

Interaction of Pt and Rh nanoparticles with ceria supports: Ring opening of methylcyclobutane and CO hydrogenation after reduction at 373–723 K

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Abstract

The catalytic properties of a Pt (4%) and a Rh (2.5%) catalyst on a low-surface area ceria support were determined as a function of hydrogen reduction in the temperature range between 373 and 723 K and compared to those of silica-supported Rh (3%) subjected to equivalent treatments. Two reactions were studied: the ring opening of methylcyclobutane (MCB) as representative for structure-sensitive hydrocarbon reactions and the hydrogenation of CO as an example for C–O bond activation. After reduction in the low- and mid-temperature range the rates of either reaction decrease significantly on ceria-supported Pt and Rh whereas they are hardly affected on Rh–silica. Annealing in vacuum at 723 K before the reduction step has a beneficial effect on the reaction rates but annealing after reduction leads to a general activity decrease. Accompanying *ex situ* high-resolution electron microscopy (HREM) investigations largely exclude particle decoration and formation of noble metal–Ce intermetallic bonds as possible effects of metal-support interaction at low and medium reduction temperatures. Taking also into account parallel surface science studies it is concluded that the observed activity decrease originates mainly from electronic perturbations at the interface between the metal nanoparticles and the increasingly reduced ceria support.

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1. Introduction

Ceria-supported platinum and rhodium are important catalysts for deNO_x and combustion reactions. Reducible oxide supports like ceria generally enhance the catalytic activity of the metal, but the catalysts are sensitive to hydrogen reduction at elevated temperature which may cause altered chemisorptive and catalytic properties, structural changes and catalyst deactivation. Strong metal-support interaction (SMSI [1]) between noble metal particles and a reducible support

under reduction in hydrogen has been under discussion for many years. Decoration of free metal surface by moieties of reduced support and inherent electronic perturbations very likely account for most SMSI phenomena observed on titania-supported [2–7] and vanadia-supported [8] noble metal particles. Decoration may be reversed upon exposure to oxygen or air [4,5,9].

On the other hand, hydrogen reduction of cerium oxide supports at 873 K and above leads to different oxides of type Ce_nO_{2n–2m}. So far, *ex situ* electron microscopy studies have revealed metal particle decoration after hydrogen treatment at 973 K and above [10–13]. Nevertheless, chemisorption data and catalytic measurements indicate appreciable interaction between ceria and noble metals already after

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reduction at 773 K and below [12,14–16]. If decoration of the metal surface by mobile oxide species is a priori excluded, the altered catalytic properties must be either due to electronic effects associated to the increasing reduction of the ceria surface, or to an incipient formation of noble metal–cerium alloys.

While most studies in the past have been concerned with reduction at 773 K and above, the present work emphasizes the influence of hydrogen reduction on the catalytic behaviour of well-characterized Pt/CeO₂ and Rh/CeO₂ catalysts at low and medium temperature [LTR (373–523 K), resp. MTR (573–723 K)] and the results are analyzed with respect to possible mechanisms of metal–oxide interaction. An Rh/SiO₂ catalyst is studied in parallel as representative for metal phases dispersed on less-reducible supports. Two standard reactions are monitored: the hydrogenolysis (ring opening) of methylcyclobutane (MCB) and the hydrogenation of carbon monoxide. It is well known that CO hydrogenation is favoured by addition of reducible oxides to noble metal catalysts [17]. After high-temperature reduction the reaction rate on Rh/ceria may be enhanced under transient conditions [18].

The hydrogenolysis of MCB, on the other hand, is an example for skeletal hydrocarbon transformations, a type of processes well known as SMSI-sensitive. It occurs easily at 373 K and below and is therefore suited to quantify the effect of reduction in the low- and mid-temperature range. At low temperature and in hydrogen excess only the ring opening products (*n*-pentane and isopentane) are formed, but reaction rate and product distribution are structure-sensitive [19,20] and also strongly hydrogen pressure-dependent [20–22]. While the sterically less hindered isopentane formation predominates on Ni [21] and on Rh [21,23], statistical ring opening may occur on Pt [20,22] and Pd [21] catalysts. The pathway to statistical ring opening is most likely connected to the ability to form a flat-lying intermediate, which in turn is determined by structural properties, e.g. facet size and metal–support interface [24]. Its occurrence depends on the hydrogen pressure [21,22], the particle size [20] and the temperature.

Finally, high-resolution electron microscopy (HREM) was used to provide information about possible alloy formation due to reduction at higher temperature. The discussion of the reported results will also take into account some recent information obtained on “inverse” CeO_x/Rh systems [25] and on “thin film” noble metal/CeO_x catalysts [26].

2. Experimental

2.1. Catalyst preparation and characterization

The Pt (4%)/CeO₂ and the Rh (2.5%)/CeO₂ catalyst used in these experiments were in part characterized in a previous high-resolution electron microscopy study [12], and their

metal dispersion and morphology were therefore well known. In order to avoid the effect of chlorine on the structural and redox properties of ceria [27–29] they were prepared by incipient wetness impregnation from aqueous solutions of chlorine-free precursors, [Pt(NH₃)₄](OH)₂ and Rh(NO₃)₃. The support was low-surface area (4 m² g⁻¹) commercial ceria (99.9% pure), from Alpha. After impregnation, both catalysts were dried, calcined and reduced at 773 K. From [12] it is known that the increase of reduction temperature up to 773 K induces moderate metal sintering, whereby the metal dispersion of the Pt/CeO₂ catalyst decreases from 50 to 40%, and that of the Rh/CeO₂ sample from 46 to 38%, while the mean particle sizes both increase from about 2.5 to 3.5 nm.

An Rh (3%)/silica catalyst with Rh particles of comparable size was prepared and treated in the same way as the ceria-supported catalysts mentioned above. A SiO₂ Cabosil M-5 sample with a BET surface area of 190 m² g⁻¹ was impregnated with an aqueous solution of Rh(NO₃)₃, and further dried, calcined, and reduced at 773 K. As revealed by HREM and chemisorption measurements, this procedure resulted in a similar metal dispersion and mean particle size of the resulting catalyst (44% and about 3 nm, respectively, as also shown previously [30]).

Finally, for an EM study of the effect of high-temperature reduction on a less-reducible support, a Pt/SiO₂ catalyst of high metal loading (20%) was prepared from the precursor described above. It was calcined and reduced at 673 K and thereafter treated in 1 bar hydrogen under exactly the same conditions as the other catalysts and also as the corresponding thin film model system [31].

The catalysts were characterized by electron microscopy and microdiffraction in a Zeiss EM 10C, a Philips CM 200 FEG and a JEOL 2000 EX.

2.2. Catalytic reactions

Initially, all catalysts were subjected to redox cycles consisting of heating in 1 bar oxygen at 673 K for 2 h, followed by reduction in 1 bar hydrogen at 523 K until they reached a constant and reproducible activity. At the end, and also after every reaction, a standard oxidative treatment (1 bar O₂ at 673 K for 120 min) was applied, sufficient to reverse metal–ceria interaction effects of purely electronic origin [12,16]. The catalyst samples were then reduced in 1 bar hydrogen for 60 min at variable temperature before being exposed to the reactants in a computer-controlled microreactor of the recirculation type [32]. Furthermore, in some experiments annealing in vacuum (at 723 K for 30 min) was included before or after the reduction step. The reactant pressures under standard reaction conditions were 10 mbar hydrocarbon and 100 mbar hydrogen for MCB hydrogenolysis and 10 mbar CO and 100 mbar H₂ for CO hydrogenation, always with He added to 1 bar total pressure. From the conversion versus time plots, initial reaction rates were determined as a function of reactant partial pressures,

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