



The several hydrotalcites investigated as precursors of catalysts by Angelo Vaccari

P. Benito^{*}, G. Fornasari, F. Basile, T. Tabanelli, C. Lucarelli, A. Fasolini, N. Dimitratos, S. Albonetti, F. Cavani, F. Trifirò^{*}

Dipartimento Chimica Industriale "Toso Montanari", Viale Risorgimento 4, Bologna 40136, Italy

ARTICLE INFO

Keywords:

Hydrotalcite
Hydrogenation
Reforming
Condensation
Environmental applications

ABSTRACT

Hydrotalcite-derived catalysts are applied in a very broad range of processes. In this paper, the contribution of Angelo Vaccari's work to the development of these catalysts is reported. His work spanned from the preparation of novel hydrotalcites in powder and in structured forms, which after thermal treatments are applied in gas phase catalytic processes for reactions of hydrogenation, steam and dry reforming, partial oxidation, condensation and environmental applications. Moreover, he reviewed several aspects of hydrotalcite-derived catalysts. In this work, we summarize the main results that Angelo Vaccari together with his numerous co-workers has achieved.

1. Introduction

Hydrotalcite (HT)-type compounds, anionic clays or layered double hydroxides are the names commonly used to describe a family of lamellar compounds with applications in several fields, such as absorbents in liquid and gas phase, drug delivery, antacids, polymers, and catalysis [1]. The structure of the hydrotalcite is described as positively charged layers of edge-sharing $\text{Mg}(\text{OH})_6$ octahedra partially substituted by Al^{3+} . The charge excess is balanced by anions located in the interlamellar space that coexist with water molecules. The general chemical formula of HT compounds is written as $[\text{M}_1^{2+}_x\text{M}_2^{3+}(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$. The nature of the cations is not limited to divalent and trivalent ions, monovalent and tetravalent cations have been also reported [2]. Their advantages as catalysts or catalyst precursors derive from the ability to host in the layers most of the metals active in catalytic processes (transition and noble metals) usually in combination with Mg^{2+} and Al^{3+} . Moreover, the interlayer region can also host anions to provide further active sites. The topotactic decomposition of hydrotalcites during thermal treatment gives rise to bulk catalysts with tailored acidic-basic character (for instance modifying the $\text{Mg}^{2+}/\text{Al}^{3+}$) and metal species highly interacting with the support. An additional reduction treatment generates metallic particles well dispersed and stabilized, even at high active phase loading. Hence, HT-derived catalysts may overcome conventional impregnated catalysts in some applications.

In this work, we would like to review the work of Angelo Vaccari in the field of hydrotalcites and catalysis. The article starts with two

general sections focusing on the preparation methods of the hydrotalcites and the catalysts, as well as the insights in the characterization of the catalysts, to later focus on the catalytic processes where they have been applied. A. Vaccari also published several review papers on the topic [2–9], the most important the one in collaboration with F. Cavani and F. Trifirò in 1991 [2], with more than 5550 citations, an index of the interest of the topic hydrotalcites and catalysis.

2. Preparation of hydrotalcite precursors and derived catalysts

The effect of the preparation method on the properties of HTs and HT-derived catalysts was investigated by A. Vaccari, including the development of novel procedures [10,11]. The selection of the preparation method was studied for Cu-containing HTs in the first works [12]. The results evidenced that the coprecipitation, which is currently the most used method, produced homogeneous precipitates. The structure depended on the composition, a pure HT structure was obtained with $\text{Cu}/\text{M}^{2+} \leq 1.0$ ($\text{M} = \text{metal}$) and $\text{M}^{3+}/(\text{M}^{3+} + \text{M}^{2+}) = 0.24\text{--}0.31$ atomic ratio. Then the level of supersaturation in the coprecipitation and/or the role of a following aging hydrothermal treatment were shown to influence the crystallinity of Ni/Cr and Ni/Al precipitates, but they did not modify their nature [13]. The key factors involved in the preparation of pure Ni/Al HT compounds were also examined, showing how several techniques allowed to verify the HT structure and decomposition products (e.g., XRD, EXAFS, ^{27}Al NMR and TG analysis) [14]. Moreover, noble metal containing HTs were prepared by coprecipitation (Rh^{3+} ,

^{*} Corresponding authors.

E-mail addresses: patricia.benito3@unibo.it (P. Benito), ferruccio.trifiro@unibo.it (F. Trifirò).

<https://doi.org/10.1016/j.cattod.2024.114791>

Received 4 February 2024; Received in revised form 1 May 2024; Accepted 6 May 2024

Available online 11 May 2024

0920-5861/© 2024 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

Ir^{3+} , Ru^{3+} , Pd^{2+} and Pt^{2+}), however in this case for the Pt-containing sample about a 20 % loss of the noble metal ions occurred [15].

Novel preparation methods of HT materials were also developed. The synthesis of HTs was performed directly on metal surfaces by the electrobase generation method. The procedure was initially developed to prepare modified electrodes [16] and it was later extended to obtain structured catalysts [17–20], studying the influence of electrodeposition parameters on the properties of the coatings. Finally, geopolymer-hydrotalcite composites shaped as beads were prepared by ionotropic gelation [21].

The first step to develop an optimized catalyst is to control the properties of the HTs, but then a thermal treatment, usually calcination followed by reduction, is required to obtain the final catalysts. A. Vaccari carefully investigated the effect of calcination and reduction parameters on the properties of several HT-derived catalysts. A kinetic study of the reduction of CuO in ternary copper-zinc-aluminum catalysts (with different atomic ratios) revealed that the reduction took place in three different steps [22]. On this topic, a great part of the work was centered on Ni-containing catalysts. The structure of Ni/Al and Ni/Mg/Al catalysts obtained by calcination in the 350–900 °C temperature range was elucidated. NiO and Ni-doped Al_2O_3 in strong interaction with partially decomposed precursor layers or with a spinel-type phase at the NiO- Al_2O_3 interface were found in Ni/Al derived catalysts [23–25]. Then the attention shifted to Ni/Mg/Al catalysts, to identify the Ni distribution and its reducibility, and in turn to control the Ni⁰ particle sizes. After calcination at 750 °C a surface spinel-type phase decreased the accessibility of the surface to the reducing mixture. The reduction of the Ni²⁺ ions is also hindered by the presence of a fraction of Al³⁺ ions inside the oxide phases. Higher calcination temperatures provoked the segregation of stoichiometric spinel and oxide or oxide solid solution. In Ni/Mg/Al catalysts, the formation of NiO/MgO solid solutions in Mg-rich samples decreased the Ni²⁺ reducibility [26,27]. The evolution of the HT phase to mixed oxide and finally the segregation of the spinel phase was investigated by Neutron diffraction using a programmed temperature control facility [28]. A model of the structure was obtained by Rietveld refinement of the diffraction patterns. The model showed that although the samples essentially show a rock-salt type structure pattern, they have a spinel-type structure. A high replacement of aluminum for magnesium in the magnesium-richer samples was proposed. In noble metal-containing catalysts (Rh^{3+} , Ir^{3+} , Ru^{3+} , Pd^{2+} and Pt^{2+}) obtained at 650 °C, the noble metal ions could segregate as oxide or metal side-phases, with the following scale of stability: $\text{Rh} > \text{Ir} > \text{Ru} > \text{Pd} > \text{Pt}$ [15]. The segregation increased after a 900 °C calcination; meanwhile the not segregated noble metal ions were always present inside the spinel-type phases and not in MgO. After reduction, small nanoparticles were obtained whose size depended on the reduction temperature, i.e. the Rh crystal size increased from 1.4 nm to 1.8 nm when the reduction temperature increased from 750 °C to 950 °C [29]. The crystalline phases at 900 °C were modified in catalysts derived from HT compounds intercalated by silicates [30,31], which were added to the composition to enhance the mechanical stability. The formation of the forsterite (MgSiO_4) altered the development of other Mg-containing phases (MgO and MgAl_2O_4).

3. HT as precursors of catalysts for hydrogenation reactions

3.1. Synthesis of methanol, hydrocarbons and higher alcohols from CO and H₂

The preparation and development of hydrotalcite-derived catalysts for the synthesis of methanol from syngas ($\text{CO} + \text{H}_2$) was the first work of A. Vaccari in the field of HTs [32–38]. The aim was to develop catalysts active at lower temperatures than the traditional ones. HTs containing $\text{Cu}_x / \text{Zn}_{76-x} / \text{Al}_{24}$ ($x = 25.3, 38$) atomic ratio, % [32] and Cu/Cr with other elements $\text{Cu}_{38} / \text{Zn}_{38} / \text{Al}_{12} / \text{Cr}_{12}$, $\text{Cu}_{38} / \text{M}_{38} / \text{Cr}_{24}$ and $\text{M}_{76} / \text{Cr}_{24}$ (with M = Zn, Co, Mn, Mg) atomic ratio, % [37,38] were prepared by

coprecipitation; the catalysts were obtained by calcination and consecutive reduction. The Cu/Zn/Al HT precursors, characterized by the presence of cations in positively charged brucite-like layers, decomposed at a lower temperature than the hydroxycarbonate to oxides, favoring the interactions among the elements and after reduction producing very small size copper crystallites (nearly 3 nm) [33,34]. However, aluminum showed an inhibitor effect on the synthesis of methanol and the delaying role on the overall reducibility at values higher than 10 atomic ratio, %, namely in catalysts $\text{Cu}_x / \text{Zn}_{76-x} / \text{Al}_{24}$ ($x = 25.3, 38, 50.7, 60.8$) and $\text{Cu}_x / \text{Zn}_{90-x} / \text{Al}_{10}$ ($x = 30, 45$) atomic ratio, % [35]. An easily reoxidizable copper (CuO and copper not detected by XRD) and copper related to the ZnO were suggested as active species [36]. In Cu/Cr HTs the presence of Zn promoted methanol synthesis, in comparison to Co and Mg; it prevented the formation of CuCrO_2 [37]. The selectivity of $\text{Cu}_{38} / \text{Zn}_{38} / \text{M}_{24}$ (with M = Al and/or Cr) catalyst could be also tailored to the production of higher molecular weight alcohols in the 250–300 °C by adding K, up to about 0.4 % by weight, or by modifying the reaction conditions (high pressure, low H₂/CO ratio in the gas mixture, and low GHSV) [39].

The addition of Co till 4 % (catalyst Co-4.0), with a corresponding decrease of Cu, in the same Cu/Zn/Cr catalyst, after an initial deactivation up to 2 % Co content, increased the activity with a high selective formation of short hydrocarbons (C₁-C₇), probably due to a synergetic effect between the cobalt containing cubic spinel type phase and highly dispersed metallic copper (Fig. 1) [40]. The activity was fully shifted to the Fischer-Tropsch reaction to hydrocarbons, till C₁₁, with typical Schulz-Flory distributions by increasing Co content and promoting the synergistic effect in catalysts $\text{Cu}_{76-(x+y)} / \text{Co}_x / \text{Zn}_y / \text{Cr}_{24}$ HT ($x = 4, 9, 12.7, 19, 25.3, 38, 76$ and $y = 0, 38, 49, 50.6$) and $\text{Cu}_{100-(x+z)} / \text{Co}_x / \text{Cr}_z$ ($x = 25, 33.3, 50$ and $z = 50, 66.7$) atomic ratio, %. The maximum yields of hydrocarbons were obtained with comparable amounts of copper and cobalt ($\text{Cu}_{19} / \text{Co}_{19} / \text{Zn}_{38} / \text{Cr}_{24}$). The relative depletion gave rise to a change in selectivity and/or catalytic activity, Fig. 1b [41].

3.2. Hydrogenation of organic compounds

HT-derived catalysts were applied in the hydrogenation of several organic compounds. $\text{Cu}_{38} / \text{Zn}_{38} / \text{M}_{24}$ HTs (with M = Al, Cr or Ga) atomic ratio, % were used as precursors of hydrogenation catalysts of maleic anhydride to γ -butyrolactone as a chromium-free alternative to chromite catalysts. The catalysts with Al (Cu/Zn/Al) reached better performances. A complete maleic acid conversion and high yields in γ -butyrolactone were obtained with an Al-content of 17 atomic ratio, % and Cu/Zn = 0.5–1.0 atomic ratio and lower tar formation [42].

Ni based HT reduced catalysts, in which the divalent cations were both Ni²⁺ and Mg²⁺, i.e. Ni/Mg(Al)O, were prepared and resulted very efficient for the gas phase hydrogenation of acetonitrile [43]. The monoethylamine selectivity depended on the Mg/(Mg + Ni) molar ratio, the acidity is partly responsible for the formation of secondary products. The catalyst with the optimal value of Mg/(Mg + Ni) ≈ 0.23 reached a maximum of monoethylamine selectivity of 92.6 % at 99 % acetonitrile conversion, due to a compromise between the reducibility of Ni and the acido-basicity of the material, both decreasing with the introduction of Mg.

The calcined commercial Mg/Al hydrotalcite (SASOL, D) was used as a support to prepare Pd/Pt catalysts for the gas phase hydrogenation of naphthalene. The use of a basic mixed oxide allowed to highlight the role of Pd/Pt active phase in the absence of acid sites of the support. The catalysts presented a high hydrogenation activity to decalin. With decreasing the Pd/Pt atomic ratio, the decalin decreased, while the yield of high molecular weight products (at high cetane number) increased, putting in evidence the role of the hydrogenolysis/ring opening reactions, catalyzed by Pt. With the lack of strong acid sites useless low molecular weight cracking compounds and tar could not be formed. Notably, the Pd/Pt pair was thio-resistant [44].

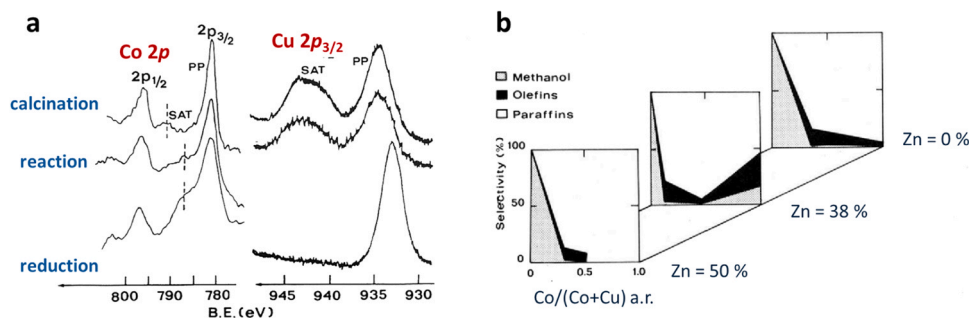


Fig. 1. Cu/Co/Zn/Cr HTs for the synthesis of hydrocarbons. a) Co 2p and Cu 2p_{3/2} XPS lines for the Co-4.0 sample after different treatments: i) calcination, ii) reaction, and iii) further reduction; b) Selectivity in methanol, paraffins, and olefins as a function of the Co/(Co + Cu) atomic ratio for catalysts with 24 % chromium and three different zinc contents, reaction temperature 290 °C, gas mixture, H₂:CO:CO₂ = 65:32:3 v/v, P = 1.2 MPa, GHSV = 3600 h⁻¹. Adapted from [40,41].

3.3. Hydrogenation of CO₂ to CH₄

In the last years, the attention has shifted to the hydrogenation of CO₂ to produce CH₄ (methanation or Sabatier reaction). By calcination of a Ni₇₅/Al₂₅ HT at 600 °C, after reduction small Ni nanoparticles were dispersed on the oxidic matrix, whose basic character was modified by adding rare-earth elements (Ni₇₀/M₅/Al₂₅ HT, with M= La, Y or Ce) atomic ratio, % [45] (Fig. 2). A high CH₄ productivity (101 L g_{Ni}⁻¹ h⁻¹) and stability at low oven temperature and high space velocity (480 L g⁻¹ h⁻¹, CO₂/H₂/N₂ = 1/4/1 v/v) was achieved with the La-catalyst. Dissociative and associative CO₂ activation on more reduced, highly dispersed, stable Ni nanoparticles and basic sites in the La₂O₃-Al₂O₃ matrix explained the catalytic results. The same catalysts were deposited on NiCrAlloy open-cell foams, and the HT precursors were prepared by electrodeposition. The combination of a stable coating, wherein Ni nanoparticles are well-dispersed, and small pore open-cell foams increased the performance of the structured catalysts in comparison to their pelletized counterpart, which could be related to an enhanced heat transfer [46]. The amount of Ni could be reduced by adding Mg to the catalyst composition (Ni/Mg/Al); however, the decreased Ni reducibility made it necessary to operate the reduction pretreatment at higher temperatures. A comparison between La and Fe promoters showed that the La-containing catalyst reached a better CH₄ productivity rate at high oven temperature (200 L g_{Ni}⁻¹ h⁻¹ at 325 °C), which could be related to the ability of lanthanum to keep smaller Ni⁰ particles and provide a higher basicity, despite in the Fe catalyst the NiFe alloy contributed to

the higher improved activity [47].

4. HTs as precursors of catalysts for syngas and H₂ production

4.1. Catalysts for steam reforming of methane

The research on catalysts for the highly endothermic steam reforming of methane to produce syngas was focused on novel HT Rh/Ni/Mg/Al catalysts, containing silicate as interlayer anion, calcined at high temperature, 900 °C for 12 h, to obtain a thermally stable catalyst. The silicates remained in the catalysts and an innovative structure was obtained. The structure was made by a forsterite-type crystalline phase (Mg₂SiO₄) as well as minor phases such as MgO, in which Ni and Rh were inserted, and a spinel defective phase. The catalysts were used in pelletized form, resulting in high activity (comparable to that of commercial catalysts) and stability with time-on-stream [48,49].

To prepare innovative catalysts with better heat transfer, a new method based on electrochemical deposition was developed. It allowed to deposit a Ni/Al HT on FeCrAlloy foams, as supports with high thermal conductivity [50]. The structured catalysts prepared by electrodeposition, after calcination at 900 °C, were made by a thin, strongly adherent film and with a suitable amount of active and stable catalyst. The optimized catalyst showed performances close to the thermodynamic equilibrium and stable with increasing the time-on-stream under industrial-like conditions [51].

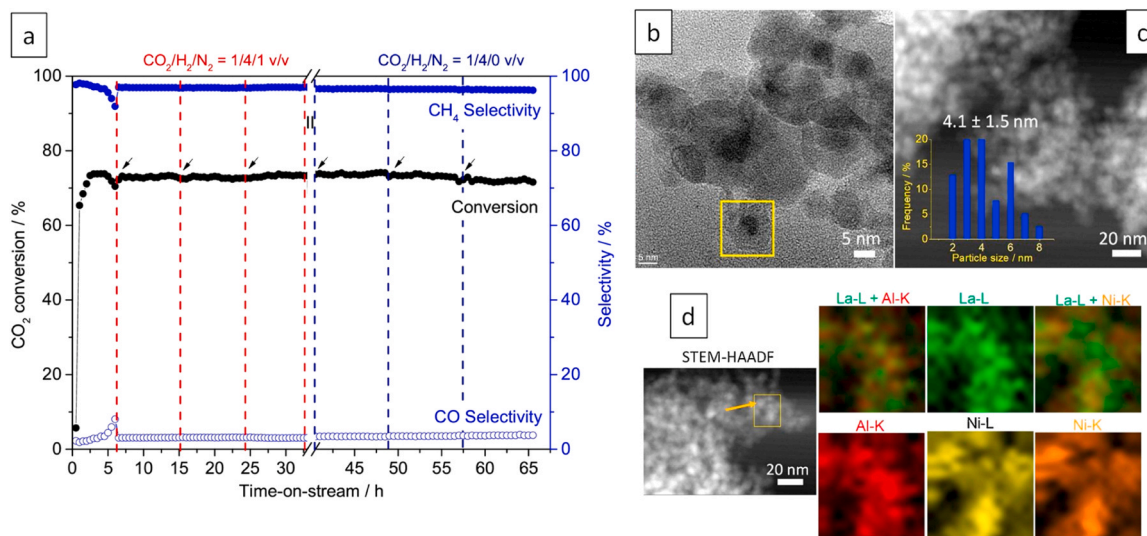


Fig. 2. CO₂ methanation on Ni₇₀/La₅/Al₂₅ catalyst: a) stability test of CO₂ methanation at 325 °C oven temperature. Flow 240 mL min⁻¹, 30 mg catalyst diluted in 470 mg quartz, 480 L g⁻¹ h⁻¹. Arrows denote shut-down to room temperature and start-up in N₂ flow; b) HRTEM and c) HAADF images of the spent catalyst, Ni particle size distribution (insets of Fig.); d) STEM-HAADF and elemental distribution in the yellow square. Adapted from [45].

4.2. Catalysts for partial oxidation of methane

The thermal stability and homogeneity of HT-derived catalysts were exploited for the preparation of materials for the exothermic catalytic partial oxidation (CPO). A wide variety of HTs were used as catalyst precursors based on noble metals, nickel, and bimetallic noble metal-transition metal.

For an industrial application HTs containing rhodium and ruthenium (Rh/Mg/Al and Ru/Mg/Al) were used after calcination at 900 °C to obtain new catalysts with well dispersed and reproducible noble metal particles, active in CPO and stable under severe reaction conditions [52].

The rhodium and ruthenium species in HT precursors, contained in low amounts, $\text{Rh}_x/\text{Mg}_{71}/\text{Al}_{29-x}$ ($x = 0.04, 1, 5$) and $\text{Ru}_x/\text{Mg}_{71}/\text{Al}_{29-x}$ ($x = 1, 5$) atomic ratio, %, after calcination at 900 °C were stabilized in an inert matrix and the used catalysts did not show any sintering or segregation phenomena [53]. HTs containing other noble metals were prepared: besides Rh and Ru also Ir, Pd and Pt ($\text{Ir}_5/\text{Mg}_{71}/\text{Al}_{24}$; $\text{Pd}_5/\text{Mg}_{66}/\text{Al}_{29}$; $\text{Pt}_4/\text{Mg}_{67}/\text{Al}_{29}$). Among all the catalysts investigated the partial oxidation activity decreased according to the order $\text{Rh} > \text{Ru} = \text{Ir} \gg \text{Pd} > \text{Pt}$. The best catalysts were those prepared from a Rh/Mg/Al HT with a 1 % Rh atomic ratio [54] (Fig. 3). Using a model catalyst with a 5 % Rh atomic ratio, highly dispersed Rh particles were obtained after reduction, active and stable after 100 h of time on stream, due to the formation of Rh dissolved in the Mg and Al matrix. The metal support interaction using HT-derived catalysts was superior to that obtainable by impregnation or deposition methods. The total amount of Rh was distributed 41 % in the spinel type and 59 % in the MgO phase [55]. The crystal structure refinements of $\text{M}/\text{MgAl} = 5:71:24$ atomic ratio, % ($\text{M} = \text{Ru}, \text{Rh}$ or Ir) HTs calcined at 650 or 900 °C showed different solubilities of noble metals in the oxide phases but an invariable substitution in the 16d site of spinel structure. The variation of the Mg/Al ratio, i.e. $\text{Rh}/\text{MgAl} = 5/71/24, 5/65/30, 5/80/15, 1/71/28, 1/65/34, 1/80/19$ atomic ratio, %, changed the distribution of the Rh and Ru in the MgO and MgAl_2O_4 phases and consequently the activity in the partial oxidation of methane. The activity and syngas selectivity were higher at high Mg/Al ratios, when Rh and Ru were almost completely mixed in the MgO [56,57] (Fig. 3c). Catalytic tests were carried out in autothermal conditions as a function of the residence time, using a $\text{Rh}/\text{MgAl} = 1/71/28$ atomic ratio, %. The temperature on the catalyst surface by IR thermography showed that the exothermic reactions are confined in the first part of the catalytic bed, while the reforming reactions happened at the end of the bed (Fig. 3b). Very short residence times evidenced that CO and H_2 had to be considered mainly as primary products [58].

The high price of Rh made it necessary to decrease its loading in the HT-derived catalysts without decreasing the performance trying to replace or combine it with the less expensive Ni active phase [59–62]. In Ni-based catalysts with different Ni content, i.e. $\text{Ni}_x/\text{Mg}_{71-x}/\text{Al}_{29}$ ($x =$

10, 34, 61, 71) atomic ratio, %, the reducibility and activity depended on the Ni content, due to the different distribution of Ni species among NiO , $(\text{Ni}, \text{Mg})\text{Al}_2\text{O}_4$ and NiO-MgO structures. High-loaded Ni catalysts required mild reduction conditions but were quickly deactivated due to carbon formation. Contrarily, catalysts with low Ni-content needed a severe reduction treatment but they were stable during the reaction at short contact times [59]. In these conditions, large temperature gradients and hot spots were measured. However, some parts of the Ni^0 at the entrance of the catalytic bed could be oxidized. The combination of small amounts of Rh with Ni, i.e. $\text{Rh}_1/\text{Mg}_{71}/\text{Al}_{28}$, $\text{Rh}_{0.1}/\text{Ni}_5/\text{Mg}_{66}/\text{Al}_{29}$, $\text{Rh}_{0.1}/\text{Ni}_6/\text{Mg}_{59}/\text{Al}_{35}$ atomic ratio, % helped to keep nickel in the reduced state during reaction in the first part of the bed and improved the reducibility of Ni^{2+} during the pretreatment. The scale of activity and syngas selectivity, also in comparison with a $\text{Ni}_{10}/\text{Mg}_{61}/\text{Al}_{29}$ catalyst, was the following: $\text{Ni}_{10} > \text{Rh}_{0.1}\text{Ni}_6 > \text{Rh}_1$, which could be explained based on the heat distribution and outlet surface temperature [60,61]. Bimetallic Rh/Ni, Ru/Ni, Ir/Ni catalysts prepared from HT precursors, i.e. $\text{Ni}_6/\text{M}_{0.1}/\text{Mg}_{59}/\text{Al}_{35}$ ($\text{M} = \text{Rh}, \text{Ru}, \text{Ir}$), $\text{Rh}_x/\text{Mg}_{71}/\text{Al}_{29-x}$ ($x = 1, 5$) atomic ratio, %, were investigated at very low residence times, in conditions where O_2 was still present. The high activity of the Rh/Ni catalysts, in which the Rh maintained the Ni in the reduced state, was highlighted [62].

All the above reported works deal with catalysts prepared by the conventional coprecipitation method. In addition, Ni/Mg/Al and Rh/Ni/Mg/Al catalysts were obtained by calcination of HTs aged by microwave hydrothermal treatment [63]. Moreover, Rh was added by chemical vapor deposition to the calcined Ni/Mg/Al catalyst, instead of being incorporated into the parent HT in the coprecipitation [64]. The characterization and catalytic activity tests demonstrated the strongest Rh/Ni interaction in coprecipitated catalysts, which yielded better performances with a lower carbon formation and high resistance towards metallic particle sintering.

The ability of intercalating anionic species different from carbonates in the interlayer region was exploited to prepare Ni, Rh, and Rh/Ni catalysts with enhanced mechanical stability for the catalytic partial oxidation due to the formation of a forsterite phase (MgSi_2O_4) [48, 65–68]. The low-loaded Rh catalyst prepared by HT silicate was more active and selective than the one prepared by CO_3^{2-} [62]. The activity of both Rh and Ni catalysts depended on the silicate content since it modified the available MgO and MgAl_2O_4 phase to incorporate Rh^{3+} or Ni^{2+} in the calcined catalyst and in turn to disperse their metallic particles after reduction [64,68]. In the case of Ru-based catalysts, i.e. $\text{Ru}_x\text{Mg}_{80}\text{Al}_{20-x}$ HT ($x = 0.1, 0.25$) atomic ratio, %, the inclusion of silicates fostered the segregation of RuO_2 and therefore the deactivation after tests at high temperature and 55–65 ms [69].

To decrease the formation of hot spots in the catalytic partial oxidation of CH_4 and increase the mass transfer, structured catalysts based on small pore FeCrAlloy and NiCrAl foams were studied. Most of the works were performed with Rh/Mg/Al catalytic coatings prepared

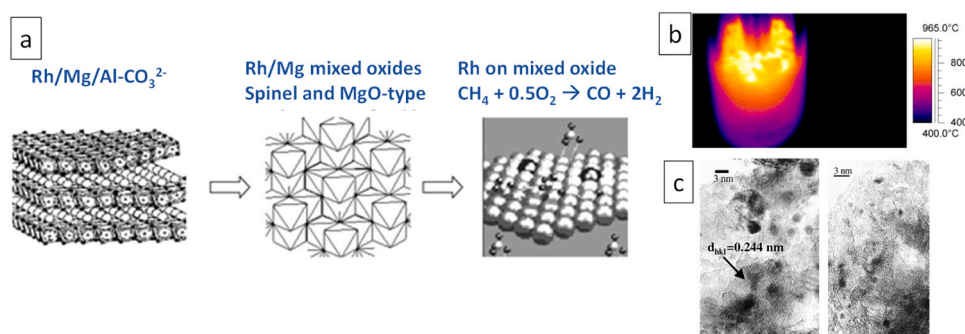


Fig. 3. Rh/Mg/Al HTs for the CPO of CH_4 : a) schema of the structure of the HT precursor, the calcined catalyst and the reaction over reduced catalyst; b) IR thermography of the top $\text{Rh}_5/\text{Mg}_{71}/\text{Al}_{24}$ catalyst bed recorded under autothermal conditions $\text{CH}_4/\text{O}_2/\text{He} = 2/1/4$ v/v, $\tau = 1.8$ ms, catalyst: 0.05 g; c) HRTEM after calcination of $\text{Rh}_1/\text{Mg}_{71}/\text{Al}_{28}$ at 900 °C and reduction at 750 °C spinel zone (left) MgO zone (right). Adapted from [55–57].

by electrodeposition of the HT precursors directly on the foam surface followed by calcination at 900 °C [70–78]. The reduced catalysts were made by thin coatings, highly adherent to the metallic surface due to their chemical interaction [73], but that contained enough well-dispersed and stabilized Rh⁰ particles to provide a high catalytic activity in the syngas production [74,75] (Fig. 4). The use of NiCrAl foams allowed, under reaction conditions, a decrease of the hot spots in comparison to FeCrAl foams [76]. Likely, the heat generated in the first part of the bed due to the total methane oxidation is transferred to the second part and used for the endothermic steam reforming.

4.3. Catalysts for steam and dry reforming of clean biogas

Ni-based catalysts promoted by different amounts of Rh, for instance, Ni/Rh/MgAl = 10/0.5/35.6/14.6 wt %, were used as precursors of catalysts of the combined dry and steam reforming of clean biogas (CH₄/CO₂ = 50/50 v/v) to produce syngas suitable for Fischer-Tropsch or methanol synthesis. The addition of a small amount of Rh increased the CO₂ conversion and significantly decreased the carbon formation. While increasing the M²⁺/M³⁺ atomic ratio from 3 to 4 (and consequently the basicity of the catalyst) enhanced the affinity of the CO₂ with the catalytic surface and favoured the formation of highly dispersed, stable and more reducible Ni-Rh nanoparticles, therefore improving the activity [79]. The incorporation of Rh using a {Ni₁₀Rh(CO)₁₉}{(CH₃CH₂)₄N}₃ cluster as a precursor of the active particles promoted the Ni-Rh interaction. Low metal loaded catalysts with highly dispersed bimetallic nanoparticles on the MgO and MgAl₂O₄ matrix displayed better catalyst activity and stability, with low carbon deposition with time-on-stream [80].

The heat transfer was also enhanced in the endothermic combined steam and dry reforming by using Rh and Ru HT-derived catalysts, Rh or Ru_x/Mg₇₀/Al_{30-x} (x = 2,5) atomic ratio, %, coated on metallic foams [81]. The structured catalysts operated at high space velocities and low Steam to CH₄ ratio, increasing the biogas valorization and thus the productivity.

4.4. Catalysts for the water gas shift

HT-derived catalysts were applied in water gas shift reaction to further produce H₂ from syngas through the conversion of CO [82]. Medium temperature water gas shift catalysts, operating at 250–350 °C, were obtained by calcination at 550 °C and reduction of Cu/Zn/Al HTs with a Cu content lower than 30 wt %. The best catalyst had a 20 wt %

Cu, M²⁺/M³⁺ = 2.0 atomic ratio, reaching the equilibrium value like a commercial catalyst. The catalytic behavior was related to the Cu⁰ surface area and the Cu/ZnO interactions.

5. HT as precursors of catalysts for environmental applications

HT-derived catalysts were also used in environmental catalytic processes such as the removal of NO_x for lean-burn gasoline or light-duty diesel vehicles by selective catalytic reduction and storage/reduction.

The selective catalytic reduction with NH₃ in the absence or in the presence of oxygen to decrease NO emissions was investigated with catalysts obtained from Cu/Mg/Al HT precursor and compared with a catalyst obtained by Cu impregnation on a Mg/Al mixed oxide [83]. HT-derived catalyst performed better than the CuO-supported catalyst feeding the gas mixture containing excess oxygen due to the presence of well dispersed and stable octahedrally coordinated Cu²⁺ ions. The competitive NH₃ oxidation on the surface of the Mg/Al mixed oxide was suppressed by controlling the catalyst composition. The optimized catalyst exhibited a behaviour comparable to that of a commercial V₂O₅-WO₃/TiO₂ catalyst. The role of Cu and the Mg/Al matrix on the properties of the catalyst and in the reaction mechanism were elucidated and identified by FT-IR feeding NH₃ and NO [84].

For the NO_x storage-reduction (NO_xSR) novel catalysts were prepared by impregnation of calcined commercial Mg/Al HTs with Pt (1 wt %), 1Pt/HT-x (x =Mg/Al atomic ratio), and/or with Cu (4 wt %) [85–89]. The optimized catalyst, 1Pt-4Cu/HT-2.0 was renamed 1Pt-4Cu/HT-C (HT-C= Condea with Mg/Al 2.0 at. ratio). This catalyst showed better performances than 1Pt-15Ba/Al₂O₃ Toyota-type NO_xSR catalysts at reaction temperature lower than 250 °C and improved resistance to deactivation by SO₂, Fig. 5. Using HTs with different Mg/Al atomic ratios, 1Pt/HT-x (x =1.3, 2.0 and 3.0, respectively) the catalytic activity and the stability increased with increasing the Mg/Al, Fig. 5b,c, also after hydrothermal treatment. The basicity of the well-dispersed Mg (Al)O mixed oxide particles, lower than the one of BaO, was responsible for the promoted low-temperature activity, due to a lower inhibition of Pt activity and thermal stability of the stored NO_x. The catalyst 1Pt/HT-2.0, having a most compact morphology, showed a slightly higher deactivation. The presence of Cu slightly inhibited activity at low temperature, although improved activity and resistance to deactivation at 300 °C.

The decomposition of N₂O to N₂ under conditions of industrial interest for its removal in adipic acid plants, N₂O concentration about 18 % v/v also in the presence of 10 % O₂, was investigated over Rh/

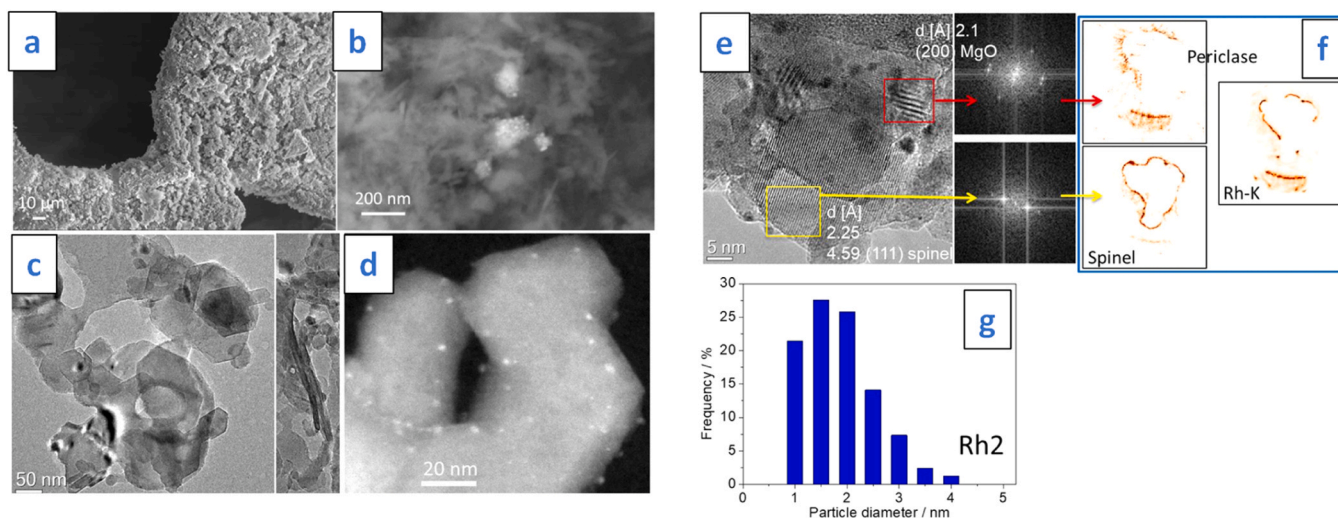


Fig. 4. Characterization of Rh₂/Mg₇₀/Al₂₈ catalyst after CPO of CH₄ tests: a, b) FE-SEM images; c, d) HRTEM and STEM-HAADF images; e) FFT of regions indicated in the TEM image; f) nano-XRF/XRD distributions; g) Rh particle size distribution. Adapted from [75].

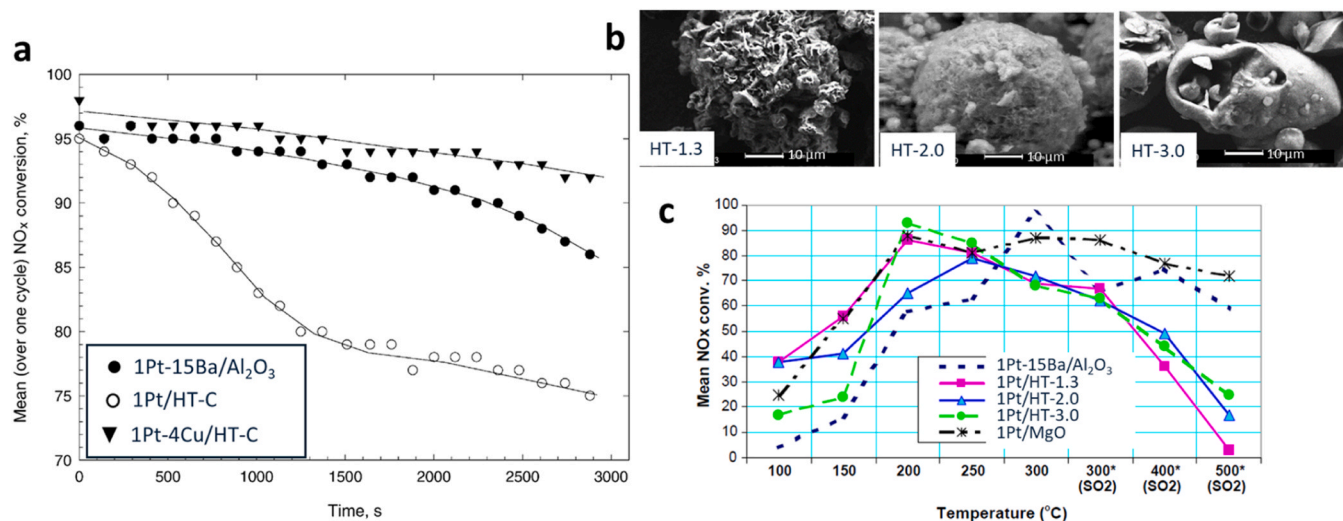


Fig. 5. Commercial Mg/Al HTs impregnated with Pt for NO_x storage-reduction: a) Mean NO_x conversion (over one cycle) at 300 °C as a function of time-on-stream in NO_xSR tests in the presence of 20 ppm SO₂; b) SEM replicas for the different HT-*x* (*x* =Mg/Al atomic ratio) precursors; c) NO_xSR activity as a function of the reaction temperature for the 1Pt/HT-*x* (*x* =Mg/Al atomic ratio) and the reference 1Pt-15Ba/Al₂O₃ and 1Pt/MgO catalysts. The optimized catalyst, 1Pt-4Cu/HT-2.0 was renamed 1Pt-4Cu/HT-C (HT-C= Condea with Mg/Al 2.0 atomic ratio) *(SO₂)=after deactivation by SO₂. Adapted from [85,88].

Mg/Al and Rh/Co/Al HT, Rh_{*x*}/Mg₇₁/Al_{29-*x*} (*x* = 0, 5, 1) and Rh_{0.5}/Co_{74.5}/Al₂₅ atomic ratio, %, derived catalysts [90]. The catalysts were active and stable under severe reaction conditions. Other active elements, i.e. Pd 1 % or La 1 % atomic ratio, were added in the HT structure to develop synergetic effects, without any interactions due to side phase segregation, or lack of homogeneity.

HT-derived catalysts were tested in the decomposition of N₂O in very diluted feeds (1000 ppm), also in the presence of inhibitors (O₂ + NO), to simulate a stream from nitric acid production [91]. A thin coating of RhMgAl catalysts, i.e. Rh₂/Mg₇₀/Al₂₈, Rh₁/Mg₇₀/Al₂₉, was deposited on open-cell FeCrAlloy foams, which became reduced to Rh⁰ during the reaction. The activity of the structured catalyst was comparable with that of a pelletized counterpart for constant Rh loading. However, the low amount of active phase in the thin catalytic coating provoked a steady deactivation during the first 20 h of time-on-stream and then a stable level was reached.

6. Miscellaneous

The gas phase Beckman rearrangement, the transformation of cyclohexanoneoxime to caprolactam, was performed with Mg/Al or Ni/Al catalysts containing boron species as the active phase. Borate species were incorporated in the interlayer space of the parent HTs and the catalysts were obtained by calcination at 400 °C. A high boron content led to higher caprolactam selectivity and cyclohexanone-oxime conversion. However, only a part of boron was stabilized in the HT structure and surface borates were more easily obtained by washing with ammonium tetraborate the solid with more satisfactory catalytic results [92–94].

A Pd₅/Mg₆₆/Al₂₉ HT atomic ratio, % was a precursor of a catalyst for the total oxidation of methane [95]. The thermal treatment led to the segregation of PdO and/or Pd⁰, in amounts and size that depended on the atmosphere. The catalyst containing a mixture of PdO and Pd⁰ was more active at low temperatures, while Pd⁰ was the active specie at higher temperatures.

Mg/Al HTs intercalated by OH⁻, were used as basic catalysts for the condensation of aromatic aldehydes with acetone [96]. The catalysts were prepared by calcination of Mg/Al HTs at 500 °C and rehydration at room temperature in absence of CO₂. High reaction temperature and long reactions favoured the formation of arylideneacetone, meanwhile, the best catalytic performance was achieved with a Mg/Al = 2.5 atomic

ratio. A semi-continuous process was developed consisting in the addition of the aromatic aldehyde during the process when the conversion was below 80 %; this significantly increased the productivity per kilogram of catalysts.

Bifunctional HT-derived catalysts were used for the synthesis of isobutyl alcohol from methanol and *n*-propanol through the Guerbet condensation. The catalysts contained the basic MgAlO_{*x*} mixed oxide and a dehydrogenating/hydrogenating metal (Pd, Rh, Ni or Cu) [97]. The CuMgAlO_{*x*} mixed oxide catalysts showed the best activity and selectivity values. These values were similar to those achieved with the mixture of copper chromite and MgAlO_{*x*} mixed oxides [98], but reducing pollution problems related to the use of chromite. Similar catalysts were later used in the Guerbet condensation of ethanol to give *n*-butanol [99]. The Cu content was the key to control the selectivity; a low Cu-content favored the condensation to *n*-butanol and higher alcohols (hexanol), while a high Cu content promoted the ester formation. The differences were related to the metallic/acid/basic sites in the fresh catalysts, a decrease in the Cu content provoked an increase of the basic sites and a decrease of the Cu reducibility. However, the catalysts were partially reconstructed to the parent HT structure due to the coproduced water.

7. Conclusions

The work performed by A. Vaccari together with his numerous co-workers demonstrated that hydrotalcite-derived catalysts have been, are, and will be optimal materials not only for catalytic processes requiring metallic particles highly dispersed on supports with tailored acidic-basic properties, but also in unexpected areas, thanks to the possibility of tailoring the catalysts for specific substrates and/or reactions. The basis for their wide applicability in hydrogenation, oxidation, reforming, condensation, organic, and environmental application reactions relies on the high versatility of the layered structure: i) a variable M²⁺/M³⁺ ratio (e.g. Mg/Al, Zn/Al); ii) ability to host the cations of catalytic active elements (e.g. Ni²⁺, Co²⁺, Cu²⁺, Rh³⁺, Ru³⁺) or promoters (e.g. La³⁺), so capitalizing on unusual synergistic effects, and iii) the possibility for intercalating different anions. But other features make them materials with unique catalytic properties. The catalysts are obtained by thermal decomposition of the layered structure from medium (350–600 °C) to high (up to 900 °C) temperature. The calcination temperature determines the crystalline phases, hence the distribution of

the active species, reducibility, and metal-support interaction, but also surface area, porosity, and acidic-basic sites, and it is possible to reconstruct to the parent hydrotalcite by exploiting the memory effect. Regardless of the calcination temperature the catalysts show a high dispersion and stability of the metallic particles after reduction (and reaction). This is true for a wide range of active phase loadings, making them an alternative to conventional impregnated catalysts. The synthesis of HTs is easily and reproducibly performed by coprecipitation, but other methods can be used to directly precipitate them on the surface of supports. The electrodeposition of HTs on metallic supports is one example that increases the applicability of the catalysts not only for thermocatalytic processes limited by mass and heat transfer, but also for electrochemical processes. Thus, A. Vaccari's work highlighted and contributed to the understanding of the properties of cheap, non-corrosive, environmentally friendly HTs for application in catalysis, in the laboratory and in industrial processes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

No data was used for the research described in the article.

References

- R. Trujillano, F.M. Labajos, V. Rives, Hydrotalcites, a rapid survey on the very recent synthesis and applications procedures, *Appl. Clay Sci.* 238 (2023) 106927, <https://doi.org/10.1016/j.clay.2023.106927>.
- F. Cavani, F. Trifirò, A. Vaccari, Hydrotalcite-type anionic clays, *Catal. Today* 11 (1991) 173–301, [https://doi.org/10.1016/0920-5861\(91\)80068-K](https://doi.org/10.1016/0920-5861(91)80068-K).
- A. Vaccari, Synthesis and catalytic applications of hydrotalcite-type anionic clays, *La Chim. e l'Ind.* 74 (1992) 174–181.
- A. Vaccari, Preparation and catalytic properties of cationic and anionic clays, *Catal. Today* 41 (1998) 53–71, [https://doi.org/10.1016/S0920-5861\(98\)00038-8](https://doi.org/10.1016/S0920-5861(98)00038-8).
- A. Vaccari, Clays and catalysis: a promising future, *Appl. Clay Sci.* 14 (1999) 161–198, [https://doi.org/10.1016/S0169-1317\(98\)00058-1](https://doi.org/10.1016/S0169-1317(98)00058-1).
- F. Basile, A. Vaccari, Applications of hydrotalcite type anionic clays (layered double hydroxides) in catalysis, in: V. Rives (Ed.), *Layered Double Hydroxides: Present and Future*, Nova Science Publishers, New York, 2001, pp. 323–365.
- F. Basile, G. Fornasari, A. Vaccari, Catalytic activity of layered double hydroxides or hydrotalcite-type anionic clays, in: A. Hubbard (Ed.), *Encyclopedia of Surface and Colloidal Science*, vol. 1, Dekker, New York, 2002, pp. 909–930.
- S. Albertazzi, F. Basile, A. Vaccari, Catalytic properties of layered double hydroxide (hydrotalcite-type anionic clays) in F. Wypych and K.G. Satyanarayana (Eds.), *Clay Surface: Fundamentals and Applications*. Elsevier, Amsterdam, 2004, vol. 1, pp. 496–546.
- A. Vaccari, F. Basile, G. Fornasari, Anionic Clays: Catalytic Activity of Layered Double Hydroxides or Hydrotalcite-Type, in F. Wypych and K.G. Satyanarayana (Eds.), *Interface Science and Technology* book series, Elsevier, 2015, pp. 416–435.
- A. Vaccari, Preparation and catalytic properties of cationic and anionic clays, in G. Bellussi (Ed), *Materials Design for Catalytic Application*, Melegnano, 1996, pp. 50–71.
- F. Trifirò, A. Vaccari, Hydrotalcite-like anionic clays (layer double hydroxides), in J.L. Atwood, J.E.D. Davies, D.D. MacNicol et al. (Eds) *Solid-state Supramolecular Chemistry: Two- and Three- Dimensional Inorganic Networks*, Pergamon, Oxford, 1996, vol. 7, pp. 251–291.
- F. Trifirò, A. Vaccari, G. Del Piero, Preparation and properties of copper synthetic anionic clays in K.K. Unger, J. Rouquerol, K.S.W. Sing, H. Kral (Eds), *Characterization of porous solids*, Elsevier, Amsterdam 1988, vol. 39, pp. 571–580.
- O. Clause, M. Gazzano, F. Trifirò, A. Vaccari, L. Zatorski, Preparation and thermal reactivity of nickel/chromium and nickel/aluminium hydrotalcite-type precursors, *Appl. Catal.* 73 (1991) 217–236, [https://doi.org/10.1016/0166-9834\(91\)85138-L](https://doi.org/10.1016/0166-9834(91)85138-L).
- O. Clause, M. Goncalves Coelho, M. Gazzano, D. Matteuzzi, F. Trifirò, A. Vaccari, Synthesis and thermal reactivity of nickel-containing anionic clays, *Appl. Clay Sci.* 8 (1993) 168–186, [https://doi.org/10.1016/0169-1317\(93\)90035-Y](https://doi.org/10.1016/0169-1317(93)90035-Y).
- F. Basile, G. Fornasari, M. Gazzano, A. Vaccari, Synthesis and thermal evolution of hydrotalcite-type compounds containing noble metals, *Appl. Clay Sci.* 16 (2000) 185–200, [https://doi.org/10.1016/S0169-1317\(99\)00053-8](https://doi.org/10.1016/S0169-1317(99)00053-8).
- B. Ballarin, M. Gazzano, R. Seeber, F. Gulmanelli, D. Tonelli, A. Vaccari, Electrodes coated by hydrotalcite-like clays. Effect of the metals and the intercalated anions on ion accumulation and retention capability, *J. Electroanal. Chem.* 445 (1998) 27–37, [https://doi.org/10.1016/S0022-0728\(97\)00538-X](https://doi.org/10.1016/S0022-0728(97)00538-X).
- M. Monti, P. Benito, F. Basile, G. Fornasari, M. Gazzano, E. Scavetta, D. Tonelli, A. Vaccari, Electrodeposition of Ni/Al and Mg/Al layered double hydroxides on Pt and FeCrAlloy supports: study and control of the pH near the electrode surface, *Electrochim. Acta* 108 (2013) 596–604, <https://doi.org/10.1016/j.electacta.2013.06.143>.
- P.H. Ho, M. Monti, E. Scavetta, D. Tonelli, E. Bernardi, L. Nobili, G. Fornasari, A. Vaccari, P. Benito, Reactions involved in the electrodeposition of hydrotalcite-type compounds on FeCrAlloy foams and plates, *Electrochim. Acta* 222 (2016) 1335–1344, <https://doi.org/10.1016/j.electacta.2016.11.109>.
- P.H. Ho, E. Scavetta, F. Ospitali, D. Tonelli, G. Fornasari, A. Vaccari, P. Benito, Effect of metal nitrate concentration on the electrodeposition of hydrotalcite-like compounds on open-cell foams, *Appl. Clay Sci.* 151 (2018) 109–117, <https://doi.org/10.1016/j.clay.2017.10.019>.
- P.H. Ho, E. Scavetta, D. Tonelli, G. Fornasari, A. Vaccari, P. Benito, Hydrotalcite-type materials electrodeposited on open-cell metallic foam as structured catalysts, *Inorganics* 6 (2018) 74–92, <https://doi.org/10.3390/inorganics6030074>.
- E. Papa, A. Natali Murri, A. Vaccari, E. Landi, V. Medri, Geopolymer-hydrotalcite hybrid beads by ionotropic gelation, *Appl. Clay Sci.* 215 (2021) 106326, <https://doi.org/10.1016/j.clay.2021.106326>.
- S. Gusi, F. Trifirò, A. Vaccari, Kinetic study of the reduction of copper-zinc-aluminum mixed oxide catalysts, *React. Solids* 2 (1986) 59–71, [https://doi.org/10.1016/0168-7336\(86\)80064-X](https://doi.org/10.1016/0168-7336(86)80064-X).
- O. Clause, B. Rebours, E. Merlin, F. Trifirò, A. Vaccari, Preparation and characterization of nickel-aluminum mixed oxides obtained by thermal decomposition of hydrotalcite-type precursors, *J. Catal.* 133 (1992) 231–246, [https://doi.org/10.1016/0021-9517\(92\)90200-2](https://doi.org/10.1016/0021-9517(92)90200-2).
- F. Beccat, J.C. Roussel, O. Clause, A. Vaccari, F. Trifirò, High thermal stability of nickel-aluminum mixed oxides obtained from hydrotalcite-type precursors, in T.J. Dines, C.H. Rochester, J. Thomas (Eds), *Catalysis and Surface Characterization*, Royal Society of Chemistry London, 1992, pp. 32–41.
- F. Trifirò, A. Vaccari, O. Clause, Nature and properties of Ni-containing mixed oxides obtained from hydrotalcite-type anionic clays, *Catal. Today* 21 (1994) 185–195, [https://doi.org/10.1016/0920-5861\(94\)80043-X](https://doi.org/10.1016/0920-5861(94)80043-X).
- D. Matteuzzi, F. Trifirò, A. Vaccari, M. Gazzano, O. Clause, Synthesis and properties of high surface area Ni/Mg/Al mixed oxides via anionic clay precursors, J. Rouxel, M. Toumoux R. Brec (Eds) *Soft Chem. Routes N. Mater. - Chim. Douce Sci.*, Trans. Tech. Aedermannsdorf 152-153 (1994) 391–394.
- G. Fornasari, M. Gazzano, D. Matteuzzi, F. Trifirò, A. Vaccari, Structure and reactivity of high-surface-area Ni/Mg/Al mixed oxides, *Appl. Clay Sci.* 10 (1995) 69–82, [https://doi.org/10.1016/0169-1317\(95\)00022-V](https://doi.org/10.1016/0169-1317(95)00022-V).
- M. Gazzano, W. Kagunya, D. Matteuzzi, A. Vaccari, Neutron diffraction studies of polycrystalline Ni/Mg/Al mixed oxides obtained from hydrotalcite-like precursors, *J. Phys. Chem.* 101 (1997) 4514–4519, <https://doi.org/10.1021/jp963761q>.
- F. Basile, I. Bersani, P. Del Gallo, S. Fiorilli, G. Fornasari, D. Gary, R. Morterra, B. Onida, A. Vaccari, *In-situ* -IR characterization of CO interacting with Rh nanoparticles obtained by calcination and reduction of hydrotalcite-type precursors, *Intern. J. Spectr.* (2011). ID 458089.
- S. Albertazzi, F. Basile, P. Benito, P. Del Gallo, G. Fornasari, D. Gary, V. Rosetti, A. Vaccari, Effects of silicates on the structure of Ni-containing catalysts obtained from hydrotalcite-type precursors, *Catal. Today* 128 (2007) 258–263, <https://doi.org/10.1016/j.cattod.2007.06.067>.
- I. Pettiti, D. Gazzoli, P. Benito, G. Fornasari, A. Vaccari, The reducibility of highly stable Ni-containing species in catalysts derived from hydrotalcite-type precursors, *RSC Adv.* 5 (2015) 82282–82291, <https://doi.org/10.1039/C5RA13863A>.
- F. Trifirò, A. Vaccari, G. Del Piero, V. Fattore and B. Notari, Preparation and characterization of Cu-Zn-Al mixed oxides for low-temperature methanol synthesis in D. Shopov, A. Andreev, A. Palazov, L. Petrov (Eds), *Proc. Vth Intern. Symp. Heterogeneous Catalysis*, Publishing House of the Bulgarian Academy of Sciences, Sofia, 1983, Vol. II, pp. 303–307.
- P. Gherardi, O. Ruggeri, F. Trifirò, A. Vaccari, G. Del Piero, G. Manara, B. Notari, Preparation of Cu-Zn-Al mixed hydroxycarbonates precursors of catalysts for the synthesis of methanol at low pressure, *Stud. Surf. Sci. Catal.* 16 (1983) 723–731, [https://doi.org/10.1016/S0167-2991\(09\)60062-8](https://doi.org/10.1016/S0167-2991(09)60062-8).
- C. Busetto, G. Del Piero, G. Manara, F. Trifirò, A. Vaccari, Catalysts for low-temperature methanol synthesis. Preparation of Cu-Zn-Al mixed oxides via hydrotalcite-like precursors, *J. Catal.* 85 (1984) 260–266, [https://doi.org/10.1016/0021-9517\(84\)90130-1](https://doi.org/10.1016/0021-9517(84)90130-1).
- S. Gusi, F. Trifirò, A. Vaccari, G. Del Piero, Catalysts for low-temperature methanol synthesis, *Catal. Behav. Cu/Zn /Al mixed Oxide*, *J. Catal.* 94 (1985) 120–127, [https://doi.org/10.1016/0021-9517\(85\)90087-9](https://doi.org/10.1016/0021-9517(85)90087-9).
- G. Fornasari, S. Gusi, F. Trifirò, A. Vaccari and G. Del Piero, Role of different copper species in low-temperature methanol catalysts in D. Shopov, A. Andreev, A. Palazov, L. Petrov (Eds), *Proc. Vth Intern. Symp. Heterogeneous Catalysis*, Publishing House of the Bulgarian Academy of Sciences, Sofia, 1987, Vol I, pp. 241–246.
- S. Gusi, F. Pizzoli, F. Trifirò, A. Vaccari, G. Del Piero, Preparation of multicomponent catalysts for the hydrogenation of carbon monoxide via hydrotalcite-like precursors, in: B. Delmon, P. Grange, P.A. Jacobs, G. Poncelet (Eds.), *Preparation of Catalysts IV*, vol. 31, Elsevier, Amsterdam, 1987, pp. 753–765.
- F. Cavani, O. Clause, F. Trifirò, A. Vaccari, Anionic clays with hydrotalcite-like structure as precursors of hydrogenation catalysts. *Adv. Catal. Design, World Scientific Publisher*, 1991, pp. 186–190.
- G. Fornasari, S. Gusi, T.M.G. La Torretta, F. Trifirò, A. Vaccari, Synthesis of higher alcohols on low-temperature methanol catalysts in A. Crucq and A. Frennet (Eds),

- Catalysis and Automotive Pollution Control, Elsevier, Amsterdam, 1987, pp 469–482.
- [40] G. Fornasari, A.D. Huysser, L. Mintchev, F. Trifirò, A. Vaccari, Cobalt modified Cu-Zn-Cr catalysts in the synthesis of methanol, *J. Catal.* 135 (1992) 386–399, [https://doi.org/10.1016/0021-9517\(92\)90041-F](https://doi.org/10.1016/0021-9517(92)90041-F).
- [41] G. Fornasari, S. Gusi, F. Trifirò, A. Vaccari, Cobalt mixed spinels as catalysts for the synthesis of hydrocarbons, *Ind. Eng. Chem. Res.* 26 (1987) 1500–1505, <https://doi.org/10.1021/ie00068a002>.
- [42] G.L. Castiglioni, M. Ferrari, A. Guercio, A. Vaccari, R. Lancia, C. Fumagalli, Chromium free catalysts for selective vapor phase hydrogenation of maleic anhydride to γ -butyrolactone, *Catal. Today* 27 (1996) 181–186, [https://doi.org/10.1016/0920-5861\(95\)00209-X](https://doi.org/10.1016/0920-5861(95)00209-X).
- [43] F.M. Cabello, D. Tichit, B. Coq, A. Vaccari, N.T. Dung, Hydrogenation of acetonitrile on nickel-based catalysts prepared from hydrotalcite-like precursors, *J. Catal.* 167 (1997) 142–152, <https://doi.org/10.1006/jcat.1997.1523>.
- [44] S. Albertazzi, G. Busca, E. Finocchio, R. Glockler, A. Vaccari, New Pd/Pt on Mg/Al basic mixed oxides for the hydrogenation and hydrogenolysis of naphthalene, *J. Catal.* 223 (2004) 372–381, <https://doi.org/10.1016/j.jcat.2004.01.024>.
- [45] P.H. Ho, G. Sanghez de Luna, S. Angelucci, A. Canciani, W. Jones, D. Decarolis, F. Ospitali, E. Rodriguez-Aguado, E. Rodriguez-Castellon, G. Fornasari, A. Vaccari, A.M. Beale, P. Benito, Understanding structure activity relationship in highly active La promoted Ni catalysts for CO₂ methanation, *Appl. Catal. B* 279 (2020) 119256, <https://doi.org/10.1016/j.apcatb.2020.119256>.
- [46] P.H. Ho, G. Sanghez de Luna, F. Ospitali, G. Fornasari, A. Vaccari, P. Benito, Open cell coated by Ni/X/Al hydrotalcite -type derived catalysts (X=Ce, La, Y) for CO₂ methanation, *J. CO₂ Util.* 42 (2020) 101327, <https://doi.org/10.1016/j.jcou.2020.101327>.
- [47] P.H. Ho, G. Sanghez de Luna, N. Schiaroli, A. Natoli, F. Ospitali, M. Battisti, F. Di Renzo, C. Lucarelli, A. Vaccari, G. Fornasari, P. Benito, Effect of Fe and La performance of NiMgAl HT-derived catalysts in the methanation of CO₂ and Biogas, *Ind. Eng. Chem. Res.* 61 (2022) 10511–10521, <https://doi.org/10.1021/acs.iecr.2c00687>.
- [48] A. Vaccari, F. Basile, G. Fornasari, V. Rosetti, D. Gary, P. Del Gallo, Supported catalysts for producing H₂ and/or CO from low molecular weight hydrocarbons, *World Patent WO 108,276* (2004) *Air Liquide*.
- [49] F. Basile, S. Albertazzi, P. Arpentinier, P. Del Gallo, G. Fornasari, D. Gary, V. Rosetti, A. Vaccari, New Catalyst for the syngas production obtained by the hydrotalcite-type precursor containing silicate, *Stud. Surf. Sci. Catal.* 147 (2004) 211–215, [https://doi.org/10.1016/S0167-2991\(04\)80053-3](https://doi.org/10.1016/S0167-2991(04)80053-3).
- [50] F. Basile, P. Benito, P. Del Gallo, G. Fornasari, D. Gary, V. Rosetti, E. Scavetta, D. Tonelli, A. Vaccari, Highly conductive Ni steam reforming catalysts prepared by electrodeposition, *Chem. Commun.* (25) (2008) 2917–2919, <https://doi.org/10.1039/B801645C>.
- [51] F. Basile, P. Benito, G. Fornasari, V. Rosetti, E. Scavetta, D. Tonelli, A. Vaccari, Electrochemical synthesis of novel structured catalysts for H₂ production, *Appl. Catal. B* 91 (2009) 563–572, <https://doi.org/10.1016/j.apcatb.2009.06.028>.
- [52] L. Basini, G. Fornasari, F. Trifirò, A. Vaccari, Material having layered structure of hydrotalcite type, and uses thereof, EP0725038 (1995) *Snamprogetti*.
- [53] F. Basile, L. Basini, G. Fornasari, M. Gazzano, D. Gary, V. Trifirò, A. Vaccari, New hydrotalcite-type anionic clay containing noble metals, *Chem. Commun.* (1996) 2435–2436, <https://doi.org/10.1039/C9960002435>.
- [54] F. Basile, L. Basini, G. Fornasari, M. Gazzano, F. Trifirò, A. Vaccari, Anionic clays as precursors of noble metal based catalysts for methane activation, *Stud. Surf. Sci. Catal.* 118 (1998) 31–40, [https://doi.org/10.1016/S0167-2991\(98\)80165-1](https://doi.org/10.1016/S0167-2991(98)80165-1).
- [55] F. Basile, G. Fornasari, M. Gazzano, A. Kiennemann, A. Vaccari, Preparation and characterisation of a stable Rh catalyst for the partial oxidation of methane, *J. Catal.* 217 (2003) 245–252, [https://doi.org/10.1016/S0021-9517\(03\)00021-6](https://doi.org/10.1016/S0021-9517(03)00021-6).
- [56] F. Basile, G. Fornasari, M. Gazzano, A. Vaccari, Rh, Ru and Ir catalysts obtained by HT precursors: effect of the thermal evolution and composition on the material structure, *J. Mater. Chem.* 12 (2002) 3296–3303, <https://doi.org/10.1039/B205146J>.
- [57] F. Basile, G. Fornasari, V. Rosetti, F. Trifirò, A. Vaccari, Effect of the Mg/Al ratio of the hydrotalcite-type precursor on the dispersion and activity of Rh and Ru catalysts for the partial oxidation of methane, *Catal. Today* 91–92 (2004) 293–297, <https://doi.org/10.1016/j.cattod.2004.03.047>.
- [58] F. Basile, G. Fornasari, F. Trifirò, A. Vaccari, Reactivity and thermal profile of methane partial oxidation at very short residence time, *Stud. Surf. Sci. Catal.* 130 (2000) 449–454, [https://doi.org/10.1016/S0167-2991\(00\)80998-2](https://doi.org/10.1016/S0167-2991(00)80998-2).
- [59] F. Basile, L. Basini, M.D. Amore, G. Fornasari, A. Guarinoni, D. Matteuzzi, G. Del Piero, F. Trifirò, A. Vaccari, Ni/Mg/Al anionic clay derived catalysts for the catalytic partial oxidation of methane, *Resid. Time Depend. React. -Features, J. Catal.* 173 (1998) 247–256, <https://doi.org/10.1006/jcat.1997.1942>.
- [60] F. Basile, L. Basini, G. Fornasari, A. Guarinoni, F. Trifirò, A. Vaccari, Catalytic behaviour of Ni- and Rh-containing catalysts in the partial oxidation of methane at short residence times, *Stud. Surf. Sci. Catal.* 119 (1998) 693–698, [https://doi.org/10.1016/S0167-2991\(98\)80512-0](https://doi.org/10.1016/S0167-2991(98)80512-0).
- [61] F. Basile, G. Fornasari, F. Trifirò, A. Vaccari, Partial oxidation of methane. Effect of reaction parameters and catalyst composition on the thermal profile and heat distribution, *Catal. Today* 64 (2001) 21–30, [https://doi.org/10.1016/S0920-5861\(00\)00505-8](https://doi.org/10.1016/S0920-5861(00)00505-8).
- [62] F. Basile, G. Fornasari, F. Trifirò, A. Vaccari, Rh-Ni synergy in the catalytic partial oxidation of methane: surface phenomena and catalyst stability, *Catal. Today* 77 (2002) 215–223, [https://doi.org/10.1016/S0920-5861\(02\)00247-X](https://doi.org/10.1016/S0920-5861(02)00247-X).
- [63] F. Basile, P. Benito, G. Fornasari, F.M. Labajos, V. Rives, V. Rosetti, A. Vaccari, Microwave-assisted catalysts for the CPO of methane, *Stud. Surf. Sci. Catal.* 162 (2006) 761–768, [https://doi.org/10.1016/S0167-2991\(06\)80978-X](https://doi.org/10.1016/S0167-2991(06)80978-X).
- [64] P. Benito, V. Del Santo, V. De Grandi, M. Marelli, G. Fornasari, R. Psaro, A. Vaccari, Coprecipitation versus chemical vapour deposition to prepare Rh/Ni bimetallic catalysts, *Appl. Catal. B* 179 (2015) 150–158, <https://doi.org/10.1016/j.apcatb.2015.05.016>.
- [65] P. Arpentinier, F. Basile, P. Del Gallo, G. Fornasari, D. Gary, V. Rosetti, A. Vaccari, Role of the hydrotalcite-type precursor on the properties of CPO catalysts, *Catal. Today* 99 (2005) 99–104, <https://doi.org/10.1016/j.cattod.2004.09.028>.
- [66] P. Arpentinier, F. Basile, P. Del Gallo, G. Fornasari, F. Gary, V. Rosetti, A. Vaccari, New catalysts with low amount of active phase for CPO processes, *Catal. Today* 117 (2006) 452–457, <https://doi.org/10.1016/j.cattod.2006.06.022>.
- [67] S. Albertazzi, F. Basile, P. Benito, P. Del Gallo, G. Fornasari, D. Gary, V. Rosetti, A. Vaccari, Effect of silicates on the structure of Ni-containing catalysts obtained from hydrotalcite-type precursors, *Catal. Today* 128 (2007) 258–263, <https://doi.org/10.1016/j.cattod.2007.06.067>.
- [68] F. Basile, P. Benito, G. Fornasari, D. Gazzoli, I. Pettiti, V. Rosetti, A. Vaccari, Ni-catalysts obtained from silicate intercalated HTLcs active in the catalytic partial oxidation of methane: influence of the silicate content, *Catal. Today* 142 (2009) 78–84, <https://doi.org/10.1016/j.cattod.2009.01.013>.
- [69] A. Ballarini, P. Benito, G. Fornasari, O. Scelza, A. Vaccari, Role of the composition and preparation method in the activity of hydrotalcite-derived Ru catalysts in the catalytic partial oxidation of methane, 15128–1539, *Int. J. Hydrog. Energy* 38 (2013), <https://doi.org/10.1016/j.ijhydene.2013.08.135>.
- [70] F. Basile, P. Benito, G. Fornasari, M. Monti, E. Scavetta, D. Tonelli, A. Vaccari, Novel Rh-based structured catalysts for the catalytic partial oxidation of methane, *Catal. Today* 157 (2010) 183–190, <https://doi.org/10.1016/j.cattod.2010.04.039>.
- [71] F. Basile, P. Benito, G. Fornasari, M. Monti, E. Scavetta, D. Tonelli and A. Vaccari, A novel electrochemical route for the catalytic coating of metallic supports In “Preparation of Catalysts 10” (E.M. Gaigneaux, M. Devillers, S. Hermans, P. Jacobs, J. Martens and P. Ruiz, Eds.), Vol. 175, Elsevier, Amsterdam NL, 2010, pp. 51–58. [https://doi.org/10.1016/S0167-2991\(10\)75007-2](https://doi.org/10.1016/S0167-2991(10)75007-2).
- [72] P. Benito, M. Monti, I. Bersani, F. Basile, G. Fornasari, E. Scavetta, D. Tonelli, A. Vaccari, Coating of FeCrAlloy foam with Rh catalysts: optimization of electrosynthesis parameters and catalyst composition, *Catal. Today* 197 (2012) 162–169, <https://doi.org/10.1016/j.cattod.2012.07.034>.
- [73] P. Benito, W. De Nolf, G. Nuyts, M. Monti, G. Fornasari, F. Basile, K. Janssens, F. Ospitali, E. Scavetta, D. Tonelli, A. Vaccari, Role of coating-metallic support interaction in the properties of electrosynthesized Rh-based structured catalysts, *ACS Catal.* 4 (2014) 3779–3790, <https://doi.org/10.1021/cs501079k>.
- [74] P. Benito, G. Nuyts, M. Monti, W. De Nolf, G. Fornasari, K. Janssens, E. Scavetta, A. Vaccari, Stable Rh particles in hydrotalcite-derived catalysts coated on FeCrAlloy foams by electrosynthesis, *Appl. Catal. B* 179 (2015) 321–332, <https://doi.org/10.1016/j.apcatb.2015.05.035>.
- [75] P.H. Ho, W. de Nolf, F. Ospitali, A. Gondolini, G. Fornasari, E. Scavetta, D. Tonelli, A. Vaccari, P. Benito, Coprecipitated-like hydrotalcite-derived coatings on open-cell metallic foams by electrodeposition: Rh-nanoparticles on oxide layers stable under harsh reaction conditions, *Appl. Catal. A* 560 (2018) 12–20, <https://doi.org/10.1016/j.apcata.2018.04.014>.
- [76] P.H. Ho, W. De Nolf, F. Ospitali, D. Beton, L. Torkuhl, G. Fornasari, A. Vaccari, P. Benito, Insights into coated NiCrAl open-cell foams or the catalytic partial oxidation of CH₄, *React. Chem. Eng.* 4 (2019) 1768–1778, <https://doi.org/10.1039/C9RE000178F>.
- [77] P.H. Ho, F. Ospitali, G. Sanghez de Luna, G. Fornasari, A. Vaccari, P. Benito, Coating of Rh/Mg/Al hydrotalcite-like materials on FeCrAl fibers by electrodeposition and application for syngas production, *Ener. Technol.* 8 (2020) 1901018, <https://doi.org/10.1002/ente.201901018>.
- [78] P.H. Ho, F. Ospitali, G. Sanghez De Luna, G. Fornasari, A. Vaccari, P. Benito, Electrodeposition of Rh/Mg/Al hydroxides with different Mg-contents on metallic foams as catalyst precursors, *Appl. Clay Sci.* 191 (2020) 105599, <https://doi.org/10.1016/j.clay.2020.105599>.
- [79] N. Schiaroli, C. Lucarelli, G. Sanghez de Luna, G. Fornasari, A. Vaccari, Ni-based catalysts to produce synthesis gas by combined reforming of clean biogas, *Appl. Catal. A* 582 (2019) 117087, <https://doi.org/10.1016/j.apcata.2019.05.021>.
- [80] N. Schiaroli, C. Lucarelli, M.C. Iapalucci, G. Fornasari, A. Grimaldi, A. Vaccari, Combined reforming of clean biogas over nanosized Ni-Rh bimetallic clusters, *Catalysts* 10 (2020) 1345–1361, <https://doi.org/10.3390/catal10111345>.
- [81] P. Tarifa, N. Schiaroli, P.H. Ho, F. Cañaza, F. Ospitali, G. Sanghez de Luna, C. Lucarelli, G. Fornasari, A. Vaccari, A. Monzon, P. Benito, Steam reforming of clean biogas over Rh and Ru open-cell metallic foam structured catalysts, *Catal. Today* 383 (2022) 74–83, <https://doi.org/10.1016/j.cattod.2021.03.024>.
- [82] C. Lucarelli, C. Molinari, R. Faure, G. Fornasari, D. Gary, N. Schiaroli, A. Vaccari, Novel Cu-Zn-Al catalysts obtained from hydrotalcite-type precursors for middle-temperature water-gas shift applications, *Appl. Clay Sci.* 155 (2018) 103–110, <https://doi.org/10.1016/j.clay.2017.12.022>.
- [83] B. Montanari, A. Vaccari, M. Gazzano, P. Kabner, H. Papp, J. Pasel, R. Dziembaj, W. Makowski, T. Lojewski, Characterization and activity of novel copper-containing catalysts for selective catalytic reduction of NO with NH₃, *Appl. Catal. B* 13 (1997) 205–217, [https://doi.org/10.1016/S0926-3373\(96\)00106-3](https://doi.org/10.1016/S0926-3373(96)00106-3).
- [84] M. Trombetta, G. Ramis, G. Busca, B. Montanari, A. Vaccari, Ammonia adsorption and oxidation on Cu/Mg/Al mixed oxide catalysts prepared via hydrotalcite-type precursors, *Langmuir* 13 (1997) 4628–4637, <https://doi.org/10.1021/la960673o>.
- [85] G. Centi, G. Fornasari, C. Gobbi, M. Livi, F. Trifirò, A. Vaccari, NOx-storage-reduction catalysts based on hydrotalcite. Effect of Cu in promoting resistance to deactivation, *Catal. Today* 73 (2002) 287–296, [https://doi.org/10.1016/S0920-5861\(02\)00012-3](https://doi.org/10.1016/S0920-5861(02)00012-3).
- [86] G. Fornasari, F. Trifirò, A. Vaccari, F. Prinetto, G. Ghiotti, G. Centi, Novel low temperature NOx storage-reduction catalysts for diesel light-duty engine emissions

- based on hydrotalcite compounds, *Catal. Today* 75 (2002) 421–429, [https://doi.org/10.1016/S0920-5861\(02\)00092-5](https://doi.org/10.1016/S0920-5861(02)00092-5).
- [87] F. Basile, G. Fornasari, M. Livi, F. Tinti, F. Trifirò, A. Vaccari, Performance of new Pt and Pt-Cu on hydrotalcite-derived materials for NOx storage/reduction, *Top. Catal.* 30 (2004) 223–227, <https://doi.org/10.1023/B:TOCA.0000029753.61106.ef>.
- [88] G. Fornasari, R. Glockler, M. Livi, A. Vaccari, Role of the Mg/Al atomic ratio in hydrotalcite-based catalysts for NOx storage/reduction, *Appl. Clay Sci.* 29 (2005) 258–266, <https://doi.org/10.1016/j.clay.2005.02.002>.
- [89] S. Morandi, F. Prinetto, G. Ghiotti, M. Livi, A. Vaccari, FT-IR investigation of NOx storage properties of Pt-Mg(Al)O and Pt/Cu-Mg(Al)O catalysts obtained from hydrotalcite compounds, *Micro Mesop. Mater.* 107 (2008) 31–38, <https://doi.org/10.1016/j.micromeso.2007.03.014>.
- [90] S. Alini, F. Basile, A. Bologna, B. Montanari, A. Vaccari, Preparation of stable catalysts for N₂O decomposition under industrial conditions, *Stud. Surf. Sci. Catal.* 143 (2002) 131–139, [https://doi.org/10.1016/S0167-2991\(00\)80650-3](https://doi.org/10.1016/S0167-2991(00)80650-3).
- [91] P.H. Ho, M. Jablonska, R. Palkovits, E. Rodriguez-Castellon, F. Ospitali, G. Fornasari, A. Vaccari, P. Benito, N₂O catalytic decomposition on electrodeposited Rh-based open-cell metallic foam, *Chem. Eng. J.* 279 (2020) 122259, <https://doi.org/10.1016/j.cej.2019.122259>.
- [92] L. Forni, G. Fornasari, R. Trabace, F. Trifirò, A. Vaccari, L. Dalloro, Beckmann rearrangement over anionic clays, *Stud. Surf. Sci. Catal.* 130 (2000) 3513–3518, [https://doi.org/10.1016/S0167-2991\(00\)80567-4](https://doi.org/10.1016/S0167-2991(00)80567-4).
- [93] R. Bechara, A.D. Huysse, M. Fournier, L. Forni, G. Fornasari, F. Trifirò, A. Vaccari, Synthesis and characterization of boron hydrotalcite-like compounds as catalyst for gas-phase transposition of cyclohexanone-oxime, *Catal. Lett.* 82 (2002) 59–67, <https://doi.org/10.1023/A:1020535923499>.
- [94] L. Forni, G. Fornasari, E. Miserazzi, R. Trabace, F. Trifirò, A. Vaccari, I. Dall'Oro, Vapour phase Beckmann rearrangement over HT-like materials, *Proc. 8th Int. Symp. . Varna (Bulg.)* (2000) 507–512.
- [95] F. Basile, G. Fornasari, A. Gazzano, A. Vaccari, Thermal evolution and catalytic activity of Pd/Mg/Al mixed oxides obtained from hydrotalcite type precursors, *Appl. Clay Sci.* 18 (2001) 51–57, [https://doi.org/10.1016/S0169-1317\(00\)00030-2](https://doi.org/10.1016/S0169-1317(00)00030-2).
- [96] M. Campanati, S. Franceschini, O. Piccolo, A. Vaccari, A. Zicmanis, Catalytic condensation of aromatic aldehydes with acetone on activated Mg-Al mixed oxides, *Catal. Commun.* 5 (2004) 145–150, <https://doi.org/10.1016/j.catcom.2003.12.004>.
- [97] C. Carlini, M. Marchionna, M. Novello, A.M. Raspolli Galletti, G. Sbrana, F. Basile, A. Vaccari, Guerbet condensation of methanol with n-propanol to isobutyl alcohol over heterogeneous bifunctional catalysts based on Mg-Al mixed oxides partially substituted by different metal components, *J. Mol. Catal. A: Chem.* 232 (2005) 13–20, <https://doi.org/10.1016/j.molcata.2004.12.037>.
- [98] C. Carlini, C. Flego, M. Marchionna, M. Novello, A.M. Raspolli Galletti, G. Sbrana, F. Basile, A. Vaccari, Guerbet condensation of methanol with n-propanol to isobutyl alcohol over heterogeneous copper chromite/Mg-Al mixed oxide catalysts, *J. Mol. Catal. A* 220 (2004) 215–222, <https://doi.org/10.1016/j.molcata.2004.05.034>.
- [99] P. Benito, A. Vaccari, C. Antonetti, D. Licursi, N. Schiaroli, E. Rodriguez-Castellón, A.M. Raspolli Galletti, Tunable copper-hydrotalcite derived mixed oxides for sustainable ethanol condensation to n-butanol in liquid phase, *J. Clean. Product.* 209 (2019) 1614–1623, <https://doi.org/10.1016/j.jclepro.2018.11.150>.