Microwave assisted heterogeneous vapor-phase oxidation of 3-picoline to nicotinic acid over vanadium–titanium oxide catalytic system

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ABSTRACT

Binary vanadium–titanium oxide catalysts as well as pure V_2O_5 and TiO_2 (anatase) were studied in microwave assisted vapor-phase oxidation of 3-picoline by oxygen in the presence of nitrogen and water vapors. The main product of the reaction over all catalysts was nicotinic acid. 3-pyridinecarbaldehyde, 3-cyanopyridine, and CO_2 were obtained at smaller amounts. The highest rate of the reaction calculated per square meter of the catalyst surface was observed over pure vanadium oxide. Decrease in vanadium oxide content in the binary catalysts led to decrease in the rate of 3-picoline conversion. Titanium dioxide (anatase) demonstrated the lowest activity. Much more energy was necessary to heat pure titanium oxide to the reaction temperature when compared to the pure vanadium oxide. The microwave heating effect can be located on the V_2O_5 catalyst active component. Due to specific temperature distribution, the lattice oxygen in the microwave effective dielectric vanadium oxide becomes more mobile inducing the rate of 3-picoline oxidation to nicotinic acid. The data obtained under microwave heating were compared to the results produced over the same catalysts by applying classical conventional energy.

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1. Introduction

The main product of 3-picoline selective oxidation is nicotinic acid, more commonly known as niacin or vitamin B_3. Nicotinic acid is a building block for important co-enzymes (NAD and NADP) which are required by all living cells. Niacin is widely used in the fields of medicine, food industry, and agriculture. It has been industrially produced by oxidation of 3-methylpyridine or 2-methyl-5-ethylpyridine with strong oxidizers (potassium permanganate or nitric acid) under high pressure in the liquid phase or by a two-step gas-phase catalytic ammoxidation of 3-methylpyridine to 3-cyanopyridine followed by a hydrolysis of the latter to nicotinic acid [1–3]. A recent discovery has shown that a better and cleaner way to obtain nicotinic acid is a one-step heterogeneous gas-phase oxidation of 3-picoline over vanadium–titanium oxide catalysts using air as an oxidizing agent [4–10]. This continuous flow method meets all the "green" process requirements: no liquid and gaseous wastes

and ease of product (nicotinic acid) isolation. However, this method of preparing nicotinic acid still needs to be improved. First, the process capacity is low due to the kinetic restrictions in the oxygen/3-picoline concentrations ratio (>40) which is needed to keep the catalyst activity at a high level. Second, considerable conventional energy consumption occurs when the reactor with a catalyst is heated.

One of the environmentally friendly energy sources is microwave energy. Microwave irradiation is becoming increasingly popular as a clean, cheap, convenient method of heating, increasing yields, and decreasing reaction times while using less power input [11–13]. Microwave irradiation is a way of applying energy directly to the reaction system rather than through other media. The conversion of electromagnetic energy in heat occurs simultaneously and evenly by heating a solid catalyst while microwave transparent materials (insulation, reactor wall and gas phase) are penetrated without energy consumption.

The aim of this work is to investigate the influence of microwave energy on heterogeneous vapor-phase oxidation of 3-picoline over V—Ti—O catalytic system.

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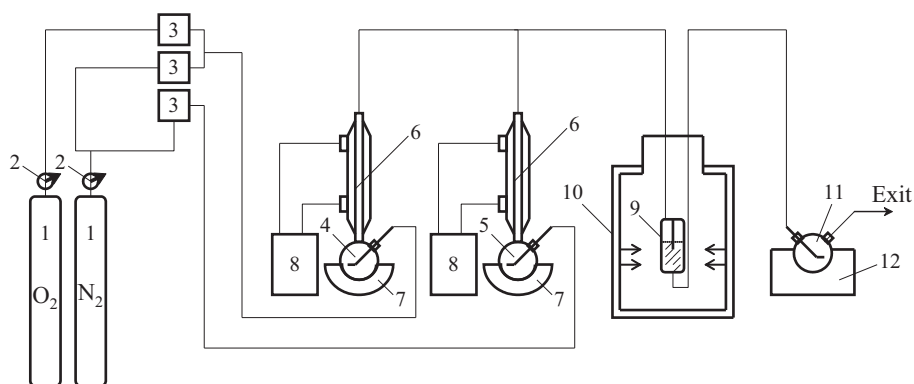E-mail addresses: alkayeva@fordham.edu, alkayeva@yahoo.com (Y. Alkayeva).

Fig. 1. Schematic diagram of the experimental set up.
1 – gas cylinder, 2 – gas regulator, 3 – flow mass controller, 4 – flask with distilled water,
5 – flask with 3-picoline, 6 – condenser, 7 – heating mantel, 8 – water circulator,
9 – reactor, 10 – microwave oven, 11 – receiving flask, 12 – cooler.

2. Experimental

2.1. Catalytic testing

Microwave "Discover" system with "Open vessel" option (CEM Corporation) was used to heat the catalyst. A sample of the catalyst (0.25–0.50 mm fraction) mixed with quartz of similar size particles was placed on a frit support in a tubular quartz reactor (diameter 15 mm, length 50 mm) with a coaxial thermocouple pocket (diameter 5 mm). "Discover open vessel" application is equipped with attenuator providing access for the reactor and thermocouple into the instrument cavity while preventing microwave leakage during operation. A non-metallic Fiber Optic thermocouple was used to control and measure the temperature in a catalyst layer. "Discover" system has an option which allows programming the amount of microwave power applied and a maximum temperature threshold above which the system will not apply microwave energy. However, during the experiment with set power and temperature, the measured parameters constantly varied. When the temperature reached the set point, the power decreased and produced temperature fluctuations. Observed temperature variations were $\pm(6–10^\circ$ C) around the set temperature. Another condition affecting the experiment in microwave "Discover" system dealt with the catalyst layer. It was discovered that to a large degree microwave energy irradiated only up to 3 cm of the catalyst layer, which limited the volume of catalyst sample in the reactor.

The set parameter ranges used in our experiments are: microwave power 18–160 W, temperature 170–220 °C. The measured temperature can be considered as an average temperature; because the real temperature on the surface of catalyst particles and the temperature of localized "hot spots" accompanying microwave heating are unknown. The effects of hot spot formation are described in literature [14,15].

Fig. 1 represents an experimental set up. The feeding system delivering all components of the reaction mixture into reactor is comprised of two tanks containing gaseous oxygen (99.9%) and nitrogen (99.9%), a heated Pyrex flask with liquid 3-picoline (Sigma–Aldridge, 99%), and a heated Pyrex flask with a distilled water. The gas flows were controlled and measured by Flow mass controllers (Aalborg Co). To provide proper concentrations of 3-picoline and water vapors, a reflux system with condensers connected to water circulators was used. Vapors were directed into reactor by using nitrogen for 3-picoline, and a mixture of nitrogen and oxygen for water. SS tubing carrying a four-component gas mixture into reactor as well as a mixture of the gas reaction products were heated to approximately 150 °C to prevent vapor condensation.

The optimal initial total gas volume passing through the microwave heated reactor was around but never less than 25 L/h. It provided a proper linear rate of a gas mixture preventing diffusion complications and ensuring high activity, high partial oxidation products selectivity, and stability of the catalyst.

Experiments involving classical conventional energy were performed using the same set up with the exception of a MW oven being substituted for electrical oven and a Fiber optic thermocouple for metal K-thermocouple.

The initial components and reaction products were analyzed by Gas Chromatography (Shimadzu GC-8A). A mixture of unconverted 3-picoline, 3-pyridinecarbaldehyde and 3-cyanopyridine collected in a receiving flask was separated in Carbowax column; CO_2 taken from the gas phase was separated from air in Porapak Q column. For separation of O_2, N_2 and CO (not found in our experiments), molecular sieves were used. All three columns were attached to the chromatograph equipped with a thermal conductivity detector. A small amount of nicotinic acid in a receiving flask was analyzed by using an Equity capillary column (Sigma–Aldrich) and a flame ionization detector.

The main amount of Nicotinic acid as a white powder was deposited in the outlet arm of the reactor below the frit holding a catalyst. The melting point as well as the mixed melting point of the collected nicotinic acid confirmed its purity. To simplify the balance calculations, series of experiments with nicotinic acid collection were performed under conditions when the reactor was weighed before and after the reaction with the catalyst off. The amount of nicotinic acid obtained was added to the amounts of other products in accordance with their stoichiometry. The calculated balance was about 98%. This number was used to calculate the selectivity for nicotinic acid in all other experiments.

2.2. Catalyst preparation and characterization

Binary V—Ti—O catalysts were prepared by spray drying of a mixture of titanium dioxide (anatase form) and vanadyl oxalate solution followed by calcination in a flowing air at 400–500 °C for 4 h. Vanadium oxide (99.9%, Sigma–Aldrich) was calcined at 450 C for 4 h. A detailed description of catalysts preparation and characterization can be found in [16–23].

Catalysts characteristics (chemical composition, phase composition, specific surface area, and particle size) are given in the Table 1.