Metal/activated carbon systems as catalysts of methane decomposition reaction

CrossMark

Małgorzata Szymańska, Anna Malaika, Paulina Rechnia, Aleksandra Miklaszewska, Mieczysław Kozłowski*

Faculty of Chemistry, Adam Mickiewicz University in Poznań, Umultowska 89b, 61-614 Poznań, Poland

ARTICLE INFO

ABSTRACT

Catalytic decomposition of methane (CDM) is an attractive approach to CO_x-free production of hydrogen. This reaction is often performed with the use of metal catalysts, however, their common drawback is a fast deactivation of the metal caused by accumulation of carbonaceous deposit on the catalyst surface. The catalyst stability can be improved by the proper choice of the support of the metallic active phase. In this aspect much attention has been paid to activated carbon (AC) as it can be used in CDM reaction both as a catalyst on its own and as a support of active phase. In this study, thermo-catalytic decomposition of methane with the use of different metals (Pt, Pd, Cr) supported on activated carbon was performed. The active phase support was prepared from ash wood by chemical activation with KOH and the final catalytic systems were obtained by incipient wetness impregnation of support with salts of the above metals. The systems prepared were tested in the methane decomposition reaction carried out at three different temperatures: 750, 850 or 950 °C. The most effective catalysts among the tested ones were Pd/AC systems, whereas Cr supported on AC showed even worse catalytic performance than unloaded activated carbon used as a catalyst.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

It is now clear that the natural resources of fossil fuels will be depleted soon because of the rapid increase in demand for them and their limited reserves in the earth. In this situation hydrogen has raised much attention, especially in the last two decades [1]. However, hydrogen is not a primary energy source and should be produced from other resources. The present commercial production of hydrogen is mainly based on steam reforming and partial oxidation of hydrocarbons and carbonaceous feedstocks, such as natural gas, petroleum fractions and coal [2]. However, these processes produce carbon dioxide which significantly contributes to the global warming. To circumvent this, CO_x-free hydrogen production via catalytic decomposition of methane has been suggested. Since only hydrogen and carbon are formed in the decomposition process, separation of products is not an issue. Another main advantage is the simplicity of the methane decomposition process as compared to conventional methods [3].

It has been shown that effective catalysts of CDM are some metals and carbon materials [4]. A number of metallic catalysts have been studied in this reaction, including Co, Cr, Ni, Fe, Mo, Pt, Pd and Rh [5,6]. It has been reported that the rate of methane decomposition by the transition metals follows the order: Co, Ru, Ni, Rh > Pt, Re, Ir > Pd, Cu, W, Fe, Mo [4]. It has been shown that Raney-type systems are also quite good catalysts for the decomposition of methane into hydrogen and carbon [7–9]. Excellent results were obtained for La_2O_3 doped Ni and Ni-Cu Raney-type catalysts [10]. La_2O_3 was found to be a good promoter for these catalysts.

Metals have been also applied as the active phase supported on the surface of various materials. The effects of using of different kinds of zeolites as supports on the catalytic activity of Ni have been investigated by Inaba et al. [11], who found that Ni supported on USY zeolite showed a longer catalytic lifetime, and considered it to be the best catalyst for hydrogen production by methane decomposition. In another study, methane decomposition at 550 °C over Ni supported on HY, USY, SiO_2 and SBA-15 has been conducted and among all the catalysts tested, the Ni/HY catalyst was found to have the highest activity [12]. Chen et al. [13] have found that the activity order for Fe/Al_2O_3, Co/Al_2O_3 and Ni/Al_2O_3 catalysts is the reverse of that of their melting points and is also the reverse of that of their initial temperatures of deactivation. In the study of Sun et al. [14],

a 70 wt% Ni/Al_2O_3 catalyst was prepared and applied for decomposition of methane. The methane conversion and the hydrogen content in the effluent gas reached 71% and 83%, respectively, at an operating temperature of 700 °C under ambient pressure.

The use of carbon-based catalysts for CO_x-free hydrogen production via catalytic decomposition of methane and other hydrocarbons have been reported recently [3–6,15,16]. The carbon catalysts show several advantages over metal catalysts, such as low cost, easy availability, high thermal stability, resistance to poisoning by sulphur compounds and other substances, etc. Muradov [6,15,17–19] has investigated the reaction over several kinds of carbon including activated carbons, carbon blacks, graphite, diamond, glassy carbon, fullerenes, carbon fibres and carbon nanotubes. Among these, activated carbons and carbon blacks showed reasonable activity and stability at 850 °C. Besides the group of Muradov, many other research groups have been working on decomposition of methane over different carbon materials [20–22]. Also our group has been interested in this subject. We have analysed the problem of carbon catalysts deactivation, which is a consequence of blocking of the active sites of the catalysts by the carbonaceous deposit forming in the reaction. We have tried to reduce the process of catalyst deactivation by adding admixture of ethylene or propylene to methane directed to the reactor [23,24]. It has been shown that these hydrocarbons also form a carbonaceous deposit but in contrast to the methane-originated deposit, the ethylene- or propylene-originated one shows good catalytic properties in the reaction of methane decomposition. Good results have also been obtained when ethylene was generated in situ in the CDM reactor by oxidative coupling of methane [25] or decomposition of ethanol [26]. The catalyst deactivation was also successfully restricted by gasification of methane-originated carbonaceous deposit by carbon dioxide [27].

Only a few papers on methane decomposition over metal/carbon catalysts have been published so far. Interesting results were obtained for carbon nanotubes containing iron or molybdenum particles on their surface [28]. In that study, the conversion of methane increased steadily with temperature and was very close to the thermodynamic value, usually not achieved even using the nickel catalysts. There was also no tendency for catalyst deactivation at high temperature, normally observed in other works. Reshetenko et al. [29] have used nickel supported on catalytic filamentous carbon (CFC) as a catalyst for low-temperature decomposition of methane. The results obtained indicated that CFCs with 10–15% content of nickel show similar catalytic properties as those of Ni/Al_2O_3 catalyst with the nickel content of 90%. The stability and activity of Ni/CFC catalysts depended both on textural properties of the support and on the surface structure of CFC filaments [30]. Ni/CFC catalysts showed high stability in methane decomposition reaction at 550 °C [31] and it was suggested that ~20 nm Ni crystallites were most active in this process [32].

To the best of our knowledge, only three papers have been published about methane decomposition over metal loaded on activated carbon (AC). In the study performed by Bai et al. [33], the Ni/AC catalyst was investigated in a fixed-bed reactor, and the results were compared with those of the methane decomposition over AC alone. It has been found that the Ni/AC catalyst shows higher activity than the original carbon. Unfortunately, the increase in Ni crystal size and formation of the new crystallite Ni_3C during the process led to the deactivation of the catalyst. Prasad et al. have also studied decomposition of methane over Ni/AC catalysts with different loading of nickel [34]. Their studies indicated that the sample with Ni content of 23.3 wt% had the highest catalytic activity among all the catalysts tested and carbon fibres were formed during the activity test. The same scientific team have applied Pd/AC catalysts for decomposition of methane [35] and reported that for

a sample with 10% Pd content the methane conversion of 50 mol% can be obtained. Moreover, carbon nanofibers formation has been revealed by TEM and SEM images.

As follows from the above review, the literature on the use of metals supported on carbons as catalysts in CDM is rather scarce. In view of the above, the main aim of this study was the preparation of catalysts made of metals supported on activated carbon and evaluation of their catalytic performance in the reaction of methane decomposition. In this work, noble metals (platinum and palladium) were tested. For comparison also a base metal (Cr) supported on activated carbon was examined.

2. Experimental

2.1. Preparation of catalysts

Decomposition of methane was conducted in the presence of a carbon catalyst obtained from ash wood biomass (*Fraxinus excelsior* L.). The precursor was ground to the grain size of ≤2.0 mm and then it was chemically activated by KOH at 800 °C for 45 min. The weight ratio of KOH to precursor was equal to 2:1. The product obtained was washed with a 5% HCl aqueous solution, next with distilled water and then dried overnight at 110 °C.

The activated carbon prepared was impregnated with solutions of different salts: $Cr(NO_3)_3 \cdot 9H_2O$, $Pd(acac)_2$ and $Pt(acac)_2$ (the incipient wetness impregnation method was used in this case). In order to obtain metal/activated carbon samples, impregnated materials were subjected to thermal treatment in He flow at 460 °C for 1 h and then reduced in hydrogen flow at the same temperature for 2 h. The content of active phase in the final samples was assumed to be 1%, 5%, 10% or 20%. The samples were labelled according to scheme: amount and type of active phase supported on activated carbon/AC, where AC means the activated carbon prepared from ash wood.

2.2. Characterisation of catalysts

Activated carbon and Me/AC samples were subjected to different analyses including textural characterisation, ICP and XRD analyses, SEM and TEM investigations.

The porous structure of samples obtained was determined by a Micromeritics Sorptometr ASAP 2010 with nitrogen as adsorbate at −196 °C. The apparent specific surface area (S_{BET}) was calculated using the BET equation, whereas t-plot method [36] was applied to calculate the micropore volume (V_{micro}) and "external" (mesopores + macropores) surface area (S_{ext}). The total pore volume (V_{tot}) was obtained from the N_2 amount adsorbed at a relative pressure close to unity. The volume of meso- and macropores was calculated from the difference ($V_{ext} = V_{tot} - V_{micro}$). In order to determine the real content of metal in the sample, all catalysts obtained were analysed by ICP-OES (inductively coupled plasma-optical emission spectrometry) method. Three portions of each sample were first treated with the nitro-hydrochloric acid in a Mars 5 microwave oven (CEM Corporation, USA). The determination of the content of metal in the sample was then carried out using Varian ICP-OES VISTA-MPX apparatus. Powder X-ray diffraction (XRD) measurements of selected samples were carried out using a Bruker AXS D8 Advance apparatus, equipped with Johansson monochromator ($\lambda Cu\ K\alpha_1 = 1.5406$ Å) and silicon strip detector LynxEye. Morphological appearance of the fresh and spent catalysts was studied by scanning electron microscopy (SEM) using a Philips 515 apparatus and transmission electron microscopy (TEM) using TEM JEOL 200 CX apparatus. TEM images were also used to get information about sizes distribution and average size of metal particles supported on activated carbon surface (about 200–900 particles were measured).