Coke promoters improve acrolein selectivity in the gas-phase dehydration of glycerol to acrolein

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ABSTRACT

Commercial processes partially oxidize propylene to acrolein but glycerol can replace the petroleum derived feeds as a bio-feedstock for this large volume specialty chemical. Metal oxides, particularly acid catalysts, dehydrate glycerol at elevated temperature. Dehydration of glycerol to acrolein is usually performed in traditional fixed-bed reactors. We tested phosphotungstic acid (HPW) loaded on titania catalysts (a weight fraction of 10, 20 and 30%) at 280 °C in a fluidized-bed reactor. With time-on-stream, the acrolein selectivity increased and the coke selectivity decreased. As much as 85% of the glycerol formed coke in the first hour and less than 20% acrolein. We developed a new method to spray the liquid feed directly on the catalyst bed and the reaction occurred in the gas phase.

We also compared the performance of pure titania supports with respect to the acrolein selectivity. Acrolein selectivity was 13% higher on TiO$_2$ with an average pore diameter of 17.3 nm versus the TiO$_2$ support with a pore of 5.6 nm. Three times more coke formed on the small pore diameter TiO$_2$. We treated the catalyst with hydrogen rich coke promoters – tetralin and decalin – to passivate non-selective catalytic sites and to evidence hydrogen transfer reactions. This treatment increased acrolein selectivity from 10% to 30% in the first 30 min of reaction. As expected, they hydrogenated the intermediates to undesired compounds including acetone and propanaldehyde (propanal).

1. Introduction

Renewable feedstocks could replace petroleum to produce energy and chemicals. Researchers and industries endeavour to develop sustainable processes based on bio-resources. Adding biodiesel to petro-diesel is a first step to substitute petroleum fuel with bio-based fuels. Microalgae [1] and waste cooking oil [2] are possible large volume sources for biodiesel synthesis.

Glycerol is the main co-product of biodiesel synthesis (a mass fraction of 10%) and with the growing biodiesel industry the market has been overwhelmed resulting in low prices. Due to its multifunctional structure, glycerol is widely applied in various industries such as, food, cosmetics, pharmaceuticals and plastics. However, crude glycerol contains NGOM (non-glycerin organic matter), water, methanol and traces of fatty acids and must be purified. Distillation is an extra step in refining and thereby increases the cost of the process. Acrolein is versatile intermediate for the

chemical industry and is a feedstock for acrylic acid and its esters, glutaraldehyde, methionine, polyurethanes and polyester resins [3–5]. The principal commercial process to synthesize acrolein relies on propylene as a feedstock and multi-tubular fixed bed reactors. Mixed-metal oxide containing Mo and Bi catalyses this reaction at 250–400 °C [6,7].

Due to the availability of glycerol from biodiesel synthesis, dehydration of glycerol to acrolein is a potential economic alternative to propylene oxidation. The early studies of glycerol dehydration were patented in 1930 by Kahlbum [8]. The yield of acrolein was 75% over lithium phosphate catalyst.

Synthesis of acrolein from glycerol has been studied in both gas and liquid phase reactions. Generally, gas-phase dehydration is preferred due to the environmental and operational issues of liquid-phase reactions.

Several classes of catalysts such as zeolites, mixed-metal oxides and heteropoly acids dehydrate glycerol to acrolein. Brønsted acids are active and selective in acrolein synthesis, but deactivation of the catalyst is the major drawback in this case. Dubois et al. [9] suggested in situ regeneration of the catalyst by co-feeding of molecular oxygen. They observed that molecular oxygen not

only decreased the coking rate, but also improved the acrolein selectivity. Additionally, the catalyst maintained its activity and reduced the by-products such as acetol and phenol. Few studies have focused on the effect of coke formation on catalyst performance. Erfle et al. [10] analysed used vanadium based catalysts by FTIR spectroscopy and concluded that coke forms on Brønsted sites. This conclusion was confirmed by Suprun et al. [11] who evaluated carbon deposits on phosphate catalysts. They also observed that higher reaction temperatures and small pore diameter of the catalyst lead to further carbon formation. Pethan Rajan et al. [12] characterized spent VPO by TPD-NH$_3$ and FTIR-pyridine. The results showed that the acidity and Brønsted acidic sites of the catalyst decreased after 40 h time-on-stream. Consequently, the conversion and selectivity of the catalyst decreased. The selectivity of acrolein over coked WO$_3$/TiO$_2$ catalysts is higher than on fresh catalyst and it remains active even after 6 h reaction time [13]. As a first step, we evaluated the performance of the coked catalyst and observed that partial regeneration of the catalyst improved the selectivity of acrolein and less coke formed in the early stages of reaction.

Although gas-phase dehydration of glycerol to acrolein has been studied since 1930 [8], most of the focus in this area is dedicated to fixed-bed reactors. Fixed-bed reactors are associated with some major drawbacks such as poor heat and mass transfer and hot spot formation in case of exothermic reactions. Considering the rapid deactivation of acid catalysts, catalyst regeneration is necessary in dehydration of glycerol. A fluidized bed reactor is the most suitable choice for this case as it provides a homogeneous heat and mass transfer and avoids local accumulation of the coke in catalytic bed.

Here, we tested three loadings of tungsten oxide over large pore and narrow pore titania supports. We focused on the effect of pore diameter on acrolein, by-products and coke selectivity. As preserving some coke on the surface of WO$_3$/TiO$_2$ improved acrolein selectivity in the first 15 min of reaction [13], we developed a novel method to treat our catalysts with hydrogen rich coke promoters such as tetralin and decalin to passivate non-selective sites of the catalyst and increase acrolein selectivity and to evidence the hydrogen transfer reactions taking place in the early phases of the reaction.

2. Methodology

2.1. Catalyst preparation

We prepared catalysts with a mass fraction of 10, 20 and 30% phosphotungstic acid (H$_3$PW$_{12}$O$_{40}$ or HPW) on large pore and narrow pore titania supports provided by ARKEMA (Hombikat 11010 – HKT-1 and Hombikat 11060 – HKT-2). A LA-950 (Horiba) laser diffractometer measured the particle size distribution (PSD) of the pure titania. The mean particle size of the supports was 95 μm and 106 μm for the HKT-1 and the HKT-2 samples, respectively. The HPW (Nippon Inorganic Color & Chemical Co., Ltd.) dissolved in 10 ml of distilled water in a rotavapor flask (BUCHI R-210). We subsequently loaded 10 g of titania to the flask. The rotavapor mixed the slurry for 2 h at room temperature. We applied a 60 mbar vacuum and heated the flask to 60 °C. The samples then dried for 10 h at 120 °C and calcined for 3 h at 500 °C [14].

2.2. Characterization techniques

An Autosorb-1 porosimeter (Quantachrome) measured the N$_2$ adsorption/desorption isotherms at −196 °C. We assigned the surface area based on the multi point BET (Brunauer, Emmett and Teller) equation and the pore size and pore volume of the samples on the BJH (Barrett–Joyner–Halenda) equation.

A TA-Q50 thermogravimetric analyzer measured the weight loss as a function of temperature. A Platinel II thermocouple placed 2 mm above the sample pan monitored the temperature. For each run, we loaded 20 mg of sample to a 10 μm aluminium crucible. The resolution and accuracy of the balance were 0.1 μg and >±0.1%.

A Philipps Xpert diffractometer scanned samples at room temperature (Cu anode, K = 0.15406 nm recorded the patterns at 50 kV voltage and 40 mA current) and produced the diffraction pattern (XRD) from which we deduced the HPW/TiO$_2$ crystal phases. The diffraction angle (2 theta range) varied between 20° and 90° at a 0.020° step size.

A JEOL JSM-7600TFE Field Emission Scanning Electron Microscopy recorded the microscopic images of the prepared catalysts. The samples were mounted on an aluminium sample holder containing a double graphite adhesive layer. We used both LEI (lower secondary electron image) and LABE (low-angle backscattered electron) detectors.

The samples prepared for FESEM analysis were also analysed at the same time for EDX imaging. An OXFORD (X-Max) instrument recorded the EDX images for elemental analysis of the samples.

For Fourier transform infrared spectroscopy (FTIR) a Spotlight 400 – PerkinElmer FTIR spectrometer was used. Prior to the analysis, the catalyst samples were treated with pyridine as the probe molecule. We recorded the background spectra of samples before analysing any samples. Then we treated the samples with pyridine at room temperature and desorbed the excess pyridine at 100 °C for 1 h. After cooling to room temperature, the instrument recorded the spectra. The IR range of the analysis was 600–4000 cm^{-1} with resolution of 16 cm^{-1}.

A heat flow calorimeter (Setaram C80) connected to a volumetric apparatus measured the acidity and basicity of the catalyst at 150 °C. The instrument was equipped with a Barocel capacitance manometer to monitor pressure. The probe molecules (ammonia for acidity and sulphur dioxide for basicity) were purified by successive freeze–pump–thaw cycles. First, 100 mg sample was pre-treated overnight at 250 °C under vacuum. To record the differential heats of adsorption, small doses of the adsorbate were introduced onto the catalyst and the pressure reached 66 Pa. The samples outgassed for 30 min at the same temperature, and the procedure was repeated at 150 °C and 27 Pa. The difference between the amounts adsorbed in the first and second steps represents the irreversibly adsorbed quantity (Virr) of a respective gas from which we estimate the number of acidic/basic sites.

2.3. Experimental

2.3.1. Catalytic reaction set-up

HPW/TiO$_2$ catalysts dehydrated glycerol in a quartz fluidized-bed reactor. The reactor height was 52 mm and its inner diameter was 8 mm. A 20 μm ceramic frit distributed the gas uniformly across the reactor. Fluidized-beds are ideal reactors to regenerate catalysts: the high solids mixing rate minimizes thermal and concentration gradients. In fixed bed reactors, coke may build up on catalysts preferentially at the entrance of the reactor and in the central region, which complicates interpreting reaction kinetics [15]. A three-zone furnace heated the reactor and a thermocouple 100 mm above the distributor monitored the bed temperature (Fig. 1).

A mixture of argon and oxygen fluidized the catalyst. To determine the minimum fluidization velocity (U_{mf}), we recorded the pressure drop at ascending and descending gas flow rates (Fig. 2a). The U_{mf} of all samples was 1.4 cm s^{-1}. The total gas velocity was held three times higher than this value for all the experiments.

The molecular oxygen (a mixture of 21 mol% O$_2$/Ar) co-fed with glycerol to maintain the catalyst life time and increase acrolein selectivity while decreasing aromatic and hydrogenated by-products [9,13].