Electronic Supplementary Material (ESI) for Green Chemistry.

## SUPPLEMENTARY INFORMATION

# One-step propylene formation from bio-glycerol over Molybdena-based catalysts

**Vasiliki Zacharopoulou[a], Efterpi S. Vasiliadou[a], Angeliki A. Lemonidou [a,b*]**

[a]Department of Chemical Engineering, Aristotle University of Thessaloniki, University Campus, Thessaloniki 54124, Greece

[b]Chemical Process Engineering Research Institute (CERTH/CPERI), P.O. Box 60361 Thermi, Thessaloniki 57001, Greece

Corresponding author

Angeliki A. Lemonidou

Phone: +30 2310 996273

Fax: +30 2310 996184

Email: alemonidou@cheng.auth.gr

## Experimental

### Temperature-Programmed Reduction (TPR)

Catalysts' reduction characteristics were studied via temperature-programmed reduction. The TPR experiments were performed in a gas flow system equipped with a quadrupole mass analyzer (OMNIStar™, PFEIFFER). Catalyst samples (0.1g) were placed in a U-shaped quartz reactor and were pretreated at 250ºC, under He Flow (30cm$^3$ min$^{-1}$) for 0.5h, and then cooled to room temperature. Samples were reduced in a flow of 10% $H_2$/He flow (30 cm$^3$ min$^{-1}$) and heated up to 800ºC, with a ramp rate of 10ºC/min.

### $NH_3$ – Temperature-Programmed Desorption (TPD-$NH_3$)

The acidity of the samples was investigated via temperature-programmed desorption of ammonia (TPD-$NH_3$). The experiments were conducted in a gas flow system, equipped with a quadrupole mass analyzer (OMNIStarTM, Pfeiffer), using a U-shaped quartz reactor. The catalytic samples (0.1g) were first reduced under $H_2$ flow for 0.5h at 500 ºC and then cooled to 100ºC. At 100 ºC, samples were saturated with $NH_3$ (30 cm$^3$ min$^{-1}$) for 1h and subsequently purged with He (60 cm$^3$ min$^{-1}$), for 2h, to remove the physisorbed ammonia. Finally, TPD was performed by heating the sample up to 800 ºC, at a heating rate of 10ºC/min, under He flow (30 cm$^3$ min$^{-1}$). The following (m/z) fragments were registered: He=4, $NH_3$ = 15, $H_2O$ = 18, $N_2$ = 28. Quantitative analysis of the desorbed ammonia was based on (m/z) 15.

### He – Temperature-Programmed Desorption (He-TPD)

Temperature-programmed desorption, in inert atmosphere, has been employed in order to identify the functional groups on the catalytic surface. The experiments were conducted in the same equipment as that of TPD-$NH_3$. The catalytic samples (0.1g) were first reduced under $H_2$ flow for 0.5h at 500 ºC and then cooled to 80ºC. The technique was also applied to fresh catalysts prior to reduction treatment. All samples (0.1g), including the supports, were then subjected to heating up to 700 ºC, at a heating rate of 10ºC/min, under He flow (30 $cm^3$ $min^{-1}$). The following (m/z) fragments were registered: He=4, CO = 28 and $CO_2$ = 46.

### Thermogravimetric Analysis (TGA)

TGA experiments were carried out on SDT Q600 (TA Instruments) apparatus. SDT Q600 works in conjunction with a controller and associated software to make up a thermal analysis system. A small amount of the sample was placed in an aluminum sample cup and then heated from room temperature to 800 ºC at 10 ºC/min, under air or nitrogen flow (100 $cm^3$ $min^{-1}$).

## Characterization

### Temperature-Programmed Reduction (TPR)

In order to assess the reduction properties of catalysts, temperature-programmed reduction method has been employed. TPR profiles of selected samples are presented in Figure S1. The peak centered at 450ºC can be attributed to the partial reduction of $MoO_3$ to $MoO_2$ species and to the reduction of $Fe_2O_3$ to FeO, while the peak at 690ºC can be attributed to the reduction of the latter, to Fe.[1] Under the specific conditions, molybdenum oxides ($MoO_2$) cannot be further reduced to Mo[2,3].

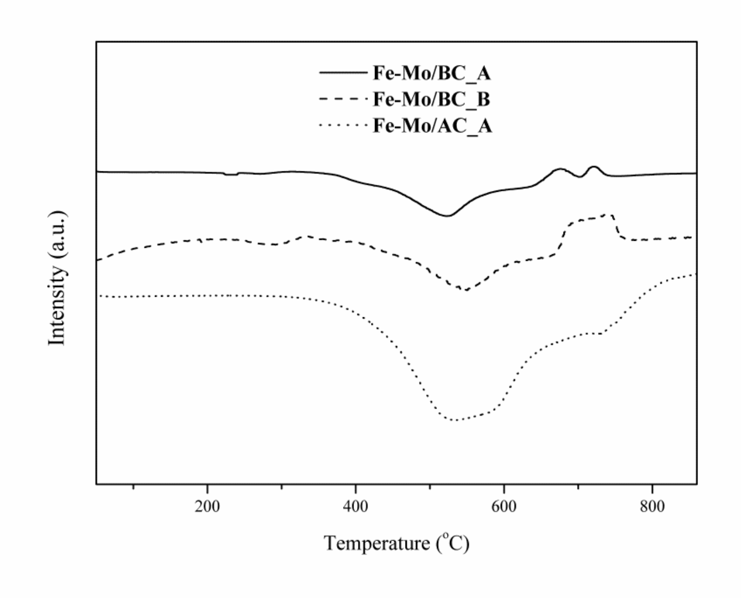

**Figure S1 TPR Profiles of Fe-Mo/C Catalysts**

## $NH_3$ – Temperature-Programmed Desorption

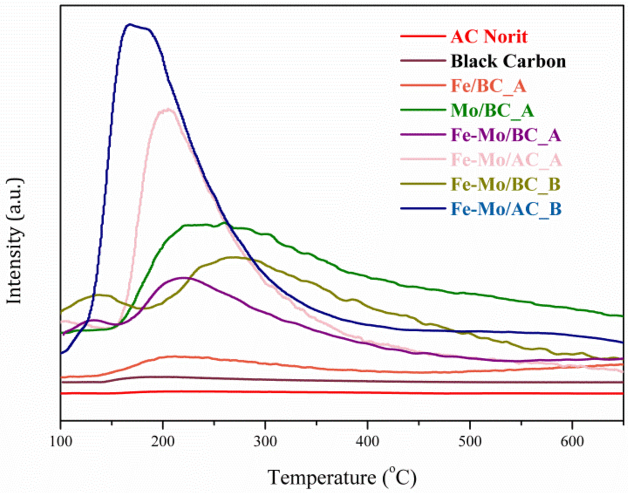

**Figure S2 TPD-$NH_3$ Profiles of all Samples**

In Figure S2, TPD-$NH_3$ profiles of all samples, post reduction treatment, are presented. Both carbons used as catalyst carriers show very low $NH_3$ desorption peaks and the amount of desorbed $NH_3$ per surface area (Table 2) indicates that both supports are not acidic. Among black carbon catalysts, the Mo catalyst presents the highest desorption peak, located in the temperature range of weak and medium acidity. Mo/BC_A acidity, per surface area, is the highest among all samples. It has been reported that, as acidity is a surface property, increased amount of dispersed $MoO_3$ will result in higher acidity values[4].

The Fe catalyst shows very low acidity with a small peak centered at 160 ºC, indicating the presence of weak acid sites, and a second peak at 650 ºC, pointing to the presence of strong acid sites. Acidity values of Fe-Mo catalysts remain between those of the corresponding Fe or Mo samples, leading to the conclusion that the surface acidity increases due to Mo presence[5,6]; Fe addition impedes surface acidity of the samples. All Fe-Mo samples present broad desorption peaks mainly within the region of weak acid sites. The different atmospheres used during calcination treatment (*i.e.* air and nitrogen) seem to slightly affect $NH_3$ desorption profiles, as calcination under nitrogen flow leads to a shift of the broad peak of Fe-Mo/BC catalyst towards higher temperatures, while the exact opposite phenomenon is observed for the Fe-Mo/AC catalysts. However, this shift does not significantly affect the amount of desorbed $NH_3$; for AC supported catalysts, calcination under air flow leads to relatively lower acidity values due to the formation of basic oxygen groups that reduce surface acidity and increase the available metal anchoring sites[7].

### He – Temperature-Programmed Desorption

Surface groups of all calcined samples and supports have been examined using temperature programmed desorption prior to and post reduction treatment. Upon heating, surface oxygen groups of carbonaceous materials decompose, producing CO and $CO_2$[8]. Presence of oxygen groups on the support surface is of extreme importance as they act as adsorption sites for metallic species, thus affecting metal dispersion and catalyst activity[9-11].

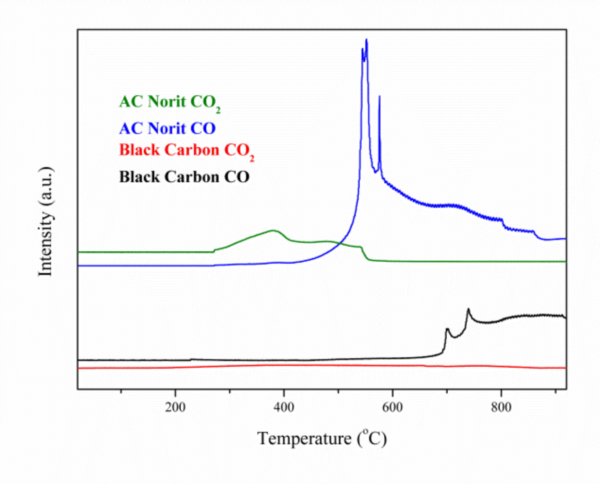

**Figure S3 TPD-He Profiles of Supports**

Figure S3 shows CO and $CO_2$ desorption signals for both catalytic supports (*i.e.* black and activated carbon). The CO and $CO_2$ signal intensity of activated carbon was two orders of magnitude greater than that of black carbon, stressing that the surface of the former contains more oxygen groups. The $CO_2$ profile of activated carbon consists of two broad peaks centered at 400 and 500°C. The former peak is associated with the presence of carboxylic groups[12], the second $CO_2$ peak at 540°C to lactone groups[13]. CO peaks attributed to phenolic groups[14] are extended to broad temperature region with $T_{onset}$ at 500°C. Black carbon gives only two lower intensity CO peaks at considerably higher temperature; 700 and 750°C respectively, due to ether or quinone groups[13]. Both supports showed low weight loss during TGA analysis (under nitrogen flow); activated carbon lost 15% of its weight while black carbon only 1%, suggesting relatively low concentration of the above-mentioned oxygen groups on the catalytic surface (Figure S6).

TPD-He profiles of all calcined and reduced catalysts differ from those of the supports (Figure S3) as a result of synthesis procedure and calcination/reduction treatments, affecting surface oxygen groups.

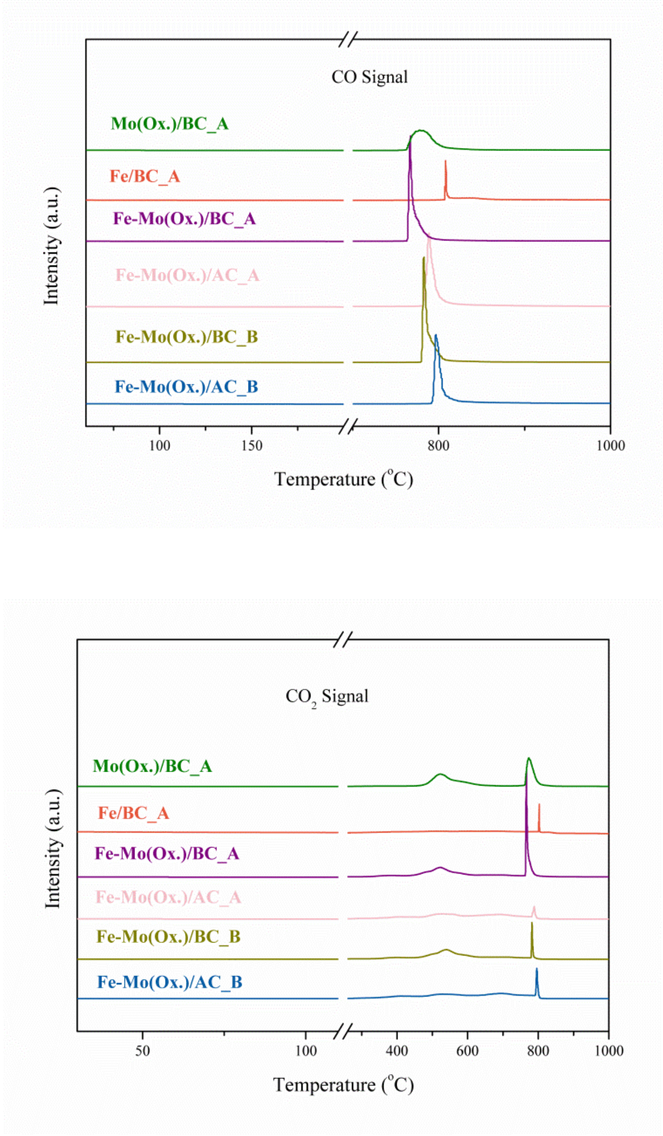

**Figure S4 TPD-He Spectra of Catalysts a) CO Signal b) $CO_2$ Signal**

TPD-He Spectra of all calcined catalysts are presented in Figure S4. All samples give a first $CO_2$ peak at 500°C- apart from Fe/BC_A, and a second around 800°C, which can be attributed to carboxylic groups and anhydrides respectively[15]. The carboxylic/lactone groups of the activated carbon are also present in the Fe-Mo/AC samples, while the ether/quinone groups of black carbon are not present in the Fe-Mo/BC catalysts. The calcination process appears to affect the surface groups, as the $CO_2$ peak at 800 °C, of Fe-Mo/BC_B is quite smaller than that of Fe-Mo/BC_A. The CO/$CO_2$ ratio has been calculated and the results are presented in Table S1. As CO, for all catalysts, is produced due to anhydride groups, the highest ratio indicates more anhydride groups on the catalytic surface. The Fe-Mo/AC_A gave the highest CO/$CO_2$ ratio, thus, having more anhydrides on its surface than the other samples.

**Table S1 CO/$CO_2$ Ratio of all Samples**

| **Catalyst** | **CO/$CO_2$ Ratio**[**] |
|---|---|
| | Fresh |
| **Activated Carbon** | 5.6 |
| **Carbon Black** | 1.5 |
| **Mo/BC_A** | 2 |
| **Fe/BC_A** | 0.7 |
| **Fe-Mo/BC_A** | 2.5 |
| **Fe-Mo/AC_A** | 5.1 |
| **Fe-Mo/BC_B** | 4.4 |
| **Fe-Mo/AC_B** | 3.1 |

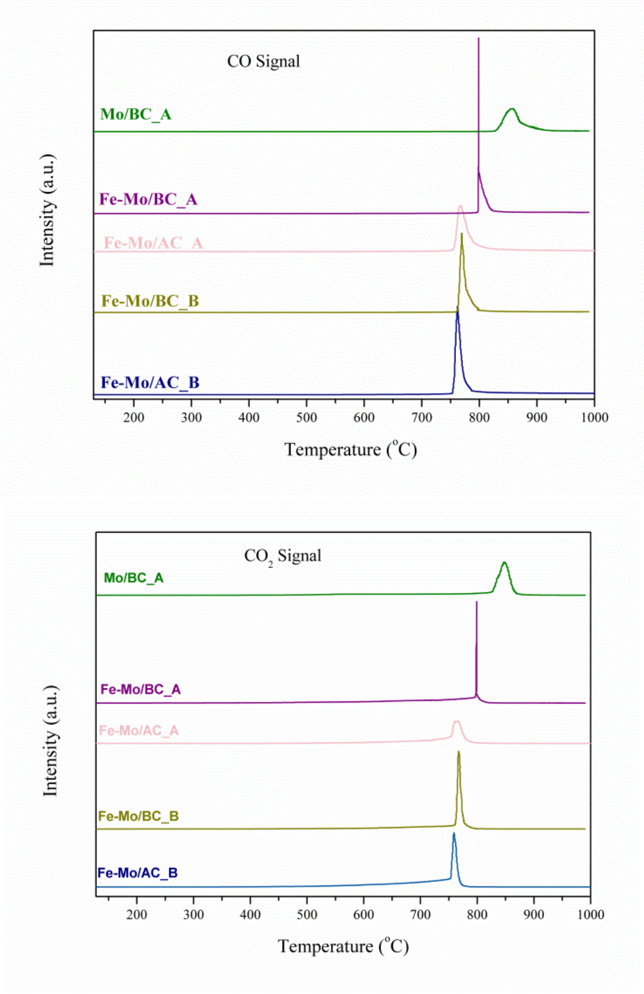

**Figure S5 TPD-He Profiles of Reduced Catalysts a) CO Signal b) $CO_2$ Signal**

All reduced samples give a single $CO_2$ peak after 750°C, which can be attributed to anhydride groups, as CO signals of all samples also present a single peak at this temperature[12]. The carboxylic/lactone groups of the activated carbon are not present in the reduced Fe-Mo/AC catalysts, as well as the ether/quinone groups of black carbon are not present in the reduced Fe-Mo/BC catalysts, probably due to calcination and reduction treatments. The calcination process appears to affect the surface groups, as the $CO_2$ peaks (around 800°C) of catalysts calcined under synthetic air flow are quite smaller than those calcined under nitrogen flow. The $CO/CO_2$ ratio has been calculated and the results are presented in Tables 2 and S1. Upon reduction the $CO/CO_2$ ratio increases by 73-86%, compared to that of calcined samples, as reductive treatment at this temperature (*i.e.* 500$^{o}$C) leads to the decomposition of oxygen groups, attributed to carboxylic groups, present in the calcined samples (Figure S4). As a result, $CO_2$ generated from those oxygen groups, at temperatures around 500$^{o}$C, is reduced and the $CO/CO_2$ ratio increases.

## Thermogravimetric Analysis (TGA)

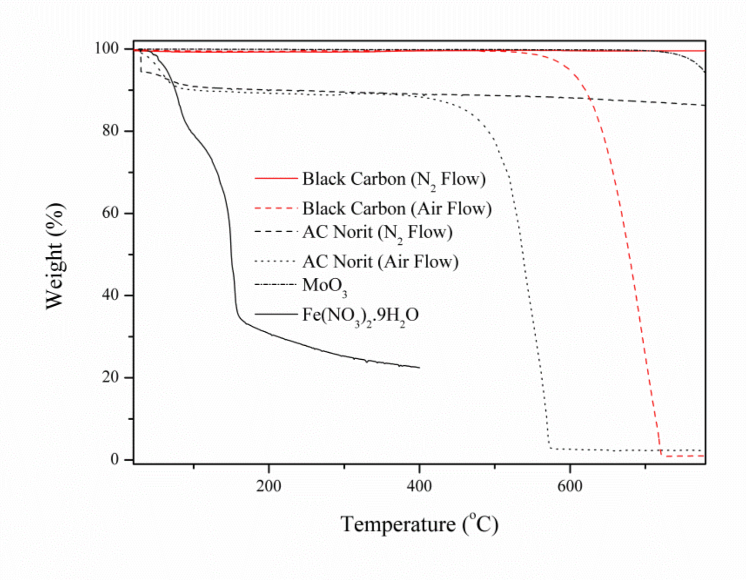

**Figure S6 TGA Profiles of Precursors and Catalyst Supports**

Thermogravimetric analysis of the metal precursors, as well as of carbon supports, has been performed under nitrogen and air flow, in order to obtain information regarding their decomposition profiles and stability upon calcination (Figure S6). Carbon black appears to be more stable, compared to activated carbon, as the weight loss of the former starts above 600ºC while for the latter starts at 400 ºC, under air flow. The increased BET surface area of the activated carbon and thus, the smaller particles, enhance decomposition. For both carbon supports, the weight loss is ~98%, due to the various impurities present in the samples, attributed to the manufacture process. Carbon supports contain impurities (e.g. Ca, Mg, Si, Fe); Si is observed in XRD spectra of activated carbon and Fe-Mo/AC catalysts, in the form of $SiO_2$. Under nitrogen flow, black carbon is also stable up to 800 ºC, while at the same temperature there is a 12% weight loss for the activated carbon.

For the Fe precursor, the first decomposition step at 70 ºC is attributed to a water and nitrate removal. The second step represents the removal of a second water-$NO_3$ group while the third group is removed at higher temperature. After the final decomposition step, the oxide a-$Fe_2O_3$ is obtained. $MoO_3$, the Mo precursor, is a very stable compound within the temperature range of 0-700 ºC; only above 750 ºC, a 10% weight loss is observed due to its evaporation. [1,12]

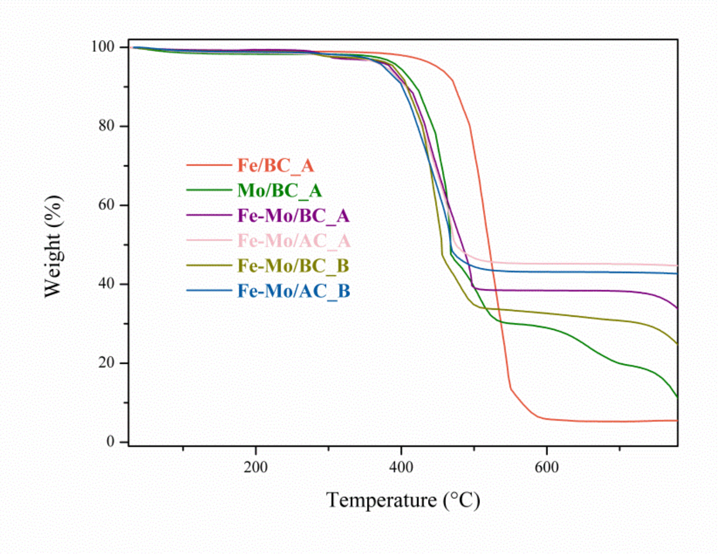

**Figure S7 TGA Profiles for all Catalysts under Air Flow**

Thermogravimetric analysis profiles of all catalytic samples after calcination, under air flow, are illustrated in Figure S7. The Fe/BC_A catalyst TGA profile appears to be identical to the carbon support (Figure S6), although the major weight loss commences at 500ºC and not at 600ºC, probably due to the presence of iron that catalyzes carbon burn off. For all Fe-Mo samples, the decomposition of Fe oxides takes place at higher temperatures, since $MoO_3$ retards their decomposition[1]. As demonstrated in Figure S6, $MoO_3$ does not decompose before 750ºC. The next weight-loss step at 750ºC can be related to the $MoO_3$ disintegration. The Fe-Mo/AC_A sample has the lowest weight loss (55.5%), similar to Fe-Mo/AC_B sample. This difference is evident, comparing these samples to Fe-Mo/BC_A and Fe-Mo/BC_B that not only show greater weight loss (69.7% and 77.9% respectively), but also their final decomposition step takes place at higher temperatures, around 750ºC.

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