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Unravelling the Mechanism of Glycerol Hydrogenolysis over Rhodium Catalyst through Combined Experimental–Theoretical Investigations

Florian Auneau,^[a, b] Carine Michel,^[b] Françoise Delbecq,^{*[b]} Catherine Pinel,^{*[a]} and Philippe Sautet^[b]

Abstract: We report herein a detailed and accurate study of the mechanism of rhodium-catalysed conversion of glycerol into 1,2-propanediol and lactic acid. The first step of the reaction is particularly debated, as it can be either dehydration or dehydrogenation. It is expected that these elementary reactions can be influenced by pH variations and by the nature of the gas phase. These parameters were consequently investigated experimentally. On the other hand, there was a lack of knowledge about the behaviour of glycerol at the surface of the metallic catalyst. A theoretical approach on a model Rh(111) surface was thus imple-

Keywords: density functional calculations • lactic acid • propanediol • reaction mechanisms • rhodium

phase reforming.^[16]

mented in the framework of density functional theory (DFT) to describe the above-mentioned elementary reactions and to calculate the corresponding transition states. The combination of experiment and theory shows that the dehydrogenation into glyceraldehyde is the first step for the glycerol transformation on the Rh/C catalyst in basic media under He or H_2 atmosphere.

cetone^[13-15] has been targeted over recent years. Due to its

availability, glycerol has also been envisaged as a potential

source of renewable fuels through, for instance, aqueous-

Glycerol hydrogenolysis in the presence of metallic cata-

lysts has always been challenging because of selectivity con-

siderations under the moderate to high hydrogen pressures

usually employed (0.1 to more than 100 bar). PDO-selective

formation is usually the aim, and it is consequently necessa-

ry to avoid C-C bond ruptures, which lead to undesired C1

and C2 cracking products such as ethylene glycol, ethanol,

methane, methanol and carbon dioxide. Historically, first at-

tempts with Co, Ni Raney, Cu Raney, Cu, Ru, Rh, Ir and Pt catalysts were conducted by Montassier et al.^[17,18] The addi-

tion of a second metal was proven to be useful to enhance

the selectivity into 12-PDO, for instance, in the case of Cu-

chromite,^[8] Cu–Ag,^[19] Ru–Cu^[20] or Ru–Pt.^[21] More recently, important works allowed significant improvements in the se-

lective hydrogenolysis into 13-PDO with Ir-Re^[9] or Pt-

dration coupled to a hydrogenation: glycerol+ $H_2 \rightarrow$

 $PDO+H_2O$. Dehydration is known to be strongly sensitive

to the pH medium, whereas hydrogenation is expected to be

dependent on the gas-phase atmosphere composition as well

as on the nature of the catalyst. Thus, both the pH solution

and the atmosphere composition may be key parameters to

control the selectivity of the glycerol conversion into PDO

Indeed, the pH of the solution influences the activities of

various metal catalysts. On the one hand, acidic co-catalysts

have shown good abilities to accelerate reaction rates and

obtain at the same time good selectivity into 12-PDO, as

in the presence of a metallic catalyst.

The glycerol transformation into PDO is formally a dehy-

Introduction

In the actual context of shortage of petroleum resources, biomass is considered a renewable alternative for fuels and chemical substitution. More importantly, the chemical transformation of bio-resources has a reduced impact on greenhouse gas emissions compared to petroleum-dependent industrial processes. Glycerol, obtained as a co-product of the transesterification of vegetable oils to produce bio-diesel, is a potential building block to be processed in bio-refineries.^[1,2] The valorisation of this abundant C₃-platform molecule has been intensively implemented experimentally along several routes.^[3-5] Its heterogeneously catalysed transformation into important value-added products such as acrolein through dehydration,^[6] glycerol esters or ethers through esterification or etherification,^[7] 1,2-propanediol (12-PDO)^[8] or 1,3-propanediol (13-PDO)^[9-12] through hydrogenolysis and oxidation products such as glyceric acid or dihydroxya-

[a] F. Auneau, Dr. C. Pinel Université de Lyon, Institut de Recherches sur la Catalyse et l'Environnement de Lyon IRCELYON, Université Lyon I, CNRS, UMR5256
2, Avenue Albert Einstein
69626 Villeurbanne Cedex (France) Fax: (+33)4-72-44-53-99
E-mail: catherine.pinel@ircelyon.univ-lyon1.fr

- [b] F. Auneau, Dr. C. Michel, Dr. F. Delbecq, Dr. P. Sautet Université de Lyon, CNRS, Institut de Chimie de Lyon ENS Lyon, Laboratoire de Chimie, UMR CNRS 5182 46 Allée d'Italie, 69364 Lyon Cedex 07 (France) Fax: (+33)4-72-72-88-60 E-mail: francoise.delbecq@ens-lyon.fr
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evidenced by the group of Tomishige et al.^[22-25] On the other hand, as initially reported by Montassier et al., the Cu Raney activity is increased in alkaline conditions.^[17] However, the distribution of the products is strongly affected with the appearance of lactic acid (LA) and the decreased yield for cracking products such as ethylene glycol (EG) compared to neutral pH. These trends were confirmed for other catalytic systems, namely, carbon-supported Pt, Ru, PtRu and AuRu catalysts.^[26,27] In addition, the formation of formic acid (FA) and gaseous species was reported. The appearance of oxidation products such as LA and FA under reductive conditions raises questions about the underlying mechanism.

As expected, the role of the gas-phase atmosphere is also debated. Recently, glycerol conversion toward 12-PDO (together with EG) was carried out by D'Hondt et al. in the absence of added hydrogen with a Pt/NaY catalyst.^[28] Montassier's group had originally mentioned for a Cu Raney catalyst that the reaction rate of glycerol transformation into 12-PDO and EG at neutral pH was poorly affected by the presence or absence of hydrogen, whereas LA was only formed in low amounts in both cases (<1%).^[17] These reports are astonishing at first sight: they demonstrate the feasibility of the hydrodeoxygenation of glycerol under inert atmosphere, whereas, as said before, glycerol conversion into PDO should require the presence of hydrogen. This raises again questions about the mechanism. The hydrodeoxygenation of glycerol under inert atmosphere has not been investigated systematically since these results, though some studies have dealt with this interesting issue.^[8,21,29-32]

All these parameters (second metal, pH and gas-phase composition) have a pronounced influence on the reactivity. The simple picture of a hydrogenation coupled to dehydration is not sufficient to understand all the experimental results. In particular, the first step of the reaction is still under debate. It has been proposed to be a dehydration, or more surprisingly, under H₂ atmosphere a dehydrogenation (Scheme 1). The dehydration has been proposed for copper-based^[33] catalysts, including copper–zinc^[34] and copper–chromite^[8] catalysts. Noble metals are also concerned with this dehydration mechanism, as shown with ruthenium carbon-based catalysts in the presence of an acidic co-catalyst.^[22–25,32] However, the mechanism originally suggested by Montassier et al.^[17] puts forward the dehydrogenation as the first step of the reaction in neutral water and alkaline condi-

Scheme 1. Glycerol transformation into 12-PDO and LA.

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tions with a copper Raney catalyst. It was also supported by Hawley et al.^[35] and reported for carbon-based Ru, Pt, PtRu and AuRu catalysts in alkaline conditions.^[26,27] Nevertheless, the exact mechanism still remains in question, as dehydration and dehydrogenation can occur simultaneously, for instance, with platinum supported on alumina catalysts together with reforming processes.^[30] For this kind of catalyst, not only the support but also the platinum metal is shown to play a role in the dehydration of glycerol.^[29] Recently, it was demonstrated that even for copper–zinc catalysts, traditionally associated with the dehydration mechanism, dehydrogenation takes place on the metallic copper.^[31] Concerning rhodium, this metal has often been associated with the dehydration mechanism in past studies either in association with an acidic co-catalyst^[36] or with the assistance of rhenium.^[37]

The interpretation of this complex system would benefit from a better comprehension of surface phenomena from a fundamental point of view. For this aim, theoretical modelling appears as a useful complementary tool to experiments. Some of us have already investigated from density functional theory (DFT) calculations the adsorption of glycerol and its dehydration intermediates at the surfaces of Ni(111), Rh-(111) and Pd(111) to identify the key points that control the selectivity of the hydrogenolysis reaction.^[38] The adsorption and reactivity of other small oxygenated compounds such as methanol^[39-45] (MeOH) or ethanol^[46-56] (EtOH) on the model surfaces of transition metals can also provide helpful clues. Despite the tremendous number of works realised until now, only a few have performed a mixed experimental and theoretical approach (using DFT) to gain further insights into the reactivity of glycerol. This is the case for Davis, Neurock and their co-workers^[57] who have considered the oxidation mechanism of glycerol in alkaline aqueous conditions by using Au, Pd and Pt catalysts on various supports (TiO₂ and C). The theoretical part focused on the oxidation of ethanol into acetic acid on Au(111) and Pt(111) assisted by surface-bonded hydroxide species in liquid water. In the direct line of our experimental investigations on glycerol hydrogenolysis into PDO,^[12,58] we focus here on the glycerol hydrogenolysis over an Rh/C catalyst in alkaline solution. We report in detail the behaviour of this catalyst as a function of various reaction parameters. In particular, we have observed the concomitant formation of hydrogenolysis (12-PDO) and oxidation (LA) products under both reductive and inert atmospheres. This raises the question: Is this process really a hydrogenolysis? To arrive at an answer, we aim at a better comprehension of the elementary steps of the reaction. The first step is of particular interest, as it can be either dehydration or dehydrogenation. We have focused on the energy profiles of these two competitive first steps, dehydrogenation and dehydration with theoretical DFT calculations performed on a model rhodium Rh(111) surface. We gather here our experimental results together with the theoretical results to gain a better insight into the unexpected processes that occur during the glycerol conversion and to provide a unified picture of the reaction mechanism.

Experimental Results

First, we detail the behaviour of the 0.7% Rh/C catalyst we have prepared as a function of various reaction parameters such as solution pH and gas-atmosphere composition. We focus in particular on their influence on the products distribution and the kinetics. Then we provide the gas-phase analysis and check the stability of the reaction products.

Catalytic tests: Table 1 shows how the pH of the solution can impact the conversion and the product distribution in the presence of rhodium-based catalyst. At neutral pH

Table 1. Influence of the pH on the reactivity.^[a]

Entry	Solvent	Conv.	Mass balance	Yield [%]		
		[%]	[%] ^[b]	12-PDO	LA	Others ^[c]
1	H_2O	2	100	<1	0	ε
2	NaOH 0.1 м	11	96	4	5	2
3	NaOH 1 м	23	100	9	9	5

[a] Conditions: glycerol (6 mL, 5 wt%) in solvent, SPR16, 50 bar H_2 , 453 K, 12 h. [b] TOC analysis. [c] Others including EG, 13-PDO, formic acid (FA), EtOH, MeOH, acetol, acetic acid (AA).

under hydrogen atmosphere, almost no glycerol was converted (< 2%) in 12 h, and only some traces of 12-PDO (< 1% yield) were analysed. The reaction rate increases with the alkalinity of the glycerol solution to give 12-PDO but also LA as the major products. The best conversion reached is nonetheless still low (23% after 12 h). Moreover, glyceral-dehyde (GAL) was observed (together with glyceric acid) at neutral pH, whereas acetol was not observed regardless of the pH (Scheme 1).

Interestingly, a catalytic transformation of glycerol also happens in the absence of hydrogen when glycerol comes into contact with the metallic catalyst at basic pH (Table 2). The conversion is even surprisingly higher under He (55%) than under H₂ (22%). Moreover, the product distribution is strongly modified upon atmospheric change. Whereas 12-PDO is the major product under H₂, LA becomes the major product under inert He atmosphere (its yield is multiplied by 5). However, it is striking that 12-PDO, which is the product of the hydrogenolysis reaction (hence requiring H atoms to be formed), is still produced under He (with a yield reduced by 50% relative to the reaction under H₂). In addition, when performing the reaction in water at neutral

Table 2. Gas-phase influence on reactivity of glycerol in alkaline conditions. $^{\left[a\right] }$

Entry	Cas	Conv.	Mass balance	Yield [%]		
	Gas	[%]	[%] ^[b]	12-PDO	LA	Others ^[c]
1	He	55	94	4	25	26
2	H_2	22	100	9	5	8

[a] Conditions: glycerol (100 mL, 5 wt %) in NaOH 1 M, Hastelloy autoclave equipped with a Teflon pot, 50 bar $H_2/30$ bar He, 453 K, 8 h. [b] TOC analysis after 24 h reaction. [c] Others including EG, 1,3-PDO, FA, EtOH, MeOH, acetol, AA. pH under He, the conversion of glycerol was less than 1% after 12 h and traces of GAL (together with glyceric acid), pyruvaldehyde, acetol and 12-PDO were detected.

Kinetic study: A kinetic study was implemented to analyse the evolution of the reaction. The glycerol conversion profile (Figure 1) is very different under He or H_2 atmosphere. Glycerol reacts indeed faster under He than under H₂, and after 24 h reaction, the glycerol is almost totally converted under He (91%), whereas half (49%) of the initial glycerol is still present under H₂. The initial activity of the reaction is $0.8 \operatorname{mol} \min^{-1} \operatorname{mol}_{Rh}^{-1}$ under hydrogen and 3.3 mol $\min^{-1} \operatorname{mol}_{Rh}^{-1}$ under helium (hence larger by a factor of 4). The evolution of the yields as a function of the conversion provides information about product formation, stability and reactivity. From the beginning, the product yield increases linearly along the conversion for 12-PDO and LA, regardless of the type of atmosphere (Figure 2). This indicates that LA and 12-PDO are the primary products of the reaction.



Figure 1. Glycerol conversion over reaction time: glycerol (100 mL, 5 wt%) in NaOH 1 M, Hastelloy autoclave equipped with a Teflon pot, 50 bar $H_2/30$ bar He, 453 K.

Data can be extracted from the kinetic study to compare the distribution of products at similar glycerol conversion (Table 3). After 24 h, 49% conversion is obtained under 50 bar H₂, thus yielding 22% 12-PDO and 15% LA. Under He, similar conversion (46%) is achieved after 6 h. LA is clearly the major product with a 20% yield; the 12-PDO production reaches only 3% yield.

Gas-phase analysis: Gas-phase analysis has been motivated by the increase of the pressure in the reactor along time at constant temperature under inert atmosphere (Figure 3). The pressure rises rapidly at the very beginning of the reaction but evolves more gradually after 100 min. There is therefore generation of gaseous species, and it is important to identify these compounds. Under hydrogen atmosphere, the initial increase in pressure is interestingly slower than under helium, and rapidly (20 min) the pressure starts to decrease, thereby indicating hydrogen consumption. The final gas-phase composition reflects the observed pressure evolu-



Figure 2. Evolution of the product yields as a function of the conversion of glycerol (linear regression): glycerol (100 mL, 5 wt%) in NaOH 1 m, Hastelloy autoclave equipped with a Teflon pot, 50 bar $H_2/30$ bar He, 453 K.

Table 3. Products distribution at glycerol isoconversion.^[a]

Entry	Gas	<i>t</i> [h]	Conv. [%]	Yield [%]		
				12-PDO	LA	Others ^[b]
1	He	6	46	3	20	23
2	H_2	24	49	22	15	12

[a] Conditions: glycerol (100 mL, 5 wt%) in NaOH 1 M, Hastelloy autoclave equipped with a Teflon pot, $50 \text{ bar H}_2/30 \text{ bar He}$, 453 K. [b] Others including EG, 1,3-PDO, FA, EtOH, MeOH, acetol, AA.



Figure 3. Continuous pressure acquisitions as a function of reaction time under He or H_2 pressure: glycerol (6mL, 5 wt%) in NaOH 1M, 30 bar He or 50 bar H_2 , 453 K.

tion along the reaction (Table 4). Under hydrogen only trace amounts of water, propane and propene were analysed. Under helium, analysis of the gas phase after 24 h reveals the presence of a large fraction of hydrogen, the origin of which is to be discussed, together with traces of carbon monoxide water.

Aqueous-phase reforming (APR) of oxygenated compounds is a well-known reaction to produce H_2 and other fuels from biomass.^[59–61] For glycerol, APR into synthesis gas is usually performed at 498–573 K.^[62] Our reactions were performed at a lower temperature of 453 K. Moreover, gasphase analysis only showed traces of CO under helium and

Entry	Initial			Final gas	phase
	gas phase	He [%]	$H_{2}[\%]$	CO [%]	Others
L	He	81	18	0.5	H_2O
2	H_2	0	>99	ε	propane, propene, H ₂ O

[a] Conditions: glycerol (100 mL, 5 wt%) in NaOH 1 M, Hastelloy autoclave equipped with a Teflon pot, 50 bar H₂/30 bar He, 453 K, 24 h. Helium, hydrogen and carbon monoxide percentages refer to a volumic percentage. Products not quantified were only detected in traces amount.

a small content of C_3 alkane (propane) and alkene (propene) under hydrogen. In both cases, the only gaseous product in any significant amount is hydrogen. It is supposed to be responsible for the small pressure increase noticed under hydrogen at the beginning of the reaction, and for the continuous pressure increase all over the reaction observed under helium. If APR were occurring, other gases such as methane, carbon monoxide and carbon dioxide would have been detected in significant amounts. Furthermore, all the mass balances of the organic soluble products were in the range of 94–100 %. We can consequently exclude APR from playing a key role in the pressure augmentation and the H₂ production observed.

Product stability: The stability of LA and 12-PDO has been evaluated under the reaction conditions (5 wt% of product in NaOH 1M with Rh/C catalyst). LA does not show any conversion after 12 h at 453 K either under He or under H₂. On the contrary, 12-PDO is found to be reactive, especially under inert atmosphere, and yields mainly LA, formic acid (FA), and degradation products (Table 5).

Table 5. Reactivity of the reaction products, 12-PDO and LA, under reaction conditions $^{\left[a\right] }$

Entry	Substrate	Gas	Conv.	Mass balance ^[b]	Yield [%]	
			[%]	[%]	LA	Others ^[c]
1	12-PDO	He	62	100	13	10
2	12-PDO	H_2	8	100	2	3
3	LA	He	0	100	_	ε
4	LA	H_2	0	100	-	ε

[a] Substrate (6 mL, 5 wt%) in NaOH 1M, SPR16, 50 bar H₂/30 bar He, 453 K, 12 h. [b] TOC analysis. [c] Others including EG, 1,3-PDO, FA, EtOH, MeOH, acetol, AA.

Theoretical Calculations

In this part, we report the theoretical study on the relative stabilities of glycerol, the products and the potential intermediates when adsorbed on the Rh(111) surface. Then we focus on the first elementary steps of the catalytic reaction and provide energy barriers. The (111) face was chosen because it is the main face of Rh particles.

Glycerol adsorption: Glycerol is a C3 polyalcohol with three hydroxyl groups on terminal (positions 1 and 3 of the alkyl chain) and central (position 2) carbon atoms. Those hydrox-

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yl groups will be respectively designated as terminal and central hydroxyl groups in the following. Glycerol exhibits numerous stable conformations in the gas phase.^[63,64] The most stable one has been re-optimised with our method to give the lowest conformation in energy represented in Figure 4 (left panel) and to show two internal hydrogen

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Figure 4. Most stable conformations of glycerol in the gas phase and on the Rh(111) surface. Black, white, dark grey and light grey spheres correspond to C, H, O and Rh atoms, respectively. Hydrogen bonds are represented in dashed dark grey lines. Bond lengths are expressed in Å. Colour version of the figure is available in the Supporting Information (Figure S3).

bonds. Glycerol can adopt several adsorption modes on the Rh(111) surface.^[38] The optimal structure (Figure 4, right panel) shows two oxygen atoms adsorbed atop sites of Rh and one hydrogen bond from the adsorbed terminal hydroxyl group to the other terminal hydroxyl, farther from the surface. The corresponding adsorption energy is $E_{\rm ads} = -0.60 \text{ eV}$. It is higher than the typical adsorption energy of monoalcohols ($\approx -0.40 \text{ eV}$).^[51]

Stability of products and intermediates on the Rh(111) surface: Experimentally, glycerol can be converted into two products: 1,2-propanediol (12-PDO) and lactic acid (LA). In the gas phase, the corresponding reactions can be formally written [Eqs. (1) and (2)]:

$$Glycerol + H_2 \rightarrow 12 \text{-PDO} + H_2O \tag{1}$$

$$Glycerol \rightarrow LA + H_2$$
 (2)

From a thermodynamic point of view, the first reaction is exothermic ($\Delta E_{\text{react}}(1) = -1.00 \text{ eV}$), whereas the second one is almost athermic ($\Delta E_{\text{react}}(2) = 0.03 \text{ eV}$). On the surface, the situation is reversed. Indeed, the previous chemical reactions can be rewritten in the following manner, taking into account the dissociated character of H₂ and H₂O on Rh(111) [Eqs. (3) and (4)]:

$$Glycerol + 2 H \rightarrow 12 \text{-PDO} + H + OH$$
(3)

$$Glycerol \rightarrow LA + 2H \tag{4}$$

When considering each species being adsorbed on Rh(111) at low coverage, both reactions are exothermic but the formation of LA is strongly favoured by 0.71 eV ($\Delta E_{\text{react}}(3) = -0.16 \text{ eV}$ and $\Delta E_{\text{react}}(4) = -0.87 \text{ eV}$, Figure 5).

Two pathways are plausible to convert glycerol into these products. They differ by the first step that can consist of



Figure 5. Relative stabilities of intermediates and reaction products adsorbed onto the Rh(111) surface. Dashed lines and continuous lines stand for dehydration and dehydrogenation paths. All the products and atoms considered are adsorbed on the slab. Energies are given in eV. The reference energy taken here is the glycerol adsorbed at the Rh(111) surface plus two isolated hydrogen adsorbed at the Rh(111) surface.

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either dehydration or dehydrogenation. We report in Figure 5 the relative stability of the reaction intermediates when adsorbed onto the Rh(111) surface.

Through the dehydration path, glycerol can first lead to two different enols almost isoenergetic on Rh(111): 1) the propene-2,3-diol, namely, Enol 1; or 2) the propene-1,3-diol, namely, Enol 2. On Rh(111) the C=C bond is coordinated in a π mode and a terminal hydroxyl group is bound to the surface (Figure 6). The conversion of Enol 2 into 13-PDO



Figure 6. Structures of Enol 1 (propene-2,3-diol), Enol 2 (propene-1,3diol), DHA and GAL chemisorbed onto the Rh(111) surface. Black, white, dark grey and light grey spheres correspond to C, H, O and Rh atoms, respectively. Dashed dark grey lines represent hydrogen bonds. Colour version of the figure is available in the Supporting Information (Figure S4).

through hydroxypropanaldehyde has not been considered, since 13-PDO is not seen in the experiment. Enol 1 can be rearranged further in acetol ($\Delta E = -0.09 \text{ eV}$) and then acetol can be hydrogenated into 12-PDO ($\Delta E = 0.54 \text{ eV}$). Acetol can also be dehydrogenated toward pyruvaldehyde (PAL) ($\Delta E = -0.59 \text{ eV}$), finally giving LA by an intramolecular Cannizzaro reaction under basic conditions ($\Delta E =$ 0.42 eV).

Considering the dehydrogenation path, glycerol leads first to dihydroxyacetone (DHA) or glyceraldehyde (GAL). In the gas phase, DHA is more stable than GAL by 0.17 eV but those two compounds are almost isoenergetic once adsorbed at an Rh(111) slab. Both molecules are adsorbed with a lateral interaction of the C=O bond with the surface (Figure 6). Whereas DHA cannot easily undergo a further dehydration step, GAL can be dehydrated into an enol (Enol 3, with a very exothermic reaction, $\Delta E = -0.73 \text{ eV}$) that rearranges into PAL (Figure 5). Then LA is reached by an intramolecular Cannizzaro reaction, whereas 12-PDO results from a double hydrogenation through acetol.

Thus, the main difference between the two routes lies in the nature of the first step. Dehydration, dehydrogenation and enol rearrangements into ketone or aldehyde are exothermic on the surface. On the contrary, C=O bonds hydrogenation steps and LA formation are endothermic. **Glycerol dehydrogenation path**: The two possible products GAL and DHA result from successive C–H and O–H bond ruptures on the Rh surface. We describe first the structures of the four mono-dehydrogenated intermediates and the eight transition-state (TS) structures. Then we report the four possible reaction paths.

Intermediate and transition-state structures: The first X–H bond scission can take place at the central (CHc) or terminal (CHt) carbon atom, or at the central (OHc) or terminal (OHt) oxygen atom that leads to alkyl intermediates (Int_{CHc} , Int_{CHt}) and alkoxy intermediates (Int_{OHc} and Int_{OHt}), respectively (Figure 7). Both alkyl intermediates are bound to the



Figure 7. Structure of mono-dehydrogenated intermediates on Rh(111). Black, white, dark grey and light grey spheres correspond to C, H, O and Rh atoms respectively. Dashed dark grey lines represent hydrogen bonds. Int_{CHe}, Int_{CHe}, Int_{OHt} and Int_{OHc} are the mono-dehydrogenated intermediates that resulting respectively from terminal C–H (CHt), central C–H (CHt), terminal O–H (OHt) and central O–H (OHc) bond ruptures in glycerol. The displayed structures are the ones after hydrogen diffusion away from the intermediate, that is without the co-adsorbed hydrogen atom. Energies are in eV. The reference energy taken here is the glycerol adsorbed at the Rh(111) surface. Bond lengths are expressed in Å. Colour version of the figure is available in the Supporting Information (Figure S5).

Rh atoms through the mono-dehydrogenated carbon atom and both the terminal hydroxyl groups. The Int_{CHc} intermediate is more stable than the Int_{CHt} by 0.17 eV, which is in agreement with the greater stability of secondary carbon radicals relative to primary ones. Conversely, alkoxy intermediates structures differ: in Int_{OHc}, the alkoxy in adsorbed in a ternary site, whereas it is adsorbed at a top site in Int_{OHt}. This can explain the greater stability of Int_{OHc} (by 0.19 eV) since methoxy is preferentially adsorbed at a ternary site rather than at a top site by 0.39 eV. For Int_{OHt} , the adsorption of the hydroxyl group and the position of the internal hydrogen bonds constrain the alkoxy to be in its lessstable position. The structures of the transition states for the first and the second dehydrogenation steps are shown in Figure 8 and Figure 9, respectively. The label of the TS for the second hydrogenation is built by concatenating the

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Figure 8. Structure of the transition states for the first step of glycerol dehydrogenation on Rh(111). Black, white, dark grey and light grey spheres correspond to C, H, O and Rh atoms, respectively. Dashed dark grey lines represent hydrogen bonds. Bonds implicated in the TS are represented in light grey. Energies are in eV. The reference energy taken here is the glycerol adsorbed at the Rh(111) surface. Bond lengths are expressed in Å. Colour version of the figure is available in the Supporting Information (Figure S6).

name of bonds dissociated in the first step and in the second step. TS structures can be divided into two categories: 1) TS of the C–H bond rupture are characterised by a triangle configuration Rh/C/H, the bond being broken onto an atop site 2) TS of the O–H bond rupture are characterised by a oxygen at a top site and a hydrogen atom in a neighbouring bridge position.

Reaction paths: Figure 10 illustrates the glycerol dehydrogenation pathways to GAL and DHA. The reference is the energy of adsorbed glycerol. GAL results from the successive C–H and O–H bond scissions at the terminal position of glycerol. Depending on the order of those two dissociations, two pathways are possible: 1) the alkoxy path starts



Figure 9. Structure of the transition states for the second step of glycerol dehydrogenation on Rh(111). Black, white, dark grey and light grey spheres correspond to C, H, O and Rh atoms. Dashed dark grey lines represent hydrogen bonds. Bonds implied in the TS are represented in light grey. Energies are in eV. The reference energy taken here is the glycerol adsorbed at the Rh(111) surface. Bond lengths are expressed in Å. Colour version of the figure is available in the Supporting Information (Figure S7).

with the terminal O–H bond scission to lead to Int_{OHt} and continues with the terminal C–H bond scission or 2) the alkyl path starts with the terminal C–H bond scission to lead to Int_{CHt} and continues with the terminal OH bond scission. Similarly, two routes yield DHA through glycerol dehydrogenation at the central position: 1) the alkoxy path through Int_{OHc} and 2) the alkyl path through Int_{CHc}. The two intermediates dehydrogenated at the central position are more stable on the surface than the corresponding terminal ones by around 0.2 eV. Int_{OHc} is even the most stable one (-0.32 eV). In addition, the O–H bond scission at the central position has the lowest activation barrier (E_{act} =0.67 eV) among the four possible initial dissociations, thereby making Int_{OHc} the most probable intermediate. However, from



Figure 10. Energy profiles [eV] for the dehydrogenation reaction paths of glycerol toward glyceraldehyde (GAL) and dihydroxyacetone (DHA) formation. The reference energy taken here is the glycerol adsorbed at the Rh(111) surface (Figure 4). GAL and DHA structures on the surface can be seen in Figure 6. The straight line is the alkoxy route along which the mono-dehydrogenated intermediates are Int_{OHt} and Int_{OHc} (Figure 7). The dashed line is the alkyl route along which the mono-dehydrogenated intermediates are Int_{CHt} and Int_{CHc} (Figure 7). Structures of transition states of first and second steps are displayed Figure 8 and Figure 9, respectively.

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Int_{OHc}, the following C-H bond dissociation is unfavourable, the central C-H bond being oriented towards the vacuum (Figure 7). To take advantage of the metal catalyst activation, an Rh-Ot bond (2.28 Å) has to be broken and the central oxygen has to switch from a stabilising hollow site to a top site (see Int_{OHc} in Figure 7 and $TS_{OHc-CHc}$ in Figure 9). The associated energy barrier is the highest computed for C-H and O-H bond dissociations in glycerol ($E_{act} = 1.16 \text{ eV}$, Figure 10). Consequently, the alkoxy route that leads to DHA is kinetically slow. Given the lower stability of the terminal intermediates, the OH bond rupture at the terminal position is surprisingly the second-lowest activation barrier $(E_{\rm act} = 0.70 \text{ eV})$. Then it is easily followed by the CHt bond scission with a low energy barrier ($E_{act} = 0.55 \text{ eV}$, Figure 10). Thus, the alkoxy route that leads to GAL is the most favourable route kinetically. Moreover, the alkyl route that leads to GAL is also competitive: the CHt barrier is only 0.07 eV higher than the OHt barrier and the second dissociation transition state CHt-OHt is only 0.05 eV lower in energy than OHt-CHt. Besides, the alkyl route that leads to DHA requires the crossing of higher barriers and is less probable. To conclude, GAL is the major dehydrogenation product and it is mainly obtained through the alkoxy route.

Glycerol dehydration path: The dehydration of an alcohol catalysed by a metallic surface is a two-step process: C–H bond scission followed or preceded by the adjacent C–O bond scission. Wang et al. have shown that the C–H dissociation comes first when dehydrating ethanol at a Rh(111) surface.^[50] According to their work, the initial C–O bond rupture is reported to be difficult ($E_{act}=1.76 \text{ eV}$), whereas the initial C–H bond rupture is accessible ($E_{act}=0.52 \text{ eV}$). Conversely, the C–O bond rupture as a second step from the mono-dehydrogenated CH₃CHOH species is easy ($E_{act}=0.42 \text{ eV}$). Thus, we have considered the dehydration of glycerol by adopting the following route: C–H scission followed by C–O scission.

Intermediates and transition-state structures: This process shares the first step with the alkyl routes of the dehydrogenation process (see above). The TS structures of the CO rupture are provided in Figure 11. The dissociating hydroxyl group is adsorbed onto a top site of the surface, and is already distant from the forming enol, as the CO bond length is 2.11 Å in both TS structures.



Figure 11. Structure of the transition states for the second step of glycerol dehydration (C–O bond cleavage) on Rh(111). Black, white, dark grey and light grey spheres correspond to C, H, O and Rh atoms. Dashed dark grey lines represent hydrogen bonds. Bonds implied in the TS are represented in light grey. Bond lengths are expressed in Å. Colour version of the figure is available in the Supporting Information (Figure S8).

Reaction paths: As already said, the glycerol dehydration can lead to two different enols: 1) Enol 1 (central C–H bond followed by terminal CO scission) or 2) Enol 2 (terminal C–H bond followed by central CO scission). Figure 12 shows the corresponding reaction pathways. The TS of the CO scission are rather high in energy: 0.95 eV at the terminal position, 0.86 eV at the central position with respect to adsorbed glycerol. Consequently, the main dehydration route is CHt–COc for which both barriers are lower, thus leading to Enol 2.



Figure 12. Energy profiles [eV] for the dehydration reaction path of glycerol toward Enol 1 and Enol 2 formation. Enol 1 and Enol 2 structures can be seen in Figure 6. The reference energy taken here is the glycerol adsorbed at the Rh(111) surface (Figure 4). The mono-dehydrogenated intermediates are Int_{CHt} and Int_{CHc} , which are displayed in Figure 7. Structures of transition states of first and second steps are shown in Figure 8 and Figure 11, respectively.

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Discussion

The glycerol transformation into propanediols (PDOs) is generally performed in basic or acidic media in the presence of a metal catalyst under hydrogenolysis conditions: 12-PDO is usually the main product. This transformation is formally a dehydration coupled to a hydrogenation reaction. Consequently, dehydration is commonly envisaged as the first step of the reaction. The corresponding mechanism is represented in Scheme 2 in black. The glycerol dehydration yields an enol (Enol 1, propen-1,2-diol) in equilibrium with acetol. Then this ketone is hydrogenated at the metal catalyst into 12-PDO.



Scheme 2. Dehydration mechanism usually proposed for the glycerol conversion into 1,2-propanediol (12-PDO). In grey, an extension can be easily proposed from acetol to lead to the lactic acid (LA).

As seen in the Results Section, glycerol yields the expected 12-PDO in the presence of an Rh/C catalyst at basic pH under hydrogenolysis conditions (P(H₂)=50 bar) but it also yields an oxidation product, the lactic acid (LA) with a slightly lower yield (Table 2, entry 2). This product could be obtained by the dehydrogenation of acetol into pyruvaldehyde (PAL), followed by a Cannizzaro reaction into LA (Scheme 2, additional path in grey). Moreover, when changing the atmosphere from reductive to inert, both products are still obtained but with a reversed selectivity (Table 2, entry 1). Thus, even in absence of H₂, 12-PDO can be produced. This questions the mechanism of glycerol hydrogenolysis previously described.

In the literature, an alternative mechanism has been proposed by Montassier et al.,^[17] starting with a dehydrogenation step, unfamiliar under hydrogenolysis conditions. This alternative route is represented in Scheme 3 in the particular case of Rh/C catalyst in basic media. The glyceraldehyde (GAL) formed by the dehydrogenation of glycerol is dehydrated into PAL. Finally, this intermediate is successively hydrogenated into acetol and 12-PDO. LA can be easily obtained by a Cannizzaro reaction from PAL. Dihydroxyacetone is often reported as another dehydrogenation product of glycerol, but dehydration is difficult in this case because of the absence of adjacent carbons that bear H and OH groups.

Gathering experimental and theoretical results, we will first discuss the nature of the first step, dehydrogenation versus dehydration. Then we will focus on the product selec-



Scheme 3. Proposed mechanism of glycerol conversion into lactic acid (LA) and 1,2-propanediol (12-PDO) starting with a dehydrogenation step.

tivity (LA and 12-PDO) depending on the nature of the atmosphere.

Dehydration versus dehydrogenation: The glycerol conversion and the pH increase together, and this is often associated with a dehydration mechanism. However, one should note that the basic media is essential in both mechanisms we examine here at different steps: the Cannizzaro reaction that leads to LA from PAL in both routes, the initial glycerol dehydration step in the dehydration mechanism and the dehydration of GAL into Enol 3 in the dehydrogenation mechanism.

To test the feasibility of the glycerol dehydration, glycerol was introduced in sodium hydroxide under He without catalyst. No conversion is observed after 24 h. This means that if the dehydration occurs, the metal catalyst and sodium hydroxide are both required and that there would be an assistance of the metal.^[38]

The key intermediates, GAL, PAL and acetol, are not stable in a molar solution of sodium hydroxide at room temperature. Their detection requires performing the experiments in neutral or acidic solution. When reacting glycerol in water (pH 6.5) in the presence of the Rh/C catalyst, a very low glycerol conversion is reached and traces of 12-PDO are observed, whatever the atmosphere. Under H₂ atmosphere, traces of GAL (together with glyceric acid) are seen, whereas acetol is not detected. Under helium atmosphere, traces of GAL (together with glyceric acid), PAL and acetol are detected. GAL is a key intermediate in the dehydrogenation route only, whereas PAL and acetol are expected to be key intermediates in both routes. Following those experiments, dehydrogenation seems to be the first step of glycerol deoxygenation into 12-PDO and LA. But one should wonder whether these findings could be extrapolated to the reaction in alkaline conditions.

In the operating conditions, we observed an initial increase of pressure (Figure 3) whatever the atmosphere. However, under hydrogen atmosphere, a decreasing pressure follows. Analysis of the gas phase indicates that the only gas produced in significant amount is H₂. It is consequently reasonable to attribute the pressure variations to H₂ production and consumption. Since APR is excluded under our conditions, there is necessarily a dehydrogenation step that occurs. Now there is a potential H₂ source in both mechanisms. H₂ is obviously produced from glycerol if dehydrogenation is the first step. If the dehydration is the first step, acetol can be another possible source of H₂ by dehydrogenation into PAL (Scheme 2), which is thermodynamically favoured (Figure 5). However, under hydrogen atmosphere, the pressure increases and then decreases and the main product is 12-PDO. According to the dehydrogenation mechanism (Scheme 3), the first step produces one equivalent of GAL and of H₂. Later, the formation of 12-PDO involves the consumption of two equivalents of H₂, which leads to the further decrease in the pressure. Along the alternative dehydration route (Scheme 2), H₂ production and consumption steps are not sequential as in the previous discussion, but are parallel and initiate from acetol. Consequently, the initial increase of hydrogen pressure would be observed only if LA is the main product. Now, under hydrogen, the hydrogenation product, 12-PDO, is the dominant one at all stages of the reaction. Thus, the dehydration mechanism appears incompatible with the transient formation of H₂.

The influence of the atmosphere on the conversion rate has also to be pointed out. The glycerol hydrodeoxygenation is actually found to be significantly faster under helium than under hydrogen-gas pressure: the catalyst is initially almost four times more active (Figure 1). According to the dehydrogenation mechanism, this can be explained by the reversibility of the initial dehydrogenation step. Under H₂ atmosphere, the high H₂ pressure inhibits the glycerol dehydrogenation. On the contrary, under He atmosphere, the equilibrium is inverted, thereby favouring a faster glycerol conversion. If we consider now the alternative mechanism that is initiated by a dehydration step, the production of the key intermediate acetol should not depend on the H₂ pressure. Hence the rate of transformation of glycerol should not decrease under H₂ compared to He, but only the selectivity should be modified, with more 12-PDO and less LA produced under H₂. Hence, the dehydration mechanism seems to be again incompatible with the experimental results.

Let us now look at the conclusions from the DFT calculations. The glycerol dehydration on model Rh(111) surface leads to two enols, Enol 1 and Enol 2, to yield 12-PDO and 13-PDO, respectively, after isomerisation and hydrogenation steps (Figure 5). Those two enol intermediates are isoenergetic on the metal catalyst and more stabilised than the dehydrogenation intermediates, GAL and DHA. Thermodynamically, dehydration is hence favoured over dehydrogenation on the surface. If we now look at the reaction barriers, the formation of Enol 1 goes through transition states of higher energies (0.83, 0.95 eV, Figure 12) than the reaction path to Enol 2 (0.77, 0.86 eV, Figure 12). Thus, Enol 2 is the kinetically favoured intermediate on the dehydration route.

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It would lead by hydrogenation to 13-PDO, in contradiction with the experimental selectivity. Alternatively, the dehydrogenation path can be considered. Two routes are possible, the alkyl route and the alkoxy route, depending on the first bond rupture, C–H or O–H. Obviously, the first dehydrogenation step of the alkyl routes (C–H rupture) is common with the dehydration. However, the C–H bond ruptures have higher barriers (0.83, 0.77 eV) than the alternative O–H bond ruptures (0.67, 0.70 eV). In addition, when starting with the terminal hydroxyl scission (OHt–CHt route), the first dissociation is the rate-limiting step (Figure 10). Consequently, the dehydrogenation (overall barrier of 0.70 eV) is favoured kinetically compared with dehydration (overall barrier of 0.86 eV) and leads to GAL by means of an OHt–CHt route.

To sum up, the combination of experiment and theory shows that dehydrogenation into GAL is the first step for the glycerol transformation on the Rh/C catalyst in basic media under He or H_2 atmosphere.

LA and 12-PDO selectivity: The proposed mechanism is summarised in Scheme 3. Glycerol is dehydrogenated into GAL. Then, its subsequent dehydration into Enol 3 is thermodynamically favoured on the surface ($E_{reac} = -0.73 \text{ eV}$), as shown from DFT calculations. The isomerisation of Enol 3 into PAL is straightforward, and then a double hydrogenation into 12-PDO or a Cannizzaro reaction to yield LA can occur. From our experimental results, PAL conversion into LA is irreversible, whereas PAL hydrogenation into 12-PDO is an equilibrium. Indeed, LA is stable under our experimental conditions (Table 5, entries 3 and 4), whereas 12-PDO is mainly converted into LA under He. Those final steps control the product selectivity depending on the atmosphere.

Under a hydrogen atmosphere, the main product is the 12-PDO since the equilibrium is displaced towards the hydrogenation direction (Table 5, entry 2). Moreover, the PAL hydrogenation into acetol and then 12-PDO is probably faster than the Cannizzaro reaction into LA under H_2 pressure, hence the 12-PDO being the main product.

Under helium atmosphere, the pressure increases continuously, thereby leading to a significant concentration of hydrogen in the gas phase at the end of the reaction. As already noted, hydrogen production is ensured by the glycerol dehydrogenation. However, the H₂ partial pressure is much lower than under H₂ atmosphere. Therefore, all the hydrogenation/dehydrogenation equilibria are displaced towards dehydrogenation. This contributes to the H₂ pressure increase but also to the diminution of the 12-PDO yield and to the increase of the LA yield (Table 5). Since the formation of LA is irreversible under the reaction conditions, this is the main product under He atmosphere.

In a nutshell, the product distribution is controlled by the hydrogenation/dehydrogenation equilibria, and hence by the nature of the atmosphere. Under H_2 , the hydrogenation of the intermediates into 12-PDO is favoured, whereas under neutral atmosphere, the transformation of PAL into LA by

a Canizzaro reaction is the main path since 12-PDO is potentially dehydrogenated.

Conclusion

The association of the experimental and theoretical points of view has provided a deep insight into the rhodium-catalysed transformation of glycerol into 1,2-propanediol (12-PDO) and lactic acid (LA). We have particularly focused on the determination of the first step of the reaction, as there was a need to decide between the dehydration and the dehydrogenation mechanisms. Although the conversion and the pH increase together, which could be tentatively associated with a dehydration mechanism, some clues appeared experimentally in favour of the dehydrogenation route. We established that switching the nature of the gas phase from a reductive to an inert atmosphere increased the reaction rate. It must be underlined that under inert atmosphere, although the products distribution was sharply impacted in favour of LA formation, a significant amount of 12-PDO was obtained together with the production of hydrogen. The theoretical investigations on glycerol dehydrogenation and dehydration at a model Rh(111) surface with density functional theory allowed us to distinguish between the two reaction paths. Dehydrogenation was found to be kinetically favoured at the surface over dehydration. In addition, glyceraldehyde (GAL) was found to be the favoured intermediate over dihydroxyacetone (DHA). The dehydrogenation of glycerol into GAL has thus been evidenced as the major phenomenon that initiates the hydrodeoxygenation mechanism on rhodium catalyst. Furthermore, key experimental results such as the transient production of H₂ in the gas phase and the influence of the nature of the atmosphere (H₂ or He) on the reaction rate are fully explained by the proposed mechanism, whereas they cannot be explained from the alternative route initiated by a dehydration step. We have hence revisited Montassier's dehydrogenation mechanism by highlighting the surface phenomena and by showing from the mixed experimental and theoretical study that dehydrogenation and not dehydration is the first step of the reaction.

Experimental Section

Catalyst preparation and characterisation: The rhodium catalyst supported on carbon was prepared by cationic exchange (see the Supporting Information). The effective Rh weight loading determined by ICP analysis was 0.7 wt %. XRD analysis furnished little information, given the amorphous nature of the carbon support. The absence of intense Rh peaks led us to think that Rh particles are well dispersed (Figure S1 in the Supporting Information). TEM analysis confirmed this forecast; the pictures could be seen (Figure S2 in the Supporting Information): the Rh/C catalyst shows small, well-dispersed nanoparticles (2–3 nm).

Catalytic tests and analysis: Initial screening of catalysts was conducted using a Slurry Phase Reactor 16 (AMTEC) for 12 h with glycerol (6 mL, 5 wt%) in solvent (H₂O or NaOH 1 M), 30 mg catalyst, 1000 rpm. The reactors were purged three times with 20 bar helium, heated at 453 K

(unless another temperature is specified) and pressurised at 30 bar if the reaction was performed under helium. If the reaction was run under hydrogen, the pressure was adjusted to 50 bar. For the kinetic study, the reaction was performed in a 200 mL stainless steel autoclave equipped with a graphite-stabilised Teflon container. Samples of the reaction medium were taken out regularly and analysed by HPLC using a CarboSep 107H column (0.5 mLmin⁻¹ of 0.005 N H₂SO₄, T=40 °C). 13-PDO, 12-PDO, ethylene glycol, 1-propanol, 2-propanol, ethanol, methanol, acetol, lactic acid, formic acid, acetic acid, glyceraldehyde and glyceric acid were analysed. Total organic carbon (TOC) was also measured using a Shimadzu TOC-5050A analyser. The difference between TOC measured and TOC concentration introduced into the reactor gave an estimation of gaseous products (CO, CO₂, H₂ and so on) formed during the reaction. Gas phase was collected in a gas bag at the end of the reaction and analysed using a GC-MS (Agilent Technologies, 5975C) instrument equipped with Alumina. Poraplot U and 5 Å molecular sieve columns and thermal-conductivity detectors. Backflush injectors were used for Poraplot U and 5 Å molecular sieve columns.

Computational details: Periodic density functional theory (DFT) calculations have been carried out using the Vienna Ab Initio Simulation Program (VASP).^[65] The exchange-correlation energy and potential were calculated within the generalised gradient approximation (Perdew–Wang 91 functional).^[66] A tight convergence of the plane-wave expansion was obtained with a cutoff of 400 eV. The electron–ion interactions were described by the projector augmented method (PAW) introduced by Blöch^[67] and adapted by Kresse and Joubert.^[68] The Rh(111) surface is modelled by a 3×3 surface supercell that contains a slab of four layers and a vacuum of five equivalent metal layers (11.10 Å). A Monkhorst–Pack mesh of $3 \times 3 \times 1 k$ points was used for the 2D Brillouin zone integration.^[69]

The adsorption of the molecules was realised on the upper side of the slab. The two bottom layers of the slab were kept frozen in the bulk positions, whereas the uppermost layers and the molecule were free to relax. The adsorption energy $E_{\rm ads}$ is calculated as the difference between the energy of the adsorption complex and that of the bare surface plus the molecule in the gas phase. A negative energy means a stabilising adsorption. The reaction energy E_{react} is defined as the difference between the energy of the product and the energy of the reactant. A negative energy means that the reaction is exothermic, whereas a positive energy means that the reaction is endothermic. Reactions paths have been studied by combining Nudge Elastic Band (NEB) procedures^[70] together with our local reaction path generator OpenPath^[71] and the dimer method.^[72] Then transition-state structures have been optimised with a quasi-Newton algorithm and characterised by a single imaginary frequency. The activation energy $E_{\rm act}$ is specified as the difference between the energy of the TS and the energy of the reactant. Extended calculations with a 4×4 unit cell, a five-layer slab with a 3×3 unit cell, and taking into account the dipole correction have been performed, without affecting notably the activation barriers values and the TS structures (Table S1 in the Supporting Information), hence validating the model initially chosen.

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- B. Sels, E. D'Hondt, P. Jacobs in *Catalysis for Renewables: From Feed Stock to Energy Production* (Eds.: G. Centi, R. A. van Santen), Wiley-VCH, Weinhem, **2007**, p. 223.
- [2] M. Pagliaro, M. Rossi *The Future of Glycerol: New Uses of a Versatile Raw Material*, RSC Publishing, Cambridge, 2008.
- [3] C.-H. Zhou, J. N. Beltramini, Y.-X. Fan, G. Q. Lu, Chem. Soc., Rev. 2008, 37, 527–549.
- [4] A. Behr, J. Eilting, K. Irawadi, J. Leschinski, F. Lindner, Green Chem. 2008, 10, 13-30.
- [5] M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi, C. Della Pina, Angew. Chem. 2007, 119, 4516–4522; Angew. Chem. Int. Ed. 2007, 46, 4434–4440.
- [6] B. Katryniok, S. Paul, V. Belliere-Baca, P. Rey, F. Dumeignil, Green Chem. 2010, 12, 1922–1925.
- [7] J. Barrault, F. Jerome, Eur. J. Lipid Sci. Technol. 2008, 110, 825-830.
- [8] M. A. Dasari, P.-P. Kiatsimkul, W. R. Sutterlin, G. J. Suppes, *Appl. Catal. A* 2005, 281, 225–231.
- [9] Y. Nakagawa, Y. Shinmi, S. Koso, K. Tomishige, J. Catal. 2010, 272, 191–194.
- [10] O. M. Daniel, A. DeLaRiva, E. L. Kunkes, A. K. Datye, J. A. Dumesic, R. J. Davis, *ChemCatChem* 2010, 2, 1107–1114.
- [11] L.-Z. Qin, M.-J. Song, C.-L. Chen, Greem Chem. 2010, 12, 1466– 1472.
- [12] J. Chaminand, L. Djakovitch, P. Gallezot, P. Marion, C. Pinel, C. Rosier, *Green Chem.* 2004, 6, 359–361.
- [13] Y. Shen, S. Zhang, H. Li, Y. Ren, H. Liu, Chem. Eur. J. 2010, 16, 7368–7371.
- [14] W. C. Ketchie, M. Murayama, R. J. Davis, J. Catal. 2007, 250, 264– 273.
- [15] R. Garcia, M. Besson, P. Gallezot, Appl. Catal. A 1995, 127, 165– 176.
- [16] R. R. Davda, J. W. Shabaker, G. W. Huber, R. D. Cortright, J. A. Dumesic, *Appl. Catal. B* 2005, 56, 171–186.
- [17] C. Montassier, D. Giraud, J. Barbier, J.-P. Boitiaux, Bull. Soc. Chim. Fr. 1989, 2, 148–155.
- [18] C. Montassier, J. C. Ménézo, L. C. Hoang, C. Renaud, J. Barbier, J. Mol. Catal. 1991, 70, 99–110.
- [19] J. Zhou, L. Guo, X. Guo, J. Mao, S. Zhang, Green Chem. 2010, 12, 1835–1843.
- [20] T. Jiang, Y. Zhou, S. Liang, H. Liu, B. Han, Green Chem. 2009, 11, 1000-1006.
- [21] D. Roy, B. Subramaniam, R. V. Chaudhari, *Catal. Today* 2010, 156, 31–37.
- [22] Y. Kusunoki, T. Miyazawa, K. Kunimori, K. Tomishige, *Catal. Commun.* 2005, 6, 645–649.
- [23] T. Miyazawa, Y. Kusunoki, K. Kunimori, K. Tomishige, J. Catal. 2006, 240, 213–221.
- [24] T. Miyazawa, S. Koso, K. Kunimori, K. Tomishige, Appl. Catal. A 2007, 318, 244–251.
- [25] T. Miyazawa, S. Koso, K. Kunimori, K. Tomishige, Appl. Catal. A 2007, 329, 30–35.
- [26] E. P. Maris, R. J. Davis, J. Catal. 2007, 249, 328-337.
- [27] E. P. Maris, W. C. Ketchie, M. Murayama, R. J. Davis, J. Catal. 2007, 251, 281–294.
- [28] E. D'Hondt, S. Van de Vyver, B. F. Sels, P. A. Jacobs, *Chem. Commun.* 2008, 6011–6012.
- [29] I. Gandarias, P. L. Arias, J. Requies, M. B. Güemez, J. L. G. Fierro, *Appl. Catal. B* 2010, 97, 248–256.
- [30] A. Wawrzetz, B. Peng, A. Hrabar, A. Jentys, A. A. Lemonidou, J. A. Lercher, J. Catal. 2010, 269, 411–420.
- [31] S. Wang, Y. Zhang, H. Liu, Chem. Asian J. 2010, 5, 1100–1111.
- [32] S. Bolado, R. E. Treviño, M. T. García-Cubero, G. González-Benito,
- Catal. Commun. 2010, 12, 122–126. [33] Z. Huang, F. Cui, H. Kang, J. Chen, X. Zhang, C. Xia, Chem. Mater. 2008, 20, 5090–5099.
- [34] S. Wang, H. Liu, Catal. Lett. 2007, 117, 62-67.

- [35] K. Wang, M. C. Hawley, T. D. Furney, Ind. Eng. Chem. Res. 1995, 34, 3766–3770.
- [36] I. Furikado, T. Miyazawa, S. Koso, A. Shimao, K. Kunimori, K. Tomishige, Green Chem. 2007, 9, 582–588.
- [37] Y. Shinmi, S. Koso, T. Kubota, Y. Nakagawa, K. Tomishige, Appl. Catal. B 2010, 94, 318–326.
- [38] D. Coll, F. Delbecq, Y. Aray, P. Sautet, Phys. Chem. Chem. Phys. 2011, 13, 1448–1456.
- [39] G.-C. Wang, Y.-H. Zhou, Y. Morikawa, J. Nakamura, Z.-S. Cai, X.-Z. Zhao, J. Phys. Chem. B 2005, 109, 12431–12442.
- [40] I. N. Remediakis, F. Abild-Pedersen, J. K. Nørskov, J. Phys. Chem. B 2004, 108, 14535–14540.
- [41] Y.-H. Zhou, P.-H. Lv, G.-C. Wang, J. Mol. Catal. A 2006, 258, 203– 215.
- [42] C. J. Zhang, P. Hu, J. Chem. Phys. 2001, 115, 7182-7186.
- [43] G. C. Wang, Y. H. Zhou, J. Nakamura, J. Chem. Phys. 2005, 122, 044707-1-044707-8.
- [44] D. Cao, G. Q. Lu, A. Wieckowski, S. A. Wasileski, M. Neurock, J. Phys. Chem. B 2005, 109, 11622–11633.
- [45] S. Sakong, C. Sendner, A. Gross, J. Mol. Struct. 2006, 771, 117-122.
- [46] P. Ferrin, D. Simonetti, S. Kandoi, E. Kunkes, J. A. Dumesic, J. K. Nørskov, M. Mavrikakis, J. Am. Chem. Soc. 2009, 131, 5809–5815.
- [47] Y. Choi, P. Liu, J. Am. Chem. Soc. 2009, 131, 13054-13061.
- [48] H.-F. Wang, Z.-P. Liu, J. Am. Chem. Soc. 2008, 130, 10996-11004.
- [49] H.-F. Wang, Z.-P. Liu, J. Phys. Chem. C 2007, 111, 12157-12160.
- [50] J.-H. Wang, C. S. Lee, M. C. Lin, J. Phys. Chem. C 2009, 113, 6681– 6688.
- [51] M.-M. Yang, X.-H. Bao, W.-X. Li, J. Phys. Chem. C 2007, 111, 7403-7410.
- [52] R. Alcalá, M. Mavrikakis, J. A. Dumesic, J. Catal. 2003, 218, 178– 190
- [53] Y.-W. Chen, J.-J. Ho, J. Phys. Chem. C 2009, 113, 6132-6139.
- [54] H.-L. Chen, S.-H. Liu, J.-J. Ho, J. Phys. Chem. B 2006, 110, 14816– 14823.
- [55] V. Pallassana, M. Neurock, J. Catal. 2002, 209, 289-305.
- [56] E. Vesselli, A. Baraldi, G. Comelli, S. Lizzit, R. Rosei, *ChemPhys-Chem* 2004, 5, 1133–1140.
- [57] B. N. Zope, D. D. Hibbitts, M. Neurock, R. J. Davis, *Science* 2010, 330, 74–78.
- [58] M. Besson, L. Djakovitch, P. Gallezot, C. Pinel, A. Salameh, M. Vospernik in *Catalysis of Organic Reactions*, (Ed.: M. L. Prunier), Chemical Industries, Boca Raton, **2009**, p. 313.
- [59] R. D. Cortright, R. R. Davda, J. A. Dumesic, *Nature* 2002, 418, 964– 967.
- [60] G. W. Huber, J. A. Dumesic, *Catal. Today* **2006**, *111*, 119–132.
- [61] G. W. Huber, R. D. Cortright, J. A. Dumesic, Angew. Chem. 2004, 116, 1575–1577; Angew. Chem. Int. Ed. 2004, 43, 1549–1551.
- [62] R. Soares, D. Simonetti, J. A. Dumesic, Angew. Chem. 2006, 118, 4086–4089; Angew. Chem. Int. Ed. 2006, 45, 3982–3985.
- [63] R. Chelli, F. L. Gervasio, C. Gellini, P. Procacci, G. Cardini, V. Schettino, J. Phys. Chem. A 2000, 104, 11220–11222.
- [64] C. S. Callam, S. J. Singer, T. L. Lowary, C. M. Hadad, J. Am. Chem. Soc. 2001, 123, 11743–11754.
- [65] G. Kresse, J. Hafner, Phys. Rev. B 1993, 47, 558-561.
- [66] J. P. Perdew, Y. Wang, Phys. Rev. B 1992, 45, 13244-13249.
- [67] P. E. Blöchl, Phys. Rev. B 1994, 50, 17953-17979.
- [68] G. Kresse, D. Joubert, Phys. Rev. B 1999, 59, 1758-1775.
- [69] H. J. Monkhorst, J. D. Pack, Phys. Rev. B 1976, 13, 5188-5192.
- [70] D. Sheppard, R. Terrell, G. Henkelman, J. Chem. Phys. 2008, 128, 134106-1-134106-10.
- [71] P. Fleurat-Lessard, P. Dayal, A chemist view on reaction path determination, to be published. Freely available at: http://forge.cpb.enslyon.fr/redmine/projects/openpath/wiki/WikiEnglish.
- [72] G. Henkelman, H. Jonsson, J. Chem. Phys. 1999, 111, 7010-7022.

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