

Effect of potassium content in the activity of K-promoted Ni/Al₂O₃ catalysts for the dry reforming of methane

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Abstract

In this paper the effect of the potassium content in the structure and properties of the Ni active phase and in the activity and selectivity of the NiK/Al₂O₃ catalysts for dry reforming of methane has been studied. The following characterization techniques were used: SEM, TEM, temperature programmed reduction (TPR-H₂) and reaction (TPR-CH₄), temperature programmed oxidation (TPO) and XAFS. The reforming of methane with CO₂ was carried out at 973 K using 0.18 g of catalyst and a mixture CH₄:CO₂ (50:50, 60 ml/min, space velocity of 22,500 h⁻¹). Catalytic tests for 6 and 24 h have been developed. TPR-H₂ and XAFS results reveal that potassium does not modify the arrangement of Ni atoms although facilitates the reduction of nickel species by H₂ due to the modification of the interaction between metallic species and the alumina support. The activity data indicate that the addition of a low amount of potassium (0.2 wt.% K₂O) allows to obtain a catalyst with an acceptably high activity (over 63% methane conversion, close to thermodynamic equilibrium) and very low coke deposition (below 30 mg C/g cat. during 6 h reaction). Independently of the amount of potassium, the catalytic activity remains almost constant during at least 24 h.

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1. Introduction

The dry reforming of methane allows the conversion of two undesirable greenhouse gases into synthesis gas with a low H₂/CO ratio, adequate for hydroformylation and carbonylation reactions as well as for both methanol and Fischer–Tropsch synthesis [1,2]:



That is, this reforming reaction has an economical and environmental interests because it allows the conversion of two greenhouse gases (CH₄ and CO₂) into a valuable feedstock. Furthermore, considering the reaction stoichiometry (CH₄/CO₂ = 1), it is specially convenient for gases coming from sources where similar amounts of CO₂ and CH₄ are present as, for example, biogas or some high CO₂ content gas natural streams.

The reforming of methane with CO₂ is accompanied by some side reactions that determine the selectivity of the process:



These competitive reactions modify the CO₂ and CH₄ equilibrium conversion: reaction (2) increases the CO₂ conversion and the yield of CO, reaction (3) decreases the CO₂ conversion and the yield of CO and, finally, reaction (4) increases the methane conversion and the yield of H₂. The last two reactions are, also, responsible for coke formation during reaction.

It is well known that supported metals of groups 8, 9 and 10 are good catalysts for the dry reforming of methane (reaction (1)) [2–10]. Among those metals, Ni is specially interesting for industrial application due, mainly, to its lower cost and higher availability. Thus, Ni based catalysts are under investigation in order to improve both their activity and, particularly, their selectivity with the objective of avoiding

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or, at least hindering, coke formation. As variables of such investigation, the following are attracting most of the attention: the nature of the support [11–17], the preparation method [13,18–21] and the addition of promoters [12,19,22–32]. In relation with the last variable, it can be mentioned that interesting points are the nature of the promoter, being K one the most investigated [13,29–32], and the amount used, generally considered as promoter/Ni ratio.

In a previous paper, we have reported the characterization and catalytic performance of Ni/Al₂O₃ and NiK/Al₂O₃ (K/Ni = 0.7) catalysts in the dry reforming of methane [3]. A very positive effect of potassium in decreasing coke deposition was observed, and the XAFS analysis of the catalysts allowed to conclude that potassium species behave, mainly, as an independent catalyst for the gasification of the deposited coke. Further research on this topic, subject of the present work, deals with the analysis of the effect of the potassium content both in the structure and properties of the Ni active phase and in the activity and selectivity of the catalyst for dry reforming of methane. It must be also mentioned that compared to the previous work [3], and in order to use reaction conditions closer to those in real systems (biogas), an undiluted CO₂:CH₄ (1:1) gaseous mixture has been used.

2. Experimental

2.1. Catalysts preparation

A γ -Al₂O₃ (supplied by Across, $S_{\text{BET}} = 90 \text{ m}^2/\text{g}$) was used as catalysts support. It was first impregnated, by using excess-solution impregnation method, with a KNO₃ aqueous solution of the required concentration to obtain different potassium contents, from 0.2 to 5 wt.% K₂O. After solvent removal (by an air flow at 298 K), the catalysts were dried overnight at 373 K and calcined in air at 773 K for 2 h. Ni was also introduced by excess-solution impregnation, using an aqueous solution of Ni(NO₃)₂·6H₂O of the appropriate concentration to obtain a 10 wt.% (nominal) nickel content, followed by drying overnight at 373 K.

2.2. Catalysts characterization

Nickel and potassium content was determined by atomic absorption spectroscopy (AAS). The metals were extracted from the catalyst by a reflux treatment with diluted HCl for 8 h.

The morphology of the catalysts and of the coke deposited during reforming reaction were analyzed by scanning electron microscopy using a Hitachi S-3000N equipment. Transmission electron microscopy (JEOL JEM-2010) was used to estimate the size of Ni particles in used catalysts.

Temperature programmed reduction (TPR-H₂) was performed in an automatic equipment (PulseChemisorb 2705, Micromeritics) with a thermal conductivity detector. The fresh catalyst (50mg) was submitted to a heat treatment (10 K/min up to 1173 K) in a gas flow (60 ml/min) of the mixture H₂:N₂ (5:95). Previous to the TPR experiments, the samples were heat treated under inert atmosphere, at 673 K for 2 h, to produce the

decomposition of nickel nitrate, which would lead a strong interference in the TCD analysis of H₂.

Temperature programmed reaction with methane (TPR-CH₄) was performed in quartz reactor (0.4 cm of diameter) using a mass spectrometer (Balzers Thermostar) for the product analysis. The fresh catalyst was submitted to a heat treatment (10 K/min up to 1173 K) in a gas flow (60 ml/min) of the mixture CH₄:He (5000 ppm of CH₄).

XAFS measurements were performed at the BL-7C, BL-9 and BL1B101 stations of the Photon Factory in the National Laboratory for High Energy Physics (KEK-PF) in Tsukuba, Japan. A Si (1 1 1) double crystal was used to monochromatize the X-ray beam from the 2.5 GeV electron storage ring. The NiK-edge absorption spectra were recorded in the transmission mode at room temperature, in a range of photon energy extending from 8080 to 9375 eV. A Fourier transform was done on the k^3 -weighted EXAFS oscillations over the range of 3–12 Å⁻¹ (FT-EXAFS). XAFS measurements were done on the catalysts after a reduction treatment (pure H₂, 973 K, 2 h) and after reaction (973 K, 6 h). After these treatments, the catalysts were transferred without exposure to air to a glovebox where they were vacuum packed.

The used catalysts were submitted to temperature programmed oxidation (TPO) experiments to determine the amount of carbon deposited on the catalysts. These experiments were carried out in a thermobalance (TA SDT-2960) coupled to a mass spectrometer (Balzers Thermostar) under the following conditions: 20 mg of catalyst were submitted to a heat treatment (20 K/min up to 1223 K) with a gas mixture of 16 vol.% O₂ in He (100 ml/min). To determine the amount of carbon deposited on the catalysts, $m/z = 44$ and $m/z = 28$ signals and the weight loss were simultaneously recorded.

2.3. Catalytic activity tests

The reforming of methane with CO₂ was carried out at 973 K using 0.18 g of catalyst and a gas mixture CH₄:CO₂ (50:50, 60 ml/min, space velocity of 22,500 h⁻¹). Catalytic tests were carried out for 6 and 24 h. The equipment used consisted basically of a quartz tube fixed-bed reactor coupled to gas chromatograph (HP5890 series II) with a thermal conductivity detector.

Note that the catalysts have not been reduced before reaction because previous results [33] showed that this treatment does not modify the catalytic activity.

3. Results and discussion

3.1. Characterization of catalysts

Table 1 shows the K and Ni content of the different catalysts prepared. Ni loading ranges from around 5 to 9 wt.%, approximately, and K loading (as K₂O) from 0.18 to 5 wt.%. To describe the composition of the different catalysts, the K/Ni atomic ratio has been used.

Fig. 1 shows the TPR-H₂ curves of some catalysts: Ni/Al₂O₃, NiK/Al₂O₃-3, NiK/Al₂O₃-6 y NiK/Al₂O₃-8 (nomen-

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