Catalytic glycerol conversion into 1,2-propanediol in absence of added hydrogen

Els D'Hondt, Stijn Van de Vyver, Bert F. Sels and Pierre A. Jacobs*

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Conversion of glycerol into high yields of 1,2-propanediol in absence of added hydrogen is possible with Pt impregnated NaY zeolite characterized by extra-zeolitic metal particles combined with zeolite Brønsted acidity.

1,2-Propanediol is a bulk chemical intermediate used for the production of unsaturated polyester resins, as an industrial solvent and antifreeze, an approved additive in foods, cosmetics and pharmaceutical preparations, and as a lubricant for food machinery.[1–4] Whereas the traditional industrial route involves hydration of propene oxide,[1] glycerol of renewable origin seems to be an attractive source for sustainable future production of chemical intermediates.[5,6] Glycerol is known to react with hydrogen to form 1,2-propanediol and water *via* consecutive dehydration and hydrogenation reactions.[2–4,7–21] Unfortunately, literature results imply the use of expensive bio- or petrochemically derived hydrogen. Hydrogen originating from reforming of natural gas or petroleum fractions makes the process dependent on fossil carbon.

The catalytic system discussed below is assumed to generate an autogeneous reducing environment, allowing *in situ* transformation of glycerol into 1,2-propanediol. The reducing environment for hydrogenation probably is generated *via* liquid steam reforming.[22,23] CO_2 is a side-product of the reforming, and a precursor for the dehydration catalyst.

Typical results from batch experiments in inert atmosphere devoid of any added hydrogen are shown in Table 1. Entries 1–3 show glycerol conversion over time at 503 K in presence of 2.7 wt% Pt/NaY. With increasing glycerol conversion, the carbon selectivity for liquids and in parallel to propanediol increases significantly. This indicates also that glycerol carbon conversion to gaseous products decreases over time. Typically, the gas phase composition after 1 h amounts to 81% of H_2, 10% of CO_2 and 5% of CO, while the gases at steady state only contain CO, CO_2 and CH_4, but no longer hydrogen. In qualitative terms it seems that during the initial reaction period, some feed molecules undergo steam reforming and consecutive water gas shift. Liquid reforming is well-established now.[22,23] During the initial stage of the reaction, mainly gaseous compounds are produced. Entries 1–3 also point to the consecutive formation of 1,2-propanediol from hydroxyacetone as selectivities increase and decrease with conversion, respectively. The initial low selectivity for hydroxyacetone reflects its instability in the reaction conditions (entry 1). This was also confirmed by substituting hydroxyacetone for glycerol as feed (results not shown). With added hydrogen and hydroxyacetone as feed (entry 4), initially high conversion and 1,2-propanediol selectivity can be achieved, indicating that (i) the initial gas formation period disappears upon external addition of hydrogen and (ii) 1,2-propanediol can be formed by Pt-catalyzed hydrogenation of hydroxyacetone.

It should be stressed that the new catalyst (2.7Pt/NaY) is prepared by impregnation of NaY zeolite with Pt-tetraammine chloride salt, followed by dehydration, calcination and reduction. In contrast to ion-exchanged zeolite (Pt-NaY) (eqn (1)), such a catalyst does not contain any residual acidity (eqn (2)).

$$\begin{aligned}[2Na^+\text{-}Y^- + Pt(NH_3)_4^{2+}]_x \;\rightarrow\; & [Pt(NH_3)_4^{2+}\text{-}Y^{2-} + 2Na^+]_x \\ & \qquad\downarrow \\ & (Pt^0)_x + (2H\text{-}Y)_x \end{aligned} \tag{1}$$

$$\begin{aligned}[Pt(NH_3)_4Cl_2 + 2\,NaY]_n \;\rightarrow\; & (Pt^0)_n + 2n\,NaY + 2n\,HCl \\ & +n\,N_2 + n\,H_2 \end{aligned} \tag{2}$$

Via the Scherrer equation, it was found that a significant amount of Pt is present as extra-framework particles of about 42 nm [$(Pt^0)_n$]. XRD as well as ESEEM on Pt/NaY shows an absence of metal on Pt-NaY. It is clear that after ion exchange and further catalyst activation, the ion-exchanged zeolite is acid and contains exclusively intra-framework Pt [$(Pt^0)_x$].

A comparison of the carbon selectivity at short reaction time and relatively low conversion is made for the ion-exchanged and impregnated samples (entries 5 and 1). The decreased liquids as well as 1,2-propanediol selectivity for the ion-exchanged catalyst shows that the presence of small intra-crystalline Pt clusters is the basis of extensive gas formation *via* liquid reforming. On the large extra-framework Pt particles on the impregnated sample, the hydrogenolysis reaction seems to be more specific, yielding less gas (and more propanediol *via* hydrogenation of hydroxyacetone).

As the glycerol dehydration into hydroxyacetone is probably Brønsted-acid catalyzed,[19–21] its occurrence on the non-acidic Pt/NaY requires some clarification. Some of the CO_2 formed *via* liquid reforming will dissolve in the aqueous reaction medium, generating H_2CO_3, which upon dissociation will yield free protons. NaY will accept most of these protons *via* ion exchange with Na^+, thus generating a partially exchanged H-NaY. MAS NMR characterization of this material shows bridging silanol groups in the supercages at 3.8 ppm indeed. The balance between the two types of sites, *viz.*

Centre of Surface Chemistry and Catalysis, Department of Molecular and Microbial Chemistry, Catholic University of Leuven, Kasteelpark Arenberg 23, 3001 Heverlee, Belgium.
E-mail: pierre.jacobs@biw.kuleuven.be; Fax: +32 16 32 1998;
Tel: +32 16 32 1595

Table 1 Glycerol conversion on Pt-loaded catalysts[a]

					S_i (%)			
Entry	Catalyst notation	*t*/h	X (%)	S_L (%)	PDO	EtOH	PrOH	HOAcON
1	2.7Pt/NaY	1	18.1	54.7	25.0	7.0	6.6	10.0
2	2.7Pt/NaY	4	58.8	60.3	41.5	6.7	7.1	4.0
3	2.7Pt/NaY	15	85.4	89.4	64.0	9.5	7.5	3.0
4	2.7Pt/NaY[b,c]	1	98.7	95.9	91.3	1.4	1.8	—
5	2.7Pt-NaY	2	18.4	29.4	10.8	6.6	6.5	3.2
6	3.0Pt/γ-Al_2O_3[d]	24	99.9	59.0	19.1	10.6	24.4	1.9
7	2.7Pt/C[e]	24	94.6	13.1	0.6	2.4	8.9	0.5
8	2.7Pt/HBeta	17	12.8	23.8	0.0	10.1	7.1	3.7

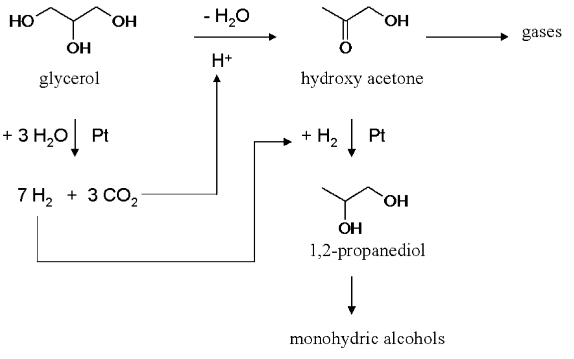
[a] 100 ml Parr batch reactor under inert atmosphere, 40 ml 20 wt% aqueous glycerol at 503 K, 575 rpm, 0.22 mmol Pt in added catalyst. [b] In presence of 4.2 MPa H_2. [c] 20 wt% aqueous hydroxyacetone feed. [d] Identical to literature catalyst.[22] [e] CMK-3 type carbon; X = conversion, S_i = carbon selectivity of PDO = 1,2-propanediol, EtOH = ethanol, PrOH = *n*-propanol, HOAcON = hydroxyacetone; S_L = carbon selectivity of total liquid products; Pt/NaY and Pt-NaY are obtained *via* impregnation and ion exchange of $Pt(NH_3)_4Cl_2$ on NaY, respectively.

protons and metal particles, seems to be subtle since results with less acidic catalyst supports such as γ-alumina (entry 6) and mesoporous carbon (entry 7) show significantly lower liquids and propanediol selectivity compared with entry 3.

Collecting all arguments shows that the conversion of glycerol into mainly 1,2-propanediol involves an acid catalysed dehydration to hydroxyacetone and subsequent hydrogenation to 1,2-propanediol (Scheme 1). Although details of the gas formation are still under study and the present note is not meant to divulge detailed kinetics, it is clear that the size of the metal particles is crucial at the start of the reaction sequences, as intrazeolitic Pt favors gas formation and decreased liquids and propanediol selectivity compared to extra-framework large Pt metal particles. The proposed mechanistic pathways on the optimally balanced catalyst (Pt/NaY) assume that initially formed CO_2 is at the origin of solution acidity and subsequently suitable zeolite acidity, catalyzing the dehydration of glycerol into hydroxyacetone. The hydrogenation of the latter preferably on metal particles external to the zeolite crystals seems to suggest the structure sensitive nature of the hydrogenation of hydroxyacetone into 1,2-propanediol.

The necessity to have a good balance between the two catalytic functions as well as a suitable acid strength/concentration is obvious from the decreased performance when a Pt impregnated zeolite Beta with high acidity is added to the reaction mixture as a second catalyst component (entry 8).

Catalytic experiments are in progress to establish a kinetic network for major as well as minor kinetic pathways on the best system (Pt/NaY). In parallel, attempts are being made to quantify the required catalytic functions, *viz.* acidity and metal, to obtain a well-balanced catalyst.



Scheme 1 Main pathways for the conversion of glycerol into 1,2-propanediol *via* bifunctional catalysis with Pt/NaY.

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