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Gas phase dehydration of glycerol to acrolein: Coke on WO_3/TiO_2 reduces by-products

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ABSTRACT

Glycerol is a renewable feedstock for specialty chemicals that is co-produced when oil and fats are transesterified to biodiesel or hydrolysed to fatty acids. Acrolein is a target specialty chemical but catalysts deactivate with time due to coke and thus require frequent regeneration cycles to maintain activity. WO_3/TiO_2 catalyst dehydrated glycerol for 14 h while the acrolein selectivity increased as coke formed on the catalyst. After the first hour of reaction the acrolein selectivity was 36% and it reached steady state after 6 h at a selectivity of 73%. The major by-products were acetone, propanaldehyde, acetaldehyde, acetol and formic acid. Coke selectivity dropped from 50% in the first hour to 9% after 14 h. Elemental analysis (CHNS/O) of the catalyst withdrawn from the reactor during the experiments confirmed that polyaromatics formed on the surface. Based on NH_3 and SO_2 adsorption calorimetry the number of strong acid sites remained constant during 14 h, while the number of the weak and medium acid sites dropped. The basic sites disappeared after 2 h; coincidentally, less by-products (acetone) formed. Samples treated with pyridine, were analysed by FT-IR and they had fewer Brønsted sites but no Lewis acid sites. Carbon deposited on walls of the cylindrical pores (based on Barrett–Joyner–Halenda method) and reduced the pore diameter.

1. Introduction

Substitution of petroleum based feedstocks and chemicals with bio-sustainable sources is a global priority. Biodiesel from vegetable oils, animal fats or cultured algae complement petro-diesel transportation fuels [1–3]. Glycerol is a co-product of triglyceride transesterification (biodiesel synthesis) and represents a mass fraction of 10% of the total biodiesel produced. It is also an oleochemical co-product of fatty acids obtained by hydrolysis of oils and fats. As a consequence of the large scale production of biodiesel, the price of crude glycerol has dropped since there was insufficient demand to absorb the additional capacity.

The low price of glycerol makes it an attractive feedstock for many specialty chemicals including acrolein. It is a large volume intermediate for acrylic acid and has several industrial applications: D,L-methionine, fragrances, polymers and detergents. Currently, the commercial process for production of acrolein is selective oxidation of propylene in the gas phase over Bi/Mo-mixed oxide catalysts [4].

Schering Kahlbum AG dehydrated glycerol to acrolein in the gas phase over lithium-phosphate and copper-phosphate catalysts in 1933 [5]. The acrolein yield reached 75% at temperatures between 300 °C and 600 °C. Zeolites, heteropolyacids (HPA), metal oxides and supported mineral acids, dehydrate glycerol to acrolein in either the gas phase or the liquid-phase. The selection of the best catalyst depends on the surface area, pore size, acid strength and the nature of the acid sites for a catalytic system. Acidity is the key factor to determine whether a catalyst is suitable to dehydrate glycerol [6–12]. For the first time, Neher et al. [13] demonstrated the effect of acidity on the catalyst performance for glycerol dehydration.

Heteropolyacids are good candidates for glycerol dehydration, due to their high Brønsted acidity which approaches superacid region (stronger acidity than pure H_2SO_4 [14]). They are also economical, environment friendly, and feature well defined structures and tunable acidity levels. The most common HPAs are HPW ($H_3PW_{12}O_{40}$), $H_4PW_{11}VO_{40}$, HSiW ($H_4SiW_{12}O_{40}$), H_4SiMoO_{40} and

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H_3PMo_{12} [14–16]. However, for catalytic applications, HPAs are usually loaded on supported materials (such as TiO_2) due to their low specific surface area. The addition of support improves the surface area of HPAs while their acidity remains high enough for the desired reaction. Dubois et al. [17] patented the application of supported HPAs for the gas-phase dehydration of glycerol. The reaction yield to acrolein was between 50% and 93% while the conversion of glycerol was 79% and 100% [17,18].

The influence of acid/base properties of zirconia and titania based catalysts on the selectivity of acrolein and by-products was studied by Stosic et al. [19]. They observed that beside the acid sites, the number of basic sites had a direct impact on acrolein selectivity in the gas-phase dehydration of glycerol. Therefore, in order to increase the selectivity of acrolein, it is necessary to control not only the strength and the amount of the acidic sites, but also to hinder the number/strength/action of the basic sites. However, the selectivity of acetol – as the major by-prodcut – was not correlated to the acid–base properties.

Although very good catalysts are developed for the dehydration of glycerol, the main disadvantage of current best catalysts is their quick deactivation. More stable catalysts (69% acrolein yield after 24 h) have been developed by Katryniok et al. [20] but the glycerol was highly diluted (10 wt%). Diluted feedstock require more energy consumption for evaporation and a larger reactor would be needed to yield in the same productivity. Erfle et al. [21] and Suprun et al. [22] reported that high reaction temperature, small catalyst pore size and high acidity of the catalyst led to severe catalyst deactivation. Erfle et al. [21] also analysed the spent catalyst by FT-IR pyridine and detected cyclic anhydride compounds. The authors stated that Brønsted sites deactivated the catalyst.

The main objective of this study was to focus on the catalytic behaviour of WO_3/TiO_2 catalyst in the dehydration of glycerol to acrolein. The increasing trend of the acrolein selectivity with reaction time motivated us to perform a 14 h reaction in a fluidized-bed reactor and withdraw catalyst samples at 1 h intervals. We also measured the by-products distribution to assess the rate of carbon deposition and its effect on catalyst performance. The main characteristics of the catalyst such as acidity/basicity, type of the acid sites, surface area and pore size distribution were correlated to coke formation and acrolein selectivity during the 14 h time-on-stream.

2. Methodology

2.1. Catalytic reaction

The fluidized bed reactor was a 46 mm ID quartz tube with a straight section (700 mm long) flanging out to 70 mm ID (300 mm long) to reduce catalyst carried by the gas to the quench. The reactor set-up has been described in detail in our previous publication [23]. A 20 µm ceramic frit, 50 mm from the bottom of the reactor, distributed the feed gases. A 1.6 mm diameter nozzle passed through the distributor and atomized the glycerol/water solution (28 wt%) directly into the WO_3/TiO_2 bed. The injector was 20 mm higher than the distributor. The quality of the spraying is crucial to prevent catalyst from agglomerating and blocking the injector which leads to the liquid accumulation at the bottom of reactor. To improve the quality of spraying, a flow of inert gas (Ar) assisted the liquid feed during the injection. The volumetric ratio of argon to glycerol solution (G/L) was qualitatively evaluated to be 400. The pressure drop in the injector at this condition reached to 0.4 bar. Although the spray quality was better at higher gas to liquid ratios, the catalyst was more exposed to attrition at higher gas velocities.

An electrical furnace heated the reactor and a 6-point thermocouple monitored the temperature of the catalyst bed and each zone of the reactor. Condensable products of the reaction were trapped in two quenches in series. A Varian HPLC (Metacarb 87H column) measured the concentration of the condensables whilst a Bruker GC equipped with Hyesep Q, Molsieve 5A and FFAP columns analysed the acrolein and other light products e.g. acetaldehyde in the gas phase. An online Pfeiffer mass spectrometer monitored the permanent gases (Fig. 1).

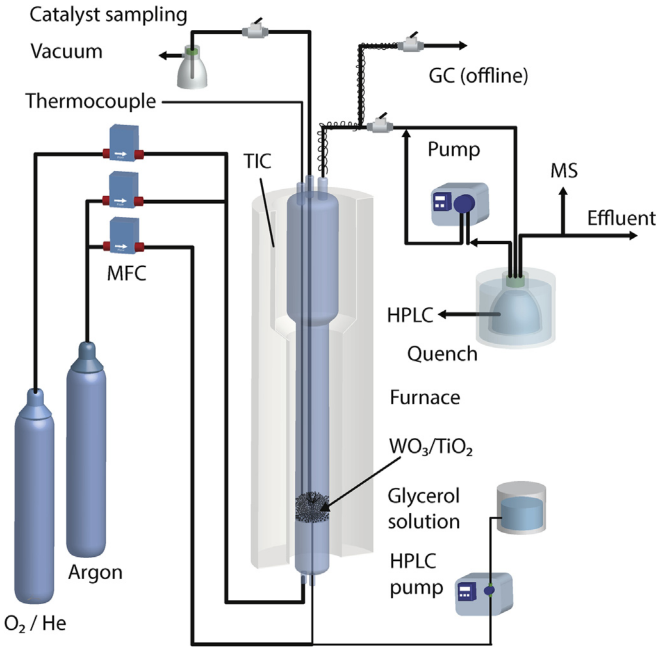

Fig. 1. Schematic of the 46 mm ID fluidized bed, inlet gas manifold, quenches and analytical.

We preheated the catalyst bed (180 g) to 400 °C for 30 min under a flow of argon. The reactor operated at 280 °C for 14 h and at 1 h intervals, catalyst, liquid and gas samples were withdrawn for analyses. The molar composition of the feed in the gas phase was glycerol/oxygen/water/argon: 0.06/0.05/1.3/8.9. These conditions were selected to study the coke build-up and its effect on the catalysts acid and base sites as well as products selectivity.

The conversion of glycerol ($X_{gly.}$) as well as selectivities towards products (S_p) and coke (S_{coke}) were calculated as follows:

$$X_{gly.}\ \ (\text{mol\%}) = \frac{n^{in}_{gly.} - n^{out}_{gly.}}{n^{in}_{gly.}} \times 100 \tag{1}$$

$$S_p\ \ (\text{mol\%}) = \frac{n_p}{n^{in}_{gly.} - n^{out}_{gly.}} \times \frac{m_p}{m_{gly.}} \times 100 \tag{2}$$

$$S_{coke}\ \ (\text{mol\%}) = \frac{n_{coke}}{n^{in}_{gly.} - n^{out}_{gly.}} \times \frac{1}{3} \times 100 \tag{3}$$

where $n^{in}_{gly.}$ and $n^{out}_{gly.}$ are the molar flow rates of glycerol at the reactor entrance and exit. In Eq. (2), n_p is the molar flow rate of each product. m_p and $m_{gly.}$ represent the number of carbon atoms of the products and glycerol. Eq. (3) is a form of Eq. (2) in which the values of m have been replaced as 1 and 3 for coke and glycerol. The molar flow rate of coke was calculated based on the results obtained from TGA analysis.

2.2. Characterization techniques

We compared the catalyst samples collected during the reaction with fresh WO_3/TiO_2. A TA-Q50 thermogravimetric analyzer (TGA) measured the weight loss of catalyst as a function of temperature. We loaded 20 mg of catalyst to a 10 µm aluminium crucible. A