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NO reduction with CO on metal nanoparticles/layered double hydroxides heterostructures obtained via the structural memory effect



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ABSTRACT

Nitrogen oxides are notorious air pollutants and the catalytic reduction of NO_x by CO for removing NO_x has attracted extensive attention. Herein, we present a series of ZnCu-layered double hydroxides (LDH) decorated with nanoparticles of metals (Me: In, Zn or Au) and the derived oxides as novel catalysts for NO reduction by CO. MeNP/ZnCu heterostructures were successfully prepared by taking advantage of the structural reconstruction of ZnCu LDH, via the structural memory effect, in the aqueous solutions of Me salts. X-ray diffraction (XRD), FTIR spectroscopy, H₂-Temperature programmed reduction (H₂-TPR), transmission electron microscopy TEM, X-ray photoelectron spectroscopy (XPS), and UV–vis spectroscopy are been used to characterize the structural, chemical composition, optical and nano/micromorphology of MeNP/ZnCu tatalysts and the mixed oxides derived after the thermal treatment. Results indicate that on MeNP/ZnCu the reduction of NO by CO was 3 times higher than that of ZnCu while CO conversion was above 90%. Further, MeNP/ZnCu and the derived oxides demonstrated good stability in subsequent catalytic cycles while NO conversion was influenced by the molar ratio O₂/CO. These findings indicate that the memory effect of the LDH can be effective as a simple strategy in the development of novel LDH-based heterostructured catalysts.

1. Introduction

Catalysis profoundly affects our everyday technologies in the conditions that over 90% of all chemical manufacturing is based on, or relies heavily on, catalytic processes [1]. A question that has recently emerged is whether it is possible to design more performant catalysts by taking the advantage of heterostructures obtained by the close junction of multiple structural units that are able to combine their properties to promote novel catalytic functionalities. In this view, tunable heterostructures of 2D layered double hydroxides (LDH) and nanoparticles of metals/metal oxides (MeNP/LDH) have received longstanding interest in catalysis [2,3]. LDH are 2D layered matrices with a brucite-like structure that consists of cationic metal hydroxide layers and exchangeable anions located in the interlayer gallery for change balance [4,5]. With the advantage of their 2-D layered structure, LDH has attracted great attention as catalysts because of their intrinsic properties such as their composition diversity, high stability, ease of preparation, large surface area, and tailored micro/nanoporosity [6]. Furthermore, the LDH-like catalysts can be transformed, by specific calcination treatments, in mixtures of mixed oxides. Moreover, most LDH are endowed with the "structural memory effect", this means that the layered structure can be reconstructed from the corresponding mixed oxides, obtained by calcination at moderate temperatures, when introduced in aqueous solutions containing anions [7,8]. Very recent findings demonstrate that the transformation of the LDH catalysts by using the "structural memory effect" can induce a higher abundance of active sites, vacancies and defects such that to improve the catalytic stability, reusability and functionality [9,10]. However, the manifestation of the structural "memory effect" of LDH in specific environments is still not well understood [11] and further research is needed. By exploiting the manifestation of the structural memory effect of LDH in the aqueous solutions of metal salts we recently reported MeNP/LDH

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Fig. 1. Catalytical experimental set-up.

heterostructured catalysts that manifest the joined characteristics of nanoparticles of metals/metal oxides (MeNP), (such as CeNP, FeNP, AuNP) and those of the LDH matrices [8,12,13]. Based on this procedure, MeNP were directly obtained and stabilized on the surface of the LDH by exploiting the manifestation of the "structural memory" of LDH, in aqueous solution of Me salts, under ambient conditions. This strategy inspired us to further challenge the preparation of advanced heterostructures based on MeNP/LDH for designing efficient catalysts. In the present work, we used this strategy to gain new insights into the exploitation of the "structural memory effect" of the LDH for obtaining novel heterostructured materials for NO - CO process. NO reduction by CO is a key step in the catalytic control of automotive exhaust. This process is responsible for the removal of NOx from the exhaust gases and it contributes to the elimination of CO as well. The most studied catalysts for this process are noble metals such as Pt, Pd, and Rh [14]. Since the noble metals mentioned are considered CRMs (critical raw materials), recent research has focussed on developing new catalysts which present high thermal stability, high resistance to sulfur and are easy to obtain. Very recently, Cu-based catalysts came to the attention of researchers. Thus, in Cu/y-Al₂O₃ catalyst, the catalytic activity for NO reduction depends strongly on the loading amount of Cu. Lower loading amount results in highly-dispersed Cu species on Al₂O₃, which is essential to establish a high catalytic activity for NO reduction [15]. Further, has been reported that the presence of Au, In or Zn in the catalyst's composition might improve the catalysts performances for NO reduction and CO oxidation processes [16-19].

Herein, we investigated the catalytic performances of MeNP/ZnCu LDH heterostructures as novel catalytic systems for the NO-CO reduction process. Specifically, we obtained MeNP (Me: In, Zn or Au) on ZnCu LDH taking advantage of the structural reconstruction by memory effect, realized by hydration of the calcined ZnCu LDH intermediates in the aqueous solutions of Me salts - and we described the entangled structures and nano/micromorphology of MeNP/ZnCu LDH and their derived oxides. Thereby, we explored the performances in NO reduction by CO for MeNP/ZnCu LDH but also for the mixed oxides obtained by calcination and ZnCu LDH catalysts. Furthermore, we evaluated how NO conversion was influenced by the molar ratio of O_2/CO .

2. Experimental

2.1. Synthesis of the catalysts

ZnCu LDH catalyst has been synthesized by the coprecipitation method [7]. Thus, the molar ratio is $Zn^{2+}/Cu^{2+}/Al^{3+}$ equal to 2/1/1, using as metal salts $Zn(NO_3)_2$.6 H₂O, $Cu(NO_3)_2$.6 H₂O and $Al(NO_3)_3$.9 H₂O (all purchased from Sigma Aldrich, p.a. >98%) and a Na₂CO₃/-NaOH solution as a coprecipitation agent, at a constant pH of 8.2.

MeNP/ZnCu catalysts were obtained using reconstruction method [13] by exploiting the "memory effect" of the LDH. Thus, the freshly calcined ZnCu (at 550 °C, 8 h) was added into an aqueous solution of 5 wt% of In (CH₃COO)₃ or Zn(CH₃COO)₂·2 H₂O or AuCl₃ respectively, (99.99% trace metals basis, Sigma Aldrich), under vigorous stirring. The obtained precipitates were aged 8 h at room temperature, separated by centrifugation and dried overnight at 80 °C in the oven. These catalysts are denoted as: In/ZnCu, Zn/ZnCu, and Au/ZnCu, respectively. Next, the mixed oxides obtained by calcination are denoted as: ZnCu-T, Au/Zn-Cu-T, In/ZnCu-T, and Zn/ZnCu-T, respectively, where T (°C) represents the temperature of the thermally treatment.

2.2. Characterization techniques

Structural characteristics and crystallinity were performed on an Xray diffractometer (PANalytical X'Pert PRO MPD) equipped with CuKa radiation ($\lambda = 0.15406$ nm); measurements were done in the 20 range of 5-80°. DRIFT spectra were obtained using Nicolet 6700 FT-IR spectrometer in the 400–4000 cm⁻¹ region with the spectra collected at 4 cm⁻¹ 1 resolution, averaging 200 scans. The samples were mixed (2% wt) with dry KBr and pure KBr was used as a reference. TEM/HRTEM images and data were collected using a UHR-TEM-Libra 200 MC/Carl Zeiss GmbH ultra-high resolution TEM microscope (Carl Zeiss Microscopy GmbH, Oberkochen, Germany). SEM-EDX (FEG-ESEM-EDX, FEI Quanta 250) was used to study the surface composition. X-ray photoelectron spectroscopy (XPS) analyses were performed using a monochromatic Al Kα source (1486.6 eV), on a K-Alpha instrument from Thermo Scientific. The C1s peak at 284.8 eV was used as an internal standard to correct the binding energy. Quantachrome iQ was used for hydrogen temperatureprogrammed reduction (H₂-TPR) measurements. Before the analyses, 20 mg of the material was outgassed at 200°C for 16 h. Following cooling, the sample was once again weighed. The sample was then pretreated for 1 h using a He flow. 25 ml/min of 5% H₂/Ar flow was used for reduction. At a rate of 10 °C/min, the temperature was increased between 100 and 800 °C. Thermal conductivity detectors (TCD) were used to track the use of hydrogen. The weight of the outgassed catalyst was used to normalize these signals. UV-vis-Diffuse Reflectance (UV-vis-DR) spectra were obtained on a Nicolet Evolution 500 UV-vis spectrometer with a diffuse reflectance accessory.

2.3. Set up of the reactor and catalytic experiment

We used a fixed bed continuous flow quartz reactor (see Fig. 1) with an inner diameter of 0.7 cm, an outer diameter of 1 cm, and the length \pm 53.5 cm, operating with a GHSV of 60000 h⁻¹. The gas feed total rate was 200 ml/min (10 ml/min NO, 0.6 ml/min CO, 1 ml/min O₂, and 188.4 ml/min N₂ [20]). The studied powders were pelletized using an IR



Fig. 2. XRD patterns of a) the reconstructed LDH as: ZnCu, Au/ZnCu, Zn/ZnCu, In/ZnCu; b) the mixed oxides derived after the catalytic tests as: ZnCu-600, In/ZnCu-600, Zn/ZnCu-600- and Au/ZnCu-600; (*) ZnO, (♦) CuO, (◊) AuNPs, (*) In₂O₃, (♦) ZnAl₂O₄.

pelletizer, crushed, and sieved, to produce particles that ranged in size from 150 to 300 μ m to avoid mass the transfer as well as the pressure drop constrains in the reactor due to clogging. The reactor tube was filled with 200 mg of the catalyst. Firstly, the catalyst was maintained at 100 °C for 1 h before switching on the gas feed and afterward, the tests were conducted by rising the temperature at a rate of 10 °C/min from room temperature to 600 °C. By calculating the O₂ conversion from the CO and NO conversion, one may follow the oxidation of CO by O₂ and the reduction of NO with CO utilizing this ratio between the gases. The formulas below were used to evaluate NO, CO conversion, and O₂ consumption [20]:

$$X_{NO} = \frac{C_{in,NO} - C_{out,NO}}{C_{in,NO}} \bullet 100\%$$
 (1)

$$X_{CO} = \frac{C_{in,CO} - C_{out,CO}}{C_{in,CO}} \bullet 100\%$$
 (2)

$$X_{O_{2}} = \frac{\left[X_{CO} - X_{NO} \cdot \left(\frac{C_{in,NO}}{C_{in,CO}}\right)\right]}{2} \frac{C_{in,CO}}{C_{in,O_{2}}}$$
(3)

where X is the conversion and C_{in} is the input concentration.

The influence of O_2 on the catalytic performance was studied for the different flows of oxygen as: 0.5 ml/min, 1 ml/min, 1.5 ml/min and 2 ml/min. Tests regarding the effect of the CO concentration was done by introducing into the reaction 0.6 ml/min, 0.7 ml/min and 0.8 ml/min of CO flow, respectively.

3. Results and discussion

3.1. Physicochemical properties of the catalysts

Structural characterization of the synthesized materials was studied by X-ray diffraction. The XRD patterns of the catalysts are shown in Fig. 2. Fig. 2a shows that all the reconstructed LDH exhibit the diffraction patterns characteristic to the LDH structure. Thus, peaks from 2θ = 11.7°, 23.54° are characteristic to the basal planes (003) and (006), and at 2θ = 34.54°, 39.14°, 46.62°, 60.14°, 61.46° are characteristic for the non-basal planes (012), (015), (018), (110) and (113), respectively.

Table 1	
Crystal lattice parameters for the synthesized catalysts.	

Sample	Cristal lattice parameters, Å		
	d ₀₀₃ , Å	a, Å	c, Å
ZnCu	7.48	3.07	22.74
Au/ZnCu	7.48	3.07	22.74
*Zn/ZnCu	12.3	3.07	36.9
*In/ZnCu	12.3	3.07	36.9

*lattice parameters calculated only for acetate intercalated LDH.

The lattice parameters $a = 2d_{110}$ and $c = 3d_{003}$ [21] were calculated and shown in Table 1. There are no significant changes for cation-cation distance represented by the a parameter between the as-synthesized LDH and the reconstructed catalysts, pointing out a well ordered LDH structure after the reconstruction. On the contrary, the increase of the *c* parameter indicates the presence of different anions in the interlayer space of ZnCu and MeNP/ZnCu LDHs [22]. The d_{003} parameter gives information about interlayer distance (which can be correlated with the interlayer anions) and the calculated value is around 7.5 Å for ZnCu and Au/ZnCu. According to the literature this value reveals the presence of CO_3^{2-} and/or Cl⁻ in the interlayers [23,24]. Moreover, a new diffraction peak at 20= 5.8° is noticed in the XRD patterns of the LDH reconstructed in zinc acetate (_) and indium acetate (_) aqueous solutions. This corresponds to the basal (003) plane with a calculated interlayer distance equal to 12.3 Å, attributed to the CH₃COO⁻ intercalated LDH [25]. For Zn/ZnCu and In/ZnCu we observed two (003) planes pointing out the presence of both CH_3COO^- and CO_3^{2-} in the interlayers. This can be due to the low concentration of CH3COO⁻ anions in the reconstructed aqueous solutions, that cannot fulfill the reconstruction of the all amount of ZnCu and the high affinity of the LDH for CO_3^{2-} . The reconstruction process was done under atmospheric conditions, therefore, during the reconstruction, ZnCu might capture the atmospheric CO2 to complete the reconstruction process [22]. After the reconstruction some peaks corresponding to ZnO, marked with (*), are also identified, revealing that the reconstruction process was not completed within 8 h [13]. Furthermore, the formation of MeNP deposited on the LDH surface could not be detected by XRD analysis in the conditions that the small size NP



and low Me content are difficult to detect by XRD.

The catalytic tests implied increasing the temperature up to 600 °C. At this temperature, the LDH structure is expected to collapse, giving rise to the mixed oxides. Consequently, we studied the XRD features of the catalysts after the catalytic tests, and the corresponding XRD patterns are presented in Fig. 2b. It clearly shows that the layered structure of the LDH-type catalysts collapsed, giving rise to well-crystallized mixed oxides identified as ZnO/CuO/ZnAl₂O₄ mixed phases as: (*) ZnO (JCPDS file No. 36–1451), (\blacklozenge) CuO (JCPDS Card no. 45–0937) and (\blacklozenge) ZnAl₂O₄ (JCPDS file Card No. 5–0669). For the reconstructed catalysts the presence of new peaks characteristic to the MeNP or Me oxides phases [26] are also noticed at 2 θ = 38.26°, 46.14°, 77.3°, attributed to the diffraction planes (111), (200) and (311) of (\diamondsuit) Au (JCPDS Card No. 65–2870) and, at 2 θ = 30.66°, 51.26°, 60.9° of (*) In₂O₃ (JCPDS Card No. 76–0152), while the intensity of the characteristic reflections of ZnO increased for Zn/ZnCu.

Further, to examine the nature of the anions in the layered LDH matrices, the FTIR results are given in Fig. 3. All the spectra showed the presence of a broad absorption band centered at 3460 cm⁻¹ that is ascribed to O-H stretching frequency. The broadness of the absorption band is related to the hydrogen bonding between water molecules and interlayers anions. Its intensity is lowering for Au/ZnCu, Zn/ZnCu and In/ZnCu compared to the pristine ZnCu indicating only a partial rehydration of ZnCu matrix due to the incomplete reconstruction process that was revealed by XRD results. IR absorption bands at 1360 and 1450 cm⁻¹ are ascribed to the split asymmetric stretching modes of interlayer carbonate ions [27]. In the case of the catalysts obtained by the reconstruction in Zn(CH₃COO)₂ and In(CH₃COO)₃ aqueous solutions, absorption bands at 1570 and 1371 cm⁻¹ are clearly recognized as asymmetric stretching mode of CH₃COO⁻ [28], indicating the presence of this anion besides the CO_3^{2-} as counter anions of the interlayers, in good agreement with XRD results. The absorption bands observed in the low frequency region (500-800 cm⁻¹) are attributed to the stretching frequencies of the lattice vibration mode of the metal-OH vibration centered at about 670 cm⁻¹ and the metal-O bending at about 550 cm⁻¹ [29]. Furthermore, slight shifts in the position of the bands observed in the low-frequency region are observed after the reconstruction and

based on the results discussed by Gevers et al. [21] these shifts reveal a higher amount of metal-O bonds thus, altered metal-O stretching vibrations due to the incomplete reformation of the LDH.

The chemical state of MeNP in MeNP/ZnCu catalysts were investigated by XPS in order to see the state of MeNP formed on the surface after the reconstruction and the obtained results are shown in Fig. 4. The high-resolution spectra of Zn2p from ZnCu pristine layered double hydroxide (Fig. 4a) presents two peaks at 1045 eV and 1022.2 eV characteristic to $Zn2p_{1/2}$ and $Zn2p_{3/2}$ which reveals the presence of Zn^{2+} from Zn-O bonds. Compared with ZnCu, the chemical state of Zn from Zn/ZnCu heterostructure (Fig. 4b) is also represented by a doublet but it presents additionally shoulders with lower binding energies indicating the presence of Zn⁰ [30]. Next, Fig. 4c shows two peaks with binding energy of 335.6 eV and 353.5 eV that can be clearly ascribed to Au $4d_{5/2}$ respectively 4d_{3/2} characteristic to Au⁰ chemical state [31,32]. Additional small peaks characteristic to Au⁺ and Au³⁺ can also be noticed pointing out the presence of a mixed state of Au in Au/ZnCu [33]. The full XPS spectrum of In/ZnCu is shown in Fig. S1a. The chemical state of In in Fig. 4d shows a doublet, that corresponds to In $3d_{5/2}$ and $3d_{1/2}$ at 444.7 eV and 452.2 eV assigned to In^{3+} from In_2O_3 [34,35]. Small peaks at 444.0 and 451.5 eV are characteristic to In⁰ metallic state [36]. These findings proved that both In^{3+} and In^{0} are present on the LDH surface. Cu2p high-resolution XPS spectra from In/ZnCu (Fig. S1b) shows a complex spectrum with 2 main peaks at binding energies 952.2 eV and 932.5 eV characteristic for $Cu2p_{1/2}$ respectively for $Cu2p_{3/2}$, that is specific for Cu²⁺ from ZnCu LDH. The presence of two satellite peaks at 942.9 eV and 940.6 eV can be distinguished which are 3d⁹L configuration [37].

SEM and TEM analysis were performed to get information about morphology and state of the MeNP in the catalysts. SEM image in Fig. 5a shows the characteristic LDH morphology of agglomerated hexagonal plate-like particles with different sizes. Furthermore, TEM results (Fig. 5b, d and e) clearly reveal the presence of AuNP, ZnNP and InNP on ZnCu surface, that can be clearly identified as small dark dots with average sizes between 2 and 7 nm. Next, the HRTEM images in Fig. 5c evidences the lattice fringes with the interplanar distance of 0.24 nm clearly identified as faced-centered cubic fcc of Au with the (111) plane [38]. Further, the lattice fringes with D-spacings of 0.24 nm and 0.26 nm are characteristic to (012) and (015) planes of the LDH [39,40]. Furthermore, HRTEM image of Zn/ZnCu, (see Fig. 5f) shows lattice fringes with a D-spacing of 0.26 and 0.28 nm assigned to the planes (110) of ZnO [41]. Fig. 5g illustrates the HRTEM image of In/ZnCu where the lattice fringe of 0.29 nm characteristic assigned to the (222) diffraction plane of In₂O₃ [42] can be identified while in Fig. 5h the lattice fringe of 0.26 nm and 0.28 nm are assigned to (015) and (110) diffraction planes of the LDH [39,43]. Together XRD, XPS and TEM/HRTEM results reveal the formation of entangled structures of the well crystallized MeNP and ZnCu after the reconstruction. EDS mapping results are shown Fig. 5i, j and k and show that all the catalysts consist of Zn, O, Al, Cu, Au and In, respectively. The chemical composition in wt% of elements are given in Table S1 and Fig. S2 and indicate that the amount of Zn increased with 5 wt% in Zn/ZnCu in comparison to ZnCu while the content of Au is 4.5 wt% in Au/ZnCu and In content is 5 wt% in In/ZnCu catalyst, respectively.

H₂-temperature programmed reduction (H₂-TPR) analysis was used to obtain qualitative information on the redox properties of the catalysts promoted by the interactions among the as-deposited nanoparticles and ZnCu which could nonetheless be relevant for catalysis. Under the reduction conditions employed in this study all the H₂-TPR profiles (see Fig. 6) show two reduction peaks according to the Gaussian function. In the temperature range of 200–400 °C (Fig. 6a) the reduction of Cu²⁺ to Cu⁰ occurs while in the range 500–700 °C some active Cu⁺ reduces to Cu⁰ [44] or due to strong interaction Cu²⁺ reduces at higher temperatures. It has reported that Zn is not reduced with H₂ in Zn/Cu based-catalysts at temperatures below 600 °C [45–47] such that, the main reduction peak was ascribed to the reduction of Cu species [48]. As



Fig. 4. High-resolution XPS spectra of a) Zn2p in ZnCu, b) Zn2p on Zn/ZnCu, c) Au4d on Au/ZnCu and d) In3d on In/ZnCu samples.

observed, the peak position, peak areas and the temperature of the maximum reduction rate are specific for each catalyst pointing out that the catalysts composition has a strong impact on their reducibility. For ZnCu the reduction peak centered at 320 °C demonstrates a reduction behavior within (280-345)°C comparable to that previously reported by Kuhl et al. for ZnCuAl LDH [49]. Nevertheless, the interaction between Au and ZnCu is clearly manifested in Au/ZnCu that shows a peak area with an evidently smaller H₂ uptake capacity in a temperature range of (230-350)°C. For In/ZnCu the peak positions shifted 20 °C toward higher temperatures rendering Cu reduction more difficult when compared to Au/ZnCu. The reduction of In2O3 to In0 occurs around 500-600 °C [50]. Consequently, these findings suggest that the introduction of small amounts of Au, In or Zn on ZnCu plays a key role in establishing the reducibility behavior of the catalysts. Thus, it could be reasonably expected that strong electronic interactions are established between the as-deposited nanoparticles and the ZnCu lattice that are able to induce the migration of the oxygen vacancies in Cu-based catalysts, as other studies have also been proposed [51]. Compared to the reconstructed samples, the mixed oxudes derived after calcination (Fig. 6b) show smaller differences in the reduction temperature. Thus, the reduction temperature of ZnCu-750 decreased with 10 °C while In/ZnCu-750 and Zn/ZnCu-750 shifted with 10 °C towards higher temperatures. No significant changes can be seen for Au/ZnCu-750. The reduction set point below 350 °C proves that CuO is well dispersed, has a good interaction with the other oxides and spinel and are present as small sized particles [20].

The optical properties of the catalysts were determined by UV–vis-DR spectroscopy (Fig. 7). As expected, the absorption band below 300 nm can be assigned to ligand to metal charge transfer in the octahedral coordination [22]. Reconstructed samples (Fig. 7a) showed an absorption band at 380 nm which may be associated with the ZnO presence and well correlated with the XRD observations [52]. In the visible range of the absorption spectra, a broad band centered 550 nm can be noticed which corresponds to the presence of Cu^{2+} in tetrahedral coordination [53]. For the In/ZnCu sample, the absorption band characteristic to the In₂O₃ NPs from 390 nm overlaps with the ZnO band [54], while in the case of Au/ZnCu sample, the small absorption band from 500 nm corresponds to the SPR of AuNP. It is known that the intensity of SPR band is influenced by the dimension of AuNP [55]. For the thermal treated catalysts (see Fig. 7b) the absorption band assigned to ZnO expanded to almost 400 nm due to an increased crystallinity and agglomeration with ZnAl₂O₄ [56]. Furthermore, the size of AuNP increased and the absorption band shifted to 550 nm overlapping with the CuO band.

3.2. Catalytic activity

The catalytic activity was tested for the reduction of NO by CO, under the experimental conditions described in Section 2.3. For this catalytic process, the reactions that occur under the applied conditions can be described as:

$$2CO + 2NO \rightarrow 2CO_2 + N_2 \tag{4}$$

 $CO + 2NO \rightarrow CO_2 + N_2O \tag{5}$

$$CO + N_2 O \rightarrow CO_2 + N_2 \tag{6}$$

$$2NO + O_2 \rightarrow 2NO_2 \tag{7}$$

$$2CO + O_2 \rightarrow 2CO_2 \tag{8}$$



Fig. 5. a) SEM image of Au/ZnCu, b) TEM image of Au/ZnCu, c) HRTEM image of Au/ZnCu, d) TEM image of Zn/ZnCu, e) TEM image of In/ZnCu f) HRTEM image of Zn/ZnCu, g) HRTEM image of In/ZnCu, h) HRTEM image with identification of the lattice fringe of ZnCu matrix in In/ZnCu; EDS mapping of elemental distribution for i) In/ZnCu, j) Au/ZnCu and k) Zn/ZnCu.

Obviously, the most desired reaction is the equimolar reaction between CO and NO with the formation of CO₂ and N₂, shown as reaction (4). However, numerous publications reported [57–61] that at low temperatures (<250 °C) the formation of N₂O can occur through reaction (5). Nonetheless, N₂O formation is undesired since N₂O is a greenhouse gas [60]. Various mechanistic studies [62,63] indicate that N₂O is an intermediate which can react with adsorbed CO or adsorbed atomic oxygen if it remains adsorbed (reaction (6) and (7)). However, to oxidize CO in an easy way is to use O₂, which is shown in reaction (8). The catalytic efficiencies for NO and CO conversions as well as the quantified O₂ consumption during all the catalytic processes are shown in Fig. 8 for the fresh LDH -type catalysts and in Fig. 9 for the catalysts thermally treated at 600 °C.

Fig. S3 show the results when pure CuO was used as a catalyst as benchmark. This demonstrates that pure CuO can be used to oxidize CO at around 200 °C using O_2 though, very importantly, it is unable to convert any NO under the present experimental conditions, other than very low conversion around 200 °C, presumably due to the formation of N₂O. The results obtained in the present study show that all the catalysts based LDH having a ZnCu containing lattice, as well as their calcined correspondents, are able to convert NO using CO (reaction (4)) and as well CO using O_2 (reaction (8)), respectively. These results indicate that the presence of Zn in the LDH lattice for the synthesized catalysts plays an important role in promoting the conversion of NO. The overview



results also show that the non-calcined ZnCu catalysts exhibited a better catalytic performance compared to the calcined ZnCu-600. Further, heterostructuring the AuNP, ZnNP and InNP onto the LDH surface gave rise to a major increase of the catalytic performance for the NO conversion with almost 70%. In both cases, fresh and calcined materials, In/ ZnCu presented the best catalytic performance with 95% of CO conversion and almost 80% of NO conversion, followed by Zn/ZnCu and Au/ZnCu. As mentioned above, several literature reports indicate that at low temperatures (<250 °C) the formation of N₂O can occur through reaction (5) [57-61]. In our case, the possible formation of N₂O can be noticed only for calcined materials. For Au/ZnCu-600 the N₂O could be produced at temperature lower than 150 °C while for Zn/ZnCu-600 at 170 °C (Fig. 9a) [61]. which may be also correlated with the decreased CO conversion (Fig. 9b) in these cases. The formed N₂O is possibly further converted into CO₂ and N₂ by the reaction (6), as CO conversion is measured although with a decreased efficiency. The slightly better catalytic activity of the Au/ZnCu-600 compared with the Zn/ZnCu-600 may be due to the presence of AuNP and the gold oxidation state which plays a key role in the catalytic performance. It was reported that oxidated state of gold has a better interaction with the support which, because of their high level of surface unsaturation, may coordinate additional oxygen species [64]. According to the XPS results (Fig. 4c), nanogold is present as a mixture of A^0 , Au^+ , Au^{3+} on ZnCu surface. For In/ZnCu showing the best catalytic efficiency, the high NO conversion can be associated with the presence of InNP, identified by XPS as highly dispersed In₂O₃ [65,66]. The presence of ZnNP in the form of ZnO on the surface of the catalyst can promote more active sites for the catalytic reaction as previously also reported by Imyen [67]. The slightly lower catalytic efficiency observed for the calcined catalysts, as compared with the fresh catalysts, might be a consequence of growth and possibly agglomeration of AuNP, ZnNP and InNP on the surface of ZnO/-CuO/ZnAl₂O₄ (Fig. 2b) during the calcination treatment [68,69].

3.3. Effect of O_2 and CO flow on the catalytic efficiency

The influence of oxygen concentration has been studied on In/ZnCuas most performant catalysts and results are shown in Fig. 10. It shows that when O₂ is absent from the reaction feed, the NO conversion into N₂ reaches 100% (Fig. 10a) while the CO conversion into CO₂ reaches 60% and after 300 °C slightly decreases to 50% (Fig. 10b). The CO conversion increases linearly with the O₂ flow until 1.5 ml/min and then decreases. While NO conversion decreases dramatically to no conversion when O₂



Fig. 8. Overview of the catalytic efficiencies obtained using fresh LDHs for (a) NO and (b) CO conversion as well as (c) the quantified O₂ consumption as a function of temperature.



Fig. 9. Overview of the catalytic efficiencies on the derived mixed oxides catalysts as: (a) NO and (b) CO conversion and (c) the quantified O₂ consumption, as a function of temperature.

flow is 1.5 ml/min and 2 ml/min. Excess amounts of oxygen in the reaction feed promotes the oxidation of NO to N₂O meanwhile the catalyst surface is oxidized. Furthermore, the decrease in NO conversion may be also on the account that the reaction takes place in an oxidative atmosphere where CO conversion to CO₂ is favored, practically inhibiting the NO reduction by CO [70]. Similarly, the effect of the CO concentration in the reaction feed was studied and the results are shown in Fig. 11. It can be seen that increasing of CO concentration has a positive impact on the catalytic efficiency. The NO conversion increased from 77% to 100% when using 0.8 ml/min CO in the reaction feed. The CO and O₂ conversion reach 100% in all three cases. As Yamamoto reported, a higher concentration of CO prevents it's oxidation by O₂ and further reduces NO [71].

3.4. Study on stability of catalysts over multi-cycle catalytic tests

To study the stability of the catalysts in this process and investigate the possibility of their reuse over multiple cycles were done in the same experimental conditions. Results obtained using the best catalyst, namely In/ZnCu, are shown in Fig. 12, while the catalytic stability of Au/ZnCu and Zn/ZnCu catalysts is described in Figs. S4 and S5, respectively. We noticed no significant differences after 4 catalytic runs for NO, CO and O₂ conversions. Although we observed some small differences in the NO conversion after 300 °C for Au/ZnCu catalyst (Fig. S4), such that the catalytic activity decreased with approximately 5% after the 4th consecutive cycle. Nevertheless, all the catalysts in the form of the LDH (cycle 1) or the derived mixed oxides (cycles 2–4)



Fig. 10. Effect of O₂ concentration on the conversion of a) NO, b) CO and c) follow up of the O₂ consumption using In/ZnCu catalyst.



Fig. 11. Effect of CO concentration on the conversion of a) NO, b) CO and c) follow up of the O2 consumption using In/ZnCu catalyst.



Fig. 12. Catalytic efficiency over 4 cycles on In/ZnCu as conversion of a) NO, b) CO and c) O2 consumption using the In/ZnCu catalyst.

preserved their high catalytic performances demonstrating their high stability and reusability for this catalytic process.

4. Conclusion

A series of metal nanoparticles (In, Zn, Au)/LDH heterostructures, obtained by exploiting the memory effect strategy of the LDH, and the derived mixed oxides were obtained and their performances as promising catalysts for NO reduction by CO were confirmed. The reconstructed LDHs and the mixed oxides derived after the thermal treatment entangled the phases characteristics of MeNP and that of the LDH. MeNP/ZnCu and the mixed oxides derived after their thermal treatment showed high activity and good stability for NO reduction by CO. The best catalytic performances were obtained for In/ZnCu, as 95% CO conversion and 80% NO conversion. Further we showed that O_2 and CO concentrations play a key role in the studied catalysis. This work establishes the memory effect strategy as a rational and effective approach in the development of MeNP/LDH heterostructures for NO-CO catalysis and we are currently exploring further implications of these findings on other relevant catalytic processes.

CRediT authorship contribution statement

Gabriela Carja, Pegie Cool: Conceptualization, Supervision. Diana Gilea, Elena Mihaela Seftel, Gabriela Carja: Writing – original draft preparation. Diana Gilea, Gabriel Ababei, Tim Van Everbroeck: Performing the experiments and data analyses. Diana Gilea, Pegie Cool, Gabriela Carja: Writing – review & editing. All authors read and approved the final manuscript contents.

Declaration of Competing Interest

The authors declare that they have no known competing financial

Data availability

the work reported in this paper.

Data will be made available on request.

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interests or personal relationships that could have appeared to influence

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.cattod.2023.114342.

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