

Fluidized bed plasmas reactor for catalyst pretreatment. Application for SCR NO_x by hydrocarbons in stationary and mobile sources

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Introduction

Nowadays, almost all major chemicals are produced by catalytic processes. Among them, heterogeneous catalysis plays a very active role, because of environmental concerns. The use of plasmas for catalysis is now well developed and some authors have used plasma treatment in a low pressure system to replace the thermal calcination of the catalysts [1]. Fluidized bed reactors offer the possibility to lead to homogeneous treatment and have the additional advantage of excellent heat transfer rates between the gas and the particles, so that it can modify the catalytic properties of the prepared materials [2,3].

The aim of our work is to prepare catalysts dedicated to NO_x abatement in stationary (natural gas combine heat power) or mobile sources (Diesel engines). For stationary sources, the palladium based catalyst was chosen since the main reducing agent is methane [4]. In the case of mobile sources, we have worked with silver [5] based catalysts since ethanol can be chosen as a reducer for mobile sources to replace NH₃ [6]. After the preparation of the different catalysts, we have used the low fluidized bed plasma reactor to modify Pd/γ-alumina and Ag/γ-alumina catalysts. A comparison with "classical calcination" in air at 500°C was performed in order to show the advantages of plasma treatments. Concerning the plasma process, we have studied the role of the plasma treatment time as well as the nature of the gas treatment (Ar and Ar/O₂). The characterization of the catalysts is in course in order to understand the influence of plasma treatment parameters on catalytic results.

Materials and Methods

The γ-alumina, which was used as a support, was sieved between 200 and 350 μm in order to obtain a homogeneous fluidization, and to avoid the loss of powders in the pumping system. The alumina supported Ag(2.5wt.%) and Pd(0.5wt.%) were prepared by an excess impregnation method. The impregnations were achieved using a solution of AgNO₃ for silver catalyst and Pd(NH₃)₄(NO₂)₂ for the preparation of palladium catalysts. The γ-Al₂O₃ powders were dipped in aqueous solution with the appropriate amount of silver or palladium nitrate. Then, the excess of solution was evaporated at 60°C under reduced pressure. Finally, the catalyst was dried at 120°C overnight, prior to the two different process, i.e. (i) calcination in air at 500°C for 2 h (10°C/min) or (ii) *plasma treatment in the fluidized bed reactor*. The fluidized bed reactor (FBR) consisted of a cylindrical Pyrex glass tube. The impregnated powders were fluidized by an Ar gas or a mixture of Ar/O₂ gas passing through a porous glass plate. Two external electrodes were connected to the radio frequency generator in order to create the plasma in the fluidized bed region. The first catalytic test was performed with a fixed-bed flow reactor by passing a mixture of 500 ppm NO, 2500 ppm C₂H₆O, and 10 vol.% O₂ in high pure Ar over Ag/γ-alumina catalyst (GHSV=190 000 h⁻¹). The second one was done

with a fixed-bed flow reactor by passing a mixture of 150 ppm NO, 9000 ppm CH₄, and 7 vol.% O₂ in high pure Ar over Pd/γ-alumina catalyst (GHSV=40 000 h⁻¹).

Results and discussion

According to our first results, the Ag/Al₂O₃ prepared after a plasma treatment in Ar (30 min) leads to the higher level of NO_x conversion. The conversions obtained after a typical calcination in air follows the same trend but the maximum is obtained at a higher temperature (410°C). Moreover, the C₂H₆O conversion for Ag/Al₂O₃ plasma treated catalyst was shifted to lower temperature in comparison with calcined catalyst. Those results show that the level of oxidation of the catalyst is higher with calcination with respect to plasma treatment. XPS analyses confirmed this point. In order to confirm the positive effect of plasma treatment on NO_x reduction activity, we decided to perform the same type of treatments on another active phase, i.e. alumina supported palladium catalysts. In that case, methane has been used as reducing agent, and the NO_x reduction activity was measured by Selective Catalyst Reduction (SCR). Thus, the NO_x reduction activity of Pd/γ-alumina catalysts measured at various temperatures increased with the reaction temperature and reached a maximum at 400°C for Pd/Al₂O₃ for all different plasma treatments and for the calcined sample. After 400°C, we observed a decrease as observed with the NO_x reduction of Ag/γ-alumina catalysts. Once again, the highest rate of NO_x conversion (37 %) was obtained for a plasma treatment time of 30 min whereas the minimum was obtained for short and long plasma treatment times. These results confirm the previous measurements obtained with Ag/Al₂O₃ catalysts.

Conclusions

We can conclude first that the plasma treatment realized on two catalytic systems (Ag or Pd based catalysts) is reproducible. Moreover, one could see that the treatment of the catalysts in a low fluidized bed plasma reactor leads to higher DeNO_x activity than one with typical calcination (500°C, 2h in air). Physico-chemical characterizations such as UV Vis, XPS and TEM, are in course in order to understand the differences between the plasma-treated catalysts and the calcined ones. Finally, the Radio Frequency generator will be replaced by a microwave source, which presents the advantage to create plasma with higher density of energy.

Significance

Preparations of commercial catalysts use a large amount of noble metal precursors. Moreover, during their preparation high energy is necessary for treatment processes. In order to develop a higher sustainable process, the plasma-assisted catalysts synthesis could be a solution.

References

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