom, the coordination number and the steric barrier of the alkoxide group (Gençer, 2014).

The reactivity of the silicon alkoxides is very weak and they react very slowly. Therefore, the hydrolysis and condensation reaction rates of the silicon alkoxides should be increased with an acid or base catalyst or the nucleophilic activation (Niederberger and Pinna, 2009). Transition metal alkoxides are the generally more reactive than silicon. The transition metal alkoxides need to be complexed with a suitable organic group (ligand) before sol-gel reactions to slow down and control very condensation of the control (Ogawa et al., 2003). The molecular arrangement of the alkoxide precursors used in sol-gel reactions also opens the way for the shaping new materials to be obtained.

2. MATERIALS AND METHODS

2.1 The Stages of the Sol-Gel Method

The sol-gel method takes place in the four stages. These;

- Alkoxide Hydrolysis.
- Peptidization and Polymerization.
- Gel Synthesis.
- Calcination/Sintering (Evcin, 2010).

Figure 1. The stages of the sol-gel formation process.

2.1.1 Alkoxide Hydrolysis

A metal alkoxide, a starting material (precursor), for example: TEOS (tetra ethoxysilane, Si $(OEt)_4$) reacts with water (H_2O) to hydrolyze. As a result of the reaction, silanol (tetra hedral silica) and ethyl alcohol are the formed (Ogawa et al., 2003) (Eq. (2.1)).

$$Si(OCH_2CH_3)_4 + 4\,H_2O \rightarrow Si(OH)_4 + 4\,CH_3CH_2OH \qquad (2.1)$$

Four moles of the water are consumed throughout the reaction so that all OR (alkoxy) groups can be hydrolyzed. The tetrahedral silica $Si(OH)_4$ formed forms a condensation reaction to form siloxane bonds. The condensation reaction may be water or alcohol condensation (Ogawa et al., 2003) (Eq. (2.2-2.3)).

$$Si(OH)_4 + Si(OH)_4 \rightarrow (OH)_3Si\text{-}O\text{-}Si(OH)_3 + H_2O \qquad (2.2)$$

$$OH\text{-}Si(OR)_3 + Si(OR)_4 \rightarrow (OR)_3Si\text{-}O\text{-}Si(OR)_3 + ROH \qquad (2.3)$$

In water condensation, one mole of water is the introduced into the reaction medium, while in the alcohol condensation, four moles of the alcohol are formed from the full condensation of one mole of metal alkoxide (Debecker et al., 2013). Polycondensation continues over the remaining hydroxyl groups (-OH) resulting in a SiO_2 network structure. The water and alcohol released as a result of the reaction are found in the pores in the mesh (Danks et al., 2016).

Colloidal particles act as 'sol' when a sufficient amount of the Si-O-Si bond occurs the during simultaneous walking hydrolysis and polycondensation reactions. The size of the particles in the sol and the degree of crosslinking between the particles primarily depend on the water/alkoxide ratio and many variables such as the temperature, the pH, mixing speed in the reaction medium (Chen et al., 2007). In addition, parameters such as hydroxyl (-OH) and alkoxide (-OR) relative concentrations (water/alkoxide ratio), metal alkoxide type, reaction temperature, catalysis type, reaction time and acidity of the reaction medium in the hydrolysis conditions affect of the hydrolytic polycondensation (Ogawa vd., 2003).

2.1.2 Peptidization and Polymerization

The peptidization, it is the dispersion of precipitates under the action of a solvent. A sol is the prepared by dispersing these sediments. The most suitable substances used in the peptidization are electrolytes. Electrolytes give a certain charge to the particles. The reason for the need for loading is that colloidal particles can only be found stable when loaded (Ogawa et al., 2003).

If a solution forms a negatively charged colloidal solution, they are peptidized with OH^- ions (with bases). If the same solution forms a positively charged colloidal solution, they are peptidized with H^+ ions (with acids). The amount of acid to be added is the adjusted with the pH of the medium (Anar, 2015; Evcin, 2010).

2.1.3 Synthesis of Gel

Gel is a solid and liquid phase system with a lot of liquid. The gelling reaction is the closely related to the shapes of the colloidal particles. The molecules that make up the gel connect to each other with weak or the strong bonds, forming skeletal-like tissues with fluid in the spaces between them (Evcin, 2010). The most important step of the gel formation is to dry this gel without cracking. Drying in the gels is the removing excess solvent (alcohol, water). In drying, the gel shrinks and the resulting solid contains a high amount of the porosity. This solid is called xerogel (Anar, 2015; Segal, 1994).

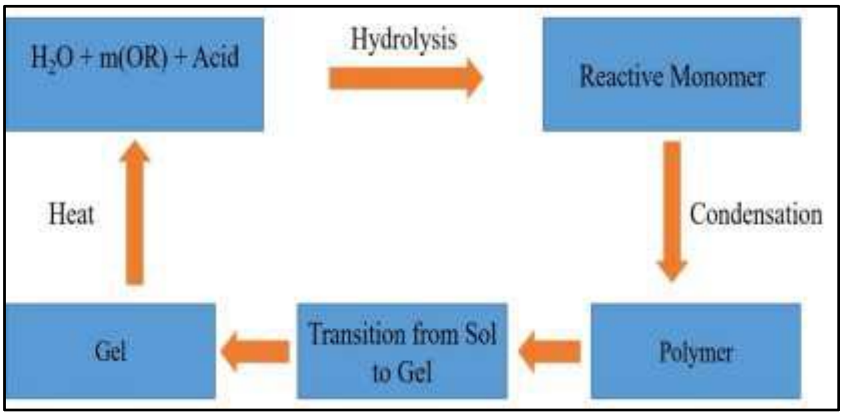

Figure 2. The stages of the gel formation process (Anar, 2015)

2.1.4 Calcination/Sintering

The breaks that occur during drying arise from to capillary forces. If the pore diameters in the gel are of nanometer size, the hydrostatic pressure of the liquid they contain will be very high. Accordingly, gels with small pores will break more quickly. In order to prevent this, the stresses that may occur can be removed by drying very slowly. The pore size of the gel can be increased and possible forces can be reduced (Anar, 2015).

3. RESULTS AND DISCUSSION

3.1 Metal Oxide Photocatalysts Synthesized by Using Sol-Gel Method

In the photocatalyst materials, metal oxides are widely used as semiconductor material. If a high energy photon is the absorbed by the semiconductor, the electrons in the valence band pass to the conductivity band and the semiconductor is stimulated (Kıranşan, 2015). As a result of the stimulation of the semiconductor materials, a positive electron space (h_{VB+}) occurs in the valence band, while an electron density (e_{CB-}) occurs in the conductivity band (Cao et al., 1999).

Photocatalyst materials can be described as a semiconductor material that becomes active when the reacting with light, forming strong oxidizing and/or reducing active surfaces (Sayılkan, 2007). A suitable photocatalyst should not be affected by the chemicals, external influences, be able to interact with visible light or near ultraviolet rays, be inexpensive, easily synthesized, non-toxic, have high photoactivity and have a large surface area and nano-size crystal structure (Kondarides et al., 2013). Only some of the semiconductors investigated can be considered effective photocatalysts, because in the most cases their optical and electronic properties do not meet all the properties of the semiconductivity. N-type metal oxide semiconductors with wide bandwidth, such as the TiO_2, WO_3, $SrTiO_3$, ZnO and Fe_2O_3, are usually effective photocatalysts because they are provide sufficiently high reduction and oxidation potentials in the conductivity and valence bands (Pfitzner et al., 2013; Kondarides et al., 2013).

3.2 Metal Oxide Photocatalyst Materials and Properties

Since they have higher oxidation power compared to other materials; Titanium dioxide (TiO_2), Zinc oxide (ZnO), Tin dioxide (SnO_2), Manganese dioxide (MnO_2), Iron (III) oxide (Fe_2O_3), Cadmium oxide (CdO), Gallium (III) oxide (Ga_2O_3), Tungsten oxide (WO_3) are the main materials preferred and used as photocatalyst (Tamirci, 2003). In order to for these semiconductor metal oxides to initiate a redox reaction, it is necessary to the perform a light stimulation process with an energy greater than valence and band cavity energy (Mori, 2004).

3.2.1 Titanium Dioxide (TiO_2)

Titanium dioxide is a white semiconductor metal oxide formulated as TiO_2, also known as the titanium (IV) oxide, with a molecular mass of the 79.866 g mol^{-1} and having a tetragonal structure (Qi et al., 2007). TiO_2; it has three forms: anatas, rutile and brokite. Of these forms, the brokite phase does not show the photocatalytic properties (Qi et al., 2007). Band gap energy of rutile phase is the 3.0 eV, band gap energy of anatas phase is the 3.2 eV.

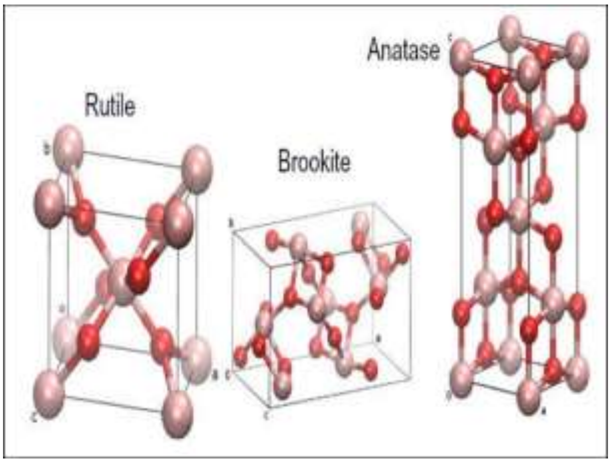

Figure 3. Crystal structure of titanium dioxide phases of rutile, brookite, and anatase (Pelaez et al., 2012)

Anatas phase has higher band gap range than rutile phase but shows higher photocatalytic effect (Qi et al., 2007). It has been the most used photocatalyst with it is strong oxidizing ability, high redox selectivity, easy supply and easy production in the laboratory, inexpensive, non-toxic, stable structure when the exposed to high-temperature UV radiation, and self-cleaning with photocatalytic effect. Since titanium dioxide is used as a catalyst it never runs out and performs it is mission over and over again (Malik et al., 2010).

3.2.2 Zinc Oxide (ZnO)

Zinc oxide is a white semiconductor metal oxide formulated as the ZnO with a molecular mass of 81.38 g mol^{-1} and having a hexagonal structure. It has found use in the many places in the paint industry, including ointments, adhesives, pigments, rubbers, plastics, ceramics, glass, cement, lubricants, as well as batteries, fire extinguishers, first aid tapes (Liedekerke, 2006).

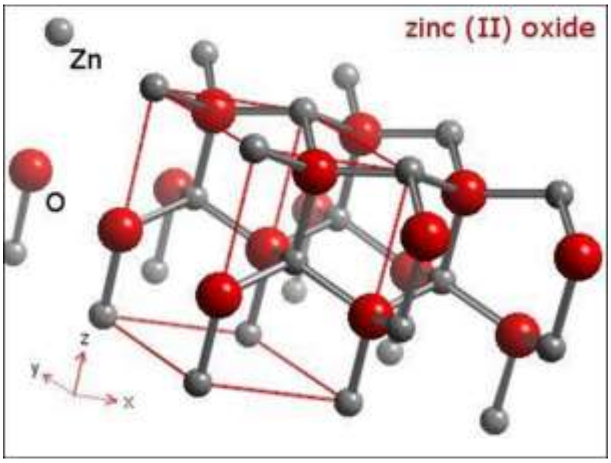

Figure 4. Crystal structure of zinc oxide (Kıranşan, 2015)

Due to it is zinc oxide photocatalytic, electronic, dermatological and antibacterial properties, it is used in many different fields. Since the band gap range is 3.37 eV and has high binding energy, it is used as a catalyst in the photocatalytic systems (Liedekerke, 2006).

3.2.3 Tin Dioxide (SnO_2)

Tin dioxide is a white solid, formulated as the SnO_2 also known as tin (IV) oxide, with a band gap range of 3.7 eV and a molecular mass of the 150.71 g mol^{-1}. SnO_2 it is a semiconductor metal oxide with a tetragonal structure, n-type broadband spacing and a member of the permeable and conductive oxide family such as the ZnO, In_2O_3 (Tang, 2004).

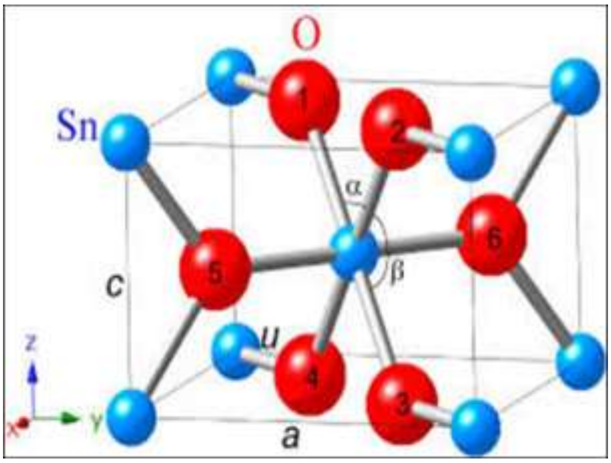

Figure 5. Crystal structure of tin dioxide (Cojocaru et al., 2017)

Since SnO_2 has many features together it has many uses. These it can be listed as heterogeneous catalysis, lithium-ion batteries, gas sensors, solar cells, infrared reflector, aircraft glasses (heater element).

3.2.4 Manganese Dioxide (MnO_2)

Manganese dioxide is an octahedral solid brown-black color with a band gap range of 3.0 eV and a molecular mass of the 86.94 g mol^{-1}, also known as manganese (IV) oxide, formulated as MnO_2. It can be said that like other oxides, MnO_2 is the polymorphic structure that crystallizes in the rutile crystal structure. Manganese dioxide is one of the oldest known natural ingredients used by people (Reidies, 2002).

MnO, it was known as an iron compound until 1774. Until 1856, while the commercial importance of manga was not yet noticed, it became important when the used by Bessemer as an additive to steel. Mangan in nature they are exist in the form of the oxide minerals and sulfides, such as the MnO_2 and MnS.

MnO_2, it has found it is own use in the dry batteries, glass surfaces and whitening of the blackened glass steel production (Reidies, 2002).

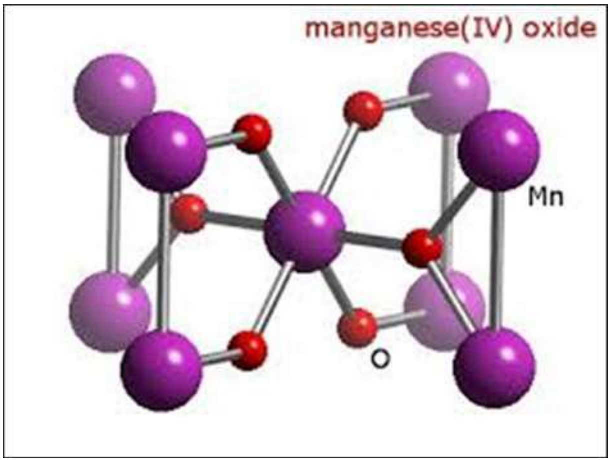

Figure 6. Crystal structure of manganese dioxide (Akhmetova et al., 2018)

4. CONCLUSION

As a result of the development of the use and applications of metal oxide semiconductor materials synthesized by the sol-gel method in the field of photocatalyst, the treatment processes of the textile organic dyes and pharmaceutical waste represent a vibrant and powerful technology that leads to superior improvement and sustainable water pollution control. The metal oxide semiconductor materials synthesized by the sol-gel method started a major revolution in the field of the environmental technologies thanks to their favorite features such as low cost and low density. Ultimately, much more dedication and further research are needed to expand this area of the research, improve the performance of the semiconductor metal oxides and expand its wide-scale application.

In addition, interdisciplinary collaboration between materials science, chemistry, physics and nanotechnology engineering needs to the provide a comprehensive understanding of the synthesis, regeneration and application of the sol-gel supported semiconductor metal oxide nanocatalysts.

ACKNOWLEDGEMENTS

The authors would like to express special thanks to the Gümüşhane University for supports.

REFERENCES

Cao L, Huang A, Spiess FJ. Suib SL 1999. Gas-phase oxidation of 1-butene using nanoscale TiO_2 photocatalysts. Journal of Catalysis, 188: 48.

Cömert AH 2019. Bor katkılı ince film kaplamaların sol-jel yöntemiyle hazırlanması ve karakterizasyonu. Yüksek Lisans Tezi, Giresun Üniversitesi, Fen Bilimleri Enstitüsü, Giresun.

Evcin A 2010. Sol-jel prosesleri ders notları. Afyon Kocatepe Üniversitesi, Seramik Mühendisliği Lisans Dersi, Ders Notları, Afyon.

Gençer A 2014. Anorganik nanopartiküller içeren ultraviyole koruyucu sert kaplamalar. Yükseklisans Tezi, Akdeniz Üniversitesi, Fen Bilimleri Enstitüsü, Antalya.

Kıranşan M 2015. ZnO/montmorillonit nanokompozitin sentezi ve bazı organik kirleticilerin fotokatalitik-ozonlama prosesi ile gideriminde kullanım etkinliğinin incelenmesi. Doktora Tezi, Atatürk Üniversitesi, Fen Bilimleri Enstitüsü, Erzurum.

Kondarides DI, Verykios XE 2013 Ch 15: Photocatalytic Production of Renewable Hydrogen. In: Triantafyllidis KS, Lappas AA, Stöcker M, Editors. The Role of Catalysis for the Sustainable Production of Bio-fuels and Bio-chemicals, Elsevier.

Kathiryelu S, D'Souza L, Dhurai B 2008. Nanotechnology applications in textiles. Indian Journal of Science and Technology, 1(5): 1-10.

Livage J, Sanchez C 1992. Sol-jel chemistry. Journal of Non-Crystalline Solids, 145: 11-19.

Liedekerke MD, Zinc Oxide: Pigments. Inorganic 1' Ullmann's Encyclopdia of Industrial Chemistry, 2006.

Malik T, Nogja S, Goyal P 2010. Self-Cleaning Textile an overview.

Mori K 2004. Photo-functionalized materials using nanoparticles: photocatalysis. J. Soc. Powder Technology, 41: 750-756.

Niederberger M, Pinna N 2009. Metal alkoxide nanoparticles in organic solvents: Synthesis, Formation. Assembly and Application XII, Springer.

Tang Y 2004. Synthesis and characterization of tin oxide for thin films gas sensor applications. PhD thesis, Deparment of Metarials Science and Engineering, Case Western Reserve University, USA,

Tamirci M 2003. Fotokatalizör ve uygulama alanları. Standart Ekonomik ve Teknik Dergi, Mayıs.

Ogawa T, Murata N, Yamazaki S 2003. Devolepment of anti-fogging mirror coated with SiO_2-ZrO_2-colloidal SiO_2 film by sol-gel process. Journal of Sol-Gel Science and Technology, 27: 237-238.

Pelaez M 2012. A review on the visible light active titanium dioxide photocatalysts for environmental applications. Applied Catalysis B: Environmental, 125: 331-349.

Pfitzner A, Dankesreiter S, Eisenhofer A, Cherevatskaya M 2013 Heterogeneous semiconductor photocatalysis. In: König B., Editor, Chemical Photocatalysis, De Gruyter.

Pierre AC 1998. Introduction to sol-gel processing. Kluwer Academic Publishers. Boston, Dordrecht, London.

Sayılkan F 2007. Nano-TiO_2 fotokatalizör sentezi ve fotokatalitik aktivitesinin belirlenmesi. Doktora Tezi, İnönü Üniversitesi, Fen Bilimleri Enstitüsü, Kimya Anabilimdalı, Malatya.

Schmidt H. 1988. Chemistry of material preparation by the sol-jel process. Journal of Non-Crystalline Solids, 100: 51-64.

Segal DD 1994. Chemical synthesis of advanced ceramic. Journal of Materials Chemistry, 4: 1611-1617.

Qi K, Xin JH, Daoud WA, Mak, CL 2007. Functionalizing polyester fiber with a self-cleaning property using anatase TiO_2 and low temperature plasma treatment. International Journal of Applied CeramicTechnology, 4(6): 554-563.