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Preparation and characterization of Pd–Ni bimetallic catalysts for CO and C_3H_6 oxidation under stoichiometric conditions

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ABSTRACT

Ni additive in the three-way catalyst (TWC) has been known for its high activity in H_2S suppression. However, the effect of Ni on the activity of TWC in stoichiometric exhaust gas conversion is less studied. In the present work characterization of bimetallic Pd–Ni catalysts supported on γ-Al_2O_3 or γ-Al_2O_3–La_2O_3 for potential TWC application was performed. The catalysts were prepared by wet co-impregnation and impregnation-evaporation methods. Brunauer–Emmett–Teller (BET), X-ray diffraction (XRD), temperature-programmed reduction (TPR), UV–vis diffuse reflectance spectrometry (UV–vis DRS), scanning electron microscopy (SEM), and scanning transmission electron microscopy (STEM) techniques were employed to confirm the effect of Ni addition on the catalysts structure. XRD, TPR, and STEM characterization was employed in order to evaluate the presence of Pd–Ni interaction. The activity of the catalysts was tested in the oxidation reaction of CO and C_3H_6 under stoichiometric conditions. Based on the obtained results, we confirmed the structure of prepared catalysts and the effect of Pd–Ni interaction on the catalytic activity of Pd–Ni catalysts in CO and C_3H_6 oxidation. XRD and TPR characterization suggested that Pd and Ni are competing for the support sites. The observed competition affected Pd-support and Ni-support interactions and consequently activity. Fresh bimetallic catalysts had higher catalytic activity compared to monometallic ones due to higher active metal loading and the presence of NiO phase. It was concluded that the catalytic activity of aged bimetallic catalysts is not affected by the addition of Ni. For that reason, addition of Ni as a second metal to Pd-based catalysts for TWC reactions can be considered in the future studies.

1. Introduction

Improvement of the air quality has been a hot research topic for the past few decades. One of the factors affecting the quality of the air is pollution of air with exhaust gases. Carbon monoxide, short hydrocarbons, and nitrogen oxides are the main pollutants produced by the vehicles running on conventional petroleum fuels. To reduce production of the toxic gases, electric engines and biofuels appeared as an alternative to commonly used petroleum fuels. Nevertheless, the number of vehicles running on petroleum fuels increases continuously. For that reason, development of catalysts for exhaust gas conversion still remains to be an important research topic.

For the reduction of exhaust gas emissions in the gasoline fueled engines, a three-way catalytic converter (TWC) has been developed. The operational principle of the TWC is simultaneous conversion of CO, C_xH_y, and NO_x pollutants. The highest conversion of exhaust gases can be achieved when TWC operates in air-fuel ratio close to stoichiometric value [1,2]. In general, commercial catalytic converters contain an active component deposited on the high surface area support, and promoters for better performance and longer life-time [1,3–7]. Platinum, palladium, and rhodium are commonly used metals in the catalytic conversion of exhaust gases [8–11]. Aluminum oxide, cerium oxide, zirconium oxide, and their combinations are well-known support materials for the noble metal catalysts [12–14]. CeO_2–ZrO_2 mixed oxides are frequently added as oxygen storage promoters, and Ba or La oxides as the promoters for thermal stability of the support [15–20].

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Nowadays the tendency in development of catalysts for the exhaust gas conversion is directed toward the search of active and relatively inexpensive materials. Modern catalysts are expected to possess higher activity during a cold start and better long term stability. In particular, palladium has appeared to be a common choice of catalyst for those reactions. Such a choice is due to its high activity in the low-temperature oxidation reactions and lower price compared with other noble metals [21–25]. However, the rising price of palladium and the deactivation of palladium catalysts during the long term work increase the demand in improvements of the existent catalysts. One possible solution of increasing the catalyst life-time is the modification of existing catalysts by addition of a second metal. Commonly, the second metal is chosen from groups 9–11 in the periodic table [26–29]. Among those metals, nickel has been proven to affect catalytic activity for exhaust gas treatment, while having comparably lower price than noble metals [27,30,31].

Ni has been widely employed as a sulfur scavenger in TWC due to its high activity in H_2S removal [32,33]. A possible concern in Ni addition to the TWC system may arise due to potential danger of Ni-carbonyl formation. Nonetheless, if Ni-containing TWC is installed in the closed-coupled position near the car engine, the operational temperature of the converter is clearly higher than the decomposition temperature of Ni-carbonyl. Considering comparably low amount of Ni in catalysts and the presence of other active metals capable of binding CO, the possibility of Ni-carbonyl formation is very low. Therefore, application of Ni as a second metal for additional TWC reactions can be considered for converters in the closed-coupled position. Prior to evaluating the role of Ni as a second metal, the effect of Ni on the activity of initial catalyst should be examined. It is important to verify that Ni addition will not deteriorate initial catalyst activity.

Beside the application of Ni as a sulfur scavenger a few studies have been conducted on the bimetallic Pd–Ni automotive exhaust catalysts operating under the stoichiometric conditions [26,27,30,31,34]. Bimetallic catalysts have been prepared with total metal loading of 2 wt.%. Catalytic activities of Pd–Ni/Al_2O_3 catalysts in stoichiometric CO and NO elimination have been unaffected by the presence of Ni [31]. Improved catalytic activity in CO oxidation has been obtained on Pd–Ni catalysts supported on alumina modified with Ce–Zr mixed oxide. It has been concluded that the presence of Ni enhanced the interaction of Pd and Ce–Zr mixed oxide, resulting in a better catalyst performance [27,31,34]. Nonetheless, no improvement on the catalytic activity has been detected on the aged Pd–Ni catalysts [27].

Although Pd and Ni belong to the same group in the periodic table, they were found to behave differently on the alumina support surface. Palladium is dispersed over the support in the form of PdO_x and tends to aggregate when exposed to high temperatures [35]. On the other hand, high temperatures improve interaction between nickel and alumina support leading to the formation of spinel-like $NiAl_2O_4$ structure [36,37]. Therefore, it could be expected that co-addition of Pd and Ni would result in the formation of separate phases of PdO_x deposited on the support and of $NiAl_2O_4$ spinel. Nevertheless, the presence of Pd–Ni interaction has been detected on the bimetallic Pd–Ni catalysts with the total metal loading above 7 wt.% [38,39]. Bimetallic Pd–Ni catalysts have been found to have a superior catalytic activity than corresponding monometallic catalysts [40–42]. The improved catalytic activity has been explained by an interaction between Pd and Ni and increase in the metal surface area [39,40]. The discovered Pd–Ni interaction improved the reducibility of both Ni and Pd metals leading to a higher catalytic activity. For that reason, the determination of the nature of Pd–Ni interaction as well as factors affecting it could help to further improve the catalytic activity of Pd–Ni catalysts.

The aim of the present study is to examine the effect of the nickel addition on the activity and stability of Pd based catalyst in CO and C_3H_6 oxidation reactions under stoichiometric conditions. Multiple factors affecting Pd–Ni interaction will be considered. For the bimetallic catalysts preparation two Pd precursors (Pd nitrate and acetylacetonate) and two supports (γ-Al_2O_3 and Al_2O_3–La_2O_3) will be used. Furthermore, influence of the concentration of Ni and calcination temperature on the catalysts structure will be examined.

2. Experimental

2.1. Catalyst preparation

A set of bimetallic Pd–Ni catalysts was prepared by the wet impregnation method. $Pd(acac)_2$ or $Pd(NO_3)_2$ in HNO_3 water solution (18.12 wt.% Pd) were chosen as an active metal source. Nickel was introduced in a form of $Ni(NO_3)_2{\cdot}6H_2O$ precursor. Palladium loading was adjusted to 3 wt.% for each of the catalysts and Pd:Ni ratio was 1:0, 1:1 or 1:3 wt.%. γ-Al_2O_3 (Sasol, particle size distribution <25 μm 37.8%, <45 μm 64.4%, and <90 μm 92.0%) or γ-Al_2O_3 promoted with La_2O_3 (3 wt.% La_2O_3, particle size distribution <25 μm 36.4%, <45 μm 64.4%, and <90 μm 98.6%) were employed as a support material. Propionic acid (Fluka, p.a.) was used as the impregnation solvent for $Pd(acac)_2$ precursor, while HNO_3 water solution was used for $Pd(NO_3)_2$. Pd and Ni nitrate precursors were deposited simultaneously on the support by co-impregnation method, while $Pd(acac)_2$ and $Ni(NO_3)_2{\cdot}6H_2O$ precursors were deposited by impregnation-evaporation method. Precursors were mixed with a support under continuous stirring at room temperature for 24 h, followed by evaporation of the solvent at 145 °C for 10 h. Calcination was carried out in air at 550 °C for 2 h, the resulting catalysts were denoted as fresh. A portion of each fresh catalyst was aged in air at 900 °C for 4 h. The preparation procedure of both the co-impregnation and the impregnation–evaporation methods was exactly the same. The difference in the method name arises from the physical properties of Ni nitrate precursor, which is insoluble in organic acids. However, its melting point is below the solvent evaporation temperature ($T = 145\,^\circ C$). Therefore, $Pd(acac)_2$ precursor was dissolved in propionic acid and deposited to the support by impregnation. The deposition of co-added $Ni(NO_3)_2{\cdot}6H_2O$ precursor occurred during drying step by evaporation. For studies of the effect of nickel on the γ-Al_2O_3 support, monometallic 3 and 9 wt.% Ni catalysts were prepared by wet impregnation and evaporation methods. Drying, calcination and aging steps were carried out under the same conditions as described above. Reference NiO sample was prepared by calcining $Ni(NO_3)_2{\cdot}6H_2O$ precursor in oven at 550 °C for 2 h. Formation of NiO phase was confirmed by powder X-ray diffraction analysis.

The catalysts prepared for the experiments are denoted as A-Ni*x*, A-Ni*x*-La, N-Ni*x* and N-Ni*x*-La, Table 1. Where A refer to $Pd(acac)_2$ and N to $Pd(NO_3)_2$ precursor. La refers to γ-Al_2O_3 promoted with La_2O_3 and x is the loading of Ni in catalyst. Reference Ni/Al_2O_3 samples were denoted as *y*Ni-P and *y*Ni-W, where *y* is the Ni weight loading, P stands for propionic acid and W for water impregnation solvent. Further, catalysts containing 3 wt.% of Ni will be referred as low Ni content and catalysts with 9 wt.% of Ni as high Ni content catalysts.

2.2. Catalyst characterization

The specific surface areas of the catalysts were measured by the Brunauer–Emmett–Teller method (BET) with a Micromeritics ASAP 2010 device. Prior to the experiment, a portion of each catalyst (220 mg) was pretreated under vacuum at 350 °C for 3 h. The measurements were carried out at the temperature of liquid nitrogen using nitrogen gas as an adsorbate. Each catalyst was tested three times.