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Reforming of CH_4 with CO_2 on Pt-supported catalysts Effect of the support on the catalytic behaviour

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Abstract

This paper reports a study about the behaviour of different Pt-based catalysts supported on Al_2O_3, Na–Al_2O_3, K–Al_2O_3 and ZrO_2 in methane reforming with CO_2. Results indicate that Pt/Na (0.3 wt%)-Al_2O_3 and Pt/ZrO_2 catalysts show both a good activity and selectivity with a very high catalytic stability at 1073 K. The Pt/K (0.3 wt%)-Al_2O_3 catalyst showed a good performance but a slightly lower conversion level than Pt/Na (0.3 wt%)-Al_2O_3. On the other hand, the Pt/Al_2O_3 catalyst displayed an important decrease of the methane conversion through the reaction time at 1073 K and hence, a lower catalytic stability due mainly to the carbon deposition. It can be concluded that either Na or K addition to Pt/Al_2O_3 enhances the catalytic stability since they provide basic sites, which favour the dissociation reaction of CO_2 into CO and O. The O species can react with the carbon deposited on the Pt, thus cleaning the metallic phase of the doped catalysts.

Keywords: Dry reforming; Metallic supported catalysts; Catalytic stability

1. Introduction

The transformation of natural gas into syn-gas or more valuable products has acquired a special importance since the reserves of natural gas in the world are higher than the petroleum ones. Alternative processes such as steam reforming and partial oxidation of methane present several difficulties due to both the high operation and equipment costs. In consequence, the study of the methane reforming with CO_2 appears as an important alternative way to obtain syn-gas.

In spite of the initial difficulties, the study of the methane reforming with CO_2 has been progressively increased. A very important driving force to develop new technologies and catalysts is derived from the potential application of this process for the preservation of the environment, since CO_2 plays an important role in the greenhouse effect. In this sense, the development of this process could contribute to the diminution of CO_2 emissions to levels close to those established in the Kyoto Protocol [1]. Furthermore, a comparative cost study about the production of acetic acid using three processes (steam reforming, partial oxidation and CH_4 reforming with CO_2) was reported in the literature and showed that the operative cost of the methane reforming with CO_2 is lower than those of the other two processes [2]. Hence, this process seems to be a promising route from an economic point of view and also appears to be an adequate tool for the environmental protection.

From the above comments, it can be inferred that it is necessary to develop new technologies for the capture and re-use of the blown CO_2. The use of CO_2 by means of proper technologies would contribute not only to the reduction of its emissions but also would introduce additional economic benefits derived from the aggregated value of the chemical products which can be obtained from CO_2. On this basis, important efforts are being done in order to develop new catalysts with high activity and selectivity and good stability in the syn-gas production by using methane reforming with CO_2 [3]. It is worth noticing that the methane reforming with

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CO_2 produces a syn-gas with a H_2/CO molar ratio close to 1, but this process has not industrial application yet [4].

The main challenge for the industrial application of the methane reforming with CO_2 is related to the development of active catalytic materials but with very low coke formation rate either on the catalysts or in the cold zones of the reactor. The carbon formation in this process can be controlled by using a support that favours the dissociation reaction of CO_2 into CO and O, the last species being the responsible for the cleaning of the metallic surface [5].

Results obtained by using supported Ni catalysts showed very high deactivation rates compared with catalysts based on noble metals [6]. Taking into account these findings, it can be inferred the promising behaviour of noble metals in this reaction [7,8]. In fact, Rostrup-Nielsen and Hansen [9] studied the behaviour of Ni, Ru, Rh, Pd, Ir and Pt supported on MgO in the reforming of methane with CO_2 process. They found that Ru/MgO and Rh/MgO exhibited both good activity and selectivity, and a very low coke deposition. Seshan et al. [10] tested several catalytic formulations containing Ni or Pt supported on γ-Al_2O_3 and ZrO_2, and they found that Pt/ZrO_2 was a very stable catalyst during the operation in contrast with Pt/Al_2O_3 and those based on Ni. Bitter et al. [8] studied the effect of the support (Al_2O_3, ZrO_2, TiO_2 and SiO_2) on Pt-based catalysts and they found that the use of an adequate support can also increase the activity of Pt. Besides, Tsipouriari et al. [11] using Rh deposited on TiO_2, γ-Al_2O_3, MgO, SiO_2, CeO_2 and ZrO_2 stabilized with Y_2O_3, observed a strong influence of the support on the specific activity and on its deactivation during the reaction.

It was reported in the literature that the behaviour of supported metallic catalysts in the methane reforming with CO_2 depends on several interrelated factors such as the nature of the metal, the support type, the metallic particle size and the characteristics of the metal–support interface [7,8,11–13].

Taking into account that there is no literature related to the use of alkali metal-doped alumina as a support of noble metals for the reaction of methane reforming with CO_2, this paper reports an study of the catalytic performance of Pt/Na-Al_2O_3 and Pt/K-Al_2O_3 catalysts with different alkali metal contents at different reaction temperatures (823–1073 K). Besides, the behavior of these catalysts was compared with that of Pt/Al_2O_3 and Pt/ZrO_2 in experiments at high temperature (1073 K) and long reaction times. Catalysts were characterized by test reaction of the metallic phase (cyclohexane dehydrogenation), temperature programmed reduction (TPR) and temperature programmed oxidation (TPO), in order to obtain a relationship between the structure of catalysts and the catalytic performance (activity, selectivity and stability).

2. Experimental

Four supports were used for the preparation of the metallic catalysts: (i) a commercial γ-Al_2O_3 (CK 300 from Cyanamid Ketjen), (ii) γ-Al_2O_3 (CK 300) doped with two different Na amounts (0.3 and 1 wt%), (iii) γ-Al_2O_3 doped with 0.3 and 0.5 wt% K and (iv) ZrO_2 (0404 T from Engelhard). The doping of γ-Al_2O_3 (previously calcined at 1073 K) with Na and K was carried out by impregnation of the support with aqueous solutions of NaOH and KOH, respectively. The amounts of the alkali metals in the impregnating solutions were such as to obtain the desired loadings. After the deposition of the alkali metal, samples were dried at 393 K for 24 h and then calcined at 1073 K for 4 h. The metallic supported catalysts were prepared by impregnation of the supports with an aqueous solution of H_2PtCl_6. The impregnating volume/weight support ratio was 1.4 ml g^{-1}, and the concentration of Pt in the impregnating solution was such as to obtain the desired Pt loading (1 wt%). The impregnation time was 6 h, and then the samples were dried at 393 K for 24 h.

In order to study the influence of the thermal treatments on the surface area of ZrO_2, Al_2O_3 and the alkali metal-doped Al_2O_3, two different He treatments were carried out on these supports: one of them at 923 K and the other one at 1073 K, both during 8 h. The measurements of the surface area were performed in a Micromeritics ASAP 2000 with N_2 at 77 K.

The effect of the previous thermal treatments in flowing He (for 4 h) on the catalytic activity in cyclohexane dehydrogenation was studied at two temperatures of the He treatment: 923 and 1073 K. Cyclohexane dehydrogenation reaction was carried out in a differential flow reactor. Prior to the reaction, samples were reduced "in situ" with H_2 at 773 K. The H_2/hydrocarbon molar ratio was 26 and the reaction temperature was 573 K.

The different catalysts were tested in the methane reforming with CO_2. The reaction was carried out in a flow equipment. The samples (0.17 g) were first reduced under flowing H_2 at 823 K for 3 h. Then, the catalysts were heated under He up to the reaction temperature (between 823 and 1073 K). After the catalysts reached the reaction temperature, the CH_4/CO_2 mixture (CH_4/CO_2 molar ratio = 1) was fed to the reactor with a flowing rate of 20 ml min^{-1}. In order to avoid diffusional effects, catalyst particle sizes were very small (<80 mesh). The reaction time was 285 min. The reaction products were analyzed by using an on-line chromatographic system (GC–TCD) containing a Supelco Carboxen 1006 PLOT (30 m × 0.53 mm) column. In order to study the catalytic stability, additional experiments were performed during longer reaction times (5800 min) at 1073 K.

TPR measurements were carried out by using a H_2 (5% v/v)–N_2 reductive mixture with a heating rate of 6 K min^{-1}. The temperature was increased from room temperature up to 850 K. Prior to the experiments, samples were calcined in flowing air at 773 K for 3 h.

Temperature programmed oxidation measurements were carried out in an apparatus with an intermediate methanation device coupled with a flame ionization detector (FID).