



## Comparative study of hydrotalcite-derived supported Pd<sub>2</sub>Ga and PdZn intermetallic nanoparticles as methanol synthesis and methanol steam reforming catalysts

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### ABSTRACT

An effective and versatile synthetic approach to produce well-dispersed supported intermetallic nanoparticles is presented that allows a comparative study of the catalytic properties of different intermetallic phases while minimizing the influence of differences in preparation history. Supported PdZn, Pd<sub>2</sub>Ga, and Pd catalysts were synthesized by reductive decomposition of ternary Hydrotalcite-like compounds obtained by co-precipitation from aqueous solutions. The precursors and resulting catalysts were characterized by HRTEM, XRD, XAS, and CO-IR spectroscopy. The Pd<sup>2+</sup> cations were found to be at least partially incorporated into the cationic slabs of the precursor. Full incorporation was confirmed for the PdZnAl-Hydrotalcite-like precursor. After reduction of Ga- and Zn-containing precursors, the intermetallic compounds Pd<sub>2</sub>Ga and PdZn were present in the form of nanoparticles with an average diameter of 6 nm or less. Tests of catalytic performance in methanol steam reforming and methanol synthesis from CO<sub>2</sub> have shown that the presence of Zn and Ga improves the selectivity to CO<sub>2</sub> and methanol, respectively. The catalysts containing intermetallic compounds were 100 and 200 times, respectively, more active for methanol synthesis than the monometallic Pd catalyst. The beneficial effect of Ga in the active phase was found to be more pronounced in methanol synthesis compared with steam reforming of methanol, which is likely related to insufficient stability of the reduced Ga species in the more oxidizing feed of the latter reaction. Although the intermetallic catalysts were in general less active than a Cu-/ZnO-based material prepared by a similar procedure, the marked changes in Pd reactivity upon formation of intermetallic compounds and to study the tunability of Pd-based catalysts for different reactions.

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### 1. Introduction

Comparative studies of different (bi- or inter)metallic phases in nanostructured catalysts often suffer from limited comparability of the catalytic materials themselves as a result of differences in their preparation history. Application of the individually synthesis recipes that have been optimized for the best performance of a given catalyst system requires special and often unique conditions like presence of certain ligands, solvents, support materials, promoters, or thermal post-treatments. As a result, differences in composition, dispersion, homogeneity, or metal-support contacts may complicate the comparison of such nanocatalysts by convolution of extrinsic and intrinsic effects. Unsupported model catalysts are an alternative [1], but with the support often also the nanostructured

nature of the active phase and with it the easy relation to real powder catalysts has to be sacrificed. Recently, aerosol-derived alloy powders were presented as an elegant compromise and useful platform for studying intermetallic metal phase in MSR and CO oxidation on PdZn particles with a surface area of 6 m<sup>2</sup> g<sup>-1</sup> [2].

While this approach successfully bridges the gap between model and real catalysts starting from the model side, we herein, present a synthetic approach to intermetallic catalysts that allows conserving the full complexity of supported nanocatalysts. At the same time, this method assures high comparability of different intermetallic compounds (IMCs) in a nanostructured form by application of a common and flexible synthesis protocol to minimize the role of different preparation history. This is achieved using a facile aqueous co-precipitation technique to prepare Hydrotalcite-like compounds (HTlc) with different elemental combinations as well-defined platform precursor materials for intermetallic compounds.

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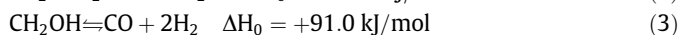
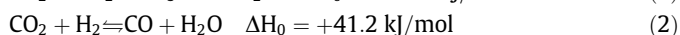
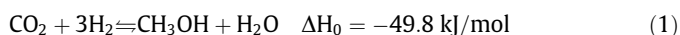
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The advantage of this precursor material is that divalent and trivalent cations are uniformly distributed in slabs of edge-sharing  $\text{MO}_6$  octahedra that allow a close interaction of all metal cations, which is thought to be prerequisite to the uniform formation of IMCs [3]. HTlcs exhibit the general composition  $(\text{M}^{\text{II}}, \text{M}^{\text{III}})_{1-x} \text{M}_3^{\text{III}}(\text{OH})_2(\text{CO}_3)_{x/2} \cdot m\text{H}_2\text{O}$  ( $0.25 \leq x \leq 0.33$ ) and a huge flexibility of reducible and non-reducible metal cations that can be incorporated into the structure, for example,  $\text{M}^{\text{II}} = \text{Mg}^{2+}, \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}$  and  $\text{M}^{\text{III}} = \text{Al}^{3+}, \text{Ga}^{3+}, \text{Fe}^{3+}, \text{Cr}^{3+}$  [4]. This flexibility makes a large number of element combinations accessible rendering HTlc a platform precursor for many IMC systems. In this work, we use the HTlc precursor approach to compare the role of different Pd-based IMCs. We used  $\text{Pd}^{2+}$  as  $\text{M}^{\text{II}}$  and added reducible species,  $\text{Zn}^{2+}$  and  $\text{Ga}^{3+}$  at the  $\text{M}^{\text{II}}$  and  $\text{M}^{\text{III}}$  sites, respectively, to obtain the IMCs PdZn and  $\text{Pd}_2\text{Ga}$ . It is noted that due to the charge distribution the formed IMCs are sometimes denoted as ZnPd and  $\text{GaPd}_2$ . Here, we use in the field of catalysis more common form PdZn and  $\text{Pd}_2\text{Ga}$  for consistency with previous work.

We have shown recently [5] that  $\text{Pd}_2\text{Ga}$  nanoparticles supported on an oxide matrix of MgO and  $\text{MgGa}_2\text{O}_4$  can be obtained by this synthetic approach and reported on their hydrogenation properties. This method presents an efficient alternative to previously used top-down methods, such as etching or milling of materials obtained from high temperature melt synthesis, used previously to synthesize this material [6]. In addition to catalyst synthesis and characterization data from a variety of complementary techniques (XRD, BET, TPR, SEM, TEM, FTIR, and XAFS), we also present catalytic performance data in two reactions involving methanol, namely its synthesis from  $\text{CO}_2$  and methanol steam reforming (MSR) to correlate structural with catalytic properties.

Methanol has been proposed as a promising energy storage molecule for portable applications such as direct methanol fuel cells, as well as fuel for automobile internal combustion engines [7]. Additionally, methanol has been proposed as hydrogen storage medium [8], whose gravimetric hydrogen density exceeds that of compressed and even that of liquid hydrogen. Furthermore, the use of  $\text{CO}_2$  as a carbon source for methanol synthesis enables the simultaneous reduction in emissions of this greenhouse gas [7].

Methanol synthesis from  $\text{CO}_2$  (Reaction (1)) and its reverse reaction, methanol steam reforming (MSR) comprise a class of reactions critical to the application of methanol as an efficient energy carrier.



Both reactions are currently carried out at similar temperatures (523–603 K) on Cu/ZnO-based catalysts. While MSR is not thermodynamically limited and is carried out at atmospheric pressure, methanol synthesis requires high pressures (30–100 bar) and lower operating temperatures due to unfavorable thermodynamics [9]. Reverse water gas shift (rWGS, Reaction (2)) is a side reaction to methanol synthesis and thus diminishes selectivity. In MSR, methanol decomposition (Reaction (3)) as well as rWGS are undesired side reactions and yield CO—a poison for fuel cell electrodes. The rates of both undesired reactions can be thermodynamically hindered by operating at lower temperatures. Lower temperature operation and low selectivity to rWGS or decomposition thus remain the driving forces behind the development and optimization of methanol catalysts [9].

The current state of the industrial Cu/ZnO catalysts are well suited to stationary operation, however suffer from pyrophoricity, sintering with long reaction times, and instability to changes in reaction conditions [10]. These shortcomings make Cu-based

catalysts unsuitable for portable applications. To that end, Pd supported on reducible oxides such as ZnO,  $\text{In}_2\text{O}_3$ , and  $\text{Ga}_2\text{O}_3$  has shown favorable reactivity similar to that of Cu-based catalysts for both methanol synthesis and MSR [11], whereas Pd supported on non-reducible supports has been shown to be selective to rWGS and methanol decomposition. Additionally, Pd-based catalysts have also shown good long-term stability and resistance to sintering. The alteration of the properties of Pd was attributed to the formation of the IMCs  $\text{Pd}_2\text{Ga}$  [12] and PdZn [11a,13] upon partial reduction in the support components rendering these systems ideal test cases for studying the potential of the HTlc precursor approach for IMC catalysts synthesis.

## 2. Experimental

### 2.1. Synthesis conditions

Ternary palladium containing and binary Pd-free *PdMgAl*, *PdMgGa*, *PdZnAl*, *MgGa*, *ZnAl*, and *MgAl* HTlc with  $\text{M}^{2+}/\text{M}^{3+}$  molar ratios of 70:30 were synthesized by co-precipitation. The nominal composition of all Pd- $\text{M}^{2+}$ - $\text{M}^{3+}$  samples was set to 1:69:30. A mixed aqueous metal nitrate ( $[\text{Pd}^{2+}] + [\text{M}^{2+}] + [\text{M}^{3+}] = 0.2 \text{ M}$ ) solution and 0.345 M basic precipitating agent solution were co-fed at pH = 8.5. For *MgGa* and *MgAl*, HTlc precursors pure sodium carbonate solution and a precipitation temperature of 328 K were used, whereas in case of *PdZnAl* HTlc a mixture of sodium carbonate (0.3 M) and sodium hydroxide (0.045 M) and a temperature of 298 K has been applied in order to obtain a homogeneous precursor sample. During precipitation, both solutions were added simultaneously dropwise into a 2-L precipitation reactor (Mettler-Toledo LabMax). The nitrate solution was automatically pumped with a constant dosing rate, and the basic solution was added to maintain a constant pH of 8.5. After completion of addition, the mixture was aged for 1 h at the same temperatures applied during synthesis. The precipitate was filtered and washed twice with warm deionized water in order to remove the nitrate and sodium ions and obtain a conductivity of the filtrate lower than 0.2 mS/cm. The solid was dried for 12 h at 353 K in air. After drying, a one-step decomposition–reduction in 5 vol%  $\text{H}_2/\text{Ar}$  (2 K/min) was performed at the temperatures extracted from  $\text{H}_2$ -TPR experiments that yielded in the intermetallic phases and in metallic Pd in case of the *PdMgAl* HTlc precursor. A reduction temperature of 523 K was applied for the *PdMgAl* and *PdZnAl* system, whereas a reduction of 773 K is needed to obtain  $\text{Pd}_2\text{Ga}$  intermetallic particles.

A HTlc-based *CuZnAl* catalyst was prepared as described previously [14] and was used as reference material for the catalytic test in methanol synthesis. Additional details about the synthesis conditions of the *CuZnAl* HTlc precursor and the synthesis protocols of the Pd-based HTlc are given in the supplementary information (Fig. S1).

### 2.2. Characterization

**X-ray diffraction.** XRD patterns of the HTlc precursor and its decomposition products were recorded on a STOE Stadi P diffractometer in transmission geometry using Cu  $K\alpha_1$  radiation, a primary Ge monochromator, and a  $3^\circ$  linear position sensitive detector.

**Specific surface area determination.** Specific surface areas (SSA) of the precursors and reduced compounds were determined by  $\text{N}_2$  adsorption–desorption measurements at 77 K by employing the BET method (Autosorb-1C, Quantachrome). Prior to  $\text{N}_2$  adsorption, the sample was outgassed at 353 K/423 K (precursor sample/reduced catalyst, respectively) to desorb moisture from the surface and pores.

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