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# Toward longer life catalysts for dehydration of glycerol to acrolein

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## ABSTRACT

In this work, tungstated zirconias were prepared by different methods and evaluated for glycerol dehydration to acrolein. For all the tested catalysts, the absence of crystalline $WO_3$ was checked by XRD and Raman microscopy. Textural properties were determined by liquid $N_2$ adsorption and mercury penetration measurements. For catalysts prepared from hydrous zirconia ($ZrO_2{\cdot}xH_2O$) incorporating W by anionic exchange, clear correlation between stability and pore diameter was shown for the first time and it was confirmed that $SiO_2$ addition favors the formation of bigger mesopores. This effect was not observed for catalysts obtained by simple W impregnation of hydrous zirconia. In this case, among different preparation parameters investigated, only the addition of a reflux step increased the pore diameter. Finally, tungstated zirconias were prepared by W impregnation of crystalline $ZrO_2$ thermally stable and owning chosen textural properties. As coking leads to pore shrinkage, much higher stability was obtained for catalysts owning high proportion of big mesopores (>10 nm) and small proportion of pores below 5 nm. These characteristics appeared to be key parameters to tailor longer life catalysts for dehydration of glycerol.

## 1. Introduction

Glycerol is a significant by-product derived from the production of biodiesel. It is predicted that by 2020, 2.7 million tons of glycerol will be generated worldwide [1], all of which should be efficiently processed in order to achieve sustainability of the biodiesel sector. Promising route to glycerol valorization is its catalytic dehydration to produce acrolein, which is an important industrial intermediate for the chemical and agrochemical industries. However, such process is limited by deactivation of catalysts with time on stream by coking.

Different groups have pointed out the interest to use mesoporous catalysts to improve the stability over time [2–10]. In particular, heteropolyacids supported on large pores (10 nm) silica have shown higher yields because of a slower decrease in conversion [6]. The use of $Al_2O_3$ with pore diameter of 12 nm instead of 5 nm to support heteropolyacids led to higher acrolein selectivity and improved catalyst lifetime [7]. Possato et al. [8] have investigated coke formation within micro/mesoporous MFI zeolites. The desilication methodology used to produce the mesoporous zeolites minimized diffusion limitations and increased glycerol conversion in the catalytic reaction due to the hierarchical system of secondary pores created in the zeolite crystals. Recently, tungstated zirconias doped with $SiO_2$ were shown to be more stable than without $SiO_2$ [9]. The larger pore diameter of these catalysts compared to undoped tungstated zirconia suggested that this parameter influences their stability. However, no detailed investigation was undertaken.

In this work, tungstated zirconias with various W and Si amounts were prepared from hydrous zirconias ($ZrO_2{\cdot}xH_2O$) incorporating W by anionic exchange or by wet impregnation. Different preparations parameters were varied to identify those determining textural properties. Their catalytic properties were compared to those of tungstated zirconias directly prepared by impregnation of crystalline $ZrO_2$ owning chosen textural properties. It allowed identification of key parameter to get better stability of tungstated zirconias used in gas phase glycerol dehydration to acrolein.

## 2. Experimental

### 2.1. Catalysts synthesis

Tungstated zirconias were prepared from hydrous zirconias or commercial zirconias incorporating tungsten by anionic exchange or impregnation method.

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#### 2.1.1. Preparation of $ZrO_2 \cdot xH_2O$

Hydrous zirconia was obtained at pH 9 mixing 0.4 M $ZrO(NO_3)_2 \cdot xH_2O$ and 28 wt.% $NH_4OH$ solutions and then aged for 1 h. The solid was recovered by filtration, washed with deionized water 4–5 times and dried at 110 °C overnight and then manually ground. For comparison, hydrous zirconias were prepared by changing either the precipitation pH, the maturation time or by adding reflux treatment at pH 12 and at 110 °C for 24 h in Teflon balloon. To obtain $SiO_2$ containing catalysts, silica was deposited on hydrous zirconia by slow TEOS (Aldrich, >99%) addition to ammonia solution containing hydrous zirconia under stirring (pH 12) followed by aging at room temperature for 24 h, filtration, washing off and drying at 110 °C overnight.

#### 2.1.2. Anionic exchange of $ZrO_2 \cdot xH_2O$

Tungsten was incorporated to hydrous zirconias containing or not $SiO_2$ by anionic exchange of peroxotungstates. For that purpose, $H_2WO_4$ (Aldrich, 99.99%) was dissolved in 35 wt.% $H_2O_2$ solution at 50 °C leading to formation of $(W_2O_3(O_2)_4(H_2O)_2)^{2-}$ dimers [11]. After ice cooling, the solids were slowly added to achieve anionic exchange with hydroxyl groups, recovered by filtration, washed 2–3 times, dried at 110 °C overnight and calcined under air flow of 100 $mL \cdot min^{-1}$ at 650 °C (heating 5 $°C \cdot min^{-1}$) for 3 h. The as-prepared catalysts are labeled *x*W*y*Si/$ZrO_2$-E in the following where *x* et *y* correspond to the W and Si surface densities respectively (expressed in $atoms \cdot nm^{-2}$).

#### 2.1.3. Impregnation of $ZrO_2 \cdot xH_2O$

Hydrous zirconias containing or not $SiO_2$ were sieved below 180 μm before wet impregnation ($V_{imp} = 0.5\ cm^3 \cdot g^{-1}$) with $(NH_4)_6H_2W_{12}O_{40} \cdot xH_2O$ aqueous solutions. The mixtures were stirred for 1 h before evaporation using rotavapor at 70 °C. The last step was calcination under 100 $mL \cdot min^{-1}$ air flow at 650 °C (heating 5 $°C \cdot min^{-1}$) for 3 h. The as-prepared catalysts are labeled *x*W*y*Si/$ZrO_2$-I in the following where *x* et *y* correspond to the W and Si surface densities respectively (expressed in $atoms \cdot nm^{-2}$).

For all the samples prepared from hydrous zirconias, precisions were added to the labeling if particular conditions were used: for instance, '-pH10', '-mat24h', '-refl' when hydrous zirconia was prepared at pH 10, aged 24 h or refluxed respectively.

#### 2.1.4. Impregnation of $ZrO_2$

W/$ZrO_2$ catalysts were also prepared from commercial $ZrO_2$ (Alfa Aesar, ref 43,815, pore size 9.3 nm, pore volume 0.32 $cm^3 \cdot g^{-1}$, $S_{BET}$ 106 $m^2 \cdot g^{-1}$, monoclinic structure) and from commercial $ZrO_2$ containing 3.2% of $SiO_2$ (Saint Gobain, ref SZ 61152, pore size 96.2 nm, pore volume 0.30 $cm^3 \cdot g^{-1}$, $S_{BET}$ 150 $m^2 \cdot g^{-1}$, tetragonal structure). After crushing the pellets and sieving below 220 μm, powder samples were impregnated with $(NH_4)_6H_2W_{12}O_{40} \cdot xH_2O$ aqueous solutions in excess, stirred for 30 min, dried using rotavapor at 70 °C and calcined at 500 °C under 100 $mL \cdot min^{-1}$ air flow. This temperature was higher than the decomposition temperature of the ammonium precursor salt. It was previously checked that the two supports were thermally stable during such thermal treatment. The corresponding catalysts are labeled *x*W/$ZrO_2$-A and *x*W/SiZrO-SG in the following where *x* corresponds to the W surface density.

### 2.2. Characterization

Si and W quantifications were obtained from ICP–OES spectra (ACTIVA/Jobin Yvon) after different dissolutions. For Si, the samples were melted in Pt-Au crucible with lithium tetraborate, heated up to 1100 °C and dissolved with 20 wt.% HCl. For W quantification, the samples were dissolved in $H_2SO_4$, $HNO_3$, HF mixture, evaporated and NaOH was finally added.

Powder X-ray diffraction patterns were achieved on a Bruker D8 Advance A25 diffractometer equipped with a Ni filter (Cu Kα radiation: 0.154184 nm) and a one-dimensional multistrip detector (Lynxeye, 192 channels on 2.95°). The crystalline phases present in the samples were identified by comparison with reference patterns available in the ICDD database. Raman spectra were recorded in ambient air using a LabRam HR spectrometer (Horiba-Jobin Yvon). The exciting line at 514.5 nm delivered by a 2018 RM Ar-Kr laser (Spectra-Physics) was focused with a power of 1 mW using a ×50 objective and the diffused light was dispersed with a 1800 $grooves \cdot min^{-1}$ diffraction grating leading to spectral resolution of ca 0.5 $cm^{-1}$ and spatial resolution of ca 2 μm. Micro-Raman mappings of ca 90 points were achieved using motorized stage to control the W dispersion.

The specific surface areas (SSA) and the pore size distributions were obtained outgasing under vacuum of $10^{-3}$ Pa for 3 h at 300 °C. Nitrogen physisorption was then achieved at −196 °C with a Micromeritics ASAP 2020 instrument applying, respectively, the BET and BJH methods. The samples were previously outgassed under vacuum of $10^{-3}$ Pa for 3 h at 300 °C. Mercury penetration measurements were achieved with Autopore 9520 apparatus (Micromeritics). The samples were previously desorbed at 200 °C for 2 h.

Carbon deposition was investigated from TGA–TDA measurements using a SETARAM TGA12 apparatus heating the aged catalysts up to 700 °C under air flow of 20 $mL \cdot min^{-1}$. They were also characterized by solid-state $^{13}C$ CPMAS NMR (100.62 MHz, pulse time 3.5l s, contact time 3 ms, 10 kHz spinning rate) using a Bruker DSX-400 spectrometer and a 4 mm CPMAS probe to obtain some information on the coke formed at the surface of the catalysts after catalytic testing.

### 2.3. Catalytic properties

Catalytic testings were achieved at atmospheric pressure and 300 °C in straight fixed bed reactor. The set up and GC analysis method have been previously described in details [12]. In standard conditions, the catalysts were preheated at 300 °C under $N_2$ flow (75 $mL \cdot min^{-1}$, NTP) before sending the reaction mixture obtained by vaporization of 20 wt.% aqueous glycerol solution with a controlled evaporator mixer (Bronkhorst) and dilution in $N_2$. The gas phase composition was glycerol/$H_2O$/$N_2$: 2.3/46.3/51.4 and the gas hourly space velocity (GHSV) was 2900 $h^{-1}$. Glycerol, water and products were collected for 1 h with a triple trap system cooled at −25 °C before off line GC analysis while CO and $CO_2$ were analyzed on line after the trap.

## 3. Results and discussion

### 3.1. Structural and textural properties

#### 3.1.1. Catalysts prepared from hydrous zirconias

Fig. 1 represents the XRD patterns of the WSi/$ZrO_2$-E catalysts. They mainly contained the bands of the t-$ZrO_2$ phase. This metastable phase is stabilized by the presence of W [13–16] and Si [17] over the crystallites. Small amounts of m-$ZrO_2$ (reflections around 24.0°, 24.4°, 28.2° and 31.2°) were also observed for the 2.3W0.5Si/$ZrO_2$-E, 3.4W1.6Si/$ZrO_2$-E and 3.8W0.9Si/$ZrO_2$-E catalysts. No band of crystalline $WO_3$ was detected by XRD for all these compounds which suggested good W dispersion in agreement with surface densities values lower than the theoretical monolayer one (4.5 $W \cdot nm^{-2}$) [18].

The $N_2$ adsorption/desorption isotherms of catalysts prepared by anionic exchange are displayed in Fig. 2A. They belong to the type IV of the IUPAC classification and are typical of mesoporous