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OXIDATION OF TOLUENE OVER VANADIUM- ALUMINOPHOSPHATE WITH AEL STRUCTURE

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Abstract

Vanadium-aluminophosphate type eleven (VAPO-11), synthesized by the hydrothermal method, was used as catalyst for oxidation of toluene, in a differential reactor, at temperature 430-470°C, varying the space time (W/F₀). The reaction products were analyzed in a gas chromatograph coupled on line to the reactor. The results obtained indicate that VAPO-11 is an active catalyst for the oxidation of toluene to benzene and benzaldehyde.

Keywords: VAPO-11, oxidation catalyst, toluene

INTRODUCTION

It is well known that vanadium oxides are widely employed as catalysts in several oxidation processes, *e.g.*, the oxidation of sulfur, carbon monoxide and hydrocarbons [1,2]. Vanadium silicalites are active oxidation catalysts in gas and liquid phase reactions [3,4]. When supported, mostly oxidic materials can be used as oxidation catalysts. In general, the influence of the method of preparation, nature of support, concentration of active component and thermal treatment of support affect the performance of the catalyst.

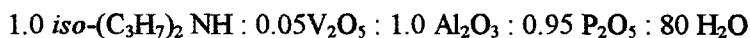
Oxidation of toluene in heterogeneous media using air as the oxidizing agent has advantages over other methods such as Friedel-Crafts carbonylation of benzene, chlorination of toluene and liquid phase oxidation of toluene.

In this study, we attempt to prepare, characterize and test a vanadium-based aluminophosphate molecular sieve (VAPO-11) in order to obtain a suitable catalyst for conversion of toluene with good selectivity to benzaldehyde. The use of several metal ions associated to molecular sieve frameworks, including VAPO-5 and VAPO-11, possible catalytic oxidation sites and some oxidation reactions have been reported [5].

EXPERIMENTAL

Catalyst preparation

The vanadium-aluminophosphate type eleven (VAPO-11) was synthesized by the hydrothermal method, starting from inorganic sources of ammonium vanadate, aluminium hydroxide (pseudoboehmite, Condea), 85% orthophosphoric acid (Merck), water. Diisopropylamine (Riedel) was used as organic template. The reactants were mixed in the following stoichiometric molar composition:



The reactive hydrogel was charged into a PTFE vessel, and autoclaved at 170°C for a period of three days, under autogenic pressure. The product was washed, dried and calcined at 500°C, with 60 mL min⁻¹ oxygen flowing.

Characterization

Infrared spectra were obtained by using the KBr technique, in the 1300 - 400 cm⁻¹, using a FT-IR MIDAC model. X-ray diffraction pattern of the sample was recorded on a Rigaku diffractometer using Cu-K α radiation, and the diffraction angle ranging from 5 to 50°. The chemical composition of the sample was estimated using a Varian AA-175 atomic absorption spectrometer. The morphology and size of the crystals were determined by scanning electron microscopy, in a Zeiss DSM microscope, at 10 kV and 77 μ A.

Catalyst testing

The catalytic tests were conducted in a differential reactor coupled on-line to a gas chromatograph. The experiments were carried out with 0.3 g of the calcined VAPO-11, at temperatures of 430, 450 and 470°C, and modified space time (W/F_o) ranging from 0 to 180 g cat mol⁻¹ h⁻¹. The toluene feed concentration was 0.5%. Before each reaction, the catalyst was activated at 470°C, in air flowing concentration of *ca.* 0.25 mol.% for 150 min.

RESULTS AND DISCUSSION

The XRD and FT-IR spectra, in the framework range, revealed the crystallization of VAPO-11, with typical AEL structure. By using a specific route of synthesis, microcrystals with typically orthorhombic morphology were obtained, as shown in Fig. 1.

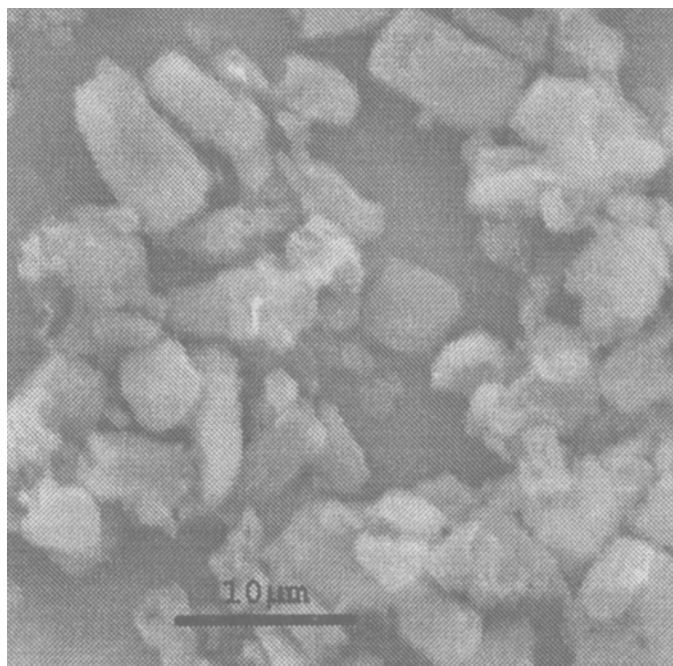
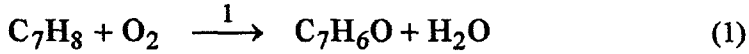


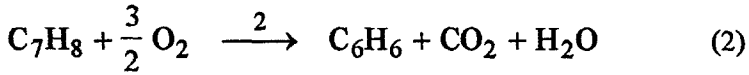
Fig. 1. Scanning electron micrograph of the as-synthesized VAPO-11

The tests indicated that VAPO-11, when acting as catalyst for toluene oxidation, forms benzene and benzaldehyde as reaction products, as shown in Fig. 2. However, the molar fraction of toluene in the products decreases with the space time. From this fact, it is supposed that high W/F_0 values must be favoring secondary reactions of complete oxidation of toluene, to carbon dioxide, according to the scheme shown below.

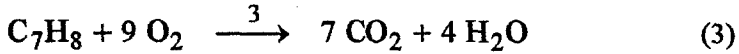
(i) Reaction of partial selective oxidation:



(ii) Reaction of disproportionation / oxidation:



(iii) Reaction of total oxidation:



The CO_2 emerges from the methyl groups, generated from toluene disproportionation, which can be oxidized to carbon dioxide, and also from the total degradation of toluene. The high selectivity to benzene evidences that the pore and channel system of VAPO-11 favors the disproportionation reaction instead of the selective oxidation, as shown in Fig. 2.

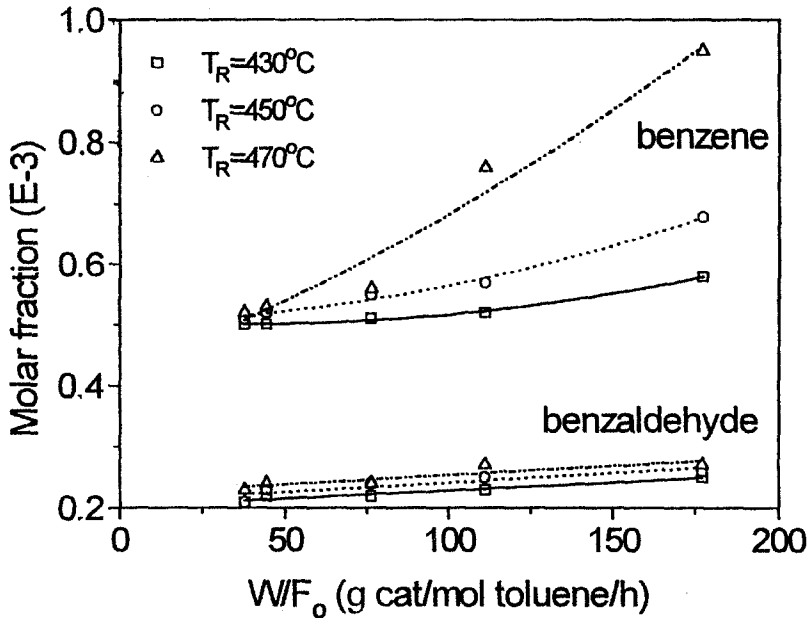


Fig. 2. Effect of the reaction temperature on the formation of products

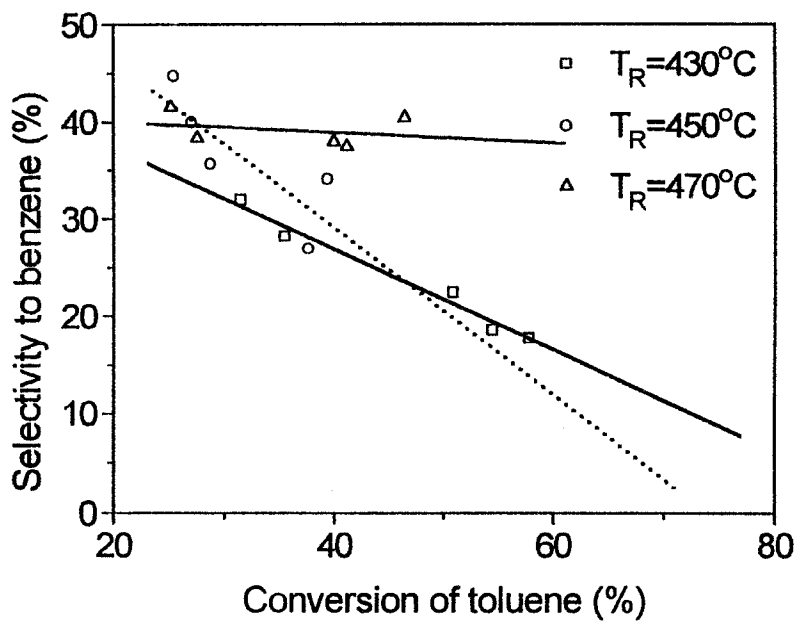


Fig. 3. Influence of toluene conversion on the selectivity to benzene

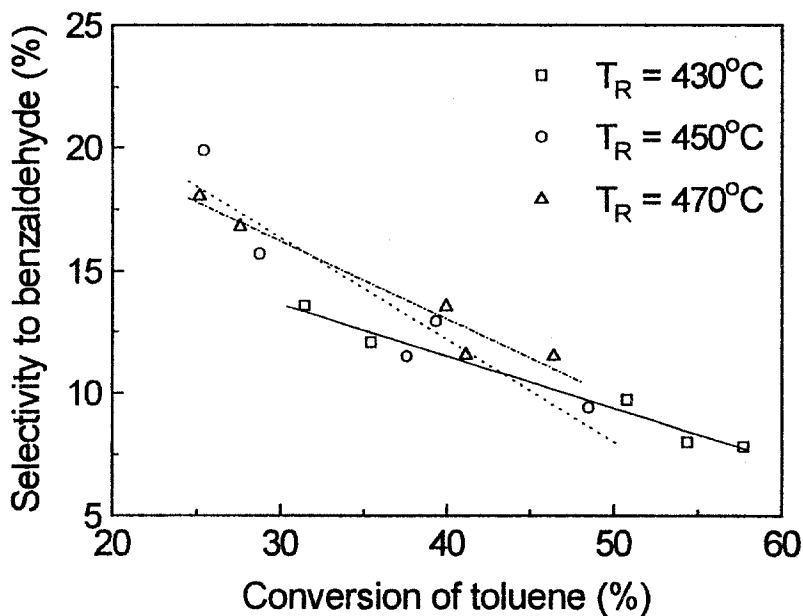


Fig. 4. Influence of toluene conversion on the selectivity to benzaldehyde

Comparing the molar fractions of benzaldehyde and benzene at 430, 450 and 470°C, it is observed that an increasing temperature to 470°C favors more the disproportionation/oxidation reaction than the selective oxidation. The high selectivity to benzene and to benzaldehyde were obtained at a reaction temperature of 450°C, as shown in Figs 3 and 4, respectively. However, the benzene selectivity is more stable at the temperature of 470°C.

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