Selectivity Enhancement of Coordinating Solvents on the Direct Synthesis of Hydrogen Peroxide

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Highlights

- Direct synthesis of hydrogen peroxide suffers from selectivity issues, promoters are needed.
- Standard promoters (H^+, CL^-, Br^-) lead to corrosion issues.
- Coordinating solvents work as novel corrosion-free promoters in ion-exchangers supported catalysts.
- The promotion mechanism lies in the nanoparticle's reconstruction mediated by the support.

1. Introduction

The direct synthesis (DS) of hydrogen peroxide (HP) aims at extending its usage as an oxidant in chemical manufacturing, having been a hot topic in heterogeneous catalysis since 90s. [1] The main issue of the DS, catalyzed by supported nanostructured palladium or palladium alloys, lies the selectivity towards the desired product. Chloride or bromide ions, combined with inorganic acids, are well-known and effective promoters, but corrosion issues prevent their application in industrial scale.[2] In the same way as halides, acetonitrile (ACN) shares good ligand properties towards Pd(II), being at the same time non-corrosive. Starting from this similarity, the effect of ACN as co-solvent in addition to methanol was investigated. After promising results, the investigation was extended to other corrosion-free coordinating solvents, namely dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). The studies were initially conducted with a semi-batch reactor (SBR), whereas in the last part of the investigation was extended to a continuous trickle-bed reactor (TBR), to better predict the behavior of the catalytic system on a technological application.

2. Methods

1% w/w Pd catalysts supported on an ion-exchange resin based on a novel mesoporous polymer (Pd/SpDVB) [3] were investigated in the DS. Further zeolite supported catalysts were investigated, together with commercial Pd on carbon as benchmark. As for the SBR, 100 mg of catalyst were studied at 25°C and 1 atm, with 300 mL of reaction mixture and a gas flow of 25 mL/min with a composition O_2 = 96%, H_2 = 4%, outside of the explosive regime. In the case of the TBR, 150 mg were tested at 15°C and 20 bar, using a liquid frow of 1 mL/min and a gas flow of 4 mL/min (pure O_2 and H_2 in CO_2 with a ratio of reactant 5:1). The outgoing gas mixture was analyzed with a micro-gc equipped with a MS5A column and HP was titrated with UV-Vis spectroscopy using a $TiOSO_4$ solution to form a colored complex. The effect of ACN, DMF and DMSO as coordinating solvent was studied by using a 10% vol of coordinating solvent in methanol as the reaction mixture. The promotion effect of ACN is proposed by comparing DS experiments and characterization of fresh and spent catalysts, mainly with XPS, TEM and XRD.

3. Results and discussion

The results of the DS experiments with SBR setup show a selectivity enhancement as well as an increase in the production of HP when coordinating solvents are present in the reaction mixture (Figure 1). This effect is obtained only when the catalyst is supported on ion-exchange materials, such as sulfonated pDVB or zeolites. In this case, the reconstruction of the metal phase occurs under reaction conditions, according to the formation of smaller Pd nanoparticles when compared to the fresh catalyst. Moreover, XPS shows an increase of the Pd(II)/Pd(0) ratio after the catalytic experiment. This is further enhanced by the presence of ACN, together with the modification of the structural properties of the metal nanoparticles. This suggests a release-and-capture mechanism of the active metal, which starts from the formation, for instance in the case of ACN, of $[Pd(ACN)_4]^{2+}$ complexes that are then grafted to the support by ion-exchange. These are eventually reduced to form metal Pd nanoparticles; in this mechanism are formed Pd species that are more active towards the DS. Moreover, is worth remarking how leaching of the active phase is not observed. By comparing the results with SBR and TBR setups, it is clearly seen that this mechanism and therefore the promotion effect depends on the reaction conditions used in the catalytic experiments.

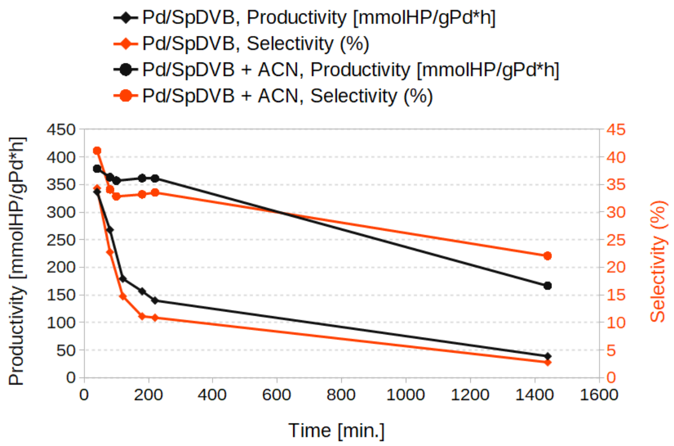

Figure 1. Caption (colored graphs and figures allowed). [Times New Roman 10].

4. Conclusions

This work demonstrates the finding of novel corrosion-free selectivity enhancers for the direct synthesis of hydrogen peroxide. The key feature to find new promoters lies in the ligand properties of the co-solvent, which enables the activation of a complex mechanism of reconstruction of the metal phase which leads to the selectivity enhancement. It is worth noting that this approach of discovery of new alternative promoters based on the chemical features of the known selectivity enhancers could theoretically be transferred to several other catalytic systems.

References

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Keywords

“Hydrogen peroxide”, “novel promoters”, “ion-exchange support”, “catalyst reconstruction”.