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Combination of flame synthesis and high-throughput experimentation: The preparation of alumina-supported noble metal particles and their application in the partial oxidation of methane

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Abstract

Mono and multi-noble metal particles on Al_2O_3 were prepared in one step by flame spray pyrolysis (FSP) of the corresponding noble metal precursors dissolved in methanol and acetic acid (v/v 1:1) or xylene. The noble metal loading of the catalysts was close to the theoretical composition as determined by WD-XRF and LA-ICP-MS. The preparation method was combined with high-throughput testing using an experimental setup consisting of eight parallel fixed-bed reactors. Samples containing 0.1–5 wt% noble metals (Ru, Rh, Pt, Pd) on Al_2O_3 were tested in the catalytic partial oxidation of methane. The ignition of the reaction towards carbon monoxide and hydrogen depended on the loading and the noble metal constituents. The selectivity of these noble metal catalysts towards CO and H_2 was similar under the conditions used (methane: oxygen ratio 2:1, temperature from 300 to 500 °C) and exceeded significantly those of gold and silver containing catalysts.

Selected catalysts were further analysed using XPS, BET, STEM-EDXS and XANES/EXAFS. The catalysts exhibited generally a specific surface area of more than 100 m^2/g, and were made up of ca. 10 nm alumina particles on which the smaller noble metal particles (1–2 nm, partially oxidized state) were discernible. XPS investigation revealed an enrichment of noble metals on the alumina surface of all samples. The question of alloy formation was addressed by STEM-EDXS and EXAFS analysis. In some cases, particularly for Pt–Pd and Pt–Rh, alloying close to the bulk alloys was found, in contrast to Pt–Ru being only partially alloyed. *In situ* X-ray absorption spectroscopy on selected samples was used to gain insight into the oxidation state during ignition and extinction of the catalytic partial oxidation of methane to hydrogen and carbon monoxide.
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1. Introduction

High-throughput experimentation (HTE) techniques have received great attention during the past years [1–4]. For heterogeneous catalysis, different aspects have been in the focus, among them high-throughput preparation of solids [5], automated catalyst testing [6], and high-throughput characterization [7]. HTE techniques conveniently open up possibilities

of repetitive catalytic test runs and long-term behaviour studies. High-throughput preparation comprises robot-controlled deposition-precipitation, impregnation, chemical vapor deposition, and sol–gel preparation methods [1,8]. The preparation routines become more complex and the task more demanding if several components are present, e.g., in supported multimetallic catalysts, and if calcinations are required to obtain a crystalline and defined metal oxide support.

In this contribution we show that flame spray pyrolysis (FSP) [9–11] gives the opportunity to prepare conveniently such multi-component catalysts in a single step. The rapid quenching after the FSP process affords materials with high

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surface area and tunable structural and chemical properties [9,10,12–14]. Furthermore, the noble metal particle size can be kept relatively small [11].

Bimetallic or multi-metallic particles are applied in a multitude of catalytic reactions including total combustion of hydrocarbons, partial oxidation of hydrocarbons, CO oxidation, and methanation reactions [15,16]. Here we used the catalytic partial oxidation (CPO) of methane as a test reaction, a promising reaction for the production of synthesis gas [17,18]. This slightly exothermic reaction can be regarded as an alternative to steam reforming, but it requires pure oxygen feed [17]. Inherent advantages comprise smaller reactor volumes, lower operating temperatures and inhibited carbon formation. Until recently, more than 20 billion cubic metres of methane were simply flared annually [19]. Thus, CPO is an alternative way of exploiting methane or natural gas in chemical industry.

The research on CPO of methane has grown during the last decade [17,18,20,21]. Mostly the catalytic performance of noble metals like Ru, Rh, Pt and Pd were studied even though Ni and Co and other transition metals are also well suited for the CPO reaction and cheaper than noble metals [18,22,23]. However, carbon formation on these materials occurs some two orders of magnitude faster than with supported noble metals [24].

The objective of the present study was to combine the opportunity and flexibility of FSP as a one-step-method with HTE techniques. The preparation and characterization of multi-component materials by FSP was evaluated. Particular focus was laid on the preparation of bi- and multi-metallic supported noble metal particles (0.1–5 wt%). The CPO of methane served as a test reaction in the low-temperature region (300–550 °C) and the catalyst structure was studied using *in situ* X-ray absorption spectroscopy. Alloy formation and structural properties of selected supported noble metal catalysts were addressed using different techniques, in particular electron microscopy and X-ray absorption spectroscopy (XAS).

2. Experimental

2.1. Flame synthesis

FSP was carried out using a solution of the corresponding precursors in either xylene or methanol-acetic acid. In one case xylene (dry, Acros), $Al(O^sBu)_3$ (75% solution in *s*-butanol, Gelest Inc.) was used as the precursor for the alumina support. Precursors for the noble metals were $Pt(acac)_2$ (purum, Fluka), $Rh(acac)_3$ (99%+, Acros), $Pd(acac)_2$, (99%, Aldrich) as well as ruthenocen (99%, Acros). Typically, the two solutions were prepared separately and then mixed. 40 ml solution was used for the spray process yielding theoretically 1.1 g of catalysts per run. The concentration of the $Al(O^sBu)_3$-precursor was typically 0.7 mol/l and that of the noble metals varied between 0.2 mmol/l (0.1 wt%) and 20 mmol/l (for 5 wt%). More details on the preparation routine can be found in Table 1 and in previous works [25,38].

In a less water and air sensitive approach, 40 ml of a fresh 50/50 (v/v) mixture of methanol/acetic acid served as a solvent

Table 1
Elemental analysis by WD-XRF and LA-ICP-MS of different multi-component alumina-supported systems (determined on the basis of dry samples)

Precursors of flame synthesis	Nominal composition	Pelletised	%Pt ($d_{50\%}$)[a]	%Ru ($d_{50\%}$)[a]	%Rh ($d_{50\%}$)[a]	%Pd ($d_{50\%}$)[a]	BET sf. area (m² g⁻¹)
Rh(acac)₂, Al(acac)₃	0.1%Rh/Al₂O₃	Yes	<0.01 (50 μm)	<0.01 (400 μm)	0.11 (450 μm)	<0.01 (510 μm)	–
Pt(acac)₂, Rh(acac)₂, Ru-ocen, Al(acac)₃	0.2%Pt–0.2%Rh–0.2%Ru/Al₂O₃	No	0.21 (50 μm)	0.18 (370 μm), 0.17[b] (1.4 μm)	0.21 (420 μm)	<0.01 (480 μm)	201.3 ± 2.6
Rh(acac)₂, Ru-ocen, Al(acac)₃	1%Rh–1%Ru/Al₂O₃	Yes	<0.01 (50 μm)	1.10 (350 μm)	1.2 (390 μm)	<0.01 (430 μm)	196.3 ± 3.1[c]
Pt(acac)₂, Rh(acac)₂, Ru-ocen, Al(acac)₃	2.5%Pt–2.5%Rh–2.5%Ru/Al₂O₃	No	2.68 (40 μm)	2.47 (180 μm), 2.55 (1.3 μm)	2.42 (200 μm)	<0.01 (220 μm)	198.8 ± 3.5[d]
		Yes	2.54[e] (40 μm)	2.53[e] (200 μm)	2.51[e] (200 μm)	<0.01 (220 μm)	
Pt(acac)₂, Rh(acac)₂, Ru-ocen, Pd(acac)₂, Al(O^sBu)₃	1%Pt–1%Rh–1%Ru–1%Pd/Al₂O₃	Yes	1.07 (43 μm), 1.19[g]	0.61 (260 μm), 0.54[g]	1.12 (290 μm), 1.13[g]	1.22 (310 μm)	108.2 ± 1.6[f]
Pd(acac)₂, Zr(acac)₄	5%Pd/ZrO₂	Yes	<0.01 (13 μm)	<0.01 (13 μm)	<0.01 (15 μm)	4.76 (16 μm)	–

[a] Information depth.
[b] These data were obtained from the L_α-line.
[c] Surface area for 3%Rh.
[d] For 5% Rh/Al₂O₃.
[e] LA-ICP-MS matrix matched calibration was based on these values
[f] For 1% Ru–1%Rh/Al₂O₃ via xylene solution.
[g] Measured by LA-ICP-MS.