Epoxidation of propylene and direct synthesis of hydrogen peroxide by hydrogen and oxygen

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The autoreduction of palladium–platinum-containing titanium silicalite leads to an effective catalyst for the epoxidation of propylene to propylene oxide by O_2 in the presence of H_2. The “one-pot” reaction is favoured compared to the two-step reaction path.

Keywords: epoxidation, propylene oxide, hydrogen peroxide, titanium silicalite, palladium, platinum

1. Introduction

The oxidation of propylene to propylene oxide (PO) has been attracting much interest [1,2]. Titanium silicalite-1 (TS-1) [3] is a new type of molecular sieve which incorporates titanium in the framework. Among other reactions it has been found to be very effective in the epoxidation of propylene, using H_2O_2 as an oxidant under mild conditions [4]. For economic reasons, attempts have been made to substitute H_2O_2 by employing a mixture of H_2 and O_2 that generates H_2O_2 *in situ* [5–9]. In these cases the TS-1 is modified with precious metals such as palladium and platinum, that catalyze the direct synthesis of H_2O_2. So far, low yields of propylene oxide, i.e., less than 3%, have been reported for such a synthesis route [5–8]. We already had found that maximum PO yield of 12% were obtained over a TS-1 loaded with 1.0 wt% and 0.02 wt% Pt and reduced under N_2 at 150 °C [9]. When H_2O_2 is used as the oxidant, the yields of propylene oxide are significantly higher [4]. Therefore, it can be assumed that the *in situ* formation of H_2O_2 is the rate-determining step for the epoxidation of propylene with hydrogen and oxygen catalyzed by Pd/TS-1. We have further validated this assumption by conducting experiments under the same conditions for the epoxidation of propylene with H_2O_2 or H_2 and O_2, respectively.

In order to obtain a better understanding of the reaction steps that are involved when a H_2–O_2 mixture is used as the oxidant, we have conducted two types of catalytic experiments: in the first type we have investigated the direct synthesis of H_2O_2, whilst the second type deals with the synthesis of propylene oxide with propylene, hydrogen and oxygen as starting materials. Since the same catalytic systems are employed for both reactions, it is possible to gain new insights by the direct comparison of the obtained results. Furthermore, we report the influence of different methods for the reduction of palladium and platinum on the synthesis of H_2O_2 and propylene oxide.

2. Experimental

2.1. Catalyst preparation

TS-1 with $\mathrm{Si:Ti} = 34.6$ was prepared according to the procedure described in the patent by Taramasso et al. [10]. The MFI-structure of the synthesized material was confirmed by X-ray powder diffractometry. The DR-UV-Vis spectra exhibited a band in the range of 190–210 nm and the IR spectra revealed a band at 960 $\mathrm{cm^{-1}}$ indicating tetrahedally coordinated titanium atoms [11]. TS-1 was impregnated with $[Pd(NH_3)_4](NO_3)_2$ and $[Pt(NH_3)_4]Cl_2$ leading to a catalyst with a loading of 1 wt% Pd and 0.1 wt% Pt. The impregnated TS-1 was reduced under an atmosphere of either H_2, a mixture of 5% H_2 + 95% N_2 or pure N_2 at a temperature of 50, 150 or 300 °C, respectively, that was maintained for 1 h. Under the pure nitrogen atmosphere, the catalyst was autoreduced by the thermal decomposition of the NH_3 ligands [12]. In another reduction method, the Pd–Pt-loaded catalyst was calcined in air at 250 °C and subsequently reduced with 5% H_2 + 95% N_2 at 50 °C.

2.2. Apparatus and reaction procedure

All reactions were carried out in an 200 ml autoclave with 0.2 g of catalyst, 15 g MeOH and 5 g H_2O as the solvent mixture, stirred with a magnetic stirrer. The reaction time was 3 h. For the epoxidation of propylene with H_2O_2, 10 g of propylene and 8 g of 30 wt% aqueous H_2O_2 were added to the reaction mixture. When H_2 and O_2 were used as oxidants, the H_2O_2 was substituted by pressurizing the autoclave with H_2 (7 bar), N_2 (15 bar) and O_2 (10 bar). In the case of the direct synthesis of H_2O_2, the vessel was

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pressurized with H_2, N_2 and O_2 as stated above, without charging propylene to the autoclave. The epoxidaton reactions were carried out at 43 °C, while the direct synthesis of H_2O_2 was conducted at 10 °C. These are the temperatures typically applied for both reactions [4,13]. Catalysts were filtered off and the aqueous phase was subjected to gas chromatographic analysis (epoxidation reactions) or iodimetric titration (H_2O_2 synthesis). For safety reasons we placed the reaction vessel and peripheral equipment in a barricaded area and used a remote control system to take samples, start, monitor and terminate the reaction.

3. Results and discussion

The yield of propylene oxide that was obtained with different oxidants (H_2O_2 or H_2 and O_2) and different catalysts (TS-1 and Pd–Pt-loaded TS-1) is presented in table 1. The highest yield of propylene oxide (40%) was achieved with unloaded TS-1 using H_2O_2 as the oxidant. When employing a TS-1 catalyst, loaded with 1 wt% Pd + 0.1 wt% Pt and autoreduced at 150 °C under nitrogen atmosphere, the yield of PO decreases by almost 50–21%. This effect can be attributed to the ability of palladium and platinum to decompose H_2O_2. When a mixture of hydrogen and oxygen was used instead of H_2O_2, no oxidation products were obtained with an unloaded TS-1 catalyst. Over the 1% Pd + 0.1% Pt/TS-1 catalyst propylene was oxidized with hydrogen and oxygen to propylene oxide with a yield of 5.3%. Since no propylene oxide was found over the unloaded catalyst, it seems that H_2O_2 has been generated at palladium and platinum sites and that the *in situ* produced H_2O_2 epoxidated the propylene over TS-1. The obtained yield of PO was heavily dependent on the oxidant used. The use of a H_2–O_2 mixture led to a decrease of the PO yield compared to the reaction with H_2O_2, thereby indicating that the rate of formation of H_2O_2 over the Pd–Pt-TS-1 catalyst was insufficient.

Table 1
Epoxidation of propylene.[a]

Oxidant	Catalyst	PO yield (%)
H_2O_2	TS-1	39.3
H_2O_2	1% Pd + 0.1% Pt/TS-1 Reduction: 150 °C, N_2	21.3
$H_2 + O_2$	TS-1	0.0
$H_2 + O_2$	1% Pd + 0.1% Pt/TS-1 Reduction: 150 °C, N_2	5.3

[a] Conditions: 0.2 g catalyst, 15 g MeOH, 5 g H_2O, 3 h, 43 °C, 10 g propylene, 8 g (30 wt%) H_2O_2, 7 bar H_2 (59 mmol), 15 bar N_2 (138 mmol), 10 bar O_2 (92 mmol).

In order to quantify the formation of H_2O_2 over the Pd–Pt-TS-1 catalyst, we carried out the batch experiments for the synthesis of H_2O_2 under the same conditions as the epoxidation reactions with a H_2–O_2 mixture, except that no propylene was added and the reaction temperature was set to 10 °C. Lower temperatures are favourable for H_2O_2 formation. The yields of H_2O_2 over differently reduced 1% Pd + 0.1% Pt/TS-1 catalyst are presented in figure 1. If we compare these results with the PO yield for the epoxidation with a H_2–O_2 mixture, as illustrated in figure 1, we find that the PO yield was always higher than the H_2O_2 yield, although one mole of H_2O_2 is required to form one mole of PO. This effect indicates more H_2O_2 was originally generated during direct synthesis of H_2O_2 than could be detected at the end of the synthesis as most of the H_2O_2 thus formed had decomposed. However, during the epoxidation experiment the generated H_2O_2 reacted rapidly with propylene before its decomposition could take place.

The low yields of H_2O_2 over any tested catalyst (<1%) are likely due to the absence of ionic additives and acids that are known to be essential promoters for the H_2O_2 synthe-

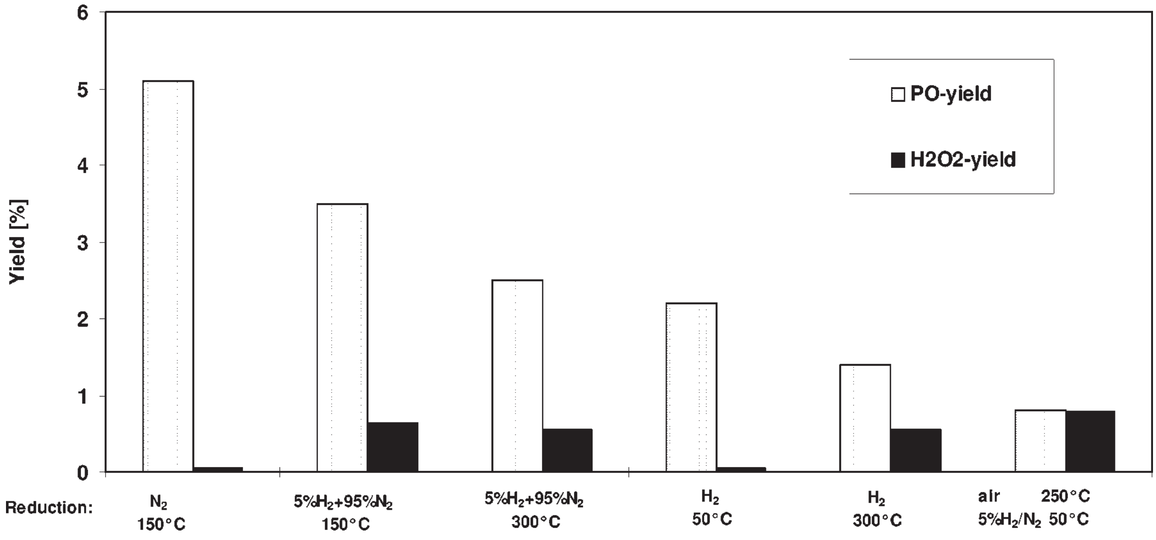

Figure 1. Effect of reduction methods on the PO yield and the H_2O_2 yield over 1% Pd + 0.1% Pt/TS-1. Conditions: 0.2 g catalyst, 15 g MeOH, 5 g H_2O, 7 bar H_2 (59 mmol), 15 bar N_2 (138 mmol), 10 bar O_2 (92 mmol), 3 h, H_2O_2 synthesis: 10 °C, PO synthesis: 43 °C, 10 g propylene added.

sis [13]. These yields were too low to draw any conclusions on the influence of the reduction method. In contrast to the H_2O_2 synthesis, the reduction methods exhibited a clear influence on the epoxidation of propylene with a H_2–O_2 mixture. We already could demonstrate that the best reduction method for the Pd/Pt/TS-1 catalyst was the autoreduction [9]. The highest PO yield (5.3%) was obtained over an autoreduced (N_2 atmosphere, 150 °C) catalyst. Increasing the reduction temperature from 50 to 300 °C and the hydrogen concentration in the reduction atmosphere (pure $N_2 \rightarrow H_2$–$N_2 \rightarrow H_2$) caused the PO yield to decrease. The lowest PO yield was obained over a catalyst that was first calcined under air and subsequently reduced. Interestingly, the same catalyst is the most effective one in the direct synthesis of H_2O_2. The two reactions seem to require differently reduced catalysts, though the formation of *in situ* H_2O_2 is necessary to produce propylene oxide.

4. Conclusion

It could be demonstrated that the epoxidation of propylene by O_2 in the presence of H_2 is favoured in a “one-pot” reaction procedure and results in higher yields rather than in a two-step reaction manner. It is also interesting to note that the autoreduction of the catalyst leads to higher yields of PO than the reduction with H_2 or H_2–N_2 mixtures. Such H_2 reduction is even worse at higher temperatures.

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