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Short Communication

Application of rhodium nanoparticles for steam reforming of propane in microchannels

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ABSTRACT

Rhodium nanoparticles were synthesized by means of the chemical reduction method and applied as precursor for the preparation of Rh/Al_2O_3 catalysts with different Rh content (1, 2.5 and 5 wt.%). High surface area alumina powder was impregnated with the nanoparticle solution. After drying and calcination, the catalyst powder was deposited in microchannels by means of a washcoating process and after repeated drying and calcination tested for steam reforming of propane. All catalysts showed full conversion at the reaction conditions applied ($T = 750$ °C, $S/C = 4$, $WHSV = 120\ Nl/(h{\cdot}g_{cat})$) including during mid-term tests of 140 h uninterrupted testing.

1. Introduction

The synthesis of noble metal nanoparticles for applications in catalysis has attracted immense attention due to their high surface-to-volume ratio [1–3]. By applying nanoparticles instead of metal salt impregnation large fractions of the metal atoms are exposed at the surface of the catalyst carrier pores and are consequently accessible to reactant molecules and available for catalysis. Among various methods, e.g. photochemical reduction or thermal decomposition, chemical reduction of metal ions using a polymer, e.g. PVP (poly(N-vinyl-2-pyrrolidone)) as a reagent preventing the growth process is one of the promising ways to prepare small noble metal particles [4–7].

For our studies, rhodium was selected as noble metal due to its important role in heterogeneous catalysis. A major application of rhodium is in three-way catalytic converters in automobiles because of its high activity and inertness against corrosion and aggressive chemicals [8]. Furthermore rhodium is often applied in the field of reactions dealing with energy generation via fuel cell technology [9], especially for steam reforming reactions of fuels. Propane is such a fuel with high potential as a hydrogen carrier due to its easy storage and existing infrastructure.

Therefore numerous papers dealing with steam reforming of propane are known [10–15]. Those applying rhodium based catalysts include the work of Schädel, Aartun and Li. Schädel et al. [16] applied a commercial rhodium-based catalyst from Umicore AG & Co. KG (Hanau, Germany) that was deposited on cordierite honeycomb monoliths. Further details concerning the catalyst composition and catalyst preparation were not provided. Aartun et al. [17] applied Rh-impregnated alumina foams and metallic microchannel monoliths made of Fecralloy for oxidative steam reforming. These monoliths were first oxidized in air at 1000 °C to form a thin alumina surface layer and were then impregnated with an aqueous solution of $RhCl_3$. Li et al. [18] improved the performance of a 2 wt. % Rh/Al_2O_3 catalyst by adding Ni or Ce, but they applied an aqueous $Rh(NO_3)_3$ solution.

However these catalysts are prepared in a different route compared to what is reported here.

In this paper, we present a route for preparing various Rh/Al_2O_3 catalysts with different Rh content (1, 2.5 and 5 wt.%) by applying rhodium nanoparticle solutions as precursor. This could be an effective method to improve the catalytic performance of rhodium catalysts by increasing their specific surface area. This would allow for the reduction of the rhodium content of the catalyst and consequent costs. Due to the costs and the availability, rhodium is currently not widely used in industrial applications although it is a more effective catalyst in terms of activity and stability, compared to nickel. The reduction of the rhodium content could improve the commercial applicability.

In order to evaluate the prepared catalysts, they were tested for their performance in the steam reforming of propane. The mid-term stability of the prepared catalysts, an aspect which is frequently not considered, was also evaluated.

2. Experimental

2.1. Preparation of the rhodium nanoparticle catalyst

The rhodium nanoparticles were formed by the chemical reduction method similar to the method described by T. Ashida et al [6]. The

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nanoparticles were synthesized by the reduction of rhodium chloride hydrate ($RhCl_3{\ast}H_2O$) in an ethanol-water solvent mixture together with the water-soluble polymer of PVP. The growth of the nanoparticles during reduction will be limited by the space restrictions imposed by the three-dimensional PVP network. Thus, the size of the nanoparticles can be controlled by changing the molecular weight of PVP and/or the water/ethanol ratio [19]. For our tests and for the purposes of this communication we focused on one kind of PVP and one ethanol-water ratio.

10 mmol PVP ((K-90, MW: 360,000, SIGMA ALDRICH) was dissolved in a water-ethanol mixture (315 ml ethanol & 35 ml deionized water). Afterwards 0.5 mmol rhodium chloride hydrate (ALFA AESAR) was added to the solution and the mixture was refluxed at 353 K for 3 h. After ca. 30 min the colour of the solution changed to dark brown thus indicating the formation of the rhodium nanoparticles. The volume of the nanoparticle solution was then reduced to about 30 ml by means of a rotary evaporator and the achieved solution was applied as an impregnating precursor for the catalysts with different rhodium content. In order to achieve catalysts with 1, 2.5 and 5 wt.% rhodium, the calculated amount of alumina (Puralox SBa-200, SASOL) was impregnated with the prepared nanoparticle solution. After the addition of the impregnating solution, the mixture was manually stirred for 2 min and after relaxing for 3 h, the mixture was calcined at 450 °C for 6 h in air.

2.2. Catalyst deposition

For the deposition of the catalyst within microchannels, an aqueous suspension containing the catalyst powder was prepared. First poly (vinyl alcohol) (PVA) as a binder was dissolved in deionized water under stirring at 65 °C for 3 h. Afterwards the catalyst powder (10 wt.%) and a small amount of acetic acid was added and the mixture was stirred again for 3 h at 65 °C. The typical components of such a suspension are binder:water:catalyst:acetic acid in the following ratios 5: 84:10:1. Stirring at room temperature was continued for 2 to 3 days until a homogeneous suspension was achieved. The microchannels were then completely filled with the as-prepared suspension and excess suspension was removed by means of a sharp blade. After drying at room temperature the coating was calcined for 6 h at 450 °C in air, again. This method was applied for the catalyst powders prepared via impregnation with nanoparticle solutions as well as for the commercial catalyst powder.

2.3. Catalyst characterisation

2.3.1. Specific surface area & XRF

The specific surface area was determined by nitrogen sorption using a Sorptomatic 1990 (Carlo Erba Instruments) automatic apparatus and calculated by the BET method.

The composition of the catalysts was measured by XRF with the ED-XRF spectrometer model 1510 (Canberra Packard, USA) equipped with a set of radioactive sources. The excitation source was Cd-109 (energy of 22 keV) for elements from Cr to Nb and from Hf to Bi or Am-241 (energy of 60 keV) for others (from Mo to Ho), respectively. After estimation of the element content in an examined catalyst, weighted samples were homogenized with SiO_2 and with appropriate internal standard (oxides of heavy metals), and then pressed to very thin pellets with surface density of $0.0478\ g{\ast}cm^{-2}$. The internal standard was chosen so that the atomic number of a standard element was close to the atomic number of the examined element. The amount of sample and internal standard was set such that the contents of the examined element and the standard did not exceed 1%.

2.3.2. X-ray diffraction (XRD)

X-ray measurements have been performed on catalyst samples in glass capillaries using a Siemens D5000 diffractometer with Cu-K_α radiation ($\lambda = 1.54$ Å) in Debye–Scherrer geometry (capillary technique) and a position sensitive detector. Samples were scanned from 5° to 85° with a step size of 0.079°.

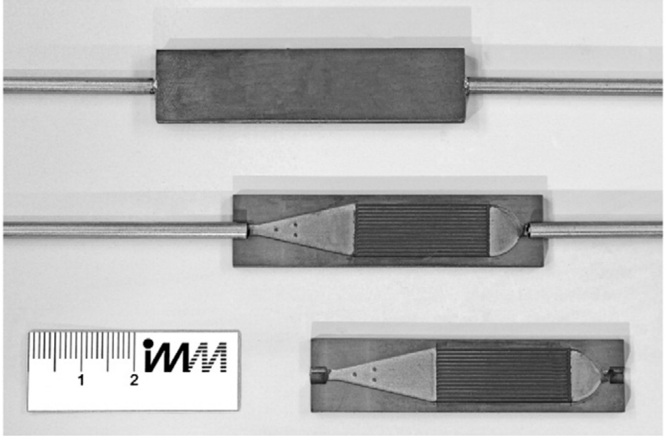

Fig. 1. Photo of the sandwich microreactor applied for the testing of the prepared Rh/Al_2O_3 catalysts.

2.3.3. Transmission electron microscopy (TEM)

The powder samples were dispersed in ethanol by ultrasonic treatment and deposited on a TEM grid. The measurements were performed either with a FEI Tecnai F30 transmission electron microscope at an accelerating voltage of 300 kV (5 wt.% Rh) or with a Philips EM-420 at an accelerating voltage of 120 kV (1 and 2.5 wt.% Rh).

2.3.4. Catalytic testing

Propane steam reforming was performed on various Rh/Al_2O_3 catalysts with different Rh content (1, 2.5 and 5 wt.-%) in a conventional lab-scale test-rig with a microchannel reactor. The feeding system was composed of conventional thermal mass flow controllers (BRONKHORST, HI-TEC) for dosage of the gaseous and liquid components (propane and water) and a homemade microstructured evaporator for evaporating the water. Water tanks pressurised with nitrogen supplied the evaporator with liquid water. Heated lines led from the evaporator to the reactor, to the reactor bypass-line and from there to the on-line Agilent Micro-GC equipped with four thermal conductivity detectors. The off-gas composition was measured every 3.5 min. The reaction temperature was set to 750 °C and the feed composition to a steam-to-carbon ratio of 4.

Table 1
Composition and specific surface area of the tested catalysts with various rhodium content prepared via impregnation with rhodium nanoparticle solutions.

Sample	Rh [wt.%]	Chemical analysis (XRF) [wt.%]	Specific surface area [m^2/g]
Rh/Al_2O_3	5	4.71 ± 0.14	204
Rh/Al_2O_3	2.5	2.29 ± 0.07	206
Rh/Al_2O_3	1	1.00 ± 0.03	206

Experiments were performed in sandwich-type reactors which are composed of two laser-welded microstructured platelets each having 14 channels with 500 μm width and 250 μm depth which have been described in more detail in previous studies [20,21]. The microchannels were etched by means of wet-chemical etching using aqueous iron chloride solutions. Inlet and outlet capillaries were attached to the reactors by laser welding. A depiction of the reactor can be seen in Fig. 1, before and after laser welding. The dimensions of the microreactor were measured to be 60 mm long and 14 mm wide with the catalyst coating being of ca. 40 μm thickness. The microreactors were placed into a metal block powered by a heating cartridge regulated by a PID temperature controller with a K-type thermocouple inserted next to the bed of the catalyst. Temperature differences between the gas outlet temperature and the