



# Direct synthesis of propylene oxide in the liquid phase under mild conditions

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## ABSTRACT

Here, we study the direct synthesis of propylene oxide (PO) on Pd-based catalysts operating under mild conditions (40 °C, 5.5 bar) and in a continuous flow microreactor. We show that the PO yield can be improved by a factor of two, with respect to the values present in literature, by using a Pd–Pt/TS-1 catalyst in excess of oxygen. Moreover, we compare the PO reaction with the hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) synthesis, being H<sub>2</sub>O<sub>2</sub> (or OOH species) the intermediate and rate limiting step of the direct PO formation. We found that the optimal conditions for the PO synthesis are not advantageous for the H<sub>2</sub>O<sub>2</sub> productivity. In this respect, the presence of Pt, which improves the PO selectivity by lowering the hydrogenation of propylene, negatively affects the H<sub>2</sub>O<sub>2</sub> productivity due to an acceleration of its side reactions. This effect is more pronounced for the Pd–Au/TS-1 catalyst, which shows a high performance for H<sub>2</sub>O<sub>2</sub> production. However, the PO formation remains relatively poor due to a very fast hydrogenation of propylene to propane. We conclude that the optimization of the H<sub>2</sub>O<sub>2</sub> synthesis is not sufficient to improve the direct PO formation. Indeed, the hydrogenation of propylene needs also to be considered.

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## 1. Introduction

Propylene oxide (PO) is an important compound largely studied in the last decades due to its broad applicability as a chemical intermediate [1,2]. Efforts were made in order to substitute the existing technologies with new alternatives to make the PO synthesis process economically and environmentally advantageous [3–6]. An attractive approach to address these limitations is the direct synthesis of PO from oxygen, hydrogen and propylene [7–18]. This two step reaction involves the in-situ formation of the intermediate species, which is the rate limiting step, and its consecutive consumption by the propylene epoxidation [6,11]. The formation of the intermediate species from the reaction of H<sub>2</sub> and O<sub>2</sub> on metal catalysts still represents an open and interesting discussion topic. Many groups acknowledge the formation of H<sub>2</sub>O<sub>2</sub> as the intermediate step for the further reaction with propylene to PO [15,16,19–22]. However, more research focused on the reaction between O<sub>2</sub> and H<sub>2</sub> shows that a mixture of H<sub>2</sub>O<sub>2</sub> and OOH species is obtained on the metal catalyst [23,24]. Water is the main by-product obtained

from this reaction. Two main research streams can be distinguished for the direct PO synthesis: gas vs liquid phase reaction.

The discovery of the bi-functional Au/Ti<sub>species</sub> as a very selective catalyst for the gas phase PO synthesis led to deep insights on its reaction mechanism and its fundamental steps [7–11,14]. Nevertheless, the achievements obtained by improving the catalyst performance [9,13] and the reactor design [11,25,26] do not overcome the issues related to the low hydrogen efficiency and PO productivity. An alternative approach is provided by the liquid phase reaction. Here, methanol or a mixture of methanol–water are the main solvents utilized. Several catalysts were implemented for the direct PO synthesis starting from Pd/TS-1 [27] to Pd–Pt/TS-1 [15–17]. The advantage of these catalysts consists in intensifying the two step reaction in a single unit reaction. This allows to improve the process by optimizing the single steps of the reaction, including the rate limiting one [6].

In the present work, we report the effect of oxygen excess on the productivity and yield of PO during the direct and continuous flow synthesis reaction. The PO production is investigated for the 1 wt% Pd/TS1 and 1 wt% Pd–0.1 wt% Pt/TS-1, catalysts developed by Hölderich [15]. The performance of these catalysts is also studied for the H<sub>2</sub>O<sub>2</sub> synthesis underlining the differences between the two reactions. These results are compared with the results obtained

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### Nomenclature

TPAOH	tetrapropylammonium hydroxide
TEOS	tetraethyl orthosilicate
TBOT	tetrabutyl orthotitanate
$[\text{Pd}(\text{NH}_3)_4](\text{NO}_3)_2$	tetraamminepalladium nitrate
$[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$	tetraammineplatinum chloride
$\text{PdCl}_4^-$	tetrachloropalladate ions
$\text{AuCl}_4^-$	tetrachloroaurate ions
$\text{NaBH}_4$	sodium borohydride
1M2P	1-methoxy 2-propanol
2M1P	2-methoxy 1-propanol
X	conversion
S	selectivity
$\text{Eff}_{\text{H}_2}$	hydrogen efficiency
P	productivity $\text{mmol}_i/\text{g}_{\text{cat}} \text{ h}$

with a Pd–Au/TS-1 catalyst, which was shown to be very active in the direct synthesis of  $\text{H}_2\text{O}_2$  [28]. The comparison provides important information on the rate limiting step and the propylene in the direct synthesis of PO.

## 2. Experimental

### 2.1. Experimental setup

PO and  $\text{H}_2\text{O}_2$  synthesis reactions were carried out in a continuous microreactor flow system. A schematic representation of the setup is shown in Supplementary information.

The gases are supplied to the system by means of mass flow controllers. Before reaching the microreactor, the gases are mixed with the solvent, that is fed to the system with an ISCO pump (Teledyne ISCO 500D). At the exit of the microreactor, the gas stream is separated from the liquid phase in a pressurized stainless steel vessel. The composition of the gases is analyzed on-line by a GC (Poraplot/Molsieve 5A, TCD/FID detector). Liquid samples are collected and analyzed in an off-line liquid Gas Chromatograph (Varian 3800 GC, FID detector, 8400 Autosampler). The pressure of the system is kept constant with a back-pressure regulator with argon for the PO production experiments (and nitrogen for the  $\text{H}_2\text{O}_2$  production experiments). The microreactor, a peek capillary tube with an internal diameter of 0.9 mm, is placed inside an oven to keep the temperature constant at 40 °C. The reactions were performed at a total pressure of 5.5 bar. In a typical reaction run, 50 mg of catalyst (particle size 250–400  $\mu\text{m}$ ) was used in a packed bed and a feed of 1.5 ml/h of methanol and 2 ml/min total gas flow was provided. The gas composition was 10/10/10/70:  $\text{H}_2/\text{O}_2/\text{C}_3\text{H}_6/\text{N}_2$  or 10/50/10/30:  $\text{H}_2/\text{O}_2/\text{C}_3\text{H}_6/\text{N}_2$ . For the  $\text{H}_2\text{O}_2$  synthesis reactions, the methanol contains traces of  $\text{H}_2\text{SO}_4$  and NaBr. These compounds are needed to stabilize  $\text{H}_2/\text{O}_2$  by avoiding the further decomposition reaction. Also, the propylene was substituted with nitrogen to keep a constant total gas flow.

### 2.2. Catalyst preparation

The TS-1 catalyst was prepared in micellar media [29]. A mixture of 1 g of Tween 20 and 16 g of distilled water was added to 9.6 g of TPAOH (32 wt%). This solution, containing 18 g of TEOS, was stirred for 1 h. Then, a mixture of TBOT and isopropanol (0.904 g:4.56 g) was slowly added to the solution. The hydrothermal synthesis and the calcination concluded the preparation of the catalyst. The Pd/TS-1 and Pd–Pt/TS-1 catalysts were prepared according to the recipe presented by Hölderich [15]. 1 g of TS-1 was suspended in 4 g of water. An aqueous solution containing

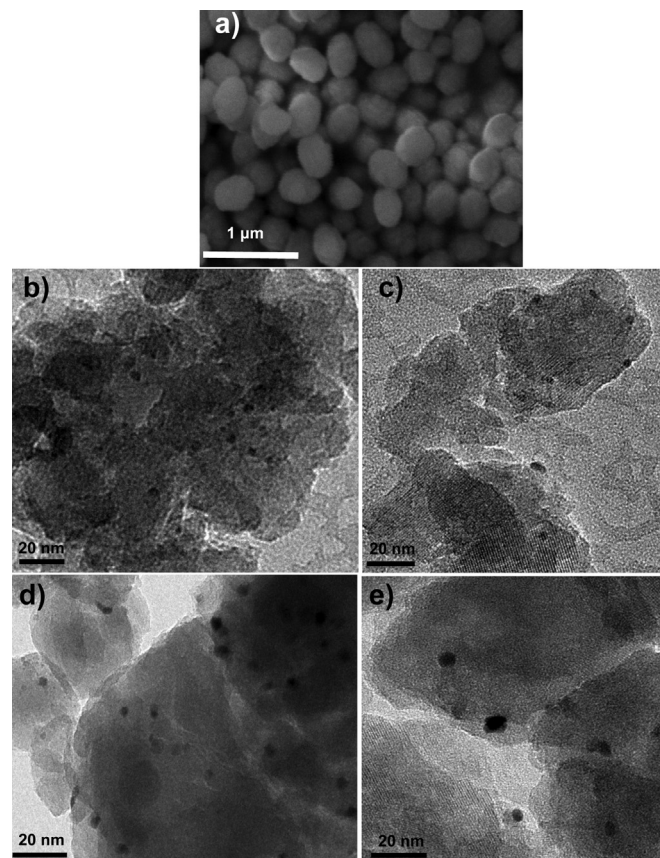
the proper amounts of  $[\text{Pd}(\text{NH}_3)_4](\text{NO}_3)_2$ , or a mixture of  $[\text{Pd}(\text{NH}_3)_4](\text{NO}_3)_2$  and  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$  (for Pd or Pd–Pt catalysts respectively) were added to the TS-1, and stirred for 24 h at 80 °C. The solvent was removed in vacuum at 60 °C, and the catalyst was dried at 60 °C for 24 h. The reduction of the catalysts was conducted at 150 °C in nitrogen for 2 h. The loading of the catalysts is 1 wt% Pd and 0.1 wt% Pt. The Pd–Au/TS-1 catalyst was synthesized as shown elsewhere [28]. The TS-1 is impregnated with Pd–Au nanoparticles synthesized with a phase-transfer procedure. The  $\text{PdCl}_4^-$  and  $\text{AuCl}_4^-$  ions are transferred from the water to the organic phase, and reduced with  $\text{NaBH}_4$ . The phase-transfer agent utilized in this procedure is tetraoctylammonium chloride. The loading of the final catalyst is a 1 wt% Pd with a Pd/Au molar ratio changing from 2 to 10.

## 3. Results and discussion

### 3.1. Catalyst characterization

Fig. 1 shows the TS-1 catalyst morphology obtained with Scanning Electron Microscope analysis (SEM, QuantaTM 3D FEG). The morphology of the metal particles (Pd–Pt, Pd–Au) on the TS-1 catalyst is studied with Transmission Electron Microscopy (TEM, FEI Tecnai G2 Sphera).

A detailed study on the performance and optimization of the Pd–Pt/TS-1 catalyst for the direct synthesis of PO in liquid phase was conducted by the group of Hölderich [15]. They demonstrated that the advantage of the Pd–Pt/TS-1 catalyst for the PO synthesis consists on the presence of Pd(II) species [15]. The oxidized species



**Fig. 1.** SEM and TEM images of the utilized catalysts. (a) SEM image of TS-1 catalyst synthesized according to the micellar procedure. (b) TEM image of the Pd/TS-1 catalyst. (c) TEM image of the Pd–Pt/TS-1 catalyst. (d) TEM image of the Pd–Au (2:1) catalyst. (e) TEM image of the Pd–Au (10:1) catalyst.

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