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# Bio-glycerol hydrodeoxygenation to propylene: advancing knowledge on Mo-based catalyst characteristics and reaction pathways under flow conditions

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In this work, the reaction pathways of one-step glycerol hydrodeoxygenation in the gas phase are exploited under flow conditions over molybdena-based catalysts (8.7 wt% Mo/black carbon). Hydrodeoxygenation (HDO) experiments with possible reaction intermediates along with temperature-programmed surface reaction spectroscopy (TPSR) experiments demonstrated two possible reaction pathways. The major one involves propylene formation *via* hydrodeoxygenation of 2-propen-1-ol which is considered to be the main intermediate of the reaction. In the secondary route, propanal formed *via* 2-propen-1-ol isomerization is further converted to 1-propanol. XPS measurements in fresh-reduced and reduced-used catalysts revealed that molybdena exists as multivalent species mostly as Mo<sup>5+</sup>, Mo<sup>4+</sup> and Mo<sup>3+</sup>, the presence of which seems to be crucial for the desired pathway of successive HDOs towards propylene. TPSR tests using methanol as the probe molecule showed that redox and acid sites co-exist on the surface of reduced molybdena catalysts, and this bifunctionality is mostly served by the undercoordinated molybdena species. The long-term catalyst test at 280 °C and 60 bar pressure under glycerol hydrodeoxygenation conditions demonstrated that the catalyst remains stable in terms of activity and selectivity for the first 10 h with a gradual drop afterwards. Regeneration of the catalyst for a short time under hydrogen flow proved to be sufficient to fully recover the initial activity and product selectivity.

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## 1. Introduction

Growing concerns about climate change along with the depletion of fossil resources have triggered the development of alternative and greener strategies to produce fuels and chemicals.<sup>1</sup> Global emissions of carbon dioxide, a major greenhouse gas, have dramatically increased resulting in its concentration in the air of 414 ppm in 2021, with the power and industry sectors mostly contributing to them.<sup>2–5</sup> More specifically, the chemical industry accounts for 20% of the total CO<sub>2</sub> emissions.<sup>6</sup> Propylene is considered an important chemical intermediate, the demand for which has undergone a booming growth as it is used to produce important chemicals (*e.g.*, polypropylene, propylene oxide, acrylic acid, and acrylonitrile).<sup>7</sup> Historically, the main routes for propylene production are energy consuming processes, such as steam cracking (SC) and fluid catalytic cracking (FCC), resulting in high CO<sub>2</sub> emissions. Both the FCC and SC processes emit approximately 1.51 kg<sub>CO2</sub>

per kg of propylene produced.<sup>6</sup> Attempting to fill the propylene gap between the market demand and propylene production, on purpose propylene technologies, such as propane dehydrogenation (PDH), olefin metathesis, and methanol to propylene (MTP), have been developed over the years. Among them, PDH appears very profitable and has been successfully industrialized worldwide.<sup>8–10</sup> However, the main disadvantage of the PDH process is the origin of the feedstock as it is still derived from fossil fuels.

The growing environmental issues along with the increased demand to fill the propylene gap can be tackled using a renewable feedstock. Biomass (*e.g.*, lignocellulosic and algae) and its derivatives (glycerol, glucose, sorbitol) can pave environmentally friendly ways for producing alternative fuels and platform chemicals owing to their null carbon footprint.<sup>11,12</sup> Biomass derived oxygenates, such as polyols, are considered promising and sustainable feedstocks to produce unsaturated hydrocarbons. Removal of their oxygen content to form olefinic compounds is important and can be realized *via* promising catalytic routes (hydrogenolysis, dehydration, *etc.*). Among them, hydrodeoxygenation (HDO) is considered the most appealing one to remove oxygen functional groups by using hydrogen as a reductant.<sup>13,14</sup>

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Different types of HDO catalytic materials have been investigated in the last few years, such as noble metal catalysts (Pd, Pt, Ru, Rh),<sup>15</sup> zeolites,<sup>16</sup> non-noble metals (Ni, Cu)<sup>17,18</sup> and catalysts based on transition metal oxides, such as Mo and W<sup>11</sup>. Among these, Mo-based catalysts have attracted much attention.<sup>19–21</sup> Likoza's group has studied HDO of lignocellulosic biomass by using Mo-based catalysts, as well as Pd and Ni unsupported and/or supported on different supports. Among the different catalysts, Mo-based ones exhibited the best performance in terms of activity and selectivity.<sup>22,23</sup> The promising performance of Mo-based catalysts has also been mentioned for the case of m-cresol conversion to toluene.<sup>24</sup> It was found that the reducibility of Mo species as well as the type of support mostly affects the HDO activity. All the above results clearly point to the high potential of Mo-based catalysts for HDO reactions.

Glycerol is a non-toxic polyol derived from several biomass processes (biodiesel transesterification, hydrolysis, *etc.*) having three –OH groups and constitutes an ideal feedstock for valorization.<sup>25–29</sup> The rapid expansion of biodiesel production, which generates substantial amounts of glycerol as a co-product, boosts the potential of bio-glycerol upgrading to value-added products, such as 1-propanol, 2-propen-1-ol, propanal, acrolein acrylic acid, C<sub>3</sub>-diols and others.<sup>30–37</sup> Complete glycerol deoxygenation along with the formation of a double carbon bond is a challenging path that could lead to propylene. The choice of the catalytic material is of outmost importance as it should favor C–O rupture instead of C–C.

To the best of our knowledge, reports in the open literature on catalytic glycerol conversion to propylene either in one step or in a tandem process are limited (Table 1). Fadigas *et al.*<sup>38</sup> explored the reaction of glycerol HDO to propylene over an Fe–Mo catalyst supported on activated carbon in the gas phase. Later, the same group<sup>39</sup> studied the same reaction in the gas phase, nonetheless at ambient pressure and high temperature (300 °C), reaching high propylene selectivity (90%) for almost complete glycerol conversion. Very recently, M. El. Doukkali and co-workers systematically investigated the performance of Mo-based catalysts on hydrophobic-inert silica supports and in the form of carbide  $\beta$ -Mo<sub>2</sub>C.<sup>40</sup> Other researchers have reported the use of bifunctional catalysts in a double bed (Ir/ZrO<sub>2</sub> and ZSM-5-30, WO<sub>3</sub>-Cu/Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, MoO<sub>3</sub>-Ni<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and ZSM-5-30, Pt/ZSM-5 and ZSM-5) for enhanced propylene formation.<sup>28,41–43</sup> Even though this seems favorable for massive propylene production, the potentiality of these processes apart from not commercially acceptable propylene productivity (Table 1) still lies ahead as some issues should be first resolved. For example, the stability and reusability of the catalytic materials have not been reported, which are important and challenging aspects for a potential commercial application. The most complete study for propylene production *via* glycerol hydrodeoxygenation is the one authored by M. El Doukkali and coworkers<sup>40</sup> as it provides insightful information covering most of the aforementioned issues. As there is a need to develop new processes that can significantly contribute to fill the propylene gap, more studies should focus not only on

Table 1 Summary of literature data of glycerol hydrodeoxygenation to propylene

Catalyst – reactor type	Operating conditions	Conversion (%)	Propylene selectivity (%)	Propylene productivity (kg <sub>C<sub>3</sub>H<sub>6</sub></sub> kg <sub>cat</sub> <sup>–1</sup> h <sup>–1</sup> )	Ref.
Fe–Mo/activated carbon – fixed bed flow unit	300 °C, 1 bar, H <sub>2</sub> /Glyc = 120, TOS ~ h	100	90	0.04	39
Ir/ZrO <sub>2</sub> & ZSM-5 – vertical fixed bed	250 °C, 5 bar, H <sub>2</sub> /Glyc = 100, TOS = 2h	73	88	0.17	28
WO <sub>3</sub> -Cu/Al <sub>2</sub> O <sub>3</sub> & SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> – fixed bed downflow glass reactor	242 °C, 1 bar, H <sub>2</sub> /Glyc = 161, TOS = 2h	100	84.8	0.0017	41
MoO <sub>3</sub> -Ni <sub>2</sub> P/Al <sub>2</sub> O <sub>3</sub> & ZSM-5 – fixed bed quartz reactor	250 °C, 1 bar, H <sub>2</sub> /Glyc = 100, TOS ~ h	100	88	0.0016	42
Pt/ZSM-5 & ZSM-5 – double bed reactor	500 °C, 1 bar, H <sub>2</sub> /Glyc = 100, TOS = 500h	100	63.7	0.0028	43
MoOx@SBA-15, $\beta$ -Mo <sub>2</sub> C@SBA-15 – single fixed bed	318 °C, 50 bar, H <sub>2</sub> /Glyc = 98, TOS = 2.4h	100	84.1	0.10	40
Fe–Mo/black carbon – batch reactor	318 °C, 50 bar, H <sub>2</sub> /Glyc = 98, TOS = 14.5h	100	64.8	0.07	44
Mo/black carbon – high pressure continuous flow reactor	300 °C, 80 bar, H <sub>2</sub> /Glyc = 53, TOS ~ h	88.8	76.1	0.48	45
Mo/black carbon – high pressure continuous flow reactor	280 °C, 60 bar, H <sub>2</sub> /Glyc = 80, TOS = 4h	100	71	0.10	45
	280 °C, 60 bar, H <sub>2</sub> /Glyc = 80, TOS = 10h	100	60	0.12	Current study



optimizing the current HDO processes, but also on improving catalytic performance that can pave the way for future scale-up studies for glycerol HDO to propylene and perhaps for similar complex molecules.

In a previous research study of our group, it was demonstrated that glycerol can be effectively converted to propylene, in one step, in the liquid phase over Mo-based catalysts.<sup>44</sup> As mentioned earlier, molybdenum catalysts are widely applied in HDO reactions, and more specifically, they are also found to be attractive candidates for glycerol HDO to propylene, as apart from their deoxygenation ability, their mild hydrogenation activity does not favor the further conversion of propylene to propane. Considering that continuous flow operation is preferred for industrial applications, molybdenum catalysts were further evaluated in glycerol HDO in the gas phase employing a high-pressure continuous flow unit.<sup>45</sup> The effect of reactor parameters was investigated over molybdenum catalysts supported on hydrophobic black carbon (Mo/BC). It was experimentally proved that increased temperature, hydrogen availability (expressed either as  $P_{\text{H}_2}^\circ$  or  $P_{\text{H}_2}^\circ/P_{\text{glyc}}^\circ$ ) and  $W/F$  are key parameters for propylene production. The reaction conditions were further optimized with predictive modelling and under the optimum conditions ( $T = 280^\circ\text{C}$ ,  $P_{\text{H}_2}^\circ = 30\text{ bar}$ ,  $P_{\text{H}_2}^\circ/P_{\text{glyc}}^\circ = 80$ ,  $\text{LHSV} = 1\text{ h}^{-1}$  and  $W/F = 422\text{ g}_{\text{cat}}\text{ mol}_{\text{glyc}}^{-1}\text{ h}^{-1}$ ) dictated by modelling, a propylene yield of 71% with almost complete glycerol conversion was experimentally validated over 8.7 wt% Mo/BC catalyst. The main byproduct was 1-propanol with 20% yield.

The scope of the current work and its novelty span from the efforts to shed more light on the mechanistic pathways of glycerol HDO to propylene under flow conditions to the determination of the nature of the active sites of the promising 8.7 wt% Mo/BC catalyst and to its stability and reusability as well as the effect of the prereduction step. The identification of the primary and secondary routes of glycerol HDO is attempted by performing experiments in the gas phase under flow conditions with the intermediate products formed, as well as by applying temperature programmed surface reaction spectrometry. Additional studies to determine the nature of the catalyst active sites by using methanol oxidation as the chemical probe reaction along with XPS measurements are performed. The stability and reusability of Mo/BC, as well as the effect of the pre-reduction step are also assessed. The results obtained lead to productivity values (Table 1) equal to 0.10–0.12  $\text{kg}_{\text{C}_3\text{H}_6}\text{ kg}_{\text{cat}}^{-1}\text{ h}^{-1}$  which are among the highest compared to others reported in the literature and can pave the way for further techno-economic assessment that might contribute to finding a sustainable way towards an industrial accelerated glycerol to propylene route in the future.

## 2. Materials and methods

### 2.1. Catalyst preparation

A molybdenum catalyst with 8.7 wt% Mo loading supported on a commercially available black carbon (BC) Vulcan XC72 was

prepared following a procedure previously described<sup>45</sup> using  $\text{MoO}_3$  as the molybdenum precursor. The obtained catalyst was calcined at  $200^\circ\text{C}$  for 2 h under synthetic air flow ( $100\text{ cm}^3\text{ min}^{-1}$ ) and then prior to the reaction was reduced at  $500^\circ\text{C}$  for 30 min under pure hydrogen flow ( $40\text{ cm}^3\text{ min}^{-1}$ ). The calcined and reduced samples were named fresh and reduced, respectively, and labeled as 'fresh Mo/BC' and 'reduced Mo/BC', respectively.

### 2.2. Catalyst characterization

The basic characterization of fresh and reduced Mo/BC samples (BET surface area, XRD,  $\text{H}_2$ -TPR, TGA) can be found in our earlier work.<sup>45</sup> The Brunauer–Emmett–Teller (BET) surface area of the used samples was determined by  $\text{N}_2$  physisorption at 77 K with an Autosorb-1 (Quantachrome, Florida, UK) flow apparatus. Thermogravimetric analysis of the reduced and reduced-used catalysts was conducted on a TG 209 F3 Tarsus (NETZSCH, Germany) apparatus. A small amount of the sample was placed in an aluminum sample cup and heated up to  $800^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$  under a nitrogen atmosphere ( $50\text{ cm}^3\text{ min}^{-1}$ ).

**2.2.1. X-ray photoelectron spectrometry (XPS).** XPS measurements were performed on a Kratos Analytical AXIS Ultra DLD spectrometer equipped with an aluminum monochromatic X-ray source ( $\lambda K\alpha = 1486.6\text{ eV}$ ). The wide scan spectra were recorded by applying 7 mA/10 kV on the X-ray source with a pass energy of 160 eV. High resolution (HR) regions were recorded with a pass energy of 20 eV on the analyzer during a three-sweep scan applying 10 mA/15 kV on the X-ray gun. Binding energy referencing was employed based on the C 1s peak at  $284.6 \pm 0.1\text{ eV}$  for the C–C bonds. Before XPS measurements, the samples were stored under vacuum and the analysis was conducted on the same day.

**2.2.2. Temperature programmed surface reaction spectroscopy studies (TPSR).** To study the nature of the catalyst active sites, as well as the intermediate species of glycerol HDO to propylene, temperature programmed surface reaction studies were performed in a specially designed lab-scale fast response flow unit, which is fully automated, and all functions are controlled by Genie Advantech software. Experiments were conducted in a U-shaped quartz reactor with a porous frit to hold the catalytic material. The reactor was placed in an electrically heated oven controlled by a programmable temperature controller. The reactor exit was connected *via* a heated capillary line to a mass spectrometer (MS) (Omnistar™, GSD 350, PFEIFFER) for online analysis of the gaseous exit stream.

TPSR experiments using pure methanol ( $\text{CH}_3\text{OH}$ -TPSR) as the probe molecule were performed to extract information on the nature of the catalyst active sites. Fresh and reduced samples (0.2 g) were placed in the reactor and were further impregnated with a drop of liquid methanol to cover the catalyst surface. Then, the reactor was heated up to  $100^\circ\text{C}$  and held for 2 h under helium flow ( $60\text{ cm}^3\text{ min}^{-1}$ ). After cooling to room temperature, the catalytic samples were heated up to  $800^\circ\text{C}$  at a constant rate of  $10^\circ\text{C min}^{-1}$  under helium flow



(30 cm<sup>3</sup> min<sup>-1</sup>). The following masses (*m/z*) were recorded: 4 (He), 15 (CH<sub>4</sub>), 18 (H<sub>2</sub>O), 29 (HCHO), 31 (CH<sub>3</sub>OH), 44 (CO<sub>2</sub>), 46 (dimethyl ether, DME), and 60 (methyl formate, HCOOCH<sub>3</sub>) and the overlapping fragmentations of the compounds were appropriately considered.

Temperature programmed surface reaction tests under H<sub>2</sub> flow (H<sub>2</sub>-TPSR) were conducted over the reduced catalyst to elucidate the reaction routes of glycerol to propylene. Prior to measurements, the catalytic samples were impregnated with 10 wt% aqueous solution of the desired feed. Apart from glycerol, 2-propen-1-ol, 2-propanol, 1-propanol, propanal and acetone were also used as feeds. The catalytic samples (0.15 g) were then flushed under flowing He, for 0.5 h at 60 °C. Afterwards, the temperature was increased up to 600 °C at a constant rate of 5 °C min<sup>-1</sup> under 50% H<sub>2</sub>/He flow (total flow 20 cm<sup>3</sup> min<sup>-1</sup>). Overlapping fragmentation contributions of all the abovementioned compounds were taken into consideration. Furthermore, TPSR experiments were also performed following the same procedure under pure He flow instead of H<sub>2</sub> using glycerol as the feed. Table 2 displays the main fragment ions of all components that were considered in the CH<sub>3</sub>OH-TPSR and TPSR tests of glycerol, products and intermediates.

### 2.3 Catalytic activity tests

Activity measurements were conducted in the gas-phase in a continuous flow high-pressure reactor unit (FlowCat, HEL) equipped with a fixed bed reactor (*d*<sub>in</sub> = 6 mm), electronic pressure and temperature controllers, a H<sub>2</sub> mass flow controller and a HP liquid pump. Typically, a certain amount of the reduced sample with the particle size between 45 and 75 μm was loaded in the middle of the reactor packed with quartz particles at both ends. Then the system temperature and pressure were set at the desired values equal to 280 °C and 60 bar, respectively. Following this step, an aqueous feed solution

containing 10 wt% (unless otherwise stated) of the oxygenate and the rest water was fed to the top of the reactor together with hydrogen flow. Before entering the reactor, the feed was preheated at 200 °C by passing it through an electrically heated line.

The reactor exit stream was separated in the liquid and gas phases by passing it through a condenser at 0 °C. The gaseous products were online analyzed in a GC (Agilent 7890A) equipped with a TCD detector and two columns in series-bypass configuration (Molecular Sieve and Plot Q). Apart from propylene, which was the main product detected in the gas phase, propane at low concentrations was found under specific conditions, while other lower alkanes and/or CO<sub>x</sub> were not detected. In addition to gaseous products, liquid products were collected hourly and analyzed offline using a GC (Agilent 8890A) with an FID detector and a capillary column (DB-Wax, UI 30 m × 530 μm × 1.0 μm). The carbon balance of all experiments was 85 ± 5%. Most of the experiments have been performed at least twice, others even three times. A simple statistical analysis was performed using the Minitab statistical program, while the analysis of variance (ANOVA) was used to evaluate the results *via* the calculation of the *p*-value and coefficient *R*<sup>2</sup>. A small *p*-value (<0.05) and a high value of *R*<sup>2</sup> (>90%) were observed confirming the reliability of the current results.

The reaction pathways of glycerol HDO to propylene were investigated by performing experiments with the possible intermediate products formed, such as 2-propen-1-ol, propanal, 2-propanol, 1-propanol and acetone, at a constant time on stream equal to 4 h and by maintaining the same values of the reaction parameters (*T* = 280 °C, *P*<sub>system</sub> = 60 bar, LHSV = 1.2 h<sup>-1</sup>, *W/F* = 211 g<sub>cat</sub> mol<sub>feed</sub><sup>-1</sup> h<sup>-1</sup>), unless otherwise noted.

The following expressions were used to determine the catalytic activity. The conversion of the reactant (eqn (1)), selectivity towards a product (based on the reactant consumed) (eqn

**Table 2** The main fragment ions of various components that were considered in the TPSR experiments

Product	Molecular Weight	Main fragment ions
H <sub>2</sub>	2	<b>2(100)</b> <sup>a</sup>
He	4	<b>4(100)</b>
Propane	44	<b>29(100)</b> , 28(59), 27(42), 44(27), 43(23), 39(18)
1-Propanol	60	<b>31(100)</b> , 29(17), 27(16), 42(13)
Propylene	42	<b>41(100)</b> , 39(73), 42(71), 27(38), 40(29), 38(20), 37(12)
Acetone	58	<b>43(100)</b> , 58(25), 42(9), 41(3), 44(2.5)
CO <sub>2</sub>	44	<b>44(100)</b> , 28(10)
2-Propanol	60	<b>45(100)</b> , 43(19), 27(16), 29(12.5), 41(8), 39(6), 42(4), 44(4)
Propanal	58	<b>58(100)</b> , 29(88), 28(58), 27(57), 57(30), 26(16)
2-Propen-1-ol	58	<b>57(100)</b> , 31(41), 39(28), 29(25), 27(23.2), 58(23)
Glycerol	92	<b>61(100)</b> , 43(77), 44(43), 31(39), 29(30), 15(22)
Methane	16	<b>16(100)</b> , <b>15(89)</b> , 14(20)
Methanol	32	<b>31(100)</b> , 32(74), 29(45)
Formaldehyde	30	<b>29(100)</b> , <b>30(58)</b> , 28(24)
Dimethyl ether	46	<b>45(100)</b> , 46(60), 29(38), 15(24)
Methyl formate	60	<b>31(100)</b> , 32(46), 29(45), <b>60(38)</b> , 15(19)
H <sub>2</sub> O	18	<b>18(100)</b> , 17(21)

<sup>a</sup> The *m/z* signals recorded appear in bold.



(2)), propylene yield (eqn (3)), propylene rate (eqn (4)) and carbon balance (eqn (5)) were calculated as:

$$\text{Feed conversion (\%)} = \frac{n_{\text{feed,in}} - n_{\text{feed,out}}}{n_{\text{feed,in}}} \times 100 \quad (1)$$

$$\text{Selectivity}_{\text{product},i} (\%) = \frac{n_{c,i}}{n_{c,\text{feed,in}} - n_{c,\text{feed,out}}} \times 100 \quad (2)$$

$$\text{Propylene yield (\%)} = \frac{n_{\text{propylene}}}{n_{\text{feed,in}}} \times 100 \quad (3)$$

$$\text{Propylene rate (mmol}_{\text{C}_3\text{H}_6} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}) = \frac{n_{\text{propylene}}}{m_{\text{catalyst}} \cdot h} \quad (4)$$

$$\text{Carbon balance (\%)} = \frac{\sum n_{c,i} + n_{c,\text{feed,out}}}{n_{c,\text{feed,in}}} \times 100 \quad (5)$$

where  $n_{\text{feed,in}}$  and  $n_{\text{feed,out}}$  are the inlet and outlet molar flows of the feed,  $n_{c,i}$  is the carbon atom molar flow of product  $i$ ,  $n_{c,\text{feed,in}}$  and  $n_{c,\text{feed,out}}$  are the carbon atom molar flow of feed in the reactor inlet and outlet respectively,  $n_{\text{propylene}}$  is the molar flow of propylene produced and  $m_{\text{catalyst}}$  is the catalyst mass.

### 3. Results and discussion

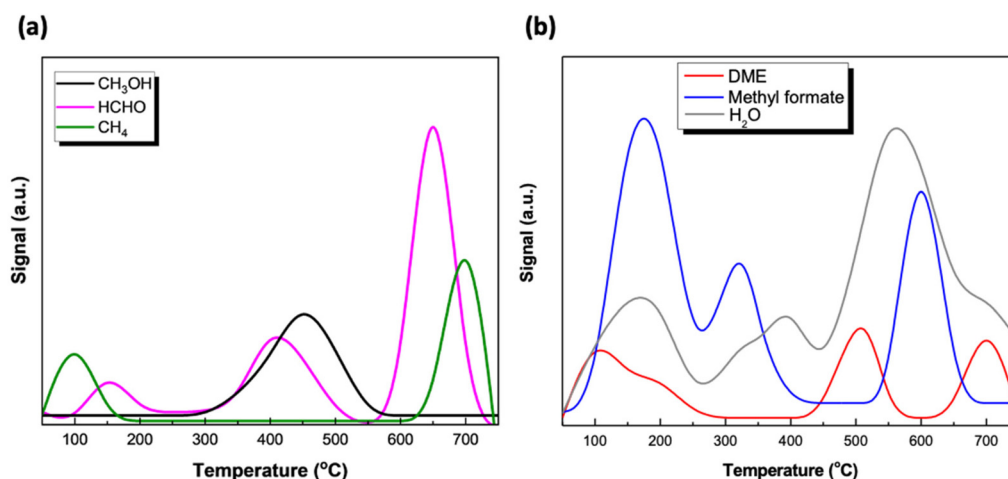
#### 3.1 Catalyst characterization

Temperature programmed surface reaction spectroscopy (TPSR) is considered a powerful technique providing valuable information about the nature of catalyst active sites, the reaction mechanism and kinetics using chemical probe molecules. Among them, methanol has attracted much attention, especially for identifying the nature of active sites, due to its ability to easily adsorb on catalytic surfaces, as well as its reactivity to metal oxides compared to the other molecules used.<sup>46,47</sup> Methanol conversion can lead to various products reflecting the nature of the catalyst active sites. Redox centers

oxidatively convert methanol towards formaldehyde, acid sites yield dimethyl ether (DME) and methyl formate, while basic sites produce  $\text{CO}_2$ .<sup>48</sup>

The  $\text{CH}_3\text{OH}$ -TPSR spectra for both fresh and reduced catalysts are presented in Fig. 1 and 2, respectively. It is interesting to see that the same reaction products, nonetheless at different reaction temperatures, were detected indicating the presence of the same active sites with different chemical activity. Another common feature of both spectra is the appearance of methanol at relatively elevated temperatures with a broad desorption peak maximizing at 400–450 °C. Considering that molecularly physisorbed methanol releases at low temperature ( $\sim 100$  °C),<sup>49</sup> the elevated temperature methanol peak in both samples derives more likely from self-hydrogenation of surface methoxy species ( $^*\text{OCH}_3$ ) which undergo protonation and desorb as  $\text{CH}_3\text{OH}$ .<sup>50–52</sup> This is mostly associated with DME and HCHO formation due to the high concentration of the surface methoxy species.<sup>51</sup> A closer look at both graphs confirms this assumption, as the  $\text{CH}_3\text{OH}$  peak centers at approximately the same temperature where the production of both HCHO and DME occur. Similarly, it is noteworthy that  $\text{CH}_4$  production appears at the spectrum of both materials, which can be attributed either to decomposition reactions of both  $\text{CH}_3\text{OH}$  and DME and/or their hydrogenolysis<sup>53</sup> with hydrogen which is a decomposition product of  $\text{CH}_3\text{OH}$  along with HCHO.<sup>54,55</sup> In fact, two TPSR  $\text{CH}_4$  peaks appear in both cases, one at 100 °C and the other one at 650 °C. The desorption peak at low temperature can be ascribed to hydrogenolysis reactions, while the other at high temperature to decomposition ones.<sup>53</sup>

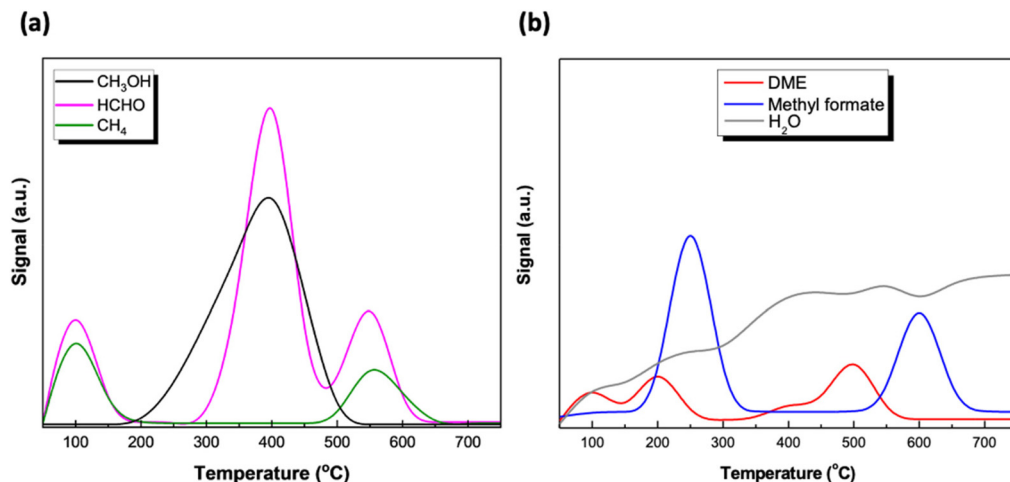
The  $\text{CH}_3\text{OH}$ -TPSR spectrum of fresh catalytic material is shown in Fig. 1. It can be easily seen that the chemisorbed surface methoxy species yield HCHO, DME and methyl formate reflecting the presence of both redox and acid active sites. Even though the present results were not fully quantified, based on



**Fig. 1**  $\text{CH}_3\text{OH}$ -TPSR spectrum of fresh catalyst. Desorption products corresponding to (a) methanol, redox sites (HCHO) and  $\text{CH}_4$  and (b) acid sites (DME,  $\text{HCOOCH}_3$ ) and water. The following masses were used:  $m/z = 31$  for  $\text{CH}_3\text{OH}$ ,  $m/z = 30$  for HCHO,  $m/z = 45$  for DME,  $m/z = 60$  for  $\text{HCOOCH}_3$ ,  $m/z = 15$  for  $\text{CH}_4$  and  $m/z = 18$  for  $\text{H}_2\text{O}$ .







**Fig. 2**  $\text{CH}_3\text{OH}$ -TPSR spectrum of reduced catalyst. Desorption peaks corresponding to (a) methanol and redox sites and (b) acid sites and water. The following masses were used:  $m/z = 31$  for  $\text{CH}_3\text{OH}$ ,  $m/z = 30$  for  $\text{HCHO}$ ,  $m/z = 45$  for  $\text{DME}$ ,  $m/z = 60$  for  $\text{HCOOCH}_3$ ,  $m/z = 15$  for  $\text{CH}_4$  and  $m/z = 18$  for  $\text{H}_2\text{O}$ .

almost similar sensitivity factors of the above products,<sup>52</sup> it can be inferred from the relevant intensities of the peaks that the fresh catalytic material possesses high selectivity towards dehydration products (DME and methyl formation). The production of DME and methyl formate occurs at three different temperature zones indicating the presence of three different intermediate methoxy species which are adsorbed on catalyst active sites with different acid strengths. The surface methoxy species at the lowest temperature correspond to the  $\text{Mo-OCH}_3$  species formed on the catalyst surface, while the other peaks reflect the high stability of the  $\text{Mo-OCH}_3$  intermediates implying that they have had their redox and/or acidic properties retarded.<sup>51</sup> This is mostly the case for the redox sites which appear to be less active, as  $\text{HCHO}$ , the product of methanol reduction, desorbs at very high temperature  $>600^\circ\text{C}$ .

The  $\text{CH}_3\text{OH}$ -TPSR experiment for the reduced  $\text{Mo/BC}$  catalyst (Fig. 2) presents the same product spectrum as that for the fresh one except for different desorption temperature, indicating the existence of both redox and acid sites. Specifically, the main desorption peak of  $\text{HCHO}$  formed on the redox sites, have shifted towards lower temperatures reflecting the higher activity of the reduced molybdenum sites than the oxidized ones.<sup>50</sup> The same is also valid for the desorption temperature of DME and methyl formate produced on acid sites. In both Fig. 1 and 2, water, which is associated with the formation of both DME and methyl formate, is also presented. As shown in Fig. 1b, three intense water peaks appear in the same temperature range with those of DME and methyl formate. Even though the resolution of the water signal in the MS analyser used (Omnistar) was not high, the recorded signals at  $m/z = 18$  are more pronounced for the fresh  $\text{Mo/BC}$  catalyst where DME and methyl formate are more favored compared to the reduced  $\text{Mo/BC}$  (Fig. 2b).

A rough calculation was performed on the number of active (both redox and acid) sites that can be made by integrating the

desorption peaks of the methanol products. The integration revealed that the total number of active sites increases by 37% upon reduction. More specifically, reduction favors product formation proving that the reduced  $\text{Mo}^{3+}$ ,  $\text{Mo}^{4+}$ , and  $\text{Mo}^{5+}$  species enhance methanol chemisorption more efficiently than the fully oxidized  $\text{Mo}^{6+}$  ones.<sup>50</sup> However, the most significant difference between the fresh and reduced catalysts is in the acid/redox ratio which in the fresh catalyst is roughly 1 while it drops to 0.15 in the reduced catalyst. The high decrease of acid in favor of redox sites on the surface of the reduced catalyst might affect the production of the target product by altering the reaction pathway as will be discussed further on. As the catalytic activity of the surface molybdenum oxide was found to increase upon reduction, it can be suggested that the reduced molybdena species which behave as both redox and acid sites are the most active ones capable of catalyzing the hydrodeoxygenation steps during glycerol HDO.

### 3.2. Catalytic performance

The catalytic results of our previous studies for glycerol HDO to propylene in the liquid phase in a batch reactor<sup>44</sup> and in the gas phase in a fixed bed reactor under flow conditions<sup>45</sup> revealed the outstanding catalytic activity of the  $\text{Mo}$ -based catalyst supported on black carbon. Employing standard reaction conditions ( $280^\circ\text{C}$ , 60 bar system pressure), under flow conditions, propylene yield exceeded 60% for almost complete glycerol conversion for the steady state TOS = 4 h. In most cases, 1-propanol was the main byproduct formed reaching a maximum yield value of 20%. Apart from 1-propanol, propanal and 2-propen-1-ol were also identified, with varying yields depending on the applied reaction conditions. After having extensively tested the effect of the reaction parameters,<sup>45</sup> the performance of the catalyst is further explored by testing its stability for extended reaction time along with its reusability at



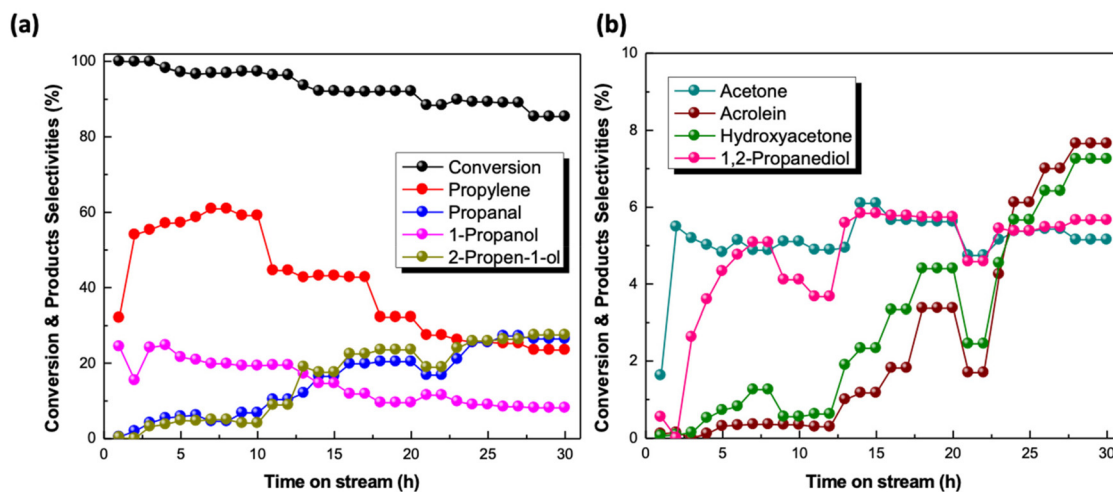


Fig. 3 Stability test in the reaction of glycerol hydrodeoxygenation over reduced Mo/BC catalyst at  $T = 280\text{ }^{\circ}\text{C}$ ,  $P_s = 60\text{ bar}$ ,  $P_{\text{H}_2}^{\circ}/P_{\text{glyc}}^{\circ} = 90$ , LHSV =  $1.2\text{ h}^{-1}$  and  $W/F = 211\text{ g}_{\text{cat}}\text{ mol}_{\text{glyc}}^{-1}\text{ h}^{-1}$ .

the selected optimum reaction conditions ( $T = 280\text{ }^{\circ}\text{C}$ ,  $P_{\text{system}} = 60\text{ bar}$ ,  $P_{\text{H}_2}^{\circ}/P_{\text{glyc}}^{\circ} = 90$ , LHSV =  $1.2\text{ h}^{-1}$ ,  $W/F = 211\text{ g}_{\text{cat}}\text{ mol}_{\text{glyc}}^{-1}\text{ h}^{-1}$ ), under which both the maximum propylene yield and formation rate were achieved.

**3.2.1. Catalyst stability.** Fig. 3 shows glycerol conversion along with product selectivity over time. During the first 10 h, the catalytic activity remains almost constant achieving the highest propylene selectivity ( $\sim 60\%$ ) for almost complete conversion. 1-Propanol is the only product detected in the liquid phase, the selectivity of which remains constant at 20%, while minor amounts of propanal and 2-propen-1-ol (selectivity values  $< 7\%$ ) are also formed. From 10 to 30 h, the conversion decreases from 96 to 85%, in parallel with the activity loss towards the pathway to propylene. More specifically, its selectivity decreases to 43% and remains constant for 7 h. From 17 to 30 h, propylene selectivity further drops almost to half (from 43.14 to  $\sim 20\%$ ), whereas at the same time, 2-propen-1-ol selectivity is notably enhanced indicating that the latter is the main intermediate towards propylene. It is worth mentioning that for the first 17 h the sum of their yield still is roughly the same and equal to 60% indicating that the catalyst activity towards conversion of 2-propen-1-ol to propylene drops. Further increase in the reaction time to 30 h decreases their sum value to 52% implying that a part of the catalytic activity is further lost. It is interesting to note also that the sum of propanal and 1-propanol yield remains the same over time and equals approximately 30%, in addition to the one of propylene and 2-propen-1-ol, indicating a change in both hydrogenolysis and hydrogenation of active Mo species over time. The decrease in the catalytic activity, due to the loss of active sites, is followed also by a drop in the selectivity to the target product (propylene) and the main by-product (1-propanol) in favor of their precursors (2-propen-1-ol and propanal respectively) indicating a change in the functionality of the active sites. Apart from the main intermediate products (2-propen-1-ol, propanal, 1-propanol), hydroxyacetone, acrolein, acetone

and 1,2-propanediol are also detected, though in significantly lower concentrations. However, a closer look in Fig. 3b reveals a slight increase in the selectivity of hydroxyacetone and acrolein. This implies a possible oxidation of the catalyst surface during the last five hours, as the oxidized Mo species favor the production of dehydration products, as it will be mentioned further on. Nonetheless, their production stays relatively low (selectivity  $< 7\%$ ).

These results suggest that not only the number of active sites, but their functionality also changes during extended catalyst testing under reaction conditions. BET measurements revealed almost 50% loss of the surface area after 30 h (BET surface area of the reduced and reduced-used catalyst: 131 and  $67\text{ m}^2\text{ g}^{-1}$ , respectively). Indication about the loss of active sites is also provided by TGA measurements of the reduced-used catalyst after 30 h TOS under inert nitrogen flow. Fig. 4 illustrates the variation in the catalyst weight as a function of

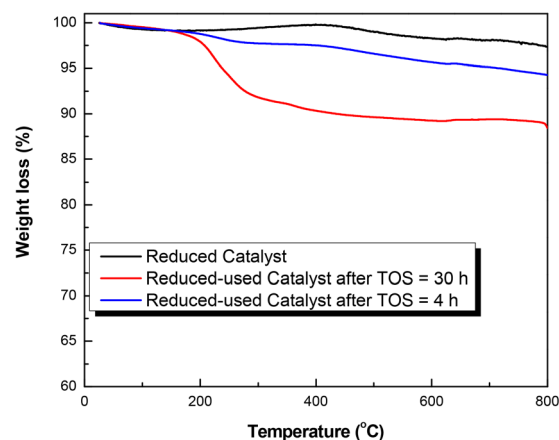


Fig. 4 Thermogravimetric analysis of Mo/BC catalysts under nitrogen flow.



temperature. For comparison, the profiles of the reduced and reduced-used after 4 h TOS for Mo-based catalysts are also included. As expected, under inert conditions the profile of the freshly reduced catalyst is almost flat. The catalyst which was used for a typical test of 4 h TOS shows a gradual loss of 4% in total, which is extended from 100–600 °C. However, the profile of the catalyst weight change after 30 h TOS is different. The loss in weight up to 200 °C, which is considered as the temperature range where water desorbs, amounts to 2.5 wt%. Further 6% weight loss up to 450 °C is seen and this can be ascribed to adsorbed intermediate species and/or products limiting thus the number of available sites for the reactions to proceed.

**3.2.2. Catalyst reusability.** Reusability is considered one of the most significant factors of heterogeneous catalysts especially for a potential commercial application. The reusability of the Mo/BC catalyst was evaluated after regeneration which was performed *via* hydrogen reduction under the same conditions applied during the initial reduction step (500 °C, 30 min). The results are shown in Fig. 5. Having performed an experiment for 6 h duration after initial reduction (1st run), the catalyst was regenerated and was used in a second run (1st regeneration use) with negligible activity loss compared to the reduced one (after the 1st run), while the selectivity towards both propylene and 1-propanol remains almost the same, 60 and 20% respectively. The used-regenerated catalyst was further regenerated and tested again in a third process run (2nd regeneration use). After the third run, no significant changes can be seen in terms of glycerol conversion and product selectivity. Specifically, propylene selectivity slightly reduces along with a minor increase in 2-propen-1-ol production, while at the same time glycerol conversion insignificantly reduces by 2%. In every case, 1-propanol is the main by-product formed, with its selectivity (20%) being still

unchanged after used 3 times. Therefore, it can be suggested that despite the reducing atmosphere under reaction conditions, short hydrogen treatment (30 min) of the catalyst at high temperature (500 °C) regenerates efficiently the active sites by removing any adsorbed species and re-establishing the oxidation states of molybdena. The former is also confirmed by TGA measurements. In the reduced-used sample for 4 h TOS before regeneration (Fig. 6) the weight loss starts at 200 °C and it is extended until 600 °C due to the removal of the water and the organic species adsorbed on the catalyst surface. Nonetheless, the regenerated catalyst (before recycle use) follows the same trend with the fresh reduced catalyst indicating that the catalyst surface is free of any adsorbed species. To clarify further the effect of reduction, catalytic samples in fully oxidized and in reduced form were tested in glycerol HDO under similar conditions, as will be discussed in detail in the following paragraph.

**3.2.3. Effect of the catalyst reduction step.** The effect of catalyst pre-treatment on its reaction performance was evaluated by comparing the activity with and without hydrogen pre-reduction. It should be mentioned that the experiments using the fresh non-reduced catalyst were performed under the typical reaction conditions, however, at time on stream equal to 5 h instead of 4 h. As depicted in Fig. 7, both glycerol conversion and product distribution are highly affected. While over pre-reduced catalyst, glycerol is almost fully converted and propylene is the main product with selectivity over 60%, this is not the case with the fresh fully oxidized molybdena catalyst. Despite the highly reducing environment ( $P_{\text{system}} = 60$  bar,  $P_{\text{H}_2}^{\circ}/P_{\text{glyc}}^{\circ} = 90$ ) the performance of the catalyst does not change during 5 h TOS. The catalyst shows high activity mostly towards dehydration products with hydroxyacetone being the product with the highest selectivity ~54%, while glycerol conversion does not surpass 50%. Production of acrolein, a product of two consecutive dehydration steps from glycerol, is also highly favored with 28% selectivity. As acidity is considered a key factor promoting HDO reactions of glycerol, it

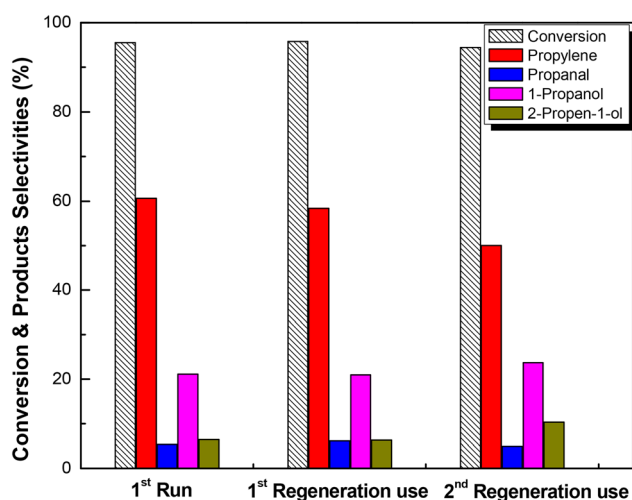


Fig. 5 Reusability test of Mo/BC catalyst in glycerol hydrodeoxygenation reaction at  $T = 280$  °C,  $P_s = 60$  bar,  $P_{\text{H}_2}^{\circ}/P_{\text{glyc}}^{\circ} = 90$ , LHSV =  $1.2 \text{ h}^{-1}$ ,  $W/F = 211 \text{ g}_{\text{cat}} \text{ mol}_{\text{glyc}}^{-1} \text{ h}^{-1}$  and TOS = 4 h. Regeneration procedure: the same with prereduction step ( $T = 500$  °C, 30 min in  $\text{H}_2$  flow).

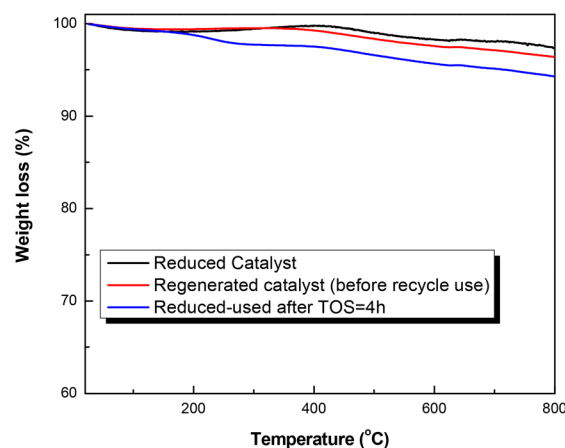


Fig. 6 Thermogravimetric analysis of Mo/BC catalysts under nitrogen flow.





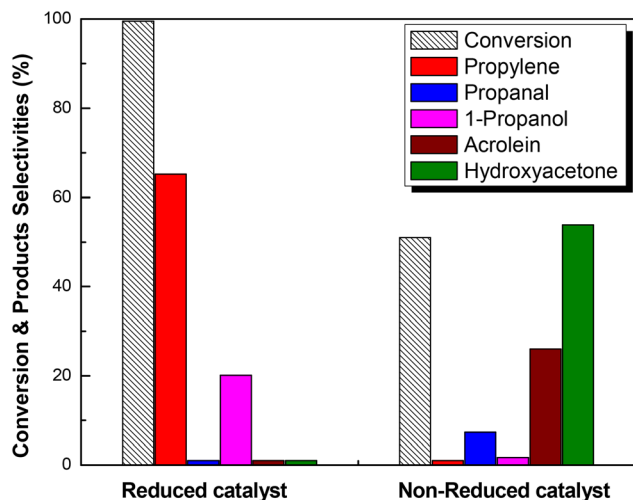


Fig. 7 Effect of hydrogen reduction as a catalyst pre-treatment step at  $T = 280\text{ }^{\circ}\text{C}$ ,  $P_s = 60\text{ bar}$ ,  $P_{\text{H}_2}^{\circ}/P_{\text{glyc}}^{\circ} = 90$ ,  $\text{LHSV} = 1.2\text{ h}^{-1}$  and  $W/F = 211\text{ g}_{\text{cat}}\text{ mol}_{\text{glyc}}^{-1}\text{ h}^{-1}$  and TOS = 4h for reduced and TOS = 5h for non-reduced catalyst.

can be suggested that the  $\text{Mo}^{6+}$  oxidized species provide the required acidity towards dehydration products.<sup>56,57</sup> However, their hydrogenation ability is negligible. It has also been reported that glycerol generates hydroxyacetone through Lewis acid sites, while acrolein *via* Brønsted acid sites. Thus, as the formation of both is highly favored, it can be assumed that both Lewis and Brønsted active sites co-exist on the catalyst surface which favor almost exclusively the formation of dehydration products.<sup>58,59</sup> Even though the production of both hydroxyacetone and acrolein require the presence of acid sites, their production from redox and/or basic sites is also feasible. In the open literature, catalytic materials having redox sites, such as copper oxide, have been applied for the dehydration reaction of glycerol.<sup>59,60</sup> These results further verify the results obtained in  $\text{CH}_3\text{OH}$ -TPSR experiments according to which the ratio of the acid/redox sites is significantly lower in the reduced catalyst compared to the fresh one. Performance data

suggest that the reduced catalyst with the low acid/redox ratio promotes the complete deoxygenation to propylene while samples with higher ratios lead to partially deoxygenated products in agreement with the work of M. El Doukkali *et al.*<sup>40</sup> Summarizing, catalyst hydrogen pre-treatment step is of utmost importance to obtaining the active sites for the reaction to proceed towards propylene production.

Considering the above results, along with that of the re-usability test, reduced Mo species are most likely the active species for the selective HDO of glycerol to propylene. To further confirm this, measurements of catalysts by XPS, which provides valuable information about the composition and the oxidation state of metal species in the upper surface layers, were performed.

Fig. 8 visualizes the Mo 3d XPS spectra of fresh, reduced Mo/BC catalyst, while Fig. 9 that of reduced-used and non-reduced-used. Mo 3d levels are split into  $3d_{5/2}$  and  $3d_{3/2}$  due to the spin-orbital coupling.<sup>61</sup> In the case of fresh sample, the observed binding energy of Mo  $3d_{5/2}$  and  $3d_{3/2}$  levels correspond to 232.5 and 236 eV, respectively. Based on the literature data<sup>61–65</sup> and as presented in Table 3, these values are close to the ones typically referred to  $\text{Mo}^{6+}$  ions indicating that in the fresh sample molybdenum species are only present at the highest oxidation state 6+. The XPS data fitting for both reduced (Fig. 8b) and reduced-used (Fig. 9a) sample indicates that the formed species are related with numerous Mo oxidation states at different percentages, as shown in Table 3, whereas the peak deconvolution indicates that four oxidation states of Mo ( $\text{Mo}^{6+}$ ,  $\text{Mo}^{5+}$ ,  $\text{Mo}^{4+}$  and  $\text{Mo}^{3+}$ ) coexist on the surface. The appearance of new molybdenum species, namely  $\text{Mo}^{4+}$  and  $\text{Mo}^{5+}$ , which is associated with a notable diminution of  $\text{Mo}^{6+}$  species suggests that during reduction almost half part of  $\text{MoO}_3$  in the upper surface layers is reduced to  $\text{MoO}_2$  (Table 3). A small amount of  $\text{Mo}^{3+}$  is also formed as shown by the peaks located at 228.6 and 231.7 eV, suggesting that a part of  $\text{Mo}^{4+}$  species undergoes an over hydrogen-reduction to  $\text{Mo}^{3+}$ . XRD measurements of the catalytic materials<sup>45</sup> showed that all the detected peaks of both reduced and reduced-used sample correspond to  $\text{MoO}_2$ , while those of fresh to  $\text{MoO}_3$ .

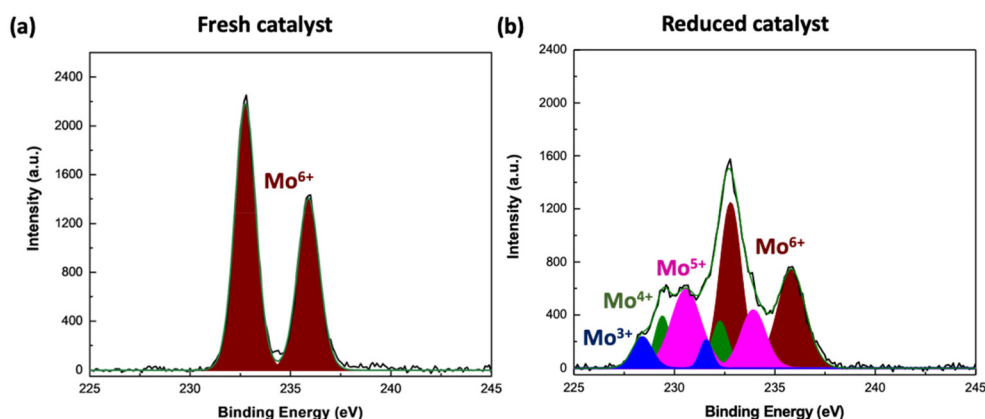


Fig. 8 XPS Mo 3d spectra (black line) and the fitted (green line) for (a) fresh and (b) reduced Mo/BC catalyst.



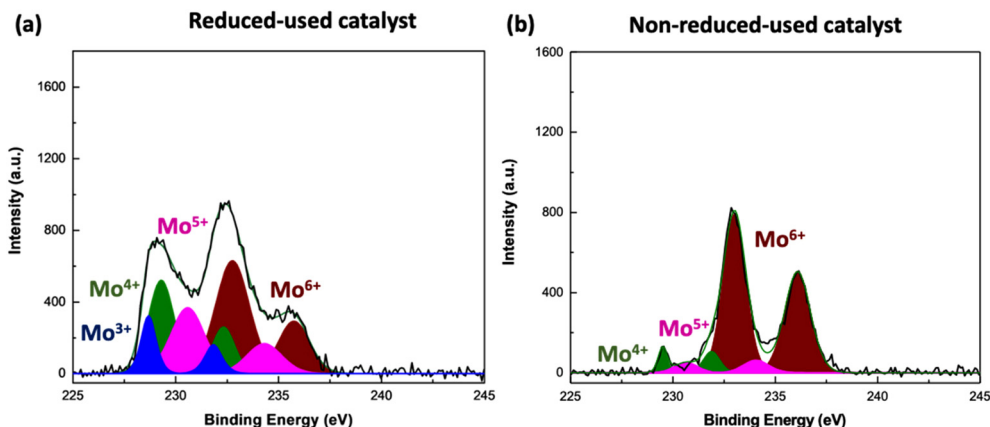


Fig. 9 XPS Mo 3d spectra (black line) and the fitted (green line) for (a) reduced-used and (b) non-reduced-used Mo/BC catalyst.

**Table 3** XPS quantification data for population of Mo at different oxidation states and XPS standard binding energies (eV) of Mo 3d levels for different oxidation states of molybdenum<sup>61</sup>

Oxidation state	Population of oxidation state of catalytic materials (%)				Standard reported values (eV)	
	Fresh catalyst	Reduced catalyst	Reduced-used catalyst	Non-reduced-used catalyst	Mo 3d5/2	Mo 3d3/2
Mo <sup>6+</sup>	100	50.10	40.20	84.40	232.5	235.7
Mo <sup>5+</sup>		29.90	24.10	7.60	231.5	234.7
Mo <sup>4+</sup>		12.40	25.30	7.90	230.1	232.2
Mo <sup>3+</sup>		7.60	10.40	—	229.3	232.6

Taking into account both XRD and XPS results it can be assumed that the bulk oxide is different than the composition of the upper surface layer of the catalyst. On the other hand, comparing reduced (Fig. 8b) and reduced-used samples (Fig. 9a), the population of Mo<sup>6+</sup> and Mo<sup>5+</sup> species further decreased from 50.10 to 40.20% and from 29.90 to 24.10%, respectively, while that of Mo<sup>4+</sup> and Mo<sup>3+</sup> increases indicating that a reductive atmosphere during experiments favors the reduction of Mo<sup>6+</sup> to Mo<sup>5+</sup> and its further reduction to Mo<sup>4+</sup> over that of Mo<sup>4+</sup> to Mo<sup>3+</sup>. XPS data for non-reduced-used catalyst (Fig. 9b) indicated the formation of Mo<sup>4+</sup> and Mo<sup>5+</sup> species which can be attributed to the reductive environment during experiments. Nonetheless, their formation is very limited not surpassing 8% which was not enough to promote propylene production. Comparing the catalytic performance data with CH<sub>3</sub>OH-TPSR and XPS results, it can be suggested that the hydrodeoxygenating activity is attributed to the reduced Mo<sup>3+</sup>, Mo<sup>4+</sup>, and Mo<sup>5+</sup> species.

### 3.3. Glycerol to propylene reaction routes

**3.3.1 Conversion of intermediates under steady state high pressure flow conditions.** To better understand the reaction routes of glycerol to propylene and other products formed in the presence of Mo/BC, a series of experiments was conducted using as feedstock the partially deoxygenated products formed (2-propen-1-ol, propanal, acetone, 2-propanol, 1-propanol). The tests were conducted in the flow unit under similar con-

ditions in terms of reactant partial pressure, total pressure, temperature and LHSV, unless otherwise noted, to allow for direct comparison. Fig. 10 shows the propylene formation rate as well as propylene productivity for glycerol and partially deoxygenated intermediates. As shown, 2-propen-1-ol leads to the highest propylene formation rate (13 mmol<sub>C<sub>3</sub>H<sub>6</sub></sub> g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>) followed by 2-propanol (2.7 mmol<sub>C<sub>3</sub>H<sub>6</sub></sub> g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>), comparable to the one from glycerol (3.1 mmol<sub>C<sub>3</sub>H<sub>6</sub></sub> g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>). On the

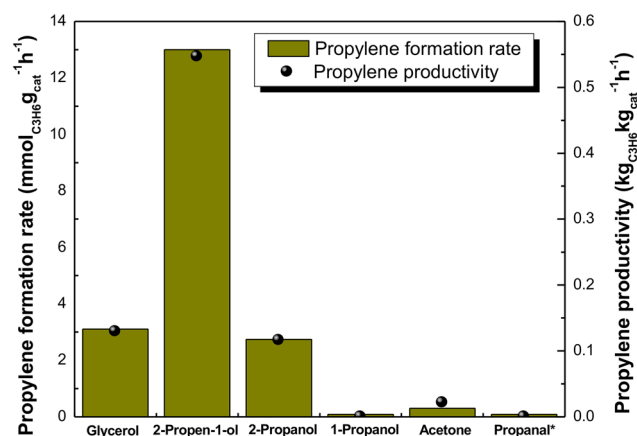


Fig. 10 Propylene formation rate and propylene productivity using glycerol and possible intermediate products as feedstocks at  $T = 280\text{ }^{\circ}\text{C}$ ,  $P_s = 60\text{ bar}$ ,  $\text{LHSV} = 1.2\text{ h}^{-1}$  and  $\text{TOS} = 4\text{ h}$ . \*2 wt% aqueous solution was used as the feed.



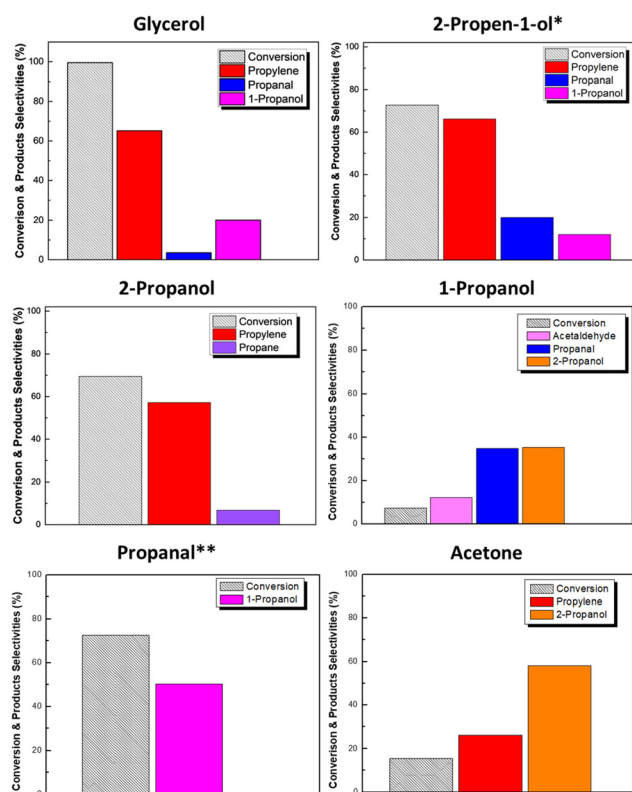
other hand, the other  $C_3$  products evaluated (propanal, acetone and 1-propanol) do not favor propylene production as the formation rate of propylene is extremely low ( $0.2 \text{ mmol}_{C_3H_6} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ ). These data confirm that 2-propen-1-ol, the primary hydrogenolysis product of glycerol, is the main intermediate towards propylene over Mo/BC catalyst in agreement with the results of our earlier work under batch conditions.<sup>62</sup>

Fig. 11 illustrates the variation of conversion levels and product distribution using each intermediate product as feedstock. The results show that 2-propen-1-ol is the most selective over Mo/BC achieving the highest selectivity, equal to 66% for 73% conversion. It should be mentioned that this test was conducted using four times lower  $W/F$  than the other tests with the intermediates confirming the high activity of the catalyst towards conversion of this compound. The product mixture consists also of propanal and 1-propanol with selectivity of 22 and 12% respectively. Apart from hydrodeoxygenation, 2-propen-1-ol undergoes isomerization to propanal, a part of which undergoes sequential hydrogenation forming 1-propanol. 2-Propanol also enhances propylene production (57% selectivity), nonetheless at relatively lower rates as was mentioned previously. Notwithstanding the above, 2-propanol formation from glycerol was not detected at the tests performed at constant reaction temperature  $280^\circ\text{C}$  and variable pressure

and flow conditions applied in the previous<sup>45</sup> and in the present studies, suggesting that the route of propylene formation *via* 2-propanol dehydration can be neglected. In addition, propylene was not detected using propanal and 1-propanol as feedstocks under the standard reaction conditions. The test with propanal was performed using a more dilute aqueous solution (2 wt%), instead of 10 wt% applied in other tests, due to difficulties in handling this volatile oxygenate. Propanal over Mo/BC catalyst shows high activity towards 1-propanol ( $\sim 50\%$  selectivity) at high conversion levels (72%). A few unidentified peaks were detected at short retention times in the analysis of gas products, which might be attributed to ethers and/or products with less than 3 carbon atoms. In fact, it was mentioned that over transition metal oxides, propanal can follow ketonization, condensation and in few cases C–C bond cracking.<sup>63</sup> The high stability of 1-propanol under the present reaction conditions was confirmed with the test in which it was used as feedstock which revealed a conversion marginally surpassing 10%. The products with the highest selectivity were its isomer, 2-propanol, and the dehydrogenation product, propanal, with 25 and 20% selectivity, respectively. Acetone, the most thermodynamically favored isomer out of 2-propen-1-ol and propanal, has also been used as feedstock. The activity of the Mo-based catalyst to convert acetone was low (15%), producing 2-propanol (58% selectivity) and propylene (26%). Acetone has been proposed as the main intermediate for propylene production from glycerol.<sup>39</sup> However, the present results do not support this reaction pathway for the formation of propylene because of the absence of acetone in the product mixture and the extremely low acetone conversion activity of the catalyst under the conditions studied.

The distribution of the products is also presented in tabular form (Table 4) as formation rates together with the consumption rate of each reactant. Under current reaction conditions, 2-propen-1-ol consumption rate is the highest among all ( $21.04 \text{ mmol}_{2\text{-propen-1-ol}} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ ) with propylene being the main product formed followed by propanal and 1-propanol. Comparing that with entry 1, both propanal's and 1-propanol's formation rates are noticeably higher ( $5.00$  and  $3.00 \text{ mmol}_{\text{product}} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ ) implying that a part of 2-propen-1-ol undergoes isomerization to propanal, which sequentially hydrogenates partially to 1-propanol due to the reductive environment. The lower rate of formation of 1-propanol from propanal (entry 5) can be ascribed to the much lower concentration of propanal as pointed also in the previous paragraph.

**3.3.3 Temperature programmed surface reaction spectroscopy (TPSR).** In addition to identifying the nature of the catalyst active sites, as was previously mentioned, TPSR can also be applied for elucidating surface reaction pathways. Although TPSR provides fundamental information for the surface chemistry of catalytic material, it has not been extensively applied due to the complexity of analysis.<sup>47</sup> Wang *et al.*<sup>64</sup> applied the TPSR method for screening several catalysts for low temperature glycerol dehydration towards acrolein, while Suprun *et al.*<sup>65</sup> studied the reaction pathways of gas-phase glycerol oxidation over mixed metal oxides.



**Fig. 11** Catalytic performance of glycerol and possible reaction intermediates products at  $T = 280^\circ\text{C}$ ,  $P_s = 60 \text{ bar}$ ,  $\text{LHSV} = 1.2 \text{ h}^{-1}$  and  $\text{TOS} = 4 \text{ h}$ . \* $W/F$  applied in 2-propen-1-ol test was 4 times lower than the other tests for the same bed volume. \*\*2 wt% aqueous solution of propanal was used as the feed.



**Table 4** Consumption rate of feedstocks and formation rate of products under flow conditions at  $T = 280\text{ }^{\circ}\text{C}$ ,  $P_s = 60\text{ bar}$ ,  $\text{LHSV} = 1.2\text{ h}^{-1}$  and  $\text{TOS} = 4\text{ h}$ 

Feed	Consumption rate ( $\text{mmol}_{\text{feed}}\text{ g}_{\text{cat}}^{-1}\text{ h}^{-1}$ )	Formation rate ( $\text{mmol}_{\text{product}}\text{ g}_{\text{cat}}^{-1}\text{ h}^{-1}$ )						
		Propylene	Propane	Propanal	1-Propanol	2-Propen-1-ol	2-Propanol	Acetaldehyde
1 Glycerol	4.68	3.10	—	0.17	0.94	—	—	—
2 2-Propen-1-ol	21.04	13.00	—	5.00	3.00	—	—	—
3 2-Propanol	4.42	3.25	0.30	—	—	—	—	—
4 1-Propanol	0.53	—	—	0.17	—	—	0.17	0.10
5 Propanal <sup>a</sup>	0.98	—	—	—	0.65	—	—	—
6 Acetone	1.10	0.28	—	—	—	—	0.71	—

<sup>a</sup> 2 wt% aqueous solution was used as the feed. Some unidentified peaks were detected which are more likely ethers without being quantified.

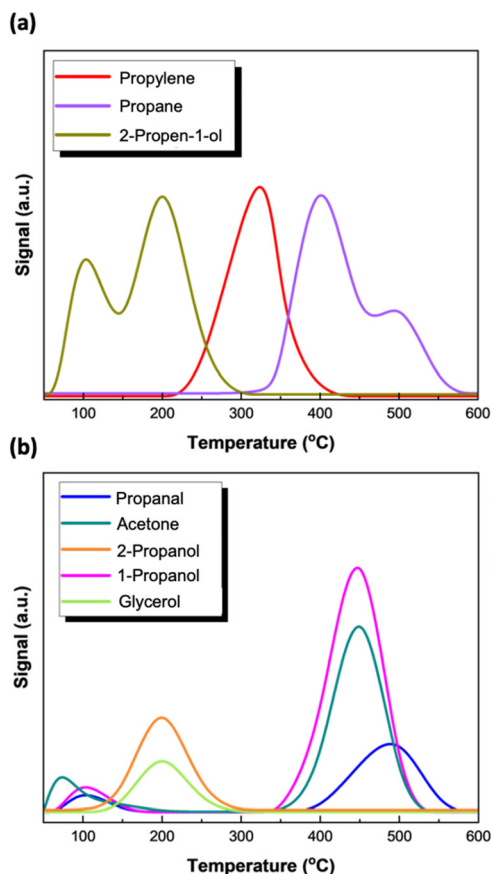
In this study, reaction pathways of glycerol conversion are also examined by TPSR under hydrogen flow. Attempting to get a general and adaptive approach to simulate the reaction, TPSR tests in  $\text{H}_2$  flow were performed over reduced Mo/BC catalyst following the procedure mentioned in section 2.2.2.

The TPSR profiles of products formed following the adsorption of glycerol are depicted in Fig. 12, that of the intermediates 2-propen-1-ol, propanal and 1-propanol are presented in Fig. 13, while that of 2-propanol and acetone are shown in Fig. 14. It is noteworthy that the desorbed species agree qualitatively with those observed during steady state HDO experi-

ments. The reduced Mo/BC catalyst shows an ability to convert all feeds to propylene, apart from propanal and 1-propanol in agreement with the steady state tests as mentioned in the previous section. In few cases, more than one desorption peak appears for the same component (2-propen-1-ol double desorption peak during glycerol TPSR experiment) implying types of active sites with varying activity<sup>66</sup> as also concluded from the  $\text{CH}_3\text{OH}$ -TPSR experiments.

The TPSR-spectrum of glycerol (Fig. 12a and b) shows that the reaction network highly depends on temperature and can be roughly divided into three different zones. Glycerol molecular desorption occurs at  $200\text{ }^{\circ}\text{C}$  with an extremely low intensity peak implying the high activity of the reduced Mo surface species to convert this oxygenate with the aid of  $\text{H}_2$  to various products. Temperatures below  $250\text{ }^{\circ}\text{C}$  mostly favor the production of partially deoxygenated products, with 2-propen-1-ol and 2-propanol being the major products desorbed with extremely high intensity. Other intermediates like propanal, 1-propanol and acetone appear in the same temperature range but with significantly lower intensity. The appearance of 2-propanol in comparable intensity with 2-propen-1-ol, highlights the difference in the reaction sequence at lower temperatures. Further temperature increase up to  $350\text{ }^{\circ}\text{C}$ , primarily promotes propylene formation and desorption. Nevertheless, at temperatures higher than  $400\text{ }^{\circ}\text{C}$  propylene production is restricted in favor of propane, while the reaction pathway changes promoting the formation and the desorption of partially deoxygenated intermediates (acetone, propanal and 1-propanol).

The evolution of products following the adsorption of 2-propen-1-ol on the catalyst surface is remarkably interesting with the appearance of propylene, which dominates in the whole temperature range, indicating the high activity of reduced Mo/BC in converting 2-propen-1-ol to propylene. This result agrees with the high rate of propylene formation obtained in the steady state runs using 2-propen-1-ol as the feed. Despite the higher activity to propylene, 2-propen-1-ol isomerization towards propanal also occurs above  $300\text{ }^{\circ}\text{C}$  with the latter being converted to 1-propanol on account of the reductive environment. Comparing 2-propen-1-ol and propanal TPSR-spectra (Fig. 13a and b), it can be seen that the activity of the catalyst surface sites towards propanal conversion is much lower as it desorbs intact in the temperature range  $200\text{--}400\text{ }^{\circ}\text{C}$  with a high intensity. The main products formed from the partial conver-



**Fig. 12** Glycerol TPSR spectrum using hydrogen over reduced Mo/BC catalyst.





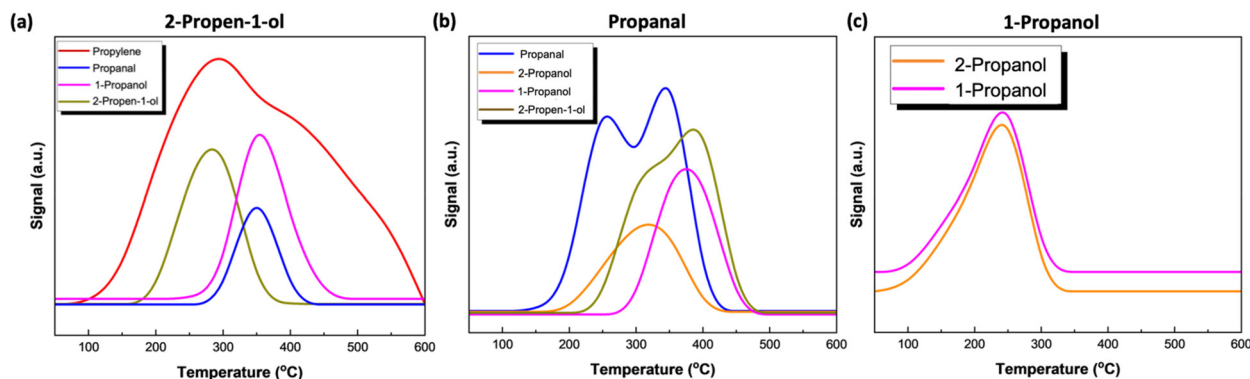


Fig. 13 TPSR spectrum of (a) 2-propen-1-ol, (b) propanal and (c) 1-propanol using hydrogen over reduced Mo/BC catalyst.

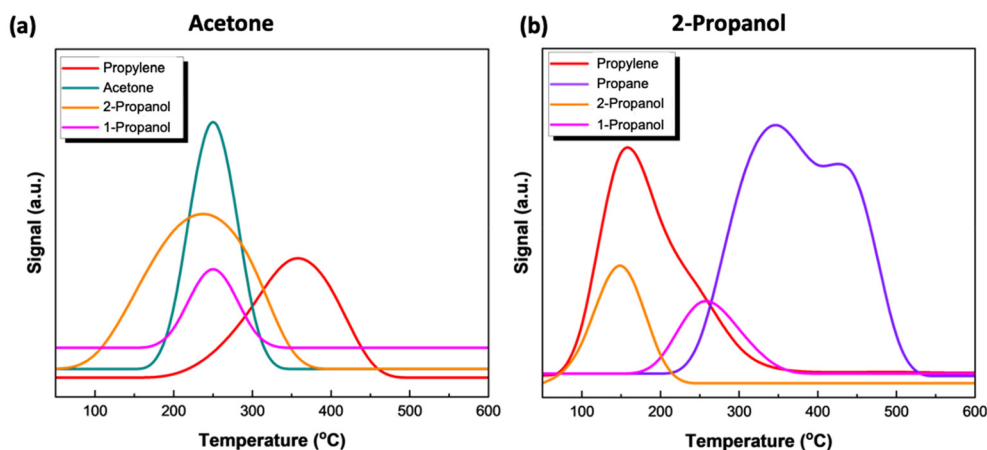


Fig. 14 TPSR spectrum of (a) acetone and (b) 2-propanol using hydrogen over reduced Mo/BC catalyst.

sion of propanal are its isomer 2-propen-1-ol which desorbs up to 450 °C and propanols, 1- and 2-. No propylene formation was detected using either propanal (Fig. 13b) or its hydrogenation product 1-propanol (Fig. 13c) as feedstock.

TPSR of acetone and 2-propanol were also conducted. As depicted in Fig. 14a, adsorbed acetone starts to hydrogenate at temperatures as low as 100 °C as evidenced by the desorption of 2-propanol, which dominates in the product spectrum. In the test with 2-propanol as the feedstock, propylene appears as the main product desorbing at low temperature (onset 100 °C). In the temperature range 300–500 °C, the adsorbed species are further hydrogenated to propane. Even though propylene formation might also be feasible using both acetone and 2-propanol as the feedstock (even at low temperatures), when glycerol is used as the feedstock, their formation is possible only at lower temperatures than the one applied during HDO experiments (280 °C). In fact, steady state experiments that took place at lower temperatures (240 °C) favored both acetone and 2-propanol production, nonetheless without being further converted to the desired product, propylene, which was not detected.<sup>45</sup> The above results confirm that the reaction pathways through which glycerol is converted to propylene are highly dependent on temperature.

TPSR of glycerol was also conducted under inert conditions using helium instead of hydrogen, to study the reaction pathway under an inert atmosphere. The profiles of the desorbed compounds as a function of temperature are presented in Fig. 15. Glycerol is converted to various products, but the extent of its conversion is much lower as depicted by the intensity of its desorption peak especially when compared with the corresponding glycerol peak under hydrogen flow (Fig. 12). Lower conversion of glycerol (69%) under inert conditions compared to 99% under hydrogen was also observed in the liquid phase under batch conditions over molybdena catalysts.<sup>62</sup> In addition, under an inert atmosphere glycerol desorbs at 50 degrees lower than that in the presence of H<sub>2</sub> with a maximum intensity at 150 °C. Further comparison of Fig. 15 with Fig. 12 shows that the products formed, and their distribution vary significantly. As expected, in the absence of hydrogen, propylene and 1-propanol appear with lower intensities (selectivity) compared to that in the presence of hydrogen. However, the striking difference is that under inert conditions, acetone dominates in the product spectrum desorbing at 200 °C. Its isomer, 2-propen-1-ol, also appears as a product at a slightly higher temperature ( $T_{\max} = 250$  °C) followed by propylene, which is the product of 2-propen-1-ol hydrogenolysis.



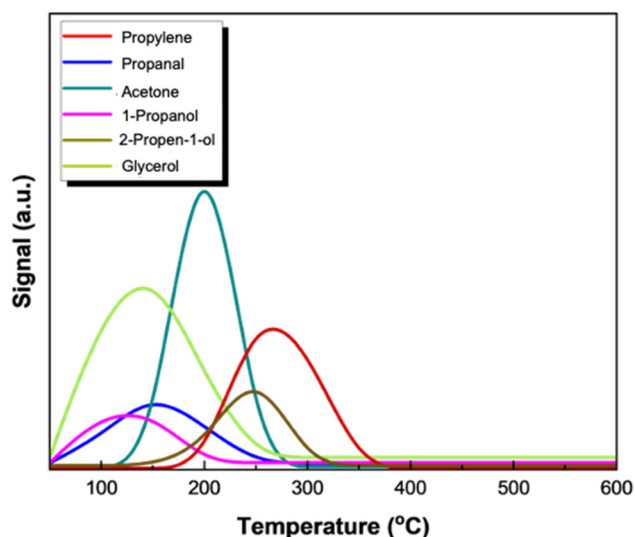


Fig. 15 Glycerol TPSR spectrum under inert gas flow (He) over reduced Mo/BC catalyst.

The formation of propylene under inert conditions might also be possible, implying that intermediate products formed function as hydrogen donors enhancing hydrogenation reactions.<sup>67</sup> However, under inert conditions or low hydrogen availability, propylene's formation is restricted in favor of dehydration and/or partially deoxygenated products (acetone, propanal, 2-propen-1-ol).

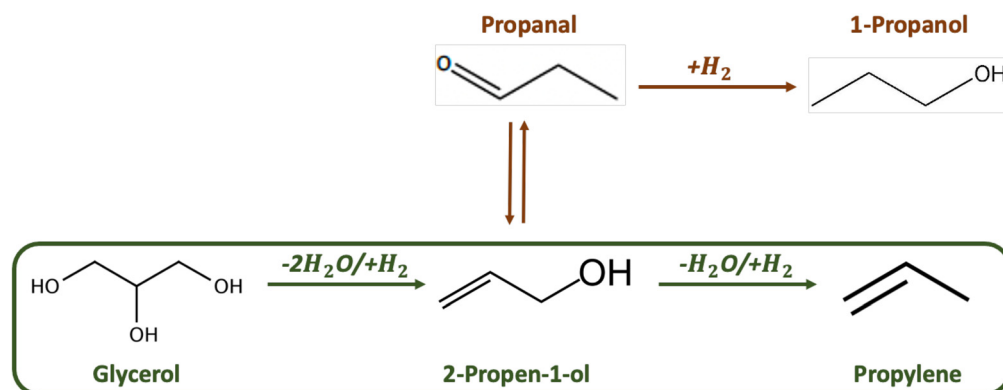
**3.3.4. Glycerol to propylene reaction network.** Considering all the above experimental results under flow conditions, it can be proposed that the main reaction route of glycerol HDO to propylene over reduced 8.7 wt% Mo/BC catalyst follows the same reaction pathway (Scheme 1) as that proposed in our previous publication regarding glycerol HDO to propylene over 20 wt% Mo/BC under batch conditions<sup>62</sup> and analogous with other redox reactions.<sup>19,68,69</sup> The mechanism is based on the reverse Mars van Krevelen (MvK) approach including two subsequent cycles. In the first step, glycerol is converted to 2-propen-1-ol through the loss of two vicinal hydroxyl groups which are adsorbed in oxygen vacancies of the catalyst surface

leading to the formation of 2-propen-1-ol. Next 2-propen-1-ol desorbs from the surface, leaving the surface in the oxidized form. The first cycle completes with the regeneration of the vacancies by H<sub>2</sub> which is present in excess. In the following cycle, 2-propen-1-ol re-adsorbs on the catalyst surface with the remaining hydroxyl group and is further deoxygenated to propylene formation *via* reverse MvK. A prerequisite for the reverse MvK mechanism is the presence of oxygen vacancies (reduced Mo species) on the catalyst surface. This is the case also with the present catalyst on the surface of which the undercoordinated Mo as +5, +4 and +3 prevail. M. El Doukkali and coworkers<sup>40</sup> proposed that the cycles proceed over the pairs Mo<sup>5+</sup>–Mo<sup>6+</sup> and Mo<sup>4+</sup>–Mo<sup>3+</sup>. Our present results do not provide enough evidence for this, requiring further characterization of the catalyst surface under *in situ* conditions.

In parallel to the desired pathway of 2-propen-1-ol re-adsorption on oxygen vacancies leading to the formation of propylene with a high rate, another pathway also proceeds. A part of 2-propen-1-ol undergoes isomerization to propanal which is sequentially hydrogenated to 1-propanol. The experimental results using glycerol as well as the intermediates 2-propen-1-ol, propanal and 1-propanol under steady state and dynamic (TPSR) conditions support this pathway as well. It was also proved that the rate of propylene produced *via* this route is negligible. The probe reaction of CH<sub>3</sub>OH-TPSR showed that both acidic and redox sites exist on the surface of the Mo catalyst; however over the reduced catalyst the ratio of acid/redox sites is much lower than that of the fresh fully oxidized catalyst. As in all the tests under typical conditions the catalyst was pre-reduced, we can propose that isomerization proceeds on Mo acid sites that exist on the surface and due to their low density, the extent of this pathway is limited.

## 4. Conclusions

In this study, an in-depth effort to elucidate the reaction pathways of bio-glycerol hydrodeoxygenation to propylene over molybdena catalysts supported on black carbon under flow conditions was made. For this, the catalytic results were



Scheme 1 Proposed reaction pathways of glycerol HDO towards propylene over reduced Mo/BC catalyst.



obtained by performing experiments with the main intermediate products formed as well as by applying a powerful technique, temperature programmed surface reaction spectroscopy (TPSR). The results showed that the presence of hydrogen is essential for the formation of 2-propen-1-ol and the final product propylene. Nonetheless, 2-propen-1-ol isomerization towards propanal is considered a secondary route with the latter being converted to 1-propanol due to the reductive environment. The presence of acid and redox sites on the surface of the catalyst was examined using  $\text{CH}_3\text{OH}$ -TPSR as the probe reaction. It was found that both sites exist on the surface and that over the reduced catalyst surface, redox sites prevail confirming the higher extent of the desired pathway of the intermediate 2-propen-1-ol hydrodeoxygenation to propylene over its isomerization which takes place over acid sites. The catalyst  $\text{H}_2$ -reduction step at a high temperature (500 °C) for 0.5 h prior to the reaction is vital for the formation of the active sites, which according to XPS measurements are  $\text{Mo}^{5+}$ ,  $\text{Mo}^{4+}$  and  $\text{Mo}^{3+}$ . Despite the reducing environment during the reaction, the catalyst without pre-reduction showed a 50% decrease in activity and more importantly poor hydrodeoxygenation selectivity with almost negligible propylene formation.

The performance of the reduced Mo/BC catalyst was further investigated during the stability test for TOS = 30 h. The selectivity to propylene was not affected for the first 10 h, while a total loss of approximately 17% of its initial activity was observed. The loss of the activity was mostly ascribed to the coverage of the active sites by adsorbed intermediate species. In addition to the stability test, the reusability of the catalyst was also evaluated. Both activity and selectivity to propylene showed no significant differences after two regeneration tests using  $\text{H}_2$  treatment proving that the catalytic active sites are fully recovered.

The current results can be considered as very promising ones offering interesting feedback that advances the scientific knowledge not only of the whole process, but of catalysts as well, strengthening the potential use of molybdenum-based catalysts in large-scale application of bioglycerol HDO to propylene, contributing at the same time for future green processes in general. In the current process, 1-propanol is the main by-product with the highest yield (20%). Nonetheless, this should not be considered as a limitation for a future scale-up scenario, as the separation of 1-propanol and propylene can easily take place *via* a distillation step due to their different boiling points. 1-Propanol, which is still considered a green chemical, can be further used as a raw material for the production of a wide variety of chemicals, and/or by applying a different catalytic material to be dehydrated to propylene, further increasing the propylene yield and improving the feasibility of the HDO process.

## Conflicts of interest

There are no conflicts to declare.

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