Journal of Molecular Catalysis A: Chemical xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Green propene through the selective hydrogenolysis of glycerol over supported iron-molybdenum catalyst: The original history

Claudio J.A. Mota[a,b,c,*], Valter. L.C. Gonçalves[a], Jhon E. Mellizo[b], Ana Maria Rocco[b], José C. Fadigas[d], Rossano Gambetta[d,1]

[a] *Universidade Federal do Rio de Janeiro, Instituto de Química. Av Athos da Silveira Ramos 149, CT Bl A. Cidade Universitária, Rio de Janeiro 21941-909, Brazil*
[b] *Universidade Federal do Rio de Janeiro, Escola de Química. Av Athos da Silveira Ramos 149, CT Bl E. Cidade Universitária, Rio de Janeiro 21941-909, Brazil*
[c] *INCT Energia e Ambiente, UFRJ, Rio de Janeiro 219041-909, Brazil*
[d] *Braskem S. A., Av. Nações Unidas, 4777, 05477-000, São Paulo, Brazil*

ARTICLE INFO

Article history:
Received 21 September 2015
Received in revised form
11 November 2015
Accepted 15 November 2015
Available online xxx

Keywords:
Glycerol
Propene
Hydrogenolysis
Iron-molybdenum catalyst

ABSTRACT

The hydrogenolysis of glycerol, a byproduct of biodiesel production, to propene was studied over supported metallic catalysts. About 100% glycerol conversion was observed for all catalysts, but the selectivity was dependent on the composition. Ru and Pd on activated carbon produced mainly propane and methane/ethane, respectively. Ni/Mo on activated carbon gave mainly propane, whereas Zn/Mo and Cu/Mo supported on activated carbon produced intermediate oxygenated compounds. Fe/Mo over activated carbon presented up to 90% selectivity to propene. This results may be explained in terms of the poor reductibility of the Fe/Mo catalysts, as shown by TPR and XRD experiments. A possible pathway from glycerol to propene involves the formation of acetol, 1,2-propanediol and 2-propanol as intermediates.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Catalysis plays an important role in biorefining processes. Enzymes or biological catalysts are key component in many transformation of sugars into fuels and chemicals, whereas several inorganic materials catalyze the conversion and upgrading of biomass. Hydrogenation and hydrogenolysis appears as one of the most important biorefinery processes to use heterogeneous catalyts. Nevertheless, they usually rely on noble metals to achieve good conversion and selectivity. Some metals used in these processes, such as Pt, Pd, Ru and Ir, are considered endangered, as their supply may be in risk in the future due to increasing use, as well as limited available reserves [1]. On the other hand, the chemical industry will still process hydrogenation reactions, as they are key to the production of improved fuels and chemicals. Many biomass-derived feedstock possesses oxygen atoms, which must be partially or totally removed during processing. Therefore, the search for hydrogenation and hydrogenolysis catalysts based on more abundant metals is of prime importance to attain more sustainable biorefinery processes.

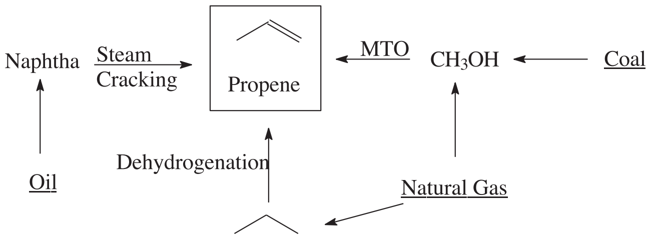
Propene is one of the most important chemicals in industry, with global production around 80 million tonnes per year. About 2/3 of the propene produced is directed to polypropylene (PP), which is a thermoplastic with increasing applications. Propene is basically obtained from fossil sources (Scheme 1), with the steam reforming of naphtha being the main process [2]. In addition, propene can also be produced from methanol over acidic molecular sieve catalysts [3]. This is an indirect route of propene from natural gas or coal, because methanol is normally produced from these fossil sources. Propene can still be produced from propane dehydrogenation over noble metal catalysts [4]. However, propane is a minor constituent of natural gas, or is formed in the catalytic cracking of petroleum fractions. On the other hand, the production of propene from renewable feedstock is poorly studied, differently from ethene, which can be obtained through the dehydration of bioethanol [5]. Thus, the development of green propene, from biomass-derived feedstock, is highly desired and pursuited in the chemical industry.

---

[*] Corresponding author at: Universidade Federal do Rio de Janeiro, Instituto de Química. Av Athos da Silveira Ramos 149, CT Bl A. Cidade Universitária, Rio de Janeiro, 21941-909, Brazil.
E-mail address: cmota@iq.ufrj.br (C.J.A. Mota).
[1] Now at: Embrapa Agroenergia. Parque Estação Biológica-PqEB s/n, Brasília, DF, 70770-901, Brazil.

http://dx.doi.org/10.1016/j.molcata.2015.11.014
1381-1169/© 2015 Elsevier B.V. All rights reserved.

Please cite this article in press as: C.J.A. Mota, et al., J. Mol. Catal. A: Chem. (2015), http://dx.doi.org/10.1016/j.molcata.2015.11.014

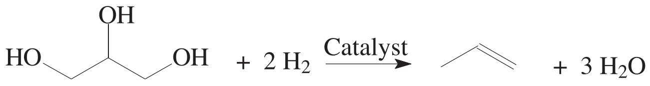


Scheme 1. Main industrial routes to propene from fossil sources (oil, coal and natural gas).

Biodiesel is an important biofuel used mainly in Europe and South America. In Brazil, there is a mandatory blend of 7% biodiesel in the regular diesel and an increase in this percentage is being considered for the next years. The transesterification of oils and fats is the main industrial process for the production of biodiesel [6]. It involves the reaction of a triglyceride with excess methanol, in the presence of a basic catalysts, to afford three molecules of fatty acid methyl esters, the biodiesel, and a molecule of glycerol, which accounts approximately to 10 wt% of the total mass of the system (Scheme 2). The use of glycerol as a renewable feedstock in biorefinery processes has motivated many studies in the recent years [7–10]. Hydrogenolysis of glycerol is one of the main studied processes. Different metal catalysts can be used, with 1,2 and 1,3-propanediols being the main target products [11–13]. Some studies reported that, at more severe conditions, isopropanol and *n*-propanol could also be observed [14,15]. This fact could open a possibility of developing a glycerol to propene route, because dehydration of propanols over acidic catalysts would afford propene as major product.

Aiming to develop a technological route to produce propene from renewable raw materials, we have began an extensive study on glycerol hydrogenolysis, which ultimately led to the development of bimetallic catalysts for the selective production of propene. The initial results were published on the patent literature [17,18]. Thereafter, Yu et al. reported a selective glycerol hydrogenolysis to *n*-propanol over Iridium supported catalysts. The coupling of this metal catalyst with acidic ZSM-5 zeolite may provide a technological route to produce propene from glycerol, in high conversion and selectivity [16]. Nevertheless, Iridium is considered an endangered element and faces serious threat, due to limited availability and increasing use. In addition, the process is carried out in two steps, using two different catalysts, which may increase the operational costs. Thus, the development of an Ir-based catalyst may not be economically and environmentally feasible for the production of green propene, a major chemical commodity.

Here, we report the original history behind the development of the iron/molybdenum-based catalyst for the selective hydrogenolysis of glycerol to propene, as reported in the previous patents [17,18] (Scheme 3). Molybdenum is highly used in oil refining, as a major component of hydrotreating catalyst to remove sulfur and nitrogen from diesel and kerosene, but there is no serious danger of supply of this element in the forthcoming years. Iron is the main catalyst for ammonia production and highly abundant on Earth. Hence, a technological route to propene from glycerol, relying on sustainable metal catalysts, can be of great relevance for developing a biorefinery process based on oils and fats.



Scheme 3. Hydrogenolysis of glycerol to propene.

2. Experimental

The catalysts were prepared by successive impregnation of the metals over an activated carbon (AC) support. Initially, molybdenum was impregnated by a slurry method [19]. About 10 g of activated carbon were placed in a 250 mL Erlenmeyer and 1.5 g (10.6 mmol) of MoO_3 were mixed together with 100 mL of deionized water. The system was kept stirring at room temperature for 24 h and then, the water was evaporated at 70 °C under reduced pressure. In the sequence, a specific mass of $Ni(NO_3)_2\cdot 6H_2O$, $Zn(NO_3)_2\cdot 6H_2O$, $Cu(NO_3)_2\cdot 3H_2O$ or $Fe(NO_3)_3\cdot 9H_2O$, corresponding to 6.93 mmol of the metals, were dissolved in the minimum amount of deionized water and put in contact with the solid obtained upon the Mo impregnation of the AC. Then, a solution of about 150 mL of 30 wt% ammonium hydroxide were added dropwise to precipitate the metal hydroxide. At the end, the system was stirred at room temperature for 24 h and then subjected to water evaporation at 70 °C and reduced pressure. The final solid was calcined at 450 °C for 2 h (rate of 10 °C min^{-1}). The atomic ratio of the catalysts were 0.4 considering the amount of the metal divided by the amount of the metal plus Mo.

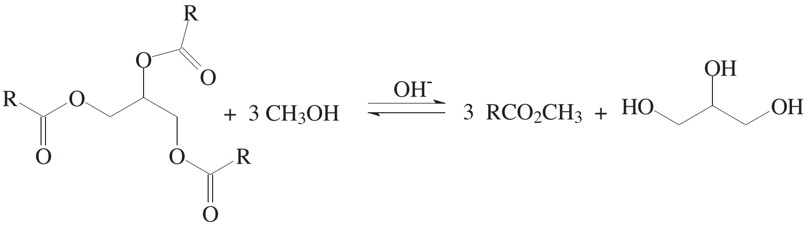
The catalysts were characterized by temperature programmed reduction (TPR), X-ray diffraction (XRD), N_2 physisorption and acidity, which was measured by *n*-butylamine termodesorption (TPD), according to a previous publish method [20]. The chemical composition was measured by X-ray fluorescence (FRX).

The catalysts were evaluated in a fixed bed flow unit at atmospheric pressure. The catalysts were initially reduced on 40 mL min^{-1} of H_2 at 550 °C for 30 min (rate of 10 °C min^{-1}). Then, the temperature was decreased to 300 °C and a solution of 90 vol% of glycerol in water was introduced into the H_2 gas flow (40 mL min^{-1}) by means of a syringe pump. The weight hour space velocity (WHSV) in relation to the glycerol was 5.4 h^{-1} in many experiments. The products were analyzed by on-line capillary gas chromatography equipped with a methyl silicone column (100m × 0.15 mm × 0.5 μm) using a flame ionization detector.

Commercial Pd and Ru supported catalysts were also tested in the hydrogenolysis of glycerol. These catalysts were kindly provided by Evonik and have 5 wt% of the metal supported over activated carbon.

3. Results

We began the studies toward a selective process of glycerol hydrogenolysis to propene using the commercial Ru and Pd cat-



Scheme 2. Transesterification of triglycerides to produce biodiesel and glycerol.

Please cite this article in press as: C.J.A. Mota, et al., J. Mol. Catal. A: Chem. (2015), http://dx.doi.org/10.1016/j.molcata.2015.11.014

Table 1
Glycerol hydrogenolysis over commercial Ru and Pd catalyst at 300 °C, atmospheric pressure, H_2:glycerol molar ratio of 60:1, WHSV = 3.45 h^{-1}.

Catalyst	Ru/C	Pd/C
Glycerol conversion (%)	100	100
Selectivity (%)		
Methane + ethane	10	26
Ethanol	–	17
Acetaldehyde	16	45
Ethylene glycol	–	9
Acetol	13	–
1,2 and 1,3-propanediol	–	–
Propane	61	3

Table 2
Chemical and textural characterization of the catalysts.

Catalyst	Mo[a] (wt%)	M[a] (wt%)	Ratio[b]	Others[c] (wt%)	Area (m^2 g^{-1})
Ni/Mo	59.5	34.8	0.37	5.7	291
Zn/Mo	61.5	33.3	0.35	5.2	291
Cu/Mo	63.6	31.0	0.33	5.4	224
Fe/Mo	64.5	30.2	0.32	5.3	275

[a] Distribution of the metals, not including C, H and O from the support.
[b] Atomic M/(M + Mo).
[c] Includes Si (major), Ca, Ti, Al, Fe.

alysts. Notwithstanding, the results clearly indicated that they are too active toward hydrogenolysis, favoring different pathways. Table 1 shows the results of conversion and product selectivity of both catalyst on the glycerol hydrogenolysis at 300 °C and 60:1 H_2:glycerol molar ratio. One can see that both catalysts gave 100% glycerol conversion. However, Ruthenium favored total hydrogenation to propane, Pd was more selective toward the cleavage of the C—C bond, ultimately leading to ethane and methane. No propene was detected in these experiments, indicating that, if this olefin was formed, it was rapidly hydrogenated to propane.

The results of glycerol hydrogenolysis over Pd and Ru supported catalysts at 300 °C were not promising toward propene, as no trace of this olefin was observed in the experiments. Thus, we decided to direct the studies toward less active hydrogenation catalysts, based on Molybdenum and another metal. This type of catalyst is used in hydrotreating of oil fractions to remove sulfur and nitrogen atoms, but are recognized to be significantly less active toward olefin hydrogenation.

Table 2 shows the results of composition and texture of the catalysts. One can see that the metal ratios were slightly lower than the nominal values, but all in a similar range. The parent AC had minor amounts of Si (0.3 wt%) and other metals (<0.04 wt%), explaining the presence of these elements in the prepared catalysts. The surface area decreased upon metal impregnation, as the AC has an area of 558 m^2 g^{-1}. This is usual in this type of impregnation procedure, but all catalysts presented similar areas. Fig. 1 shows the results of glycerol hydrogenolysis at 300 °C, atmospheric pressure and a molar ratio of H_2 to glycerol of 120. All catalysts presented high glycerol conversion, around 100%. The Ni–Mo catalysts produced mainly propane (86% selectivity), with propene and methane/ethane as minor compounds. The Zn/Mo catalysts produced mainly oxygenated compounds, with over 90% selectivity. These oxygenated were mostly acetol, 1,2-propanediol, 1,3-propanediol, isopropanol and *n*-propanol, with minor amounts ethylene glycol and ethanol, probably formed upon the cleavage of the C—C bond of glycerol. Methane, ethane and propane were the only hydrocarbons observed over this catalyst. Oxygenated compounds were also the main products observed over Cu/Mo catalyst, with selectivity close to 60%. Propane selectivity was 40% on this catalyst and the remaining hydrocarbons were methane and ethane. The results were completely different over Fe/Mo catalysts, which presented 100% of glycerol conversion and propene as the major product, with selectivity of 90%. The remaining 10% were propane plus methane and ethane. Therefore, the Fe/Mo catalyst showed high selectivity to the desired product with complete glycerol conversion and minor amount of other products. This catalyst did not show any significant change of conversion and selectivity in a test of 24 h with continuous flow of glycerol and hydrogen, indicating no appreciable deactivation within this time period. Fig. 2 shows the results of glycerol hydrogenolysis over the Fe/Mo catalysts as a function of the H_2:glycerol molar ratio. One can see that the oxygenated compounds, mostly acetol and ethylene glycol, are present in higher selectivity as the molar ratio decreases, suggesting that they are intermediates in the pathway of glycerol hydrogenolysis to propene. The excess of hydrogen is then important to achieve high selectivity to propene, suggesting the poor activity of the Fe/Mo catalyst in hydrogenation reactions.

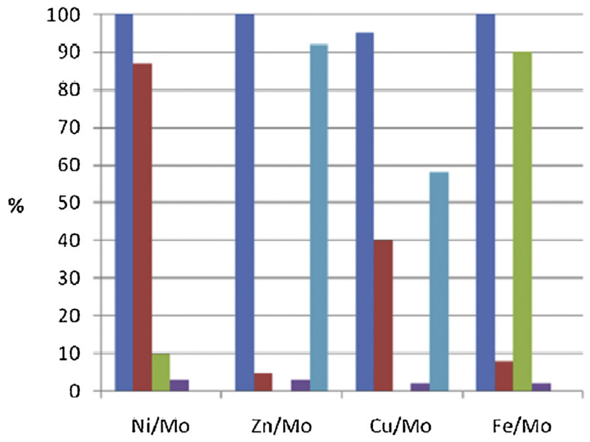


Fig. 1. Conversion and product selectivity of glycerol hydrogenolysis over supported metal/molybdenum catalysts at 300 °C, 1 atm, 5.4 h^{-1} WHSV and 120:1H_2:glycerol molar ratio; (🟦) conversion; (🟥) propane; (🟩) propene; (🟪) methane and ethane; (🟦) oxygenated compounds.

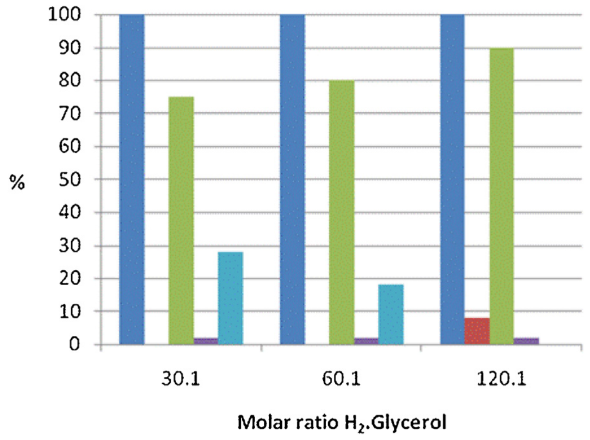


Fig. 2. Effect of the H_2:glycerol molar ratio on the conversion and selectivity of the hydrogenolysis over Fe/Mo catalyst at 300 °C, 1 atm, 5.4 h^{-1} WHSV and 120:1H_2:glycerol molar ratio; (🟦) conversion; (🟥) propane (🟩) propene; (🟪) methane and ethane; (🟦) oxygenated compounds.

Fig. 3 shows the TPR profile of the catalysts. The dotted line indicates the temperature of reduction inside the reactor, prior to the injection of the glycerol feed. The Ni/Mo and the Cu/Mo catalysts showed significant reduction peaks at temperatures lower than 550 °C, indicating a predominant metallic structure at the reaction conditions. This may explain their high selectivity to propane, a product of extensive hydrogenation. On the other hand, Zn/Mo and Fe/Mo showed significant peaks at temperatures higher than

Please cite this article in press as: C.J.A. Mota, et al., J. Mol. Catal. A: Chem. (2015), http://dx.doi.org/10.1016/j.molcata.2015.11.014

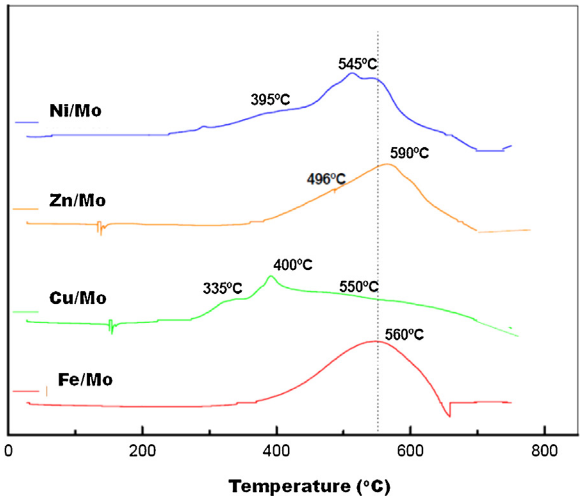


Fig. 3. TPR profile of the catalysts. The dotted line denotes the temperature of reduction prior to glycerol hydrogenolysis.

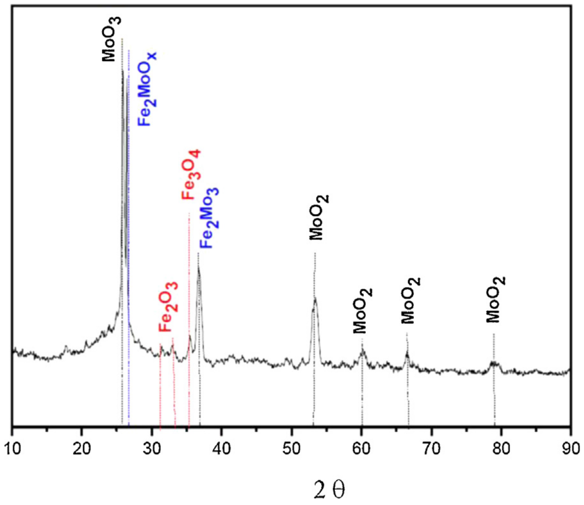


Fig. 4. XRD pattern of the Fe/Mo catalyst.

550 °C, indicating that these catalysts were only partially reduced at the reaction conditions, probably showing metal oxide phases on the surface. These results may explain the low selectivity to propane over Zn/Mo and Fe/Mo, which gave, respectively, oxygenated compounds and propene. The broad peak centered at 560 °C on the TPR profile of the Fe/Mo catalyst has been assigned to the reduction of FeO to metallic Fe, as well as the reduction of the MoO_3 to MoO_2 [21].

Fig. 4 shows the XRD of the Fe/Mo catalyst after reduction at 550 °C. One can identify the presence of MoO_2 phases, consistent with the TPR data. In addition, the diffractogram clearly shows the interaction between the two metals, with the presence of mixed oxide phases. This result is consistent with literature data of similar catalysts [22]. Formation of mixed Fe/Mo species may impair the reduction of the iron ions to the completely reduced form (Fe), due to formation of $Fe_2(MoO_4)_3$ [23,24]. With the predominance of Fe_2Mo_3 mixed oxide phase, the activity of this type of catalyst in hydrogenation is limited, explaining the high selectivity to propene.

The acidity of the parent activated carbon and the Fe/Mo catalyst are shown in Figs. 5 and 6. Upon metal impregnation the acid strength is slightly modified. One can clearly see that the peak centered at 250 °C on the parent activated carbon has disappeared, and a broad peak centered at 388 °C is present upon metal impregnation, together with a shoulder centered at 463 °C. This indicates that stronger acid sites, capable of desorbing the amine over 450 °C, are still present upon metal impregnation, conferring bifunctionality to the Fe/Mo supported on activated carbon catalyst.

Recently, Zacharopoulou et al. repeated our original procedure to prepare Fe/Mo catalysts of varying compositions. Working under batch conditions, at 300 °C and 8 MPa of H_2, they found [25] similar conversion and selectivity to propene as reported in our previous studies [17,18]. They suggested that the active phase is the MoO_2 formed upon reduction of the MoO_3. In addition, they suggested that propene was mostly formed from hydrodeoxygenation of allyl alcohol, obtained from the hydrogenation of acrolein, rather than from 1-propanol and 2-propanol, which in turn could be

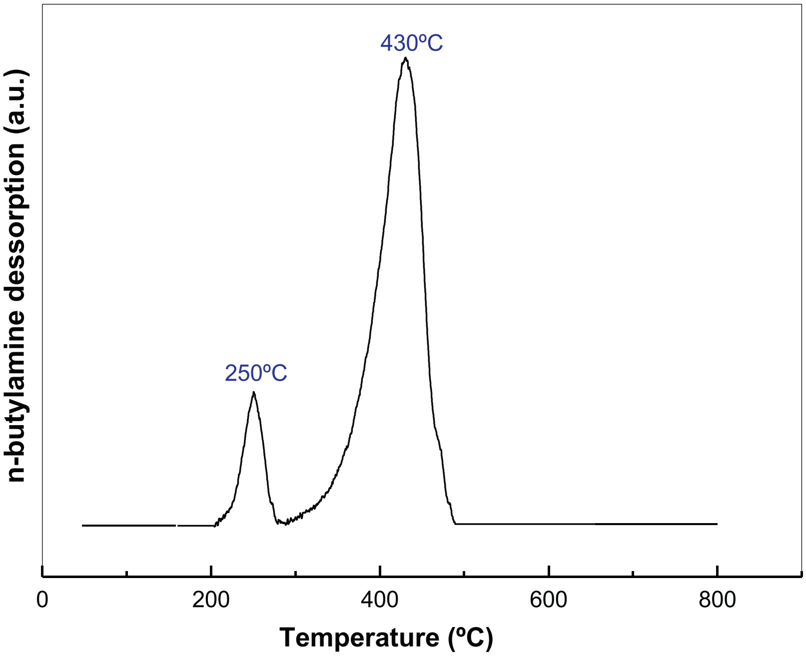


Fig. 5. TPD of *n*-butylamine of the parent activated carbon.

Please cite this article in press as: C.J.A. Mota, et al., J. Mol. Catal. A: Chem. (2015), http://dx.doi.org/10.1016/j.molcata.2015.11.014

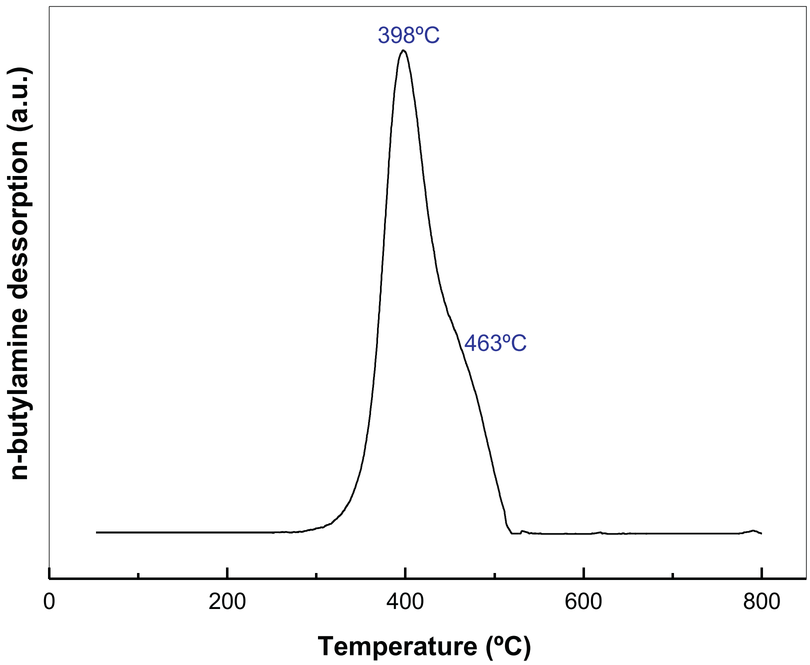


Fig. 6. TPD of *n*-butylamine of the Fe/Mo supported on activated carbon.

Table 3
Selectivity of Fe/Mo catalysts as a function of the amount of iron. Reactions carried out at 325 °C, H_2:glycerol molar ratio of 100:1 and WHSV of 2.6 h^{-1}.

Catalyst[a]	Propene	Methane + ethane	Oxygenated
Fe/Mo (0.2)[b]	75	14	11
Fe/Mo (0.4)	66	11	23
Fe/Mo (0.8)	67	16	17
Fe/Mo (1)[c]	1	–	99
Fe/Mo (0)[d]	82	13	5

[a] All catalysts presented 100% glycerol conversion.
[b] Parenthesis indicated the Fe/(Fe + Mo) ratio.
[c] Only Fe supported over the activated carbon.
[d] Only Mo supported over the activated carbon.

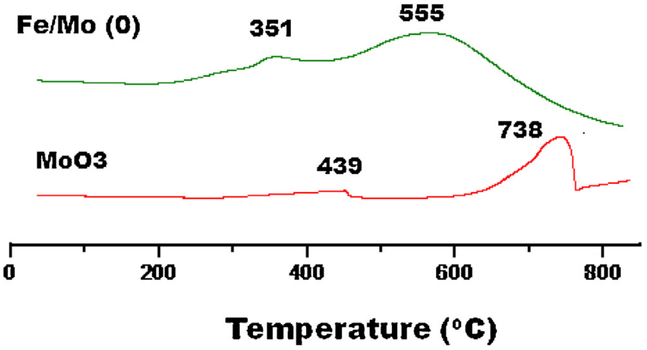
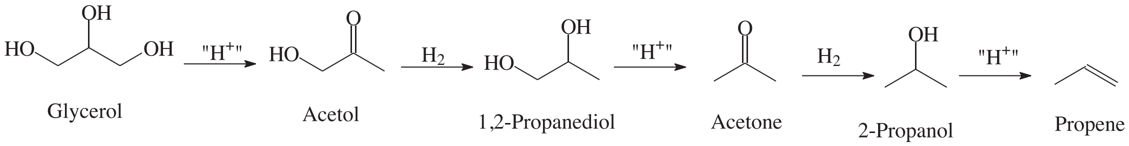


Fig. 8. TPR of the bulk MoO_3 and supported on activated carbon, designated as Fe/Mo (0).

obtained from 1,2-propanediol/1,3-propanediol and acetol. Nevertheless, allyl alcohol was not observed, or formed in minor amounts, in most of the experiments.

Table 3 shows our results of glycerol hydrogenolysis as a function of the amount of iron and molybdenum on the catalyst. One can see that, although the conditions used in the experiments were not the most favorable one to the formation of propene, as we would like to see differences among the catalysts, it is clear that iron does not have a significant role in the formation of this olefin. As the amount of iron on the catalyst increases, the selectivity to propene decreases. Pure iron on activated carbon gave low selectivity to propene, whereas pure MoO_3 gave the highest selectivity to propene. Fig. 7 shows the XRD pattern of the Fe/Mo (0) catalysts, containing only Mo on activated carbon. One can see the formation of MoC phases, which, in addition to MoO_2, may be the active phase for glycerol hydrogenolysis. In fact, supporting the MoO_3 over the activated carbon leads to the decrease of the reduction temperature compared with the bulk oxide, as can be seen in the TPR profile of Fig. 8. To have more insight into the reaction pathway of glycerol to propene, we investigated the hydrogenolysis of 1-propanol, 2-propanol, 1,2-propanediol and 1,3-propanediol over the Fe/Mo catalyst. Table 4 shows the results.

The results of Table 4 clearly show that 2-propanol and 1,2-propanediol are more reactive than their respective isomers over the Fe/Mo catalyst under the reaction conditions used. These data indicate that secondary alcohols are easily converted to products over the catalyst, as one might have anticipated. Propene was the main product from 2-propanol, but dehydrogenation also takes place with formation of acetone as secondary product. 1,2-Propanediol followed the same trend, with propene and 2-propanol as major products. These data show that dehydration of 2-propanol is the major pathway to propene over the Fe/Mo catalyst. On the



Scheme 4. Suggested main pathway of glycerol hydrogenolysis to propene.

Please cite this article in press as: C.J.A. Mota, et al., J. Mol. Catal. A: Chem. (2015), http://dx.doi.org/10.1016/j.molcata.2015.11.014

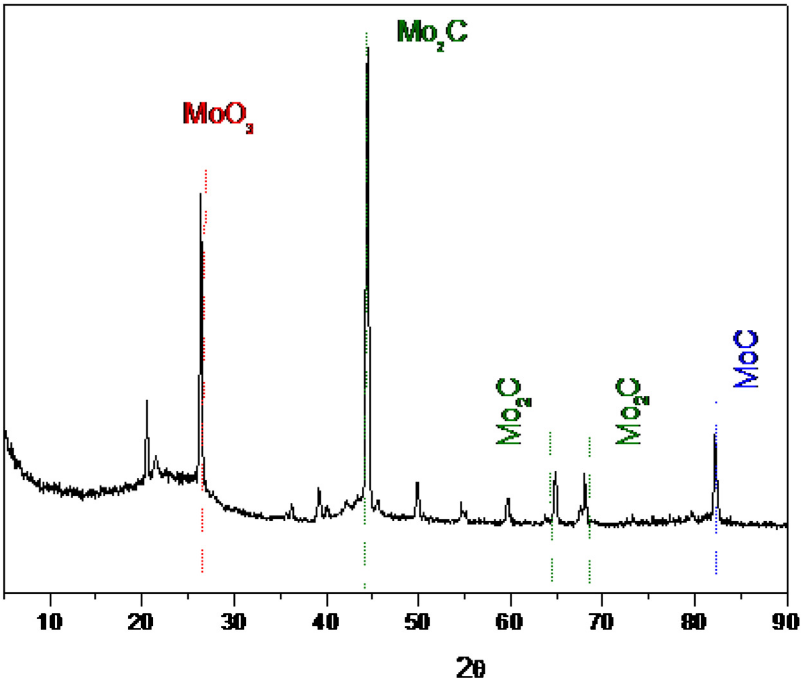


Fig. 7. XRD pattern of the Fe/Mo (0). Supporting MoO_3 alone over activated carbon.

other hand, propene and propanal are formed in approximately the same amount on the hydrogenolysis of 1-propanol over the Fe/Mo catalyst, whereas hydrogenolysis of 1,3-propanediol did not produce propene under the reaction conditions used. These data show that primary alcohols are more difficult to dehydrate over the Fe/Mo catalyst, implying that they are not involved in the main route to propene from glycerol under the reaction conditions used. These results contrast with the suggestion that propene is mainly formed from allyl alcohol, because primary alcohol are significantly less reactive over the Fe/Mo catalyst at the reaction condition used in the experiments.

It has been proposed that hydrogenolysis of glycerol to 1,2-propanediol takes place in two steps, with formation of acetol as intermediate [26]. We have shown that 1,2-propanediol can be converted to 2-propanol, which is then dehydrated to propene. A possible reaction pathway is shown in Scheme 4. This is the most preferred pathway for propene, because the route involving the hydrogenolysis of 1,3-propanediol and 1-propanol present significantly slower rates over the Fe/Mo catalyst, under the reaction conditions used.

Table 4
Conversion and selectivity of products of the hydrogenolysis of possible intermediates on the pathway of glycerol to propene ($T = 300\,^{\circ}C$, atmospheric pressure, H_2: alcohol flow ratio of 40 mL/min: 0.010 mL/min, catalyst = 50 mg).

Alcohol	1,2-Propanediol	1,3-Propanediol	2-Propanol	1-Propanol
Conversion	57%	12%	90%	9%
Selectivity				
Propene	57%		71%	48%
1-Propanol	4%	32%		
2-Propanol	31%			
Propanal		45%		52%
Acetone			29%	
Acetol	4%			
Methanol	4%	23%		

4. Conclusions

In the search for a feasible one-step process of glycerol hydrogenolysis to propene, different metal catalysts were tested. Commercial Ru and Pd catalysts yielded propane and methane/ethane, respectively, as major products, indicating that they are too active for the desired process.

Mo-based catalysts were tested and produced different types of products; Ni/Mo gave propane as major product, whereas Zn/Mo and Cu/Mo produced significant amounts of intermediate oxygenated products. On the other hand, Fe/Mo supported on activated carbon is an efficient catalyst for the continuous flow selective hydrogenolysis of glycerol to propene. It seems that the active phase may be either MoO_2 or MoC.

The reaction scheme may involve the formation of acetol, 1,2-propanediol and 2-propanol as intermediates. The low activity of hydrogenation of propene to propane over the Fe/Mo catalyst may be due to the poor reductibility of the metals at the reaction conditions. TPR and XRD experiments are consistent with the formation of mixed species between Fe and Mo, which retards the reduction of the iron, making this catalyst suitable for the desired process.

Acknowledgements

Authors thanks FAPERJ, CNPq and FINEP for funding. The former Quattor Petrochemicals, now Braskem, is acknowledged for financial support.

References

[1] E. Davies, Chem. World 8 (2011) 50.
[2] T. Ren, M. Patel, K. Blok, Energy 31 (2006) 425.
[3] D. Chen, K. Moljord, A. Holmen, Micropor. Mesopor. Mat. 164 (2012) 239.
[4] Z. Han, S. Li, F. Jiang, T. Wang, X. Ma, J. Gongo, Nanoscale 6 (2014) 10000.
[5] M. Zhang, Y. Yu, Ind. Eng. Chem. Res. 52 (2013) 9505.
[6] A.C. Pinto, L.N. Guarieiro, M.J.C. Resende, N.M. Ribeiro, E.A. Torres, W.A. Lopes, P.A.D. Pereira, J.B. Andrade, J. Braz. Chem. Soc. 16 (2005) 1313.
[7] C.H. Zhou, J.N. Beltramini, Y.X. Fan, G.Q. Lu, Chem. Soc. Rev. 37 (2008) 527–549.

Please cite this article in press as: C.J.A. Mota, et al., J. Mol. Catal. A: Chem. (2015), http://dx.doi.org/10.1016/j.molcata.2015.11.014

[8] M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi, C.D. Pina, Angew. Chem. Int. Ed. 46 (2007) 4434–4440.
[9] C.J.A. Mota, C.X.A. Silva, V.L.C. Gonçalves, Quim. Nova 32 (2012) 639–648.
[10] C.J.A. Mota, B.P. Pinto, in: K. Waldron (Ed.), Advances in Biorefineries, Woodhead Publishing, Cambridge, 2014, p. 364.
[11] J. Chaminand, L. Djakovitch, P. Gallezot, P. Marion, C. Pinel, C. Rosierb, Green Chem. 6 (2004) 359–361.
[12] T. Miyazawa, Y. Kusunoki, K. Kunimori, K. Tomishige, J. Catal. 240 (2006) 213–221.
[13] S.S. Pryia, V.P. Kumar, M.L. Kantam, S.K. Bhargava, K.V.R. Chary, RSC Adv. 4 (2014) 51893–51903.
[14] B. Casale, A.M. Gomez, US pat 527618, 1994.
[15] S. Ludwig, E. Manfred, US pat 5616817, 1997.
[16] L. Yu, J. Yuan, Q. Zhang, Y.M. Liu, H.Y. He, K.N. Fan, Y. Cao, ChemSusChem 7 (2014) 743.
[17] C.J.A. Mota, V.L.C. Gonçalves, J.C. Fadigas, R. Gambetta, W.O., pat. 155674 A2, 2009.
[18] C.J.A. Mota, V.L.C. Gonçalves, J.C. Fadigas, R. Gambetta,US pat. 0184216 A1, 2011.
[19] E. Hillerová, H. Morishige, K. Inamura, M. Zdrazil, Appl. Catal. A 156 (1997) 1–17.
[20] V.L.C. Gonçalves, B.P. Pinto, J.C. Silva, C.J.A. Mota, Catal. Today 673 (2008) 133–135.
[21] W. Ma, E.L. Krugler, J. Wright, D.B. Dadyburjori, Energy Fuels 20 (2006) 2299–2307.
[22] S. Quin, C. Zhang, J. Xu, Y. Yang, H. Xiang, Y. Li, Appl. Catal. A 392 (2011) 118–126.
[23] G. Maiti, R. Malessa, M. Baerns, Thermochim. Acta 80 (1984) 11.
[24] C.G. Hill, J.H. Wilson, J. Mol. Catal 67 (1991) 57.
[25] V. Zacharopoulou, E.S. Vasiliadou, A. Lemonidou, Green Chem. 17 (2015) 903–912.
[26] M. Dasari, P.P. Kiatsimkul, W.R. Sutterlin, G.J. Suppes, Appl. Catal. A 281 (2005) 225–231.

Please cite this article in press as: C.J.A. Mota, et al., J. Mol. Catal. A: Chem. (2015), http://dx.doi.org/10.1016/j.molcata.2015.11.014