Gas phase oxidation of furfural to maleic anhydride on V_2O_5/γ-Al_2O_3 catalysts: Reaction conditions to slow down the deactivation

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ABSTRACT

An alumina-supported vanadium oxide catalyst (13.9 wt.% vanadium oxide) has been characterized by different techniques and tested in the gas phase oxidation of furfural. These studies have shown that the catalyst unavoidably deactivates by deposition of maleates and resins over the surface. Full regeneration is accomplished by burning off these deposits at 773 K. The studies have also demonstrated that if the primary contact occurs at temperatures at which furfural conversion is low and then the temperature is increased in a low- to high-temperature mode, intense deposition of maleates and resins takes place and the catalyst is rapidly deactivated. The increase of the temperature does not result in removal of deposits but accelerates the deposition. Under this protocol, the yield of maleic anhydride never exceeded 30%, irrespective of the reaction conditions (temperature and O_2/furfural mole ratio). In contrast, if the catalyst first contacts the reaction mixture at high oxidizing potential, then the rate of maleate and resin deposition is much slower, and so is the deactivation rate, and the catalyst can display a higher yield of maleic anhydride for a longer period of time. A high oxidizing potential can be attained at a high reaction temperature (close to full conversion). A higher oxidizing potential at a given high temperature can be accomplished by increasing the O_2/furfural mole ratio. Thus, for example, first contacting the catalyst at 593 K (full conversion), 1 vol.% of furfural, and O_2/furfural mole ratio = 10, obtained an initial maleic anhydride yield of 68%, and the yield was still greater than 50% after 15 h on stream. On contacting at 573 K with 1 vol.% furfural and 20 vol.% O_2, the maleic anhydride yield was initially close to 75% and was above 60% after 15 h.

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1. Introduction

Maleic anhydride (MA) is a commodity chemical with multiple applications: production of unsaturated polyester resins, 1,4-butanediol, vinyl copolymers, curing agents for epoxy resins, lubricant additives, pharmaceuticals, and agrochemicals [1,2]. MA is a petrochemical with market volume currently above 1800 kton/year and is produced primarily by selective oxidation of *n*-butane (the benzene route became obsolete for environmental reasons) [1,2].

Renewable routes based on the oxidation of furfural (FUR) in either gas [3–5] or liquid phase [6–8] have been demonstrated technically by different research groups. Gas phase oxidation offers the advantage of using low-cost air at atmospheric pressure instead of either high-pressure O_2 [6,7] or more expensive H_2O_2 [8,9] required for liquid phase oxidation of furfural.

Recently, other renewable chemical platforms have also been reported to yield MA via oxidation, such as gas phase oxidation of biobutanol, 5-hydromethylfurfural (HMF), and levulinic acid. Thus far, the yield of MA from biobutanol is lower than that obtained from furfural [10]. From HMF an overall yield of MA and maleic acid of 80% has been reported for liquid phase oxidation and at relatively high O_2 pressure (1 MPa) [11]. A high yield of MA (ca. 70%) has also been demonstrated for gas phase oxidation of levulinic acid conducted at atmospheric pressure [12].

However, biobutanol, HMF, and levulinic acid are not yet commercially available on the scale required for replacement of MA production from oil. In contrast, FUR is one of the few commodities currently produced on a large scale from biomass and is perfectly coupled with the production of human food and animal feed, because it is produced from agricultural residues [13]. FUR has been identified as one of the top value-added chemicals derivable from biomass [14] because a number of chemicals are already produced from furfural, and a wide variety of other biofuels, commodities, and fine chemicals can also be derived from it [15,16]. This makes the gas phase oxidation of furfural highly attractive.

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Gas phase oxidation of furfural is conducted using catalytic fixed-bed reactors at temperatures ranging from 473 to 673 K and using dilute furfural fed in O_2–N_2 mixtures (below 5 vol.%) and notably short contact times (a few seconds). In addition, different vanadium oxide-based catalysts (V oxide and V–Mo and V–Bi mixed oxides) on a variety of supports (pumice, asbestos, and alumina) have been tested [3–5,17–20]. Unfortunately, most of the reports lack experimental and technical details, and a few of them date back to the first half of the 20th century. Fundamental insight into the reaction mechanism, the effect of different operational variables, and the deactivation processes is still needed.

This work shows that the catalytic properties of V_2O_5/ γ-Al_2O_3 depend on the thermal protocol to which the catalyst has been subjected. Moreover, it has been shown that the effect can be used efficiently to obtain a greater yield of MA. A frequent practice in conducting a reaction is to contact the catalyst with the reaction mixture at an initial temperature at which conversion is low, and eventually increase the temperature to achieve greater conversion and higher yields of the targeted products. The results reported in this work demonstrate that the catalytic properties depend on the thermal history. Substantially higher yields of MA can be attained at full conversion if the catalyst initially contacts the gas reaction mixture at the temperature required for full furfural conversion. In contrast, if the more frequent protocol is adopted, namely, the catalyst first contacts the gas reaction mixture at temperatures giving rise to low conversion (less than 40%) and then the temperature is increased to achieve full conversion, a much lower yield of MA is obtained. A characterization study of the fresh and used catalyst by thermogravimetric analysis (TGA), diffuse reflectance infrared Fourier transform (DRIFT), and X-ray photoelectron spectra (XPS) techniques was conducted, aiming at finding an explanation for this effect.

2. Experimental methods

2.1. Catalyst preparation

In vanadium oxide catalysts supported on Al_2O_3, surface V_2O_5 crystallites have been identified as intrinsically less active for this reaction than well-dispersed VO_x species [5]. The best alumina-supported vanadium oxide catalyst is that with the largest amount of well-dispersed vanadium oxide species. The maximum surface concentration of well-dispersed vanadium oxide species is attained in the range of 8–10 atoms of V per nm^2 of alumina support.

Al_2O_3-supported vanadium oxide with a surface V loading of 8 V atoms nm^{-2} (equivalent to a V_2O_5 loading equivalent of 13.9 wt.%) was prepared via incipient wetness impregnation of γ-Al_2O_3 (134 $m^2 g^{-1}$) at 298 K using an aqueous solution of ammonium metavanadate (NH_4VO_3, Alfa Aesar, 99.0%). Oxalic acid ($C_2H_2O_4$, Alfa Aesar, 99.5%) was added (NH_4VO_3/oxalic acid molar ratio = 0.5) to ensure the complete dissolution of NH_4VO_3 in H_2O. The impregnated solids were dried in ambient air at 393 K for 12 h and subsequently treated in ambient air at 773 K (heating rate of 0.167 $K s^{-1}$). This V loading is representative of the range at which the surface concentration of well-dispersed V oxide species is maximized [5]. The catalyst is referred to as 8VA.

2.2. Measurement of catalytic activity

Furfural oxidation was performed in a tubular fixed-bed stainless steel reactor. The catalytic bed (1.5 mL) was prepared by mixing the catalyst (0.2 g, pellet size 300–425 μm) with low surface area SiO_2 (2 g, <1 $m^2 g^{-1}$, pellet size 300–425 μm). First, the catalysts were pretreated in a 21 vol.% O_2/He flow (250 mL $min^{-1} g_{cat}^{-1}$) at 623 K for 1 h. Then the temperature was set to the desired

value, and the furfural/O_2/N_2 mixture was passed through the catalytic bed (approximately 43 mL/min was always fed, which is equivalent to an overall contact time of 2.1 s or GHSV = 1720 h^{-1}). The concentration of furfural in the gas phase was controlled using a double saturator submerged in a thermostated silicone oil bath at the required temperature. N_2 was used as a carrier gas by bubbling it through the furfural present in the saturators. Heavy oligomers (brownish-colored) are unavoidably present dissolved in furfural due to oligomerization reactions [15]. The feeding of these much less volatile heavy products may cause plugging and deactivation issues, which are prevented by using this bubbling feeding system. The O_2 required to set the gas phase concentration was incorporated into the feed line downstream of the saturator and prior to the reactor. The N_2 and O_2 flows were controlled by mass flow controllers. Furfural was purchased from Aldrich (99%). Concentrations of organics in the inlet and effluent streams were measured online via gas chromatography (Agilent 6820). A capillary column (HP-5, 30 m × 0.32 mm × 0.25 μm) connected to a flame ionization detector was used to analyze furfural and maleic anhydride, and HP-PLOT Q (30 m × 0.32 mm × 0.20 μm) and molecular sieve (30 m × 0.32 mm × 0.25 μm) capillary columns connected to a thermal conductivity detector were used to determine the O_2, N_2 (internal standard), CO, and CO_2 concentrations. All transfer lines were held at 393 K to prevent condensation of water and MA. Furfural conversion is calculated as

$$X_F = \frac{(F)_{in} - (F)_{out}}{(F)_{in}} \tag{1}$$

where $(F)_{in}$ and $(F)_{out}$ are the inlet and outlet furfural molar flow rates, respectively, and MA yield as

$$Y_{MA} = \frac{MA_{out}}{(F)_{in}} \tag{2}$$

where MA_{out} is the outlet molar flow rate of MA.

The CO_2 yield formed by total oxidation of furfural was calculated on a furfural molar basis as

$$Y_{CO_2} = \frac{(CO_2)_{out} - MA_{out}}{5 \times (F)_{in}} \tag{3}$$

where $(CO_2)_{out}$ is the outlet molar flow rate of CO_2 and MA_{out} accounts for the CO_2 released to form MA (formation of a MA molecule implies release of a CO_2 molecule by decarboxylation of furoic acid)

2.3. Catalyst characterization techniques

TGA under a controlled atmosphere (synthetic air) was performed on a Mettler Toledo TGA/SDTA 851e unit at a rate of 0.167 $K s^{-1}$ in the range 300–1000 K.

XPS were acquired with a VG Escalab 200 R spectrometer equipped with a hemispherical electron analyzer and a MgKα (1253.6 eV) X-ray source. The solids were outgassed at 393 K for 1 h at 10^{-5} mbar to remove water before transfer to the ion-pumped analysis chamber. The O1s, V2$p_{3/2}$, C1s, and Al2p core levels were scanned a sufficient number of times to obtain high signal-to-noise ratios. The static charge of the samples was corrected by referencing the binding energies (BEs) to that of the Al2p peak in Al_2O_3 (74.4 eV). The accuracy of the BE was ±0.1 eV. The areas of the peaks were computed by fitting the experimental spectra to Gaussian/Lorentzian curves after background removal (using the Shirley function). Surface atom ratios were calculated from peak area ratios normalized by the corresponding atomic sensitivity factors [21].

DRIFT spectra were obtained with a Nicolet 5700 FT spectrophotometer equipped with an in situ reaction chamber, a dif-