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Photoreduction of carbon dioxide with hydrogen using temperature programmed method

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The photocatalytic reduction of carbon dioxide with hydrogen was studied by Temperature-Programmed Surface Reaction (TPSR). This process was carried out in a flow reactor that was especially designed and constructed for this purpose. Titanium dioxide (TiO_2, Degussa P-25) was used as supports for platinum, ruthenium and nickel catalysts. The experimental results indicated that the activity of photoreduction of CO_2 changes as follows: $Ru/TiO_2 > Ni/TiO_2 >= Pt/TiO_2 > TiO_2$.

Keywords: removal of CO_2, photocatalysis, photocatalytic reduction of CO_2, methanation.

INTRODUCTION

The industrial revolution, agricultural intensification and the continuously improving quality of life have resulted in an impressive rise in carbon dioxide emission in the atmosphere. Therefore, searching for new ways of CO_2 utilization has attracted a lot of interest in recent years. An application of photocatalysis in air and water purification seems to be a very interesting strategy to reduce carbon dioxide.

Photocatalytic processes create a new and efficient method of the elimination of gaseous contaminants occurring in atmospheric air such as greenhouse gases, which are considered a major cause of global warming. These processes due to their specificity (use of catalyst and light radiation) need to apply suitably constructed reactors. Reactors for photocatalytic reactions in liquid medium where a catalyst is in a suspension state are most often described in literature. Photocatalytic processes used in air-purification are performed with the gas flow through the solid catalytic bed. Moreover, using an elevated temperature can improve the efficiency of the process and the temperature-programmed modifications make it possible to study the reaction mechanism and catalytic activity.

Temperature-programmed methods comprise one of the elementary instruments applied to investigate properties of solid catalysts. One of them is temperature-programmed surface reaction (TPSR). The TPSR experiment consists in the reaction between gaseous reactants deposited on the catalytic surface or introduced to the linear heated reactor. The formation of product concentration and changes of substrate concentration are monitored in the function of variable temperatures by an analytical apparatus. The TPSR profiles provide the information about the reaction mechanism and determine the initial and final temperatures of the reaction. These temperatures characterize the activity of the studied catalyst.

The aim of the work was to apply the temperature-programmed methods in the measurements of catalytic activity. The TPSR method was used to compare the properties and activity of the catalysts such as TiO_2, Pt/TiO_2, Ru/TiO_2 i Ni/TiO_2 in the photoreduction of carbon dioxide with hydrogen. The measurements were carried out with the apparatus constructed in our Institute. In literature, there is no information about the photocatalytic process studied in this way.

The elimination of carbon dioxide, apart from its ecological meaning, has a range of applications including the synthesis gas purification for ammonia synthesis.

EXPERIMENTAL

Supported Pt, Ru and Ni (1wt.%) catalysts were investigated in the photoreduction of carbon dioxide with hydrogen. These metals appear to be the most active in methanation of carbon dioxide, whereas Pt/TiO_2 catalysts are generally very active in the photocatalytic reaction[1]. The support used in the experiment was TiO_2, S_{BET} = 50 m^2/g (commercial powder manufactured by Degussa companies). TiO_2 is relatively inexpensive and shows high activity in different photocatalytic processes. TiO_2 surface subsidized by metals show a higher activity.

The catalysts were prepared by the wet impregnation of the support using aqueous solution of H_2PtCl_6, $RuCl_3$ and $Ni(NO_3)_2$. The samples were dried at 100°C for 12 h, calcined in air for 4h and reduced in H_2 at 400°C for 4 h.

In order to determine the degree of the metallic phase dispersion hydrogen and oxygen chemisorption was measured. The method was characterized in details[2]. The measurements were carried out with the use of PEAK4 apparatus constructed in our Institute[3].

Figure 1 shows the construction of the reactor which was used in the studies. The gas gets into the reactor through a pipe and then flows between a quartz cylinder and a tube

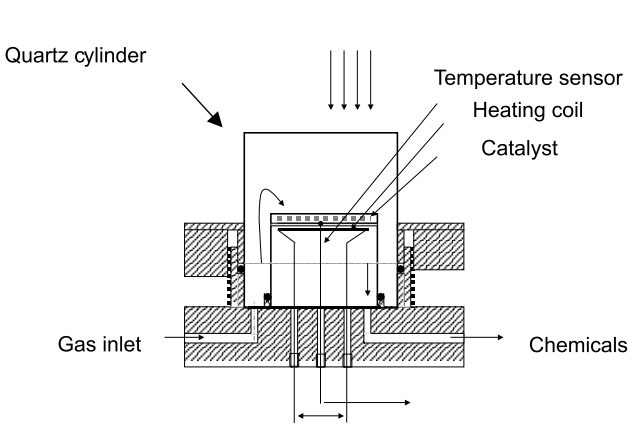

Figure 1. A scheme of using the photoreactor for the TPSR measurements

with a catalytic bed. The tube diameter is 65 mm. The catalytic bed is heated to a proper temperature with the heating coil. After the contact with the catalyst, the gas is analysed. In the reactor the gas flow rate is included in the range of 0 – 200 mil/min and the temperature range is 25 – 500°C. The temperature was measured by K type sensor. The linear increase in temperature with the rate from 0.01 to 10°C/min is carried out with an electronic programmator.

In this experiment 0.8 g of catalyst was used and a constant gas flow rate 30 cm^3/min and a controlled linear temperature growth of 5°/min were applied. The concentration of carbon dioxide was measured by CO_2 analyser with IR detector of Fuji company. The chemicals were analysed by a gas chromatograph with a detector. The type of chromatographic column was carbonex 1004 (Supelco) which measures the length of 1 m. The UV source was a PE 175B-10FM lamp with emission maximum at wavelength of λ = 386 nm. The catalytic activity was characterized by temperature of 30% CO_2 conversion – T_{30}. This temperature was used to measure the impact of UV on the catalytic activity. The bigger the change is, the more strongly UV activates the catalyst.

RESULTS AND DISCUSSION

Table 1 demonstrates the metallic phase dispersion and crystallite size for all the samples. The results were obtained by the hydrogen-oxygen titration method and oxygen adsorption measurement for Pt and Ni, Ru, respectively. The stoichiometry of the interaction between the reagents was 1:1.1 for Ru-O_2 an 1: 1.7 for Ni-O_2 [4]. Dispersion results were used to calculate the crystallite size. For this purpose, the equations presented in this paper were applied[5].

Table 1. Dispersion of the metallic phase

Catalyst	1%Pt/TiO_2	1%Ru/TiO_2	1%Ni/TiO_2
Dispersion	0.18	0.73	0.12
Crystallite size d [nm]	7.7	1.3	10.3

The results show that Ru catalyst has the highest metallic phase dispersion. It is four times higher than for platinum. Fig. 2. demonstrates how the TPSR profile changes for Pt catalyst. On the basis of the results T_{30} i $T_{\Delta 30}$ were determined. These temperatures equal 268°C and 17°C, respectively.

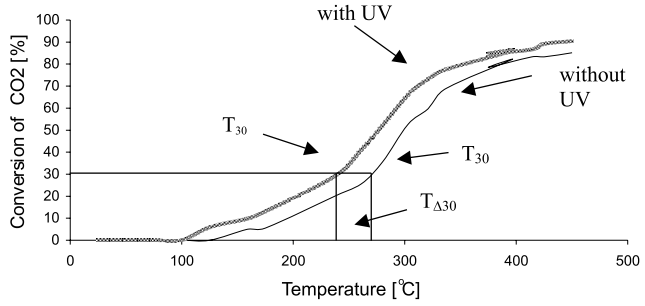

Figure 2. The TPSR profiles of the 1%Pt/TiO_2 catalyst

Table 2 summarizes T_{30} and $T_{\Delta 30}$ for all the catalysts. This clearly presents that TiO_2 shows the worst catalytic behavior in the studied reaction. It is worth noticing that the addition of metal has a promoting effect in the case

Table 2. 30% conversion temperatures for all the catalysts

Catalyst	1%Pt/TiO_2	1%Ru/TiO_2	1%Ni/TiO_2	TiO_2
T_{30} [°C]	268	245	265	380
$T_{\Delta 30}$ [°C]	17	26	5	12

of TiO_2. The activation process of semiconducting oxides with metals to get active catalysts is a well-known effect[6]. The results clearly present that Ru/TiO_2 catalyst has higher activity in the studied reaction. Moreover, UV radiation activates the slightest Ni catalyst although its catalytic activity is bigger than for TiO_2 or Pt catalyst. According to literature, the process of CO_2 reduction runs through a series of stages. At these stages the intermediate products are formed. The identification of these products makes it possible to obtain the information about the reaction mechanism. The analysis of chromatographic data shows that the only products of reaction $CO_2 + H_2$ are methane and water:

$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

The concentration of other products was so low that they cannot be detected by typical analytic methods.

CONCLUSIONS

– Application of the TPSR method in photocatalysis can be a fast and effective method in the studies of catalytic activity,

– It was found that the activity of the studied catalysts in the reduction and photoreduction of CO_2 with hydrogen changes in the following way:

Ru/TiO_2 > Ni/TiO_2 >=Pt/TiO_2> TiO_2

– The presence of UV activates Ni/TiO_2 catalyst to the slightest degree.

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