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العدد الثاني والعشرون

يناير 2023م

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-تعدل البحوث المقبولة وتصحح وفق ما يراه المحكمون .

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Manufacturing of Porous Metal Oxides HTiNbO5 Catalyst

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Abstract: Metal oxides with high porosity work very well as catalyst for the degradation of organic pesticides compared with the corresponding bulk materials. Template-assisted method is generally employed to prepare porous metal oxides. High surface area semiconductor porous material made of titanium niobium mixed oxide (HTiNbO5) catalyst has been synthesized. The manufacturing processes start with solid-state followed by acid exchange, exfoliation, precipitation, washing, and finally super critical drying. The catalytic activity of the material was investigated for degradation of halogenated compounds.

Keywords: porous metal oxides, acid exchange, exfoliation, precipitation, water pollution.

INTRODUCTION

Water pollution by organic compounds is one of the most serious environmental problems worldwide. The main sources of these pollutants are the industries, the use of fuel for transportation, aerosol sprays, pesticides, fertilizers, and detergents. Many pollutants, such as halogenated hydrocarbons and pesticides, can be persistent in the environment and are hazardous with chronic exposure at ppm and ppb concentrations (**Shertzer, et. al. 2004**). These pollutants can reach into groundwater and get into the food chain of human and other living organisms; therefore, their removal is critical (**Schiavello, et. al. M. 1988**). The most effects of chlorinated organic compounds on the human are cancer, and effects on reproduction, neurobehavior and the immune system. They have also been shown to be particularly toxic to the developing embryo, fetus and infant. some compounds which considered toxic to humans at the levels occurring in the environment are the dioxins (PCDDs and PCDFs), PCBs, DDT, as well as some other organochlorine pesticides. When PCBs are burned, even more toxic dioxins are formed. There are many physical and chemical methods for the removal of chemicals from water which include the use of anionexchange resins, flotation, ozonation, electro flotation, electrochemicaldestruction, irradiation, adsorption, and filtration (**Fujishima, et. al. 2000**,**Gao, et.al.2004**). Most of these techniques are effective for water decontamination but use more energy and chemicals. Photo-degradation is an active and cheap way to remove these contaminates. TiO_2 powder is a good catalyst for photo-degradation but hard to remove from water because it has small particles and they easily stay suspended in the water, penetrate filter materials, and clog filter membranes. This requires the need for larger catalyst particles to be used as photo-catalyst. Heterogeneous photo-catalyst which has been proven to effect full mineralization of organic pollutants has recently emerged as an efficient method for purifying water and air. HTiNbO5 which made up of titanium and niobium metal oxide is one promising TiO2-based photo catalyst to oxidize organic compounds.

Materials and methods

In this research, we synthesis high surface area semiconductor porous material made of titanium niobium mixed oxide to solve the problems of stability, crystallinity, and problems of small particle size, catalyst retrieval, and the need for high reactivity. photo-catalyst was used in the presence of UV light to remove organic compounds fromwaste water. The new materials have stable macro porous structures, suitable for effective fluid flow throughout the catalyst's surfaces and high surface areas (SA).

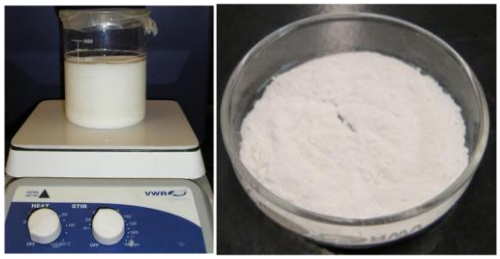
Solid State Synthetic Reaction

For the preparation of the semiconductor Potassium Titanium Niobium Pentoxide (KTiNbO5) by a conventional solid state synthesis method, a 7.0 grams of potassium carbonate (K2CO3.1.5H2O), Fisher Chemicals, Fairlawn, New Jersey, was first ground in a mortar and pestle and heated in an oven to 230 °C for two hours to remove the water. It was then added to the mixture of 8.0 grams of titanium dioxide (TiO_2, 99.9 %, Sigma-Aldrich) and 13.3 grams of niobium (V) oxide (Nb_2O_5, 99.5 %, Alfa Aesar). The mixture was then ground into a fine powder and placed in an alumina crucible and heated gradually in air to 1050 °C for 20 hours by using high temperature furnace. (BF51800 Series).

A 5% excess of K_2CO_3 was used to compensate for the loss of potassium as an oxide vapor during the heating. For this reaction, the temperature was raised to 120 °C at a rate of 10 °C per minute and held for the next 30 minutes. Then the temperature was raised to 1050°C at a rate of 10 °C per minute and held there for the next 20 hours. Finally, it was allowed to cool to 25 °C. The material $KTiNbO_5$ was then stored in the desiccators.

Preparation of HTiNbO5 from KTiNbO5 (acid exchange of KTiNbO5)

In this procedure, five grams of powdered parent material $KTiNbO_5$ were stirred in a 500.00 mL beaker with 250 mL of de-ionized water (DI) and 100 ml of concentrated hydrochloric acid (12 M) HCl for one day with no heat. The beaker was covered with a Parafilm. The mixture was centrifuged at 3000 rpm for 10 minutes using a Beckman Coulter centrifuge (Allegra X-12 R Series Centrifuge). The liquid was poured out and the solid was recuperated using DI water and placed back into the beaker. These steps were repeated every 24 hours for three days for a total of four acid exchanges. For the final and complete removal of solids from the bottom of the centrifuge tubes, a few amounts of ethanol were used to transfer the residue to a glass Petri dish. Finally, it was dried at room temperature (figure 1B). In octahedral $HTiNbO_5$, H^+ ions are emplaced between 2D anion sheets composed of TiO_6 and NbO_6. (**Colin,et.al.2006**). Acolloidal solution cannot be potassium ions are exchanged for hydrogen ions (figure 2) (Clearfield, 1988)**.**



A B

Figure 1- A-Stirring powders of KTiNbO5 B- Powder of $HTiNbO_5$

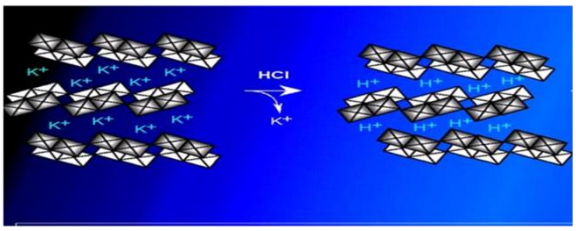


Figure: 2-$KTiNbO_5$ have layered structures with exchangeable cations

Exfoliation of HTiNbO5 into Single Sheet

Exfoliation of $HTiNbO_5$ in aqueous solutions formed colloidal single-crystal $TiNbO_5^-$ nano-sheets, which precipitated under an acidic condition to form aggregates of $HTiNbO_5$ nano-sheets. This chemical transformation of lamellar metal oxides into single sheet colloids or nano-sheets occurred when the powdered acid exchange ($HTiNbO_5$) reacted with Tetra Butyl Ammonium Hydroxide (TBAOH) by an acid base neutralization reaction (**AtsushiTakagaki. et. al.2003,Fang, er.al. 1999**)

$$HTiNbO_5 + TBA^+OH^- \longrightarrow TiNbO_5^- + TBA^+ + H_2O \quad \text{..... (Eq. 1)}$$

This reaction results the exfoliation of the individual metal oxide sheets when the hydrogen ions replaced by TBA^+ cations between the layers (Figure 3). The exfoliated metal oxide sheets ($TiNbO_5^-$) are negatively charged, therefore they allow TBA^+ counter cations on their surface to form two-dimensional (2D) macro polyanions. 2 grams of acid exchanged powder $HTiNbO_5$ was measured and added to 100 mL of DI water. Two drops from Phenolphthalein dye were added to the solution as indicator.

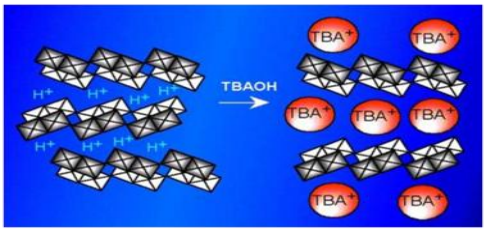


Figure: 3 Acid base neutralization reactions between $HTiNbO_5$ and TBAOH

A solution of 40% TBA^+ OH^- (Alfa Aesar) was added to the mixture drop by drop until the white color changes to light pink and pH became above 9.0. The mixture was stirred for one day to ensure the stability of the pink color. 1.3 ml of TBAOH was added. The pH of the colloid should be tested every one or two weeks or when the pink color disappears. The PH measurement was done by using a special low-leakage pH meter (Henna instruments pH 213, microprocessor pH meter, Portugal).

Precipitation procedure of exfoliated solution

The purpose of this process is to make the catalytic materials porous. Colloids of the titan niobate particles were precipitated in a glass vial with both sides closed with a vial cap and then 5mL of $HTiNbO_5$ colloid solution was added to the vial with 15 mL of water. The mixture was mixed very well. Then, 3 drops of 6 M HCl were added from each side of the vial and the vial was closed with a cap. The solid was left for two days. The nano-sheets formed aggregates during this period resulting in porous solids.

Removal of Solvent

Precipitating colloidal was rinsed with water, followed by ethanol and then acetone.The vial was placed on a clamp and stand. The precipitating sample was rinsed with 300 ml water, followed by 300 ml of ethanol and then 500 ml of acetone by using 60 mL plastic syringe through flexible polyethylene tubing and a needle which is connected to the top of the vial. Small holes were made in the bottom cap of the vial to allow the solvent out (figure 4). After that, the top cap was replaced with a wire mesh cap(to allow the passage of solvent during CO_2drying steps).

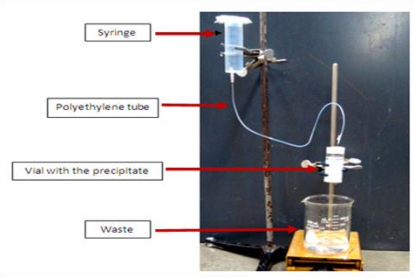


Figure: 4washing of the metal oxide aggregates.

The supercritical point CO2 drying process

The Supercritical point CO2 drying process allowed the samples to be dried without any solvent surface tension and prevent the shrinkage of the sample. Carbon dioxide is the most commonly used supercritical fluid due to its low toxicity and environmental impact. In its supercritical state, at temperature and pressure above its critical point (Tc =31.1 ◦C and Pc = 72.9 atm), CO_2 has both gas-like and liquid-like qualities. In the end of the critical point the liquid and the gas phases. Disappear to become a single supercritical phase. In this process, acetone is first used to remove away all water. The acetone is then flashed away with high pressure liquid carbon dioxide. After that, the liquid carbon dioxide is heated until its temperature goes beyond the critical point, at which time the pressure can be gradually released; allowing the gas to escape and leaving a dried product without destroy it.

A CO_2 supercritical point drying system (Quorum Technologies, East Sussex, and U.K) was used to dry the precipitating sample. This procedure is directly following solvent removal process. The chamber (figure 5 A) was cleaned filled with acetone until 3/4. The sample was placed inside the chamber and the chamber lid was closed and cooled to about 15-19 ^{o}C by circulating cold water. The CO_2 tank valve and chamber inlet valve were opened to begin liquid CO_2 goes inside the chamber and acetone flushed out from bottom outlet. After some time, the CO_2 liquid and the acetone were separated, which the acetone moved down as pure CO_2 comes in. the chamber was filled and emptied for three times with occasional agitation to promote the mixing. Then chamber was filled to 3/4, and all chamber valves were closed and the cold pump was turned off. The chamber temperature was then raised to 30 °C by turning on the heater and hot pump using circulating hot water. Then hot water circulation was stopped and the chamber temperature remained the same for 30 minutes.

A B

Figure: 5 -A chamber B- Dried porous metal oxide

The chamber was cooled again to 15 °C and the CO_2 inlet valve and the outlet valve were opened to let in and flush out CO_2 for 10 minutes. Finally, the chamber was filled 2/3 full. After that, all the valves were closed and the chamber was heated to 40 °C. During this period, the CO_2 reached the supercritical point phase. The chamber was kept at 40 °C, for 15 minutes. The top vent was opened and very slowly to release the gas. When the pressure reached the atmospheric level, the chamber was opened**.**

Topotactic dehydration of $HTiNbO_5$($Ti_2Nb_2O_9$ Synthesis)

A topotactic dehydration treatment was developed to enhance the electronic conductivity and improve the activity of the catalyst. The layers of dried porous metal oxide materials ($HTiNbO_5$) are connected to each other through their corners with two layers being interconnected through short H-O· · ·H hydrogen bonds which act as a bridge between them (**Colin, et. al. 2008**). When the distance between the layers is reduced, the electronic conduction will improve. A top otactic for the dehydration of $HTiNbO_5$ will lead to a three-dimensional (3D) structure with empty tunnels ($Ti_2Nb_2O_9$). $HTiNbO_5$($_{in}$ figure 5B)is dehydrated at 450°C for 2 hours in the furnace producing top otactic dehydrated POX by vaporizing H_2O ($Ti_2Nb_2O_9$). In this reaction, OH groups from adjacent layers condense, eliminating water and joining the corners of titanate and niobate octahedral, as shown in Figure (6). The ionic bonding between the sheets is converted in to covalent bonding by dehydrating the material top otactically(**Fang, et. al. 1999**).

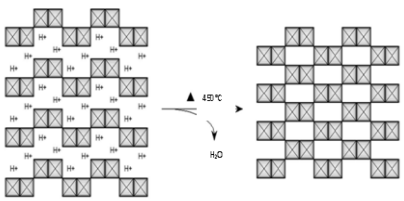


Figure: 6 condensation of $HTiNbO_5$ to $Ti_2Nb_2O_9$.

Conclusion

A porous metal oxide made of titanium and niobium ($KTiNbO_5$) was prepared via a solid-state synthesis, followed by acid exchange, exfoliation, precipitation, washing, and finally a supercritical point drying process.

The results of the (**Hadidan, et. al. 2019**). work demonstrated the effectiveness of the new catalyst in the photo-degradation of the halogenated organic compounds (1-chlorobutane ($CH_3(CH_2)_3Cl$), dichloromethane (CH_2Cl_2), chlorobenzene was adequate to determine the process of degradation; however, a more comprehensive study is needed to confirm the intermediate products of the process (**Hadidan, et. al. 2019**).

A closed photo catalytic system, where one can control the oxygen supply and detectthe released gasses should be employed. Testing this material with other widely used toxic halogenated organic compounds, like pesticides and herbicides, should be done.

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