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# Study of the properties of supported Pd catalysts for steam and autothermal reforming of methane

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## ARTICLE INFO

## ABSTRACT

The effect of support kind on the structure, surface properties and catalytic behavior of Pd catalysts supported on alumina and mixed $La_2O_3$–$Al_2O_3$ oxides, prepared by impregnation and sol–gel method was studied. It was found that the catalytic performances of Pd catalysts in steam reforming (SR) and autothermal reforming (ATR) of methane were significantly affected by the kind of support. The highest specific reaction rate and $TOFs_{CH_4}$ of La-containing Pd catalysts in SRM were related to the electronic interaction between Pd and modified alumina support surface with La oxide species and formation of $Pd^0[Pd^{\delta+}O_xLa]$ like species, promoting the $CH_4$ activation and carbon oxidation. Despite the filamentous carbon formation these catalysts exhibited the highest activity and stability in ATR caused by the presence of small Pd particles with average particle size of about 14–17 nm. It was shown that the wide particle size distribution up to 70 nm and the formation of encapsulated carbon species are responsible for the fast deactivation of non-La promoted Pd/Al catalyst.

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## 1. Introduction

Hydrogen is a widely used feedstock in the chemical, food, and refining industries. The demand for hydrogen is expected to drastically increase, because of its potential as a major energy source in the near future [1]. Hydrogen is a clean, efficient and pollution-free energy source. Therefore, much attention has been paid to hydrogen production technology in order to obtain a stable source of hydrogen.

Methane reforming is currently a well-established technology and has been the most important industrial process for the production of hydrogen and/or synthesis gas. The major reforming processes include steam reforming (SR), partial oxidation reforming (POX), catalytic partial oxidation (CPO), and autothermal reforming (ATR). Steam reforming of methane (SRM) is the common industrial process for production of hydrogen and synthesis gas, since it has the advantage of relatively low reaction temperature and high hydrogen content in the reforming products. Recently, there is a great renewal interest in the SRM process because of its potential application in the fuel cells [2]. However, steam reforming is highly endothermic and therefore demands an efficient heat supply to the system.

Catalytic partial oxidation releases energy despite of a lower $H_2/CO$ ratio and coke production. However, the catalytic autothermal reforming has received much attention in research during the recent years, because it requires less energy to produce the same amount of hydrogen. ATR is a chemical combination of steam reforming and partial oxidation and it is an economical process, since the partial oxidation reaction supplies all the heat needed to drive the catalytic steam reforming. However, the oxidation reactions are much faster than the reforming reaction and heat is usually generated at the entrance of reactor. A high thermal resistance of catalysts is required in the entrance of the bed region.

Nickel catalysts supported on γ-alumina is traditionally used for methane reforming reactions due to their low cost. However, these catalysts suffer deactivation, generally because of coke formation. Many efforts have been dedicated to development of Ni catalysts with a high resistance to cooking to achieve stable long-term operation [1,3–7].

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Supported Pd catalysts can exhibit higher activity and stability in methane reforming reactions compare to that of Ni catalysts due to the higher resistance to carbon deposition [8,9]. Recently, Yamaguchi and Iglesia [10] evaluating the effects of reactants ($H_2O$ and $CO_2$) and product concentrations on turnover rates in the steam and dry reforming of $CH_4$ reactions, showed that the C—H bond activation steps are much larger on Pd than on other metals, like Ni, Ru, Rh, Ir, Pt. According to the authors, the high reactivity of Pd surface in C—H bond activation reflects their strong binding for C and H and the concomitant stabilization of the transition state for kinetically relevant C—H activation steps. This causes the observed kinetic inhibition by chemisorbed carbon species formed in $CH_4$ and CO dissociation steps. The authors suggested that the turnover rates are similar on Pd clusters on various supports ($Al_2O_3$, $ZrO_2$, $ZrO_2$–$La_2O_3$) and independent of Pd dispersion over the narrow range accessible at reforming conditions.

Comparing the catalytic performance of alumina-supported Rh, Pt, and Pd catalysts in autothermal reforming of $CH_4$, it was found [11] that the $Pd/Al_2O_3$ catalyst showed a higher activity compared to the other metals at the entrance of the catalyst bed. However, this catalyst showed some deactivation over the catalytic bed due to the agglomeration of active phase.

Last decade, in our group much attention has been concentrated on supported noble metal catalysts, which showed high activity and stability in different methane reforming processes, depending on the support kind. Catalytic performance of supported metallic catalysts is affected by several factors such as the nature of support, the introduction of modifiers as well as the implementation of new methodologies to synthesis of supports and catalysts. To improve the catalytic activity and resistance to coking, modification of supports and various preparation methods, such as sol–gel method and impregnation method, have been proposed for reforming catalysts and for their supports [12–15]. Pt catalysts supported on mixed $CeO_2$–$La_2O_3$–$Al_2O_3$ oxides, prepared by sol–gel method, showed a high activity and cooking resistance in SRM caused by the high oxygen mobility at metal–support interface [16,17]. Improved activity and stability in partial oxidation of methane was observed for $Sm_2O_3$-doped $Pt/CeO_2$–$Al_2O_3$ catalysts [18] due to the high metallic Pt dispersion, reducibility and oxygen storage capacity of support. In situ X-ray absorption study of $Rh/Al_2O_3$ catalyst promoted with $Sm_2O_3$ and $CeO_2$ [14] showed that the structure of Rh particles in SRM was stable in the presence of $Sm_2O_3$–$CeO_2$, while the strong Rh agglomeration of un-promoted catalyst causes a deactivation. It was shown that the activity of $xCeO_2$–$Al_2O_3$-supported Pd and $xLa_2O_3$–$Al_2O_3$-supported Pt catalysts in SRM depends on $CeO_2$ and $La_2O_3$ loading, respectively [19,20]. The catalysts with higher $CeO_2$ ($La_2O_3$) loading $\geq 12$ wt.% exhibited higher activity attributed to the metal–support interface causing the increase of oxygen transfer from the support to noble metal surface and removal of carbon deposits. The high activity and stability of $Pd/CeO_2$–$Al_2O_3$ catalysts in ATR of methane was attributed to the formation of $Pd^0[CePd_xO]$ species with a high ability to promote the coke gasification [19].

Materials obtained by sol–gel method have a high surface area, high porosity and high thermal stability. It is well known that similar to $CeO_2$, the addition of $La_2O_3$ [21,22] to alumina structure can promote the stabilization of γ-alumina phase that retard the agglomeration and the loss of surface area at high temperatures. On the other hand, the sol–gel method for preparation of supports and supported metal catalysts has been useful for a large number of industrial applications.

Considering the above mentioned aspects the present study is a continuation of previously our studies of supported noble metal catalysts for methane reforming processes. The work is related to: (*i*) preparation of alumina and mixed $La_2O_3$–$Al_2O_3$ oxides by sol–gel and impregnation method; (*ii*) study the effect of the support kind on the structure and surface properties of supported Pd catalysts; (*iii*) relation between the catalyst structure and the activity and stability in the steam and autothermal reforming of methane, respectively. A combination of different techniques were applied for physicochemical characterization of the samples: $N_2$ adsorption–desorption measurement, X-ray diffraction (XRD), thermogravimetric (TG) and differential thermal analysis (DTA), X-ray photoelectron spectroscopy (XPS), UV–vis diffuse reflectance spectroscopy (UV–vis DRS), Fourier transform infrared spectroscopy (FTIR) of CO adsorption and transmission electron microscopy (TEM).

## 2. Experimental

### 2.1. Sample preparation

Two kinds of carriers for supported Pd catalysts are used in this study. (*i*) Commercial γ-$Al_2O_3$ (Stream Chem. Inc.) (Al) was impregnated with an aqueous solution of $La(NO_3)_2 \cdot H_2O$. The obtained solid was dried and calcined at 373 and 773 K for 12 h and 4 h, respectively. The obtained material $La_2O_3$–$Al_2O_3$ was abbreviated as LaAl. (*ii*) γ-$Al_2O_3$ and $La_2O_3$–$Al_2O_3$ supports were prepared by sol–gel (SG) method at room temperature. In a round bottom flask containing alcooxide aluminum 2-butanol was added (molar ratio aluminum-tri-sec-butoxide($Al(OC_4H_9)_3$)/2-butanol = 0.5). After 0.5 h of stirring deionized water was added (molar ratio $H_2O$/alcooxide = 14). After 2 h of stirring glacial acetic acid was added and again stirred for 24 h. For preparation of the mixed $La_2O_3$–$Al_2O_3$ oxide by sol–gel method a solution of $La(NO_3)_3 \cdot 6H_2O$ (99.9%, Aldrich) dissolved in 26 ml of deionized water was used. The obtained xerogels were dried in air at room temperature for 48 h. The samples were calcined under synthetic air flow of 120 ml/min, heating from room temperature to 1123 K at 10 K/min and kept at that temperature for 4 h. The supports prepared by sol–gel method were denoted as Al–SG and LaAl-SG.

Pd catalysts supported on the above mentioned materials were obtained by impregnation of the carriers with an aqueous solution of $Pd(NO_3)_2$ (Umicore). The mixture was stirred at room temperature for 3 h in a rotavapor and kept at 313 K for 1 h. The solids were dried overnight at 373 K under synthetic air. After that, the samples were subjected to a thermal treatment, heating from room temperature to 773 K at 3 K/min, using synthetic air flow of 120 ml/min, and held at 773 K for 3 h. Pd catalysts supported on commercial Al, LaAl, Al-SG and LaAl-SG carriers were abbreviated as Pd/Al, Pd/LaAl, Pd/Al-SG and Pd/LaAl-SG, respectively. The nominal content of Pd and $La_2O_3$ in all samples was 1 and 12 wt.%, respectively.

### 2.2. Sample characterization

Surface area ($S_{BET}$), pore volume ($V_p$) of the supports and Pd catalysts were measured by $N_2$ adsorption–desorption isotherms at 77 K using a Quantachrome Nova 1200 equipment. The samples were degassed at 473 K under vacuum for 2 h. The $S_{BET}$ and average pore size diameter ($D_{pore}$) were determined by the BET and BJH methods, respectively.

TG and DTA of the supports prepared by sol–gel method as well as of the spent supported Pd catalysts in ATR were obtained using a TA Micromeritics 2050 TGA instrument. The samples were heated from room temperature up to 1273 K (10 K/min) under a flow of synthetic air of 100 ml/min.

XRD patterns of the samples were collected with a Rigaku Multiflex diffractometer using Cu Kα radiation. The step-scans were taken over the range of 2θ from 5° to 80° with step-size of 0.02° and counting time of 10 s. The apparent crystallite size of xerogels was determined by Scherrer's equation using the (0 2 0) reflection of boehmite.