Effect of the preparation methods and alumina nanoparticles on the catalytic performance of Rh/Zr$_x$Ce$_{1-x}$O$_2$–Al$_2$O$_3$ in methane partial oxidation

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ARTICLE INFO

ABSTRACT

Rh supported on Zr$_x$Ce$_{1-x}$O$_2$–Al$_2$O$_3$ ($x = 1, 0.5, 0.25, 0$) catalysts are studied for catalytic partial oxidation of methane to synthesis gas. Alumina based nanocomposites are prepared through a citrate mediated route by modifying the alumina support with cerium and zirconyl nitrates via a simple evaporation-drying or a spray drying method. The effect of the commercial alumina types and the preparation method on the structure and thermostability of the nanocomposites has been studied based on the characterization by XRD, Raman spectroscopy, DTA, TEM and nitrogen adsorption–desorption measurements. Evonik Aeroxide AluC based nanocomposites prepared by spray drying give the highest thermostability concerning the sintering and phase transformation of the composites. Rh with a 0.1 or 0.5 wt.% loading is deposited on these nanocomposites by incipient wetness impregnation method. After calcination at 1173 K for 5 h, these nanocomposites supported Rh catalysts are tested in the fixed-bed reactor for methane partial oxidation. It is found that the smaller c-CeO$_2$ crystal size in the nanocomposites, i.e. the higher oxygen vacancy concentration, would be responsible of the lower ignition temperature due to the enhanced reducibility, whereas the higher Rh dispersion would be responsible of the higher methane conversion and selectivity to synthesis gas. Additionally the Rh dispersion is found to be linked to the BET surface area. The stability of the nanocomposites is also studied under reaction conditions.

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1. Introduction

Catalytic partial oxidation of methane (CPO) is an attractive route for the production of synthesis gas compared to the conventional steam methane reforming process (SMR). It gives a favorable H$_2$/CO (about 2) ratio of the produced synthesis gas, which is appropriate for processes such as methanol or Fischer–Tropsch synthesis [1]. In addition, CPO can be operated in a millisecond contact-time reactor, being able to provide a compact hydrogen processor for its use in fuel cell electric vehicles [2]. Various transition metals such as Ni [3,4], Co [5], Ru [6], Pt [7], Ir [8] and Rh [9] are found active for this reaction. Among them, Rh based catalysts are presented as the most promising materials due to a better catalytic performance with higher activity, selectivity towards H$_2$ and CO, and a good stability [10].

The catalytic partial oxidation of methane to synthesis gas is thermodynamically favored at elevated temperatures to obtain a higher conversion and selectivity to H$_2$ and CO [1]. The mechanism has been frequently studied in the literature [1,4,11–14]. The discussion has mainly focused in the occur-rence of the direct or the indirect routes. In the direct route H$_2$ and CO are the primary reaction products [12,13] whereas in the indirect one CO$_2$ and H$_2$O are initially produced by complete oxidation. Afterwards the reforming reaction and water gas shift (WGS) take place to produce syngas [11,14]. However, even though the direct route is theoretically possible, the contribution of the reforming and WGS is typically observed [15–17].

According to the indirect mechanism, the oxygen in the reactant can be rapidly consumed in this period by the deep oxidation of methane, followed by the highly endothermic steam reforming reaction [18]. Although a mild exothermicity appears if the direct conversion of methane to synthesis gas is performed, the deep oxidation of methane is found to be unavoidable in the inlet region of the reactor, even in the short-contact-time reactor [14,18,19]. The high reaction temperature together with the deep oxidation of methane will lead to a very high temperature in the catalyst bodies, especially in the inlet of the reactor, i.e. hot spots. It is well known that the presence of hot spots may also influence the stability of the catalyst and the safety of the process. Controlling the temperature profiles in the reactor is a key issue for the CPO process, which can be reached by effectively removing the produced heat. For this reaction system, metallic foams or monolith supported catalysts are employed to enhance the heat transfer by increasing the heat conductivity of catalyst support. On the other hand, the

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produced heat by combustion of methane can be consumed by the followed steam reforming reaction. Enhancing the steam reforming reaction rate can substantially reduce the temperature increase, thus making the temperature profile controllable. Wei and Iglesia [20] have pointed out that the rate of steam reforming reaction is linearly correlated with the dispersion of metallic phase. Increasing the Rh dispersion is expected to enhance the steam reforming reaction. However, the preparation of high-temperature stable Rh nanoparticles is challenging due to extreme operating conditions in the CPO. Therefore, developing a catalyst support suitable for stabilizing the Rh nanoparticles is highly interesting. Additionally, lower loading of Rh can significantly reduce the cost of the catalyst.

Although alumina is a very stable material for most oxidation reactions [21], the formation of its thermodynamically stable α-phase is observed when the temperature is increased to 1173 K or higher [21]. Such phase transformations are often accompanied with a gradual decrease in the surface area, simultaneously presenting poor mechanical properties. If the transition alumina is used as a catalyst support for high temperature reactions such as the CPO process, this gradual phase transformation will lead to the possible encapsulation of the metallic phase [22,23]. The poor mechanical properties of α-Al_2O_3 gives a higher cracking possibility as a coating layer in the monolith reactors, especially in the temperature changes such as the ignition and extinction periods [24]. Directly using α-Al_2O_3 may avoid the loss of the active phase and reduce the risk for cracking. However, the stabilization of metal nanoparticles on α-Al_2O_3 is difficult owing to its low surface area and inert surface. Therefore, developing a catalyst support aiming at obtaining high dispersed Rh nanoparticles on it in a high temperature system such as the CPO process is highly interesting.

Attempts to increase the stability of the transition alumina have been reported during the last decade [25–28]. It has been proved that the introduction of an extra phase into the parent material enhances the stability of the support [29–31]. $Zr_xCe_{1-x}O_2$–Al_2O_3 nanocomposites have been studied mainly focusing in its application towards the so-called Three Way Catalysts (TWC) [25,32–34]. Afterwards, the research has been also expanded to reactions such as methane partial oxidation [27,35,36], CO_2 reforming [37], ethanol steam reforming [38,39] or other systems [40–44]. The influence of several variables on the properties of the final product has been investigated for this system. Researchers have focused on the nature of the cerium, zirconium precursor [45], the preparation method [27,28,46,47], the Ce/Zr ratio [36], the mixed oxide–alumina ratio [23,48] or the thermal treatment effect [49]. However, to our knowledge, the nature of the alumina itself has not been yet considered. γ-Al_2O_3 can be prepared from different precursors such as $Al(NO_3)_3$ $9H_2O$ [48,50] and $Al(OC_4H_9)_3$ [29], or provided by different producers [42,44,51]. The physico-chemical properties of these Al_2O_3 powders are strongly dependent on the preparation method and the subsequent treatments. Therefore, a suitable method to combining the alumina type and doped oxide precursors are also highly crucial.

In this article, we report the influence of two commercial alumina samples and two preparation methods on the structure and thermal stability of 5 wt.% $Zr_xCe_{1-x}O_2$–Al_2O_3 nanocomposites. The evolution of the physico-chemical properties of these nanocomposites during high temperature treatments in static air is systematically studied based on the various characterization techniques. The produced composites are used as catalyst support to deposit the Rh metallic phase by impregnation. The catalytic performance of these Rh supported on $Zr_xCe_{1-x}O_2$–Al_2O_3 nanocomposites for the CPO process is evaluated in a quartz fixed-bed. The ignition and extinction behavior and the stability of these catalysts for CPO are as well studied.

2. Experimental

2.1. Catalyst preparation

Two different alumina samples are used in this contribution: Evonik Aeroxide AluC and Sasol Puralox SCCa are denoted as AluC and Puralox, respectively. AluC is an alumina powder produced by flame hydrolysis [52]. It has a crystalline structure consisting of the metastable γ- and δ-forms instead of the stable α-form. The primary particle size is in the range of 13 nm and a specific surface area around 100 m^2/g. At temperatures above 1473 K, it can be transformed to α-form [52]. Puralox is a widely employed material in the catalyst industry. The specific surface area for uncalcined Puralox powders is around 170 m^2/g with a crystalline structure of γ-phase.

$Zr_xCe_{1-x}O_2$ (5 wt.%)–Al_2O_3 nanocomposites are prepared as follows. It should be noticed that $Zr_xCe_{1-x}O_2$ is used to express the chemical composition, not for a solid solution. A certain amount of zirconyl nitrate ($ZrO(NO_3)_3$ xH_2O, 37.5 wt.% ZrO_2) cerium nitrate ($Ce(NO_3)_3$ $6H_2O$) and citric acid ($C_6H_8O_7$) are dissolved into deionized water followed by adding polyethylene glycol (0.1 g/mL_{H_2O}) to form a complex solution. Then, the weighed alumina powder is gradually added into the above complex solution under vigorous stirring to produce a suspension. A detailed study on the preparation method has been reported elsewhere [53]. Two drying procedures have been followed for obtaining the nanocomposites:

2.1.1. Evaporation-drying method
The water in the former suspension is evaporated at 358 K for 2 days to form a dried solid. Both AluC and Puralox have been used for the preparation of such nanocomposites. AluC powders prepared employing this procedure are identified as AluCev.

2.1.2. Spray drying
Using a Lab-Plant SD-06 Laboratory Scale Spray Dryer, the suspension is entrained into a chamber by the heated gases through a nozzle. The obtained powders are collected in a bottle. The pump rate is 120 mL/h, the inlet temperature 438 K and the air flow 4.3 m/s. Only AluC-based materials are prepared by this method due to the large size of the Puralox powder. The materials prepared in this way will be identified like AluCsp.

The final powdered composites are produced after these dried solids are treated in air at different temperatures (from 1173 to 1473 K) for 5 h. For the sake of comparison, $Zr_xCe_{1-x}O_2$ is also prepared by a similar procedure without including the Al_2O_3 powder. For the preparation of the Rh catalysts, rhodium nitrate is deposited on the calcined $Zr_xCe_{1-x}O_2$–Al_2O_3 support by the incipient wetness impregnation at room temperature. The prepared catalyst is kept at room temperature overnight. Subsequently, the formed solid is calcined at 1173 K for 5 h.

2.2. Catalyst characterization

2.2.1. X-ray diffraction (XRD)
X-ray diffraction (XRD) patterns of these composites are recorded at room temperature on a Bruker AXS D8 Focus diffractometer using CuKα radiation (λ = 1.54 Å). The X-ray tube voltage is set to 40 kV and the current to 50 mA. XRD patterns are collected in the range of 2θ from 20° to 85° for nanocomposites, (0.01°/step, integration time of 1 s/step) and 2θ from 27° to 32° for $Zr_xCe_{1-x}O_2$ phase (0.02°/step, integration time of 10 s/step). Diffractograms are analyzed by employing the Topas program applying the Rietveld fitting [54] to estimate the alumina phase composition and applying the Pawley method [55] to calculate the crystal size of $Zr_xCe_{1-x}O_2$ and Al_2O_3 in these composites.