



Conversion of glycerol to acrolein in the presence of WO_3/TiO_2 catalysts

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ARTICLE INFO

Article history:

Received 3 December 2010

Received in revised form 29 March 2011

Accepted 3 April 2011

Available online 14 April 2011

Keywords:

Glycerol (glycerin)

Acrolein

Alcohol dehydration

Solid acid

WO_3/TiO_2

Sustainable technology

ABSTRACT

Dehydration of glycerol to acrolein was performed on WO_3/TiO_2 catalysts in a continuous flow fixed bed reactor. A maximum of 85% acrolein selectivity was achieved at nearly complete conversion of glycerol using novel WO_3/TiO_2 catalysts for this particular reaction. The use of oxygen suppressed side product formation. In addition, correlations between carrier properties of titania and catalytic performance were observed. The outstanding properties of WO_3/TiO_2 catalyst systems for the dehydration of glycerol are revealed.

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1. Introduction

Rising crude oil prices in combination with decreasing supply is stressing the need to develop processes for sustainable chemical and material production. In parallel to that, worldwide glycerol production is increasing due to growing production of biodiesel based on triglycerides. Glycerol is an inevitable by-product of that biodiesel production and the demand for glycerol is not increasing at the same rate as the need for biodiesel. Consequently, the use of glycerol as a starting material becomes economically and environmentally feasible [1,2].

The aim of the present investigations is the heterogeneously catalysed conversion of glycerol to acrolein by dehydration. Acrolein is used in medicine, water treatment and petroleum industry as biocide. Refined acrolein is needed as starting material for the synthesis of fine and intermediate chemicals such as methionine, fragrances as well as dyes. Acrylic acid, produced by the oxidation of acrolein, is the major application of acrolein. Polymers made of acrylic acid have super absorbent properties and are the main component of hygienic pads and diapers. Polyacrylates are also used as binders in architectural coatings. Worldwide, 85% of the acrylic acid is produced by captive oxidation of acrolein [3,4].

Acrolein is currently produced by the oxidation of propylene using multi component mixed oxide catalysts [3–5]. The source of propylene is crude oil. Shifting the C3 carbon source for the production of acrolein from propylene to glycerol would not only

encourage biodiesel producers by enabling commercial pathways for their by-product, but also it would avoid the usage of crude oil in the production of acrolein. Thereby, acrolein would be a biomass based intermediate and a CO_2 -neutral production would be provided.

Starting with Sabatier and Gaudion in 1918 [6], several heterogeneous catalysts with different performances have been studied and developed [7–10]. The most remarkable catalysts are either based on silicon compounds such as zeolites [11–13], zirconia [14–16], heteropolyacids [17] or mixed oxides [18,19].

In collaboration with Arkema, the high activity of WO_3/ZrO_2 systems for the dehydration of glycerol in the gas phase was found for the first time in 2005. The experiments with up to 80% acrolein yields are described extensively in our corresponding patents [20–23]. Table 1 gives an overview of some of the important advances in this reaction since 1930.

In the present study, we present our investigations for the dehydration reaction of glycerol using a new type of catalyst systems based on WO_3/TiO_2 . Many of these catalysts show excellent catalytic performance with some of the highest selectivities known in the literature so far. Not only its catalytic performance, but also the low price of titania in comparison to zirconia catalysts increase its attractiveness as catalyst carrier.

2. Experimental

2.1. Catalysts

All TiO_2 powders were provided by Sachtleben AG, Germany, with the exception of TiO_2 P25, provided by Degussa AG, Germany.

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Table 1

Previously published results for this reaction.

Date	By	Best catalyst	X Gly (%)	Y Acr (%)	S Acr (%)	T (°C)	WHSV
21.05.1930	Schering Co. [7]	Earth/PO ₄ ³⁻	–	80	–	420	–
29.01.1948	Hoyt [25]	Earth/PO ₄ ³⁻	–	72.3	–	286	0.55
18.10.1993	Degussa Co. [9]	Al ₂ O ₃ /PO ₄ ³⁻	100	70.5	70.5	300	0.08
15.02.2005	Hölderich [26]	WO ₃ /ZrO ₂	100	72	72	280	0.14
05.12.2005	Vogel [27]	ZnSO ₄	32	12.16	38	500	–
04.12.2006	Sato [13]	H ₄ SiW ₁₂ O ₄₀ /SiO ₂	98.3	84.7	98.3	275	0.56
08.03.2007	Kijenski [28]	SiO ₂ /Al ₂ O ₃	30	30	100	300	0.7
22.06.2007	Xu [16]	WO ₃ /ZrO ₂	100	65	70	315	–
13.06.2007	Xu [10]	Nb ₂ O ₅	88	44.8	51	315	–
25.10.2007	N. Shok. Co [11]	Zr(HPO ₄) ₂	100	63	63	230	–
14.11.2007	Shang. Acr. Co [12]	ZSM-11	100	82.1	82.1	320	0.34
01.03.2008	Ding [29]	H ₄ SiW ₁₂ O ₄₀ /C	92.6	69.54	75	330	1
23.11.2009	Wang [18]	VOPO ₄	100	64	64	300	0.5
16.05.2010	Deleplanque [19]	FePO ₄	100	92	92	80	0.5

While TiO₂ P25 was a mixture of anatase and rutile (3:1) other powders had only anatase structure.

Several homemade catalysts were prepared according to the following impregnation method: A certain amount of ammonium paratungstate (NH₄)₁₀(H₂W₁₂O₄₂)·4H₂O, Sigma Aldrich, Germany) and 200 ml of water were heated to 80 °C and stirred for 2 h, yielding a clear solution. TiO₂ was added into this solution and stirred for another 4 h. After evaporation of the water, the remaining slurry was dried for 6 h at 110 °C, followed by calcination at 600 °C for 6 h.

The obtained powder was formed to round pellets under 10 tonnes/cm² pressure for 20 min, which were then crushed and sieved. A fraction of 0.5–1.0 mm particle size was used for the characterization and screening experiments.

2.2. Catalyst characterization

BET surface areas, pore volumes and average pore diameters were obtained at 77 K on a Micrometrics ASAP 2010 Gas Sorption and Porosimetry System. After activation of the samples at 300 °C for 3 h under vacuum, the adsorption–desorption curve was conducted by passing nitrogen over the solid. BET surface areas were determined over a relative pressure range from 0.05 to 0.20 bar.

Measurement of catalytic acidity and basicity were conducted with a temperature programmed desorption (TPD) unit, the TPD-Pro 1100 from CE instruments equipped with a TCD detector. After heating the sample at 500 °C for drying purposes, NH₃ or CO₂ were physisorbed at room temperature. Then the samples were heated up to 600 °C at 1°/min and the amount of desorbed gas was recorded by the TCD.

Bulk elemental analyses were carried out by means of inductive couple plasma atomic emission spectroscopy on a Spectroflame D (Spectro Analytic Instrument).

Powder X-ray diffraction (XRD) data were recorded on a Siemens diffractometer (D 5000) operated at 45 kV and 40 mA, using nickel filtered Cu K α radiation with 1.5406 Å between 1.5° and 40° (2 θ), at a scanning speed of 0.02°/min. The measured patterns were in good agreement with the literature, showing that WO₃ were existent on TiO₂ carrier [30].

2.3. Catalytic reaction

The gas-phase dehydration of glycerol under atmospheric pressure was conducted in a 100 cm continuous plug flow fixed bed reactor in form of a coil, made out of stainless steel tube (Type 316 TI) with a 0.6 cm internal diameter. The solid catalyst was filled into the reactor, which afterwards was placed in a temperature controlled, box shaped, GC-like, oven. The temperature of the oven was controlled with a thermocouple, connected to a Eurotherm controller. The temperature homogeneity within the oven was ensured

with an installed radial fan. The observed temperature fluctuation within the oven and over time was not over ± 0.5 °C.

At the adjusted reaction temperature, a 20 wt.% aqueous glycerol solution was pumped into the reactor at a rate of 23 g/h. If required, a flow of oxygen regulated by means of a mass flow controller (Brooks Mass Flow Controller 5850S) was introduced to the reactor as well.

The reaction products were collected in a double jacket flask. The temperature of the collector flask was kept at –2 °C using a cryostat at all time.

For an accurate determination of carbon and mass balance, two electronic balances were installed, one for instant observation of the amount of the glycerol solution pumped into the reactor and one to measure the collected amount of the product mixture. The reactions were usually conducted for 8 h. A sample for analysis was taken each hour from the collected product mixture and analysed on a Fisons GC 8000 gas chromatograph equipped with a flame ionization detector and a Chromosorb W-AW column (2 mm i.d., 2.5 m long), set to on-column injection.

Conversion of glycerol and product selectivity were calculated according to the following formulas:

$$\text{glycerol conversion(\%)} = \frac{(\text{moles of reacted glycerol})}{(\text{moles of glycerol fed in})}$$

$$\text{product selectivity(mol\%)} = \frac{(\text{moles of carbon in a defined product})}{(\text{moles of carbon in reacted glycerol})}$$

The mass balance was usually above 98% and the calculated carbon balance of all the detected compounds was usually above 90% except for the initial phase of 1 h. After the incubation phase, the selectivity and conversion figures reached steady values. The given conversion and selectivity figures are calculated by the values of at least three measurements.

3. Results and discussion

3.1. Different titania carriers without loading

An initial series of experiments were conducted with unmodified titania carriers in order to observe the effects of the carrier on performance, in particular on the side products. The used carriers and their physical properties are given in Table 2. Due to different preparation methods, the carriers have different SO₄²⁻ amounts, pore structure and BET surface area.

For each experiment, 4.5 ml of the catalyst, corresponding to approximately 5.0 g, were placed into the reactor, which was heated to 280 °C. A 20 wt.% aqueous glycerol solution was used as reactant which was fed into the reactor at a rate of 23 g/h together

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