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SELECTIVE OXIDATION OF ANTHRACENE TO 9,10-ANTHRAQUINONE OVER SILICA SUPPORTED VANADIUM CATALYST

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Abstract

The inner-ring oxidation of anthracene over V_2O_5/SiO_2 catalyst was investigated at various oxygen concentrations, contact times of the reactants and reaction temperatures. Up to 90 % yield to 9,10-anthraquinone is obtained at 218-220°C.

Keywords: Anthracene, anthraquinone, phthalic anhydride, oxidation

INTRODUCTION

Anthraquinone ($C_{14}O_2H_8$) is an intermediate in the manufacture of pigments and dyes, an additive in the kraft pulping process in the paper industry and is also applied in the synthesis of hydrogen peroxide. On a small scale, it is used as a catalyst in the isomerization of vegetable oils, an accelerator in nickel electroplating and as a bird repellent [1-3]. There are a variety of methods to produce anthraquinone, however, 85% of the world production is based on the vapor phase oxidation of anthracene with air. The industrial process is performed over a supported iron vanadate-potassium catalyst at 390°C with a 99% yield to the quinone [3].

Many publications and patents have been devoted to investigate the vapor-phase oxidation of anthracene over vanadium based materials that contain additives such as iron, manganese, molybdenum, cesium, potassium, chromium and others [4-10]. However, no information about the catalytic activity of vanadium pentoxide without additives is reported in the literature. The aim of the present study is to investigate the selective oxidation of anthracene with air over pure V_2O_5 supported on silica. More specifically, the influence of operative parameters such as temperature, contact time of the feeding mixture and molar ratio of reactants on the yield towards 9,10-anthraquinone was studied.

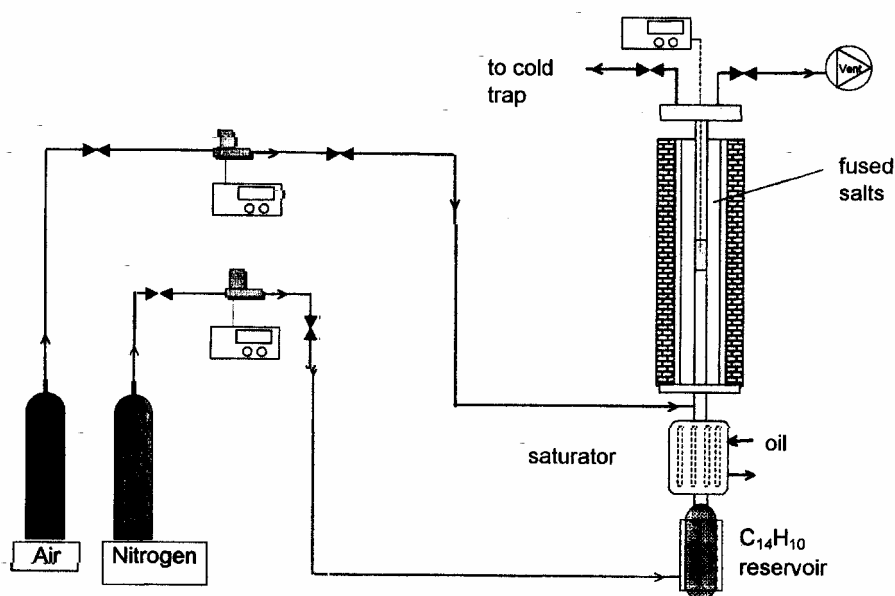


Fig. 1. Flow sheet of the equipment for the selective oxidation of anthracene

EXPERIMENTAL

Selective oxidation of anthracene. Figure 1 shows the equipment where the selective oxidation of anthracene was performed. This equipment possesses the same features of the industrial reactor [3]. Anthracene (Fluka, >95 %) is placed in a reservoir at the bottom of the reactor at 200°C. A current of nitrogen drives the vapor to a saturator at 240°C. The gas current is mixed with pre-heated air at 250°C and led into the reactor from the bottom. The flow rates of nitrogen and air are electronically adjusted with mass flow controllers (MKS) in order to maintain the concentration of anthracene below the flammability limits (0.6 % volume of anthracene in air).

The reactor is a stainless steel tube of 1.0 m long and 5.0 cm internal diameter with an electronic temperature control. Typically, the experiments were performed with 17 g of catalyst (volume = 2 cm³).

The flow of gases from the reactor goes through a cold trap at 0°C that retains condensable products. The solid sample is dissolved in chloroform (Merck PA) and analyzed by mass spectrometry to establish the composition of the mixture. The amounts of anthracene and products of reaction are determined by gas chromatography in a GC (Perkin Elmer Autosystem) equipped with a flame ionization detector and a capillary column (methyl 5% phenyl silicone, 25 m long and 0.32 mm internal diameter).

Catalytic material. The catalyst V₂O₅/SiO₂ was synthesized with the incipient wetness method from an aqueous solution of oxalic acid and the required amount of NH₄VO₃ (Baker, 99.2 %) to obtain 8 μmol of vanadium per m² of oxide support. Silica (Grace Davison Grade 59, 250 m²/g) previously calcined at 500°C was used as support of the active phase. The precursor was dried at 100°C and calcined at 500°C for 2 h under a stream of air to ensure the oxidation of the active phase.

According to the literature, the required amount of vanadium to cover silica with a bi-dimensional monolayer of VO_x species is 1 μmol/m² [11]. Therefore, it is possible to establish that the present catalyst is composed of bulk V₂O₅, since the concentration of vanadium greatly exceeds the monolayer coverage.

RESULTS AND DISCUSSION

The selective oxidation of anthracene was investigated at temperatures above the melting point of anthracene (217°C) in order to maintain the reactant in the vapor phase. The analysis of the condensable products of the selective oxidation of anthracene showed that only 9,10-anthraquinone and phthalic anhydride are produced under the reaction conditions of the experiments.

Figures 2 and 3 show the yield towards 9,10-anthraquinone versus the temperature of reaction at various molar ratios of the reactants C₁₄H₁₀/O₂ and

contact times of the feeding mixture (anthracene-nitrogen-oxygen), respectively. The "contact time" is the time that takes the feeding mixture to go through the catalyst bed. This parameter was calculated as the ratio between the volume of the catalyst bed and the flow rate of the feeding mixture.

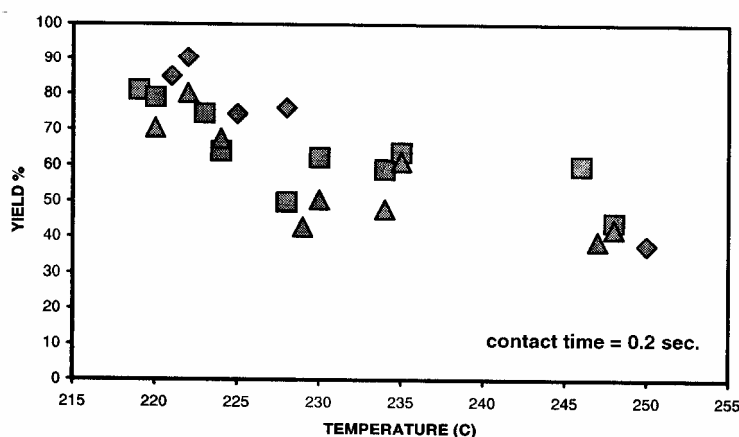


Fig. 2. Yield towards 9,10-anthraquinone versus temperature at different molar ratio of reactants. Symbols: ♦ (diamond) $C_{14}H_{10}/O_2 = 0.02$, ■ (square) $C_{14}H_{10}/O_2 = 0.03$ and ▲ (triangle) $C_{14}H_{10}/O_2 = 0.05$

The yield possesses no dependence on the concentration of oxygen in the gas phase or the contact time of the feeding mixture in the range under study. However, shows a strong dependence with the temperature of reaction. The highest yield towards 9,10-anthraquinone is obtained at low temperatures, typically 218-222°C. The yield towards the quinone diminishes and the production of phthalic anhydride increases rapidly at temperatures above 224°C (data not shown). This result suggests that the quinone is the first product of the selective oxidation of anthracene and an intermediate in the generation of phthalic anhydride in accordance with the literature [5].

The values of conversion of anthracene and products selectivity showed no modification for a week, which ensures the stability of the V_2O_5/SiO_2 catalyst under reaction conditions. An important observation that should be highlighted is that the V_2O_5/SiO_2 catalyst possesses similar yield towards 9,10-anthraquinone at a lower temperature than the industrial catalyst [3]. In fact, the temperature to achieve 90% yield to 9,10-anthraquinone (~ 220°C) is about 40% lower than the industrial process.

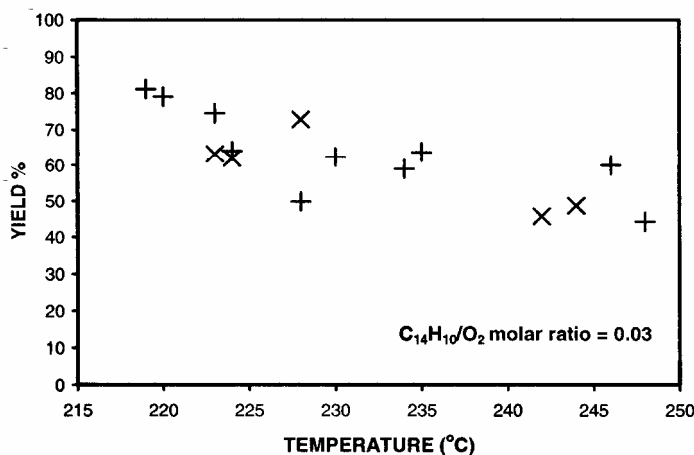


Fig. 3. Yield towards 9,10-anthraquinone versus temperature at different contact times of the feeding mixture. Symbols: + (cross) 0.2 s, x 0.4 s

Additionally, a low reaction temperature and the absence of highly oxidant promoters (Fe^{3+} , Mn^{2+} , Cr^{3+}) avoid further oxidation of the 9,10-anthraquinone to phthalic anhydride and COx which may explain the higher selectivity to quinone obtained in the present investigation than previous studies reported in the literature.

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