EFFECT OF ACTIVATED CARBON AS SUPPORT OF PALLADIUM CATALYSTS FOR THE HYDROGENOLYSIS OF CCl_2F_2 (CFC-12) INTO CH_2F_2 (HFC-32)

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INTRODUCTION

CFC-12 (CCl_2F_2) has been identified as a CFC (ChloroFluoroCarbon) which depletes the protective stratospheric ozone layer and therefore its production and use will be prohibited (per 1-1-1995 in the European Union and per 1-1-1996 worldwide). However, the depletion of stratospheric ozone will continue in spite of this prohibition. This is caused by slow diffusion of CFCs from the troposphere to the stratosphere and the eventual emission of still used CFCs. It is, therefore, of utmost importance to prevent the CFCs which are still in use from being emitted into the atmosphere. The estimated banked quantities of CFCs are 2.1 million tons worldwide. There is no dedicated destruction process available for CFCs other than combustion (incineration). At Delft University of Technology a catalytic process is under development in which the harmful CFC-12 is converted into a valuable product (HFC-32(CH_2F_2)), which can be used as an alternative, ozone friendly refrigerant. With this process both the waste materials CFC-11 (CCl_3F), which can be converted into CFC-12 by use of HF, and CFC-12, together about 90% of the banked CFCs, can be converted into a valuable product.
This presentation will deal with the influence of different types of activated carbons and the influence of purification of the activated carbon prior to use on the performance of a palladium on activated carbon catalyst.

BACKGROUND

The catalytic hydrogenolysis can be represented as the reaction of CFC-12 via HCFC-22 ($CHClF_2$) into HFC-32. A selective process to HFC-32 can be expected because fluorine is more difficult to replace with hydrogen than chlorine as has been found by Lacher and coworkers [1]. All hydrogenolysis reactions starting from CFC-12 are exothermic, irreversible reactions, and the formation of methane is thermodynamically most favoured. The reaction enthalpies are for the selective hydrogenolysis to HFC-32 -150 kJ/mol and for the complete hydrogenolysis to methane -320 kJ/mol. Besides hydrogenolysis also chlorine-fluorine exchange can take place. This leads to formation of HFC-23, a products which can only be formed via a chlorine- fluorine-exchange reaction. Also coupled products such as ethane and propane can be formed. The complete reaction scheme for one carbon containing CFCs is depicted in figure 1.

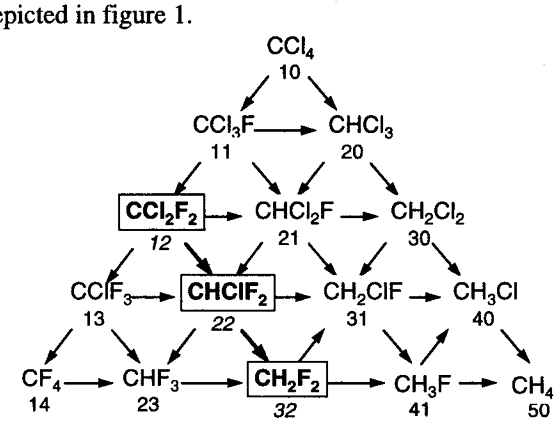

Fig. 1 Reaction scheme of C_1-type CFCs. The bold arrows represent the reactions aimed for.

Several noble metals on activated carbon support materials have been tested. Activated carbon is chosen as support material for its inertness under the corrosive reaction conditions (HF and HCl). Palladium was found to be the most suitable metal for the reaction.

EXPERIMENTAL

Catalysts were prepared by impregnation of a palladium compound on an activated carbon support. The activated carbon support was optionally treated with acid- and alkaline solution in a flow set-up prior to introduction of the noble metal. The activity tests of the CFC-12 hydrogenolysis catalysts were carried out in a Hastelloy-C microflow reactor connected to an on-line gas chromatograph with a Poraplot Q column (50 m x 0.53 mm) and a thermal conductivity detector. Reaction conditions, such as temperature, hydrogen to CFC-12 ratio, pressure and space velocity, were varied during a catalytic test. The influence of HF or HCl was tested by adding this component to the feed.

RESULTS AND DISCUSSION

The performance of the palladium on activated carbon catalyst is strongly influenced by the amount of impurities present in the activated carbon support. The effect of purification of the activated carbon support on the performance of a catalyst is depicted in figure 2. The purification of the activated carbon leads to a drastic decrease in the amount of impurities like Fe, Al and Cr, as has been found with XRF measurements. These impurities are known to act as Friedel-Crafts catalysts. After purification of the activated carbon not only the conversion of CFC-12, but also the selectivity to HFC-32 is higher. The selectivity to HFC-32 of about 80% is much higher as has been reported in literature[2], where a selectivity of 60% to 70% for palladium on graphite at low CFC-12 conversion is mentioned. The results show that the removal of the impurities very clearly suppresses both the formation of HFC-23, which can only be formed by chlorine-fluorine exchange, and the formation of coupled products. Although a considerable amount of impurities is still present in the activated carbon after the purification, the chlorine fluorine exchange activity is negligible. Apparently the remaining impurities are not accessible to the reactants.

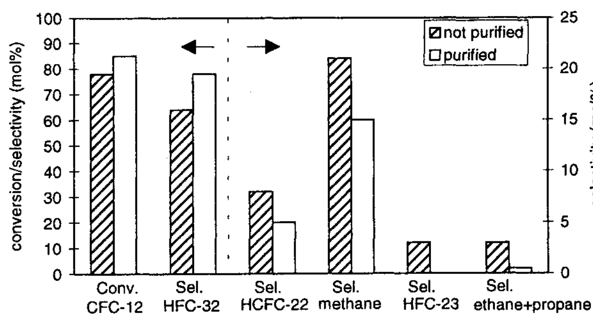

Fig. 2 Influence of purification of activated carbon on the performance in the hydrogenolysis of CFC-12.

Different types of activated carbon have been used as support material for the catalyst. The source of the carbon does not have a great effect on the catalyst performance, as long as the carbon is purified prior to use. Especially the use of a chemically activated carbon is interesting because during activation the accessible impurities might already be sufficiently removed . XRF measurements showed a low Al and Fe content for the chemically activated carbon. However the impurities were removed further in the purification procedure and were thus accessible to the reactants. Therefore the use of a naturally pure activated carbon is not always beneficial, because the small amount of impurities might still be accessible. In figure 3 the effect of the type of activation on the performance of a catalyst on purified carbons is depicted. A chemically activated carbon catalyst shows both a lower conversion and a much lower selectivity to HFC-32. The formation of methane is higher. A steam activated carbon combines a high conversion of CFC-12 with a high selectivity to HFC-32. When the activated carbon is more activated, the selectivity to HFC-32, however, becomes lower and more methane is formed. A tentative explanation for these phenomena might be that the catalysts should have a certain amount of micropores to stabilize small palladium particles. CO-chemisorption measurements on chemically activated carbon showed indeed larger palladium particles.

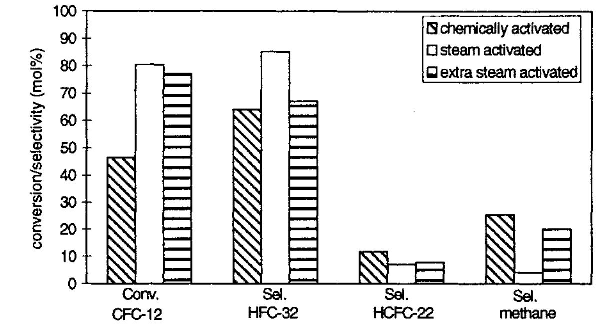

Fig. 3 The effect of different types of activated carbon on the performance of a catalyst in the hydrogenolysis of CFC-12.

CONCLUSIONS

Palladium on activated carbon is an excellent catalyst for the selective hydrogenolysis of the waste CFC-12 into a high added value product, HFC-32. The activated carbon support has to be purified to remove the accessible impurities, which can act as Friedel-Crafts catalysts. The performance of a catalyst strongly depends on the specific type of activated carbon used. Steam activated carbons are better than chemically activated carbon. When a steam activated carbon is used the performance of a catalyst depends on the grade of activation.

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