Pt Supported Catalysts for Steam Reforming Reaction

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Three platinum catalysts on different types of support (Al₂O₃, CeO₂ and SBA-15) were prepared and characterized by X-ray Diffraction in order to obtain valuable information about their structure. The XRD measurements proved the amorphous hexagonal structure of the silica supports SBA-15 and the cubic fluorite structure of CeO₂. For a complete characterization of Pt/CeO₂ catalyst, we added the results for N₂ adsorption/desorption isotherms, X-ray Photoelectron Spectroscopy (XPS) and Thermo-gravimetric analyses (TGA). All these catalysts were characterized in order to obtain complete and correct data about their physical and structural properties in order to use them in the steam reforming process.

Keywords: Platinum, Ceria, catalyst, steam reforming

The use of alcohols has been identified as a promising route for hydrogen production with high yields. Ethanol especially can be easily produced in renewable form, from several biomass sources, and does not contribute to the global warming, releasing the same amount of carbon dioxide as that absorbed by the biomass.

Production of hydrogen by steam reforming of ethanol has been performed over time by using different catalytic systems. The most effective process for hydrogen production from ethanol is this steam reforming reaction:

\[ \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + 2\text{CO}_2 \]

For this reaction Co [1,2], Ni [3] or Rh [4] based catalysts exhibited high activities. In addition for this type of process, Pt based catalysts are mentioned in several studies so far. Pt-Ni/Al₂O₃ [5] was used for ethanol steam reforming in the temperature range of 673-823 K. This type of catalyst is resistant to coke deposition and the temperature of 773 K was considered the optimum reaction temperature. At this temperature the hydrogen production is being accompanied by low carbon monoxide and methane production rates.

The oxidative reforming of ethanol over Pt catalysts supported on Al₂O₃ modified with Ce and La was studied by Navarro et al. [6]. Based on the results, the authors suggested that the catalytic behaviour of supported Pt catalysts in the reaction is strongly promoted by the presence of Cerium atoms in the support.

In addition, de Lima et al. used directly CeO₂, ZrO₂ and CeZrO₂ as supports for Pt catalysts in order to obtain hydrogen but also for the study of the influence of support nature and metal dispersion on the performance of the catalyst [7]. They concluded that the support nature significantly affects the product distribution. On Pt/CeO₂ and Pt/CeZrO₂ they obtained more hydrogen and carbon monoxide whereas on Pt/ZrO₂ more acetaldehyde and ethylene.

Finally Ahmed et al. [8] makes a review on this type of process suggesting that among the active metals used, Ni is found to be a suitable choice in terms of the activity. Cu is the most commonly used promoter, Rh also exhibits good catalytic activity, but it less preferred from economic reasons. The impregnation method is favoured in preparation of the catalyst due to its simplicity. As support γ-Al₂O₃ is preferred by many researchers because of its ability to withstand reaction conditions. Mixed oxide-supported metal catalysts are promising subjects for future research, in order to obtain an efficient catalytic system for steam reforming, able to ensure high conversion of ethanol and hydrogen yield.

Preparing a catalyst in the optimum form and studying its precise composition and shape it is an important challenge for each researcher.

Owing to its excellent thermal and mechanical stability and its rich chemistry, Al₂O₃ is the most widely used support in catalysis. Aluminium oxide, commonly known as alumina, possesses strong ionic interatomic bonds making it useful in different applications. It can exist in several crystalline phases which all revert to the most stable hexagonal alpha phase at elevated temperatures.

Ceria can be used as co-catalyst in a number of reactions, including the water-gas shift reaction and steam reforming of ethanol or diesel fuel into hydrogen gas and carbon dioxide (with varying combinations of rhodium oxide, iron oxide, cobalt oxide, nickel oxide, platinum and gold), the Fischer-Tropsch reaction and selective oxidation. Due to its fluorite structure, the oxygen atoms in a ceria crystal are all in a plane with one another, allowing for rapid diffusion as a function of the number of oxygen vacancies. As the number of vacancies increases, the mobility of oxygen around the crystal increases, allowing the ceria to reduce or oxidize molecules on its surface.

In addition mesoporous molecular sieves may play a key role in the organization of metallic particles due to their controlled pore size, pore volume, and high surface area. SBA-15 material was synthesized by Zhao et al. in 1998 using amphiphilic triblock copolymers to manage the organization of silica species under strong acid conditions. This material is a well ordered hexagonal mesoporous silica structure with uniform pore size, which can be modified from 50 to 300 Å by the use of different triblock copolymers or by adding organic molecules as cosolvent [9].

Characterization of this material represents an important issue in catalysis. X-ray diffraction is one of the oldest and most frequently applied techniques for catalyst characterization. It is used to identify crystalline phases inside catalysts by means of lattice structural parameters, and to obtain an indication of particle size. In this case of catalyst characterization, diffraction patterns are mainly used to identify the crystallographic phases that are present in the catalyst.

The limitation of XRD method is that the clear diffraction peaks are only observed when the sample possesses

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of Pluronic P123 triblock copolymer (EO20PO70EO20) and 1.5 following procedure \cite{11}: Typically, a mixture made of 2g template. The synthesis was carried out by using the impregnation process respectively PtCl2 was purchased from Fluka.

The strength of XRD for catalyst characterization gives clear and unequivocal structure information on particles that are sufficiently large, along with an estimation of their size and can reveal this information under reaction conditions. The limitation of XRD is that it cannot detect particles that are either too small or amorphous. Hence, one can never be sure that there are no other phases present than the ones detected with XRD \cite{10}.

In this study, three types of Pt supported catalyst were synthesized and characterized using the XRD techniques in order to use these catalysts further for ethanol steam reforming.

**Experimental part**

**Raw material**

Poly-(ethyleneglycol)-block-poly(propylene glycol)-block-poly-(ethyleneglycol) (EO\textsubscript{20}PO\textsubscript{70}EO\textsubscript{20}, Pluronic P\textsubscript{123}), 1, 3, 5-trimethylbenzene (TMB) and tetraethyl ortho-silicate (TEOS) were purchased from Sigma Aldrich. The hydrochloric acid (conc. 37.0 wt %) and potassium chloride were provided by Carl Roth and the metallic precursor for sulphuration that play a role in the activation of catalysts. The limitation of XRD is that it cannot detect particles that are sufficiently large, along with an estimation of their size and can reveal this information under reaction conditions. The limitation of XRD is that it cannot detect particles that are either too small or amorphous. Hence, one can never be sure that there are no other phases present than the ones detected with XRD \cite{10}.

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**Catalysts Preparation**

As support we used commercial Al\textsubscript{2}O\textsubscript{3} and CeO\textsubscript{2} (Aldrich) and SBA-15 which was prepared using Pluronic \textsubscript{123} as a template. The synthesis was carried out by using the following procedure \cite{11}: Typically, a mixture made of 2g of Pluronic P\textsubscript{123} triblock copolymer (EO\textsubscript{20}PO\textsubscript{70}EO\textsubscript{20}) and 1.5 g of potassium chloride (KCl) is dispersed in 60 g of deionized water and acid hydrochloric (HCl ~37%). A clear solution was obtained after a vigorous stirring for several hours indicating a complete dissolution of the triblock copolymer. Then, 1.5 g of 1,3,5-trimethylbenzene (TMB) was added under stirring for 10 h. Finally, 4.3 g of tetraethyl orthosilicate (TEOS) were slowly added. The gel was kept in a oven for 24 h at 35°C, followed by heating at 100°C for 24 h in a stainless steel microreactor. The solid product was separated by filtration, washed with 100 mL of deionized water several times and dried at 60°C. In order to remove the organic template, the solid product was calcinated by heating from room temperature to 540°C, the temperature was kept constant for 10 h, followed by cooling of the solid product from 540°C to room temperature. The resulted product SBA-15 was a fine white powder.

Supported catalysts were prepared by pore volume impregnation method using aqueous solutions of chloridric acid. The resulting mixture was added over a known amount of support under continuous stirring for a uniform distribution in the support pores. The impregnated samples were dried at 373 K for 48 h.

**Catalysts Characterization**

It was essential, for this type of catalysts, to detail the results obtained by XRD techniques. For a complete characterization of a catalyst it is necessary to use a series of different modern analyses like: N\textsubscript{2} adsorption/desorption isotherms, X-ray Photoelectron Spectroscopy (XPS) and Termogravimetric analyses (TGA) techniques. Because the results of Pt/Al\textsubscript{2}O\textsubscript{3} and Pt/SBA-15 catalysts characterized by N\textsubscript{2} adsorption/desorption isotherms, X-ray Photoelectron Spectroscopy (XPS) and Thermo-gravimetric analyses (TGA) were already presented in a previous paper \cite{12}, in this paper we will add the results obtained with these techniques for Pt/CeO\textsubscript{2} catalyst.

Consequently the XRD measurements were carried out using a Bruker D8 Advance, X-ray diffractometer with Cu Kα radiation (λ\textsubscript{Cu} = 1.5406Å) operating at a voltage of 40 kV and a current of 40 mA. This is a versatile, sensitive, and high resolution X-ray powder diffractometer. The monochromatic Cu Kα line is isolated by the Vario monochromater at the X-Ray tube.

The peaks from 39.62, 45.52 and 67.010° are attributed to γ-Al2O3.

**Results and discussions**

**X-ray diffraction of catalytic supports**

Figure 1 presents XRD patterns of alumina support. The catalyst sample exhibited the typical pattern for alumina. The peaks from 39.62, 45.52 and 67.01° are attributed to γ-Al2O3.

The crystalline structure of the CeO2 was confirmed by XRD (figure 2) with the characteristic diffractogram of the fluorite structure showing the main peaks at 28.8, 33.7°, 46.0 and 54.8°. Therefore, all of the peaks presented in fig. 2 can be well indexed to (111), (200), (220), (311), (222), (400), (331) and (420) phases, attributed to a face centered cubic fluorite structure. Similar results were obtained previously in the literature \cite{13}. No other impurities of the hexagonal structure of Ce(OH)\textsubscript{2}, or Ce(OH)CO\textsubscript{3} were detected. Previous studies mentioned that Ce (III) oxidation state is unstable as compared with the Ce (IV) in the presence of air. Finally the most intensive diffraction peak located at 28.8° corresponding to plane (111) of centered cubic CeO2.
For the mesoporous materials, the reflection peaks appear at low angle range, where 2\(\theta\) value is less than 10\(^\circ\) on the diffraction spectrum and these peaks are characteristic for mesopores materials.

The XRD pattern of the SBA-15 shows the characteristics of a two-dimensional hexagonal structure, where each pore is further surrounded by six pores. Consequently these results were validated by the well-ordered hexagonal array structure of the mesoporous support SBA-15.

**X-ray diffraction of synthesized Pt catalysts**

The XRD patterns for Pt/Al\(_2\)O\(_3\) catalyst is presented in figure 4.

It was observed that the diffraction peaks of Pt/Al\(_2\)O\(_3\) catalyst were the same as those of alumina support. Pt particles seem to be fairly small and hidden in the main peaks of alumina structure. It is worth mentioned that in many cases the characteristic peak position of Pt is overlapped with that of \(\gamma\) Al\(_2\)O\(_3\), so, the peak definition for Pt is rather difficult. In our synthesized Pt/Al\(_2\)O\(_3\) catalyst it was observed a small peak at 32.15\(^\circ\) which was identified as platinum oxide (Pt\(_2\)O).

In the case of Pt/CeO\(_2\), no peaks of the platinum oxides (PtO or PtO\(_2\)) were observed in the XRD patterns of all samples since the main peaks of PtO\(_2\) (27.9\(^\circ\)) and PtO (33.9\(^\circ\)) are quite close to two peaks of CeO\(_2\) (28.8 and 33.7\(^\circ\)) and probably are shielded by them.

In the case of Pt/SBA-15 catalyst the position of the prominent peak has not been modified suggesting that by impregnation of Pt the specific structure of SBA-15 was not altered.

An interesting feature of the presented XRD patterns (fig. 7) is the broad reflection centred at 2\(\theta\) = 23\(^\circ\) that was assigned to amorphous SiO\(_2\). This reflection is considerably sharper for the Pt/SBA-15, sample, which might be related to changes in the ordering towards further consolidation of the silica framework.
Beside the characteristic XRD patterns of the support materials, the XRD reflections of large Pt particles for the catalyst were also observed at 39.8 and 46.2° which can be attributed to (1 1 1) and (2 0 0) interplanar spacings of the cubic Pt metal structure, respectively.

Characterization of Pt/CeO₂ using other techniques

The surface area and porosity of the Pt/CeO₂ catalyst as in the case of the other two (Pt/Al₂O₃ and Pt/SBA-15) was investigated by means of Brunauer–Emmett–Teller (BET) analysis and nitrogen adsorption and desorption isotherm. The Pt (2.0wt%)/CeO₂ catalyst shows typical type II of isotherms and type B hysteresis loops, which closed at p/p₀ of 0.20, as shown in (fig. 8). The BET surface area of the Pt/CeO₂ catalyst was 5.48 m²/g. Note that Pt catalysts supported on SBA-15 (BET surface area 240.4 m²/g) possessed pore both mesopores and micropores and alumina (BET surface area 320.1 m²/g) were found to possess pores in the range of mesopores. For Pt/SBA-15 catalyst the N₂ adsorption/desorption isotherms is type IV with a H₁ hysteresis loops according to IUPAC classification, indicating that there are mesopores in all samples with cylindrical structure and for Pt/Al₂O₃ catalyst the isotherm is type IV with this time a H₂ desorption hysteresis loop.

The XPS investigation was conducted to explore the distribution of the elements on the surface and the variations of the oxidation states of platinum. Core levels of C₁s, O₁s and Ce₃d can be identified as 284.58 eV, 528.6 eV and 897.83 eV values of binding energy. From the Ce₃d core level peak in the XPS spectra it is clear that the cerium exists as the Ce (IV) oxidation state (897.83 eV).

After deconvolution the spectrum of Pt can be fitted by the overlapping curves associating to the two doublets of spin orbital connection at 4f⁵ and 4f⁷ respectively, as mentioned before in the case of Pt/SBA-15 catalyst.

The regional spectra were deconvoluted into sets of spin orbital doublets. Depending on the oxidation state of noble metal there are two (fig. 9) sets of noble metal peaks. In the case of Pt/CeO₂ catalyst, Pt 4f⁷/2 peak at 73.87 eV suggests the presence of Pt²⁺ and Pt 4f⁵/2 peak at 77.07 eV the presence of Pt⁴⁺. The intensity of the corresponding metallic platinum peak of Pt 4f⁷ is almost 47.9% and for Pt 4f⁵ is 52.1% of the total Pt 4f spectra in the sample.

We mention that in the case of Pt/Al₂O₃ catalyst we chose to analysed the Pt 4d lines instead of Pt 4f because of the overshadowed of Pt 4f with Al 2p.

As we have already presented in our previous paper [12], TGA analysis was performed in order to determine whether the calcination temperature for the sample are convenient and for the observation of phase transitions respectively. Weight loss under inert medium which was observed in TGA plots was attributed to the desorption of volatile fraction (e.g. water).

During the heating ramp the weight of Pt/CeO₂ shows very small change with temperature.

The weight loss in the higher temperature region is due to the removal of the last molecules of carbonaceous species. It has been shown in the literature [14] that a higher temperature is required for the oxidation of carbon on ceria.

Figure 10 shows the TGA spectra of Pt/CeO₂ catalyst. The first weight loss is observed at 165.10°C, which can be connected to the removal of physically adsorbed water; the final weight loss is observed at 356.92°C, which corresponds to the removal of carbon species. The overall weight loss would correspond to the sum of oxidation of carbonaceous species and oxidation of the reduced cerium and platinum.

For the Pt/Al₂O₃ catalyst, the losses correspond to the removal of the whole organic solvent, bulk water and physisorbed water and in principal, to the removal of structural water from the support. In the case of Pt/SBA-15 catalyst the TGA measurements were performed to determine the minimum temperature required for removal of the surfactant. The lowest weight loss was observed for Pt/CeO₂ catalyst.
Conclusions
All of the catalyst samples prepared by impregnation were successfully characterized by X-ray diffraction and different other technique (XPS, N2 isotherms, TGA) especially used for Pt/CeO$_2$ catalyst. Obviously, these catalysts were characterized by a range of solid state techniques to obtain information on their physical and structural properties in order to use them in steam reforming process.

XRD powder diffraction patterns of the catalysts were measured to analyze the crystalline structure of the supports and to assess the distribution of platinum metal in the catalysts. The method of nitrogen physisorption explores the porosity of the material. The XPS investigation was conducted to analyse the ratio of the elements on the surface and the oxidation states of platinum. By thermogravimetric analyses we calculated the weight losses, rate of the weight loss due to drying or to the decomposition of the catalyst sample when the temperature is changing.

Regardless of the type of catalyst used for the ethanol steam reforming reaction, the achievement of high stability and high catalytic activity are the main targets to attain.

As before mentioned in the literature, the CeO$_2$ supported on Pt catalyst is more active, selective and stable than Pt supported on Al$_2$O$_3$ in the range of 300–450°C. Under several reaction conditions Al$_2$O$_3$ is not able to promote the desorption of the secondary reaction products. As a consequence, its surface is poisoned and the ethanol decomposition process is impeded, leading to a marked decline in H$_2$ production. Future work on catalyst development will focus on using these catalysts under different reaction parameters in steam reforming reaction in order to evaluate their catalytic activity and to establish the optimum catalytic formula for this type of process.

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