

# Oxidative methanol steam reforming (OSRM) on a PdZnAl hydrotalcite derived catalyst

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## Abstract

Catalytic systems for the oxidative methanol reforming (OSMR) with a 1% and 2% metal loading were prepared impregnating the spinel-oxide mixture (ZnAl<sub>2</sub>O<sub>4</sub>/ZnO) obtained by thermal decomposition of a Zn–Al hydrotalcite at 1173 K with palladium nitrate solution. The samples, after thermal treatment in reducing conditions, were characterized by TEM and XRD. The catalysts showed a quite good catalytic activity in the reaction under study with high methanol conversion and good selectivity to CO<sub>2</sub>. The high activity and selectivity were attributed to the prevailing presence, on the catalyst surface, of a highly dispersed 1:1 PdZn alloy phase.

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## 1. Introduction

Increasing global energy shortage and more stringent emission regulations have recently stimulated research and development in the fuel cell area showing their potential as a clean and efficient source of electrical power for both mobile and stationary applications. The H<sub>2</sub>-fed PEMFCs fuel cells, that use polymeric electrolyte membranes, appear to be particularly suitable for automotive or naval applications [1].

The difficulty of on-board hydrogen storage and handling can be circumvented by the use of hydrocarbon fuels as hydrogen carriers [2]. Methanol is a primary candidate as a hydrogen carrier for on-board production of hydrogen for fuel-cells, because it is a low cost fluid, virtually sulphur-free, safe to handle and easy to produce [3–5].

Hydrogen can be produced from methanol by steam reforming (SRM) where the organic molecule reacts with steam, by partial oxidation (POM) in which the feed reacts with a sub-stoichiometric (with respect to the total combustion) amount of oxygen and by decomposition (DCM). Both DCM and SRM are endothermic, while POM is exothermic [6]. An attractive alternative to these reactions is a process with a zero net enthalpy known as oxidative steam reforming of methanol (OSRM), consisting in the coupling of the endothermic methanol steam reforming (SRM) with the exothermic partial oxidation (POM) that allows the production of hydrogen using an autothermal process [7–18].

Layered hydrotalcite-like anionic clays (HTlc), of general formula  $M_x^{2+}M_y^{3+}(\text{OH})_{2(x+y)}A_{y/n}^{-n} \cdot m\text{H}_2\text{O}$  where M<sup>2+</sup> and M<sup>3+</sup> are divalent and trivalent metal ions, respectively and A<sup>-n</sup> is an intercalated anion, are widely used as catalysts or catalyst precursors [19–21]. In fact, the thermal treatment of HT-like materials at high temperatures produces mixed oxides of well defined and reproducible stoichiometry [19,20].

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Very promising OSRM catalysts have been recently obtained by thermal treatment and reduction of Cu, Zn and Al hydrotalcite-like precursors with a general formula of  $(\text{Cu}, \text{Zn})_{1-x}\text{Al}_x(\text{OH})_2(\text{CO}_3)_{x/2} \cdot m\text{H}_2\text{O}$  [9,14–16].

Pd/ZnO catalysts have been recently suggested as substitute of the currently employed Cu based OSRM catalysts, because of their higher thermal stability [11,13,17,18].

In this work, we describe our preliminary data on the preparation, characterization and catalytic activity in the oxidative methanol steam reforming (OSMR) of a catalytic system which is based on Pd supported on the spinel-oxide mixture ( $\text{ZnAl}_2\text{O}_4/\text{ZnO}$ ) obtained by thermal decomposition of a Zn–Al synthetic hydrotalcite.

## 2. Experimental

### 2.1. Materials

Methanol 99.9% was obtained from Fluka, while,  $\text{Pd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ , urea, ZnO and  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  were Aldrich products. Hydrogen was obtained from SIAD.

### 2.2. Catalysts preparation

Zn–Al synthetic hydrotalcite (HTZA as) was prepared, following a procedure described by Costantino et al. [22], by precipitation of the hydroxycarbonates from a solution containing the metal chlorides and urea.

Solid urea was added to a 0.5 M solution of the metal chlorides ( $\text{Al}/(\text{Al} + \text{Zn})$  molar fraction was 0.33), to reach a urea/metal chloride molar ratio of 3.3.

The solution was heated, under vigorous stirring, at 363 K for 40 h. The recovered white solid was washed with distilled water until the complete disappearance of the chloride ions ( $\text{AgNO}_3$  test).

The sample was dried at 353 K and then calcined at 1173 K for 12 h in order to obtain the complete degradation of the hydrotalcite structure, the formation of ZnO and the spinel phase  $\text{ZnAl}_2\text{O}_4$ . The material was identified as HTZA.

The sample was successively impregnated with an aqueous solution of  $\text{Pd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ ; the loading of palladium was fixed to 1% and 2% w/w respectively. The samples were calcined at 623 K and reduced with hydrogen (40 ml/min) at 673 K for 2 h (heating rate of 5 K/min). The obtained catalysts were identified as HTZAPd1, HTZAPd2.

### 2.3. Characterization methods and catalytic tests

#### 2.3.1. Powder X-ray diffraction (XRD)

The X-ray diffraction patterns were collected with a Bragg–Brentano powder diffractometer using Cu K $\lambda$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) and a monochromator in the diffracted beam. Diffraction data were analyzed with the Rietveld method [23], using MAUD codes [24]. This program, in a fully automated version, is particularly suited for a quantitative evaluation of the phases present in the

X-ray diffraction patterns. The parameters of physical meaning such as: lattice constant, phase abundance, average crystallite size and microstrain, are worked out from the full pattern analysis and not by the comparative investigation of the peak broadening after the analysis for each peak [25].

#### 2.3.2. Transmission electron microscopy (TEM)

The samples were observed using a Transmission electron microscope (TEM, JEOL JEM-2010) equipped with a EDS probe for elemental analysis (OXFORD, LINK PENTA-FET). The samples were milled and dispersed in isopropanol in a ultrasound bath. A drop of the dispersion was then deposited on a lacey carbon film positioned on a copper grid and dried before the observation.

#### 2.3.3. Catalytic activity tests

Activity tests were carried out in a continuous flow reactor in the 523–623 K temperature range. Methanol (5.6%) was fed to the reactor at atmospheric pressure; the stream composition was:  $\text{H}_2\text{O}/\text{MeOH}/\text{O}_2 = 1.1/1/0.09$ . Total flow-rate was kept at 55 ml/min. Helium was used as a carrier. Contact time was  $0.06 \text{ gs cm}^{-3}$ .

Before the reaction, the catalyst was treated first at 673 K in air flow and then in a hydrogen stream (10%  $\text{H}_2$ ) diluted with helium under temperature-programmed conditions (heating rate of 5 K/min).

The effluent gases from the reactor were analyzed on-line using a  $25 \text{ m} \times 0.53 \text{ mm}$  CarboPLOT column ( $\text{CO}_2$ ,  $\text{CO}$  and  $\text{H}_2$ ) in a HP6890 GC and by a  $25 \text{ m} \times 0.53 \text{ mm}$  PoraPLOT-Q ( $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$ ) in a HP5890. Both GCs were equipped with TCD.

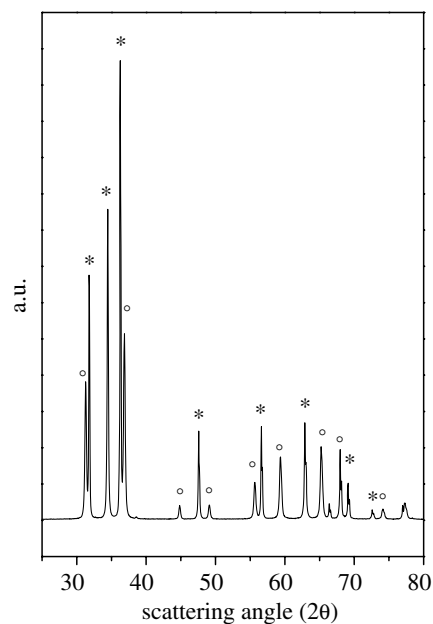


Fig. 1. XRD pattern of the HTZA obtained by calcination at 1173 K of the Zn–Al hydrotalcite. ZnO (\*) and spinel-type (○) phases were detected.

### 3. Results and discussion

#### 3.1. Catalysts characterization

##### 3.1.1. XRD measurements

The powder XRD profile of the as synthesized HTZA as sample is characteristic of a well-crystallized hydroxalcalite phase. After thermal treatment at 1173 K, the XRD pattern shows the typical reflections of zinc oxide ZnO and of a spinel phase  $\text{ZnAl}_2\text{O}_4$  (Fig. 1).

The XRD diffractograms of the palladium loaded samples HTZAPd1 and HTZAPd2 are reported in Fig. 2, along with the profiles fittings according to Rietveld methods

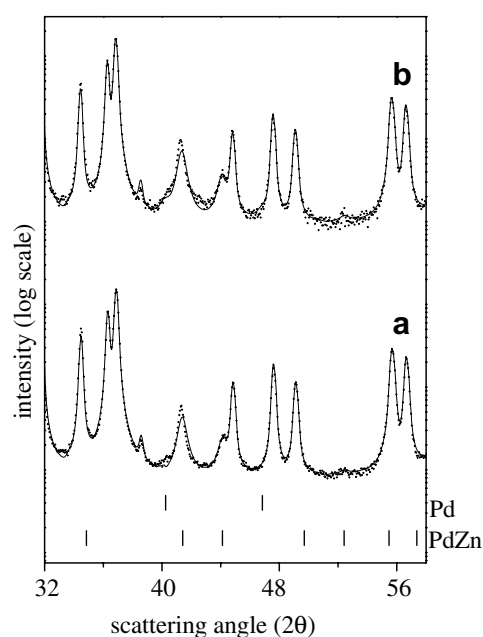


Fig. 2. X-ray diffraction patterns (logarithmic scale) vs.  $2\theta$  of (a) HTZAPd1 (Pd 1%), (b) HTZAPd2 (Pd 2%). Data points refer to experimental data and full lines to a fit according to the Rietveld methods.

[15,16]. The peaks at  $2\theta = 41.2^\circ$  and  $44.1^\circ$ , characteristic of the tetragonal PdZn (1:1) alloy, [26,27] are present in the diffraction profiles of both samples (Fig. 2). Very weak signals are also present in both profiles at  $2\theta = 40.1^\circ$ , attributable to a very small amount of metallic Pd.

The calculated (Scherrer method) particle size, for both alloyed and pure palladium is, for both samples,  $\approx 9$  nm. As can be easily seen in Fig. 2, the intensity of the PdZn peak at  $41.2^\circ$  is slightly higher for sample B, but also the shoulder at  $40.1^\circ$  increases, so that the PdZn/Pd<sub>tot</sub> atomic ratio percent remains almost the same for the two samples,  $93 \pm 2\%$  for HTZAPd1 and  $95 \pm 2\%$  for HTZAPd2.

This suggests that the increase of the Pd loading in the HTZAPd2 sample with respect to HTZAPd1 (2% and 1%) apparently does not influence the percentage of Pd that form the alloy with zinc as a result of the reducing thermal treatment.

##### 3.1.2. TEM analysis

Transmission electron micrographs of the three catalysts are reported in (Fig. 3).

The hexagonal dark particles represent the support, the small circular particles the palladium species Pd and Pd/Zn. It was, in fact, not possible to distinguish between the Pd and the alloy particles.

The mean size of the metallic particles was estimated at 5–10 nm, in good agreement with what was found by XRD.

#### 3.2. Catalytic tests

The results of the preliminary OSRM tests are reported in Table 1.

The reactivity and selectivity trends of the two samples are very similar, in accordance with the very similar phase distribution (% PdZn/Pd<sub>tot</sub>) of the two catalyst samples. The methanol conversion is 86% at 623 K on the HTZAPd1 (1% Pd) sample and, in the case of the

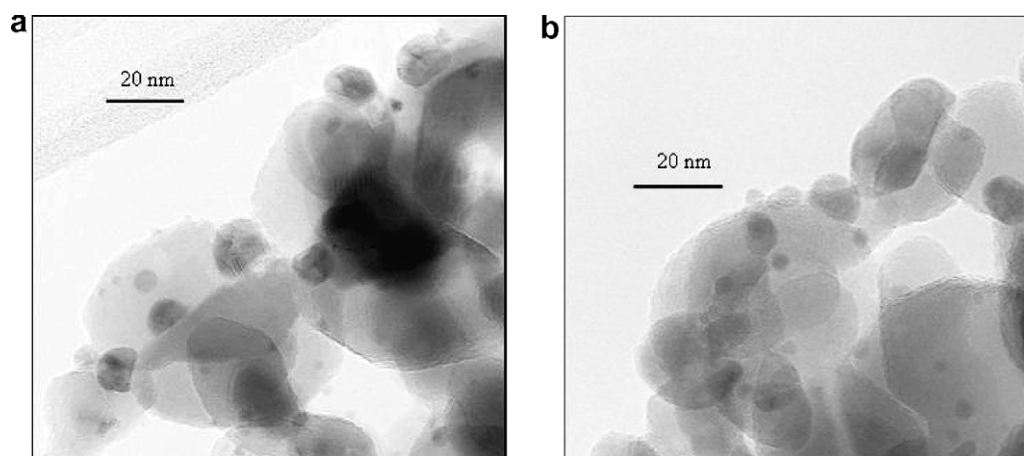


Fig. 3. TEM micrograph of the HTZAPd1(left) and HTZAPd2 (right) samples.

Table 1  
% PdZn/Pd<sub>tot</sub>, methanol conversion and %C selectivity as function of reaction temperature, for the two catalysts

Catalyst	% PdZn/ Pd <sub>tot</sub> ± 2%	Reaction temperature (K)	CH <sub>3</sub> OH conversion (%)	Selectivity/ %C	
				CO	CO <sub>2</sub>
HTZAPd1	93	523	20	24.1	75.9
		573	43	15.0	85.0
		623	86	11.9	88.1
HTZAPd2	95	523	34	25.7	74.3
		573	48	13.8	86.2
		623	100	11.5	88.5

HTZAPd2 catalyst (2% Pd), 100% at the same temperature. The CO<sub>2</sub> selectivity ranges between 75% and 88% (Table 1) for both samples, increasing with the reaction temperature. It is well documented [18–25] that the CO<sub>2</sub> selectivity, which is an indication of the occurrence of only the OSRM, of Pd/ZnO based catalytic systems is mainly related to the palladium–zinc oxide interaction or, more precisely, to the amount of PdZn alloy, formed during the thermal treatment under reducing conditions [13,17,18,28–32]. Metallic palladium is known to be an active catalyst of methanol decomposition [33,34], which is generally considered the main cause, along with the reversed WGS reaction, of the undesired carbon monoxide production. Considering the very low loading of active metal, in comparison with the values reported by other authors [11,13,17,18], the conversion values are quite high, confirming [9,14–16] that the use of layered double oxides as precursors, results in catalytic systems with highly dispersed metallic particles, much more active than those prepared by conventional dispersion methods.

#### 4. Conclusions

Impregnation with small amounts of palladium nitrate (1% or 2%) of the spinel-oxide mixture (ZnAl<sub>2</sub>O<sub>4</sub>/ZnO), obtained by thermal decomposition of a synthetic Zn–Al hydrotalcite, produce, after thermal treatment in reducing atmosphere, a metallic phase containing, in both cases, more than 93% of the Pd/Zn 1:1 alloy. These materials showed, in the preliminary tests, a quite good catalytic activity in OSRM compared to literature data of similar catalysts with much higher metal loadings [17,18]. The presence of a small amount of non-alloyed metallic palladium phase is thought to be the cause of the undesired CO production. The high activity is attributable to the homogeneous dispersion of the Pd/Zn alloy obtained using the spinel/oxide mixture obtained by decomposition a Zn/Al hydrotalcite as support. In fact, the homogeneous dispersion of the palladium and zinc species, reached in this kind of system, allows the formation of the Pd/Zn alloy at relatively low temperatures. Studies are in progress to minimize the formation of the non-alloyed palladium phase.

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