Use of carboxymethyl cellulose as binder for the production of water-soluble catalysts

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ABSTRACT

Bio-based polymers are materials of high interest given the harmful environmental impact that involves the use of non-biodegradable fossil products for industrial applications. These materials are also particularly interesting as bio-based ligands for the preparation of metal nanoparticles (MNPs), employed as catalysts for the synthesis of high value chemicals. In the present study, Ru (0) and Rh(0) Metal Nanoparticles supported on Sodium Carboxymethyl cellulose (MNP(0)s-CMCNa) were prepared by simply mixing $RhCl_3 \times 3H_2O$ or $RuCl_3$ with an aqueous solution of CMCNa, followed by $NaBH_4$ reduction. The formation of MNP(0)s-CMCNa was confirmed by FT-IR and XRD, and their size estimated to be around 1.5 and 2.2 nm by TEM analysis. MNP(0)s-CMCNa were employed for the hydrogenation of (E)-cinnamic aldehyde, furfural and levulinic acid. Hydrogenation experiments revealed that CMCNa is an excellent ligand for the stabilization of Rh(0) and Ru(0) nanoparticles allowing to obtain high conversions (>90 %) and selectivities (>98 %) with all substrates tested. Easy recovery by liquid/liquid extraction allowed to separate the catalyst from the reaction products, and recycling experiments demonstrated that MNPs-CS were highly efficiency up to three times in best hydrogenation conditions.

1. Introduction

The growing concern generated by the environmental impact of non-biodegradable fossil-based products, is pushing towards the adoption of more sustainable biobased feedstocks and products, for different industrial applications [1–11]. In particular, biobased polymers are gaining increasing interest also for the synthesis of metal nanoparticles (MNPs) [12,13]. Catalysis by MNPs is of considerable interest both at research and industrial level, since these catalysts combine features of both heterogeneous and homogeneous catalysts [14–19], allowing easy separation of products, catalyst recovery and recycling [20–22]. Additionally, the use of water soluble and bio-degradable ligands further improves the overall environmental sustainability of MNPs, and products derived [23–26]. Natural compounds, such as amino acids, peptides, proteins, sugars, and polysaccharides, have been proven to act as ligands for the stabilization of MNPs in aqueous systems [27–45]. The development of green and sustainable MNPs catalysts employing ligands

derived from renewable biomass feedstock and their use for the synthesis of value-added chemicals is currently a very active area of research [46,47]. However, difficulties encountered in catalyst recovery and recycling restrict their application on an industrial scale.

In recent years, cellulose has proved to be a suitable biopolymer able to produce highly stabilized MNPs giving highly efficient and recyclable catalysts [48–55]. Due to its abundance and unique properties, cellulose has, in fact, gained a privileged role in the development of environmentally friendly, biocompatible, MNPs acting as efficient matrix for the incorporation of a wide range of noble and transition metals [56]. Functionalization of the hydroxyl groups present in cellulose is required to introduce new functionalities able to anchor MNPs to the cellulose matrix [56–58]

In this context, cellulose derived biomass such as sodium carboxymethylcellulose (CMCNa), appears particularly attractive for the stabilization of MNPs due to its high availability, low price and biodegradability, but most of all for the large number of carboxyl acid

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groups and its solubility in water. In fact, CMCNa has been widely used for various biological [59–61], packaging [62–67] and other applications [68–71], but, according to the literature, very few examples of the use of CMCNa for the preparation of MNPs are known [72–75]. Starting from 2011, first studies were published on the use of Ni(0)-CMCNa for the hydrogenation of a number of functionalized nitrobenzenes [72], and Pd(0)-CMCNa nanoparticles as catalysts for Mizoroki−Heck reactions [73,74]. Only more recently, in 2018, Qu and co-workers [75] described the first, and to the best of our knowledge, the only example of Ru(0) nanoparticles stabilized by modified CMCNa (methyl laurate-CMCNa hereafter LM-CMCNa) and their use as catalysts for hydrogenation reactions in aqueous medium. Specifically, the hydrogenation of α-pinene in the presence of Ru(0)-LM-CMCNa was studied, reaching very high conversions, selectivities in *cis*-pinane (up to 98 %) and excellent recyclability (up to 18 times).
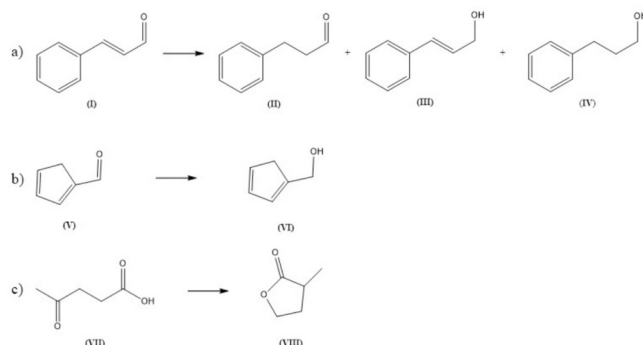
All this considered, scope of this work is to investigate the preparation and characterization of CMCNa stabilized Rh(0) and Ru(0) nanoparticles and their use as catalysts for hydrogenation reactions. Nanoparticles reported in this work were prepared by simply mixing $RhCl_3xH_2O$ or $RuCl_3$ in an aqueous solution containing CMCNa, followed by reduction with $NaBH_4$, in analogy to the protocol previously reported by Harrad and coworkers for the preparation of Ni(0)-MNPs [72]. Thus, the catalytic activity and selectivity of the Rh(0) and Ru(0)-CMCNa nanoparticles was tested in water or water/organic medium for the hydrogenation of different α,β-unsaturated substrates commonly employed for the preparation of high value chemicals (cinnamaldehyde (**I**), furfural (**V**), and levulinic acid (**VII**), (Scheme 1). Preliminary hydrogenation reactions in the presence of cinnamaldehyde were carried out to find best operational conditions, selectivity of the MNPs towards C═C or C═O hydrogenation, compare the efficiency of MNPs studied in this work with literature data [76–78]. Furfural and levulinic acid, on the other hand, have been chosen for their importance as biobased platform chemicals to produce polymers, fine chemicals, plasticizers, diols, and green solvents [16,79–88]. Easy recovery by liquid/liquid extraction was employed to separate the catalyst from the reaction products, and recycling experiments performed.

Further, MNP(0)s-CMCNa before and after reduction were characterize by XRD and FT-IR, while MNP(0)s-CMCNa before and after hydrogenation experiments were characterized by TEM and XRD.

2. Experimental

2.1. General remarks

All commercially available reagents, solvents, and chemicals were provided by Sigma Aldrich (ITALY) and used as received. CMCNa (90.000 Da) with 70 % carboxylation degree (c = 0.7), was purchased from Sigma Aldrich. The catalyst and products were characterized by different analytical and spectroscopic analysis such as, TEM, XRD, FT-IR, NMR, GC–MS. TEM images were obtained using a Philips 208 Transmission Electron Microscope. The samples were prepared by placing one drop of catalyst dispersion on a copper grid pre-coated with a Formvar film and dried in air. FT-IR spectra were recorded on a Bruker INVENIO R in the 500–4000 cm^{-1} range. The samples were prepared by placing one drop of catalyst dispersion and dried on silicon window. XRD patterns were collected with a diffractometer in Bragg-Brentano geometry (Bruker D8 Advance, Bruker AXS GmbH, Karlsruhe, Germany), provided with a Lynxeye XE-T fast detector, CuKα radiation (operative conditions: 40 kV and 40 mA, step size 0.014° 2θ, step scan 10 s). The Bruker DIFFRAC.EVA V5 software equipped with COD database was used for the phase identification. The ^1H and ^{13}C NMR spectra of the products were registered on a Bruker UltraShield 400 spectrometer operating at 400.0 and 101.0 MHz, respectively. Gas–liquid chromatography (GLC) analyses were performed on an Agilent 6850 gas chromatograph; gas chromatography–mass spectrometry (GC–MS) analyses were performed on a HP 5890 series II gas chromatograph interfaced to a HP 5971 quadrupole mass detector.

2.2. Preparation of MNP(0)s-CMCNa

Preparation of Rh(0) and Ru(0) nanoparticles stabilized with variable quantities of CMCNa using $NaBH_4$ as reductant was carried out starting from $RhCl_3x3H_2O$ or $RuCl_3$ respectively. The preparation of MNP(0)-CMCNa (CMCNa/M: 1/100 mol/mol) nanoparticles was carried out as follows: under nitrogen atmosphere, 2.0 mg (2.22×10^{-7} mol) of CMCNa and 50 mL of distilled water, were introduced into a 150 mL flask and left under stirring until a homogeneous solution was formed (1 h, CMCNa concentration 0.4 g/L).

Then, MCl_3 (2.20×10^{-5} mol), where added to the solution and after 2 h further 20 mg (5.3×10^{-3} mol) of $NaBH_4$, dissolved in 30 mL of H_2O, where added. The resulting black solution was kept under stirring for 24 h under inert atmosphere and portions of the solution used for catalytic reactions.

2.3. General procedure for the hydrogenation of model substrates with MNP(0)s-CMCNa

Hydrogenation experiments were carried out in a magnetically stirred stainless steel autoclave (total volume 150 mL) connected to a thermostatic bath in order to maintain the reaction temperature constant within ±1 °C. The same experimental protocol was used for hydrogenation reactions and recycling experiments with all different substrates tested, unless otherwise stated.

For example, the procedure for the hydrogenation of cinnamaldehyde (**I**) is reported (entry 8, Table 1). Under inert atmosphere, in a 50 mL vial equipped with a small magnetic bar were introduced 4 mL of a water/THF solution (1/1 vol/vol), 0.05 mL (0.397 mmol) of (**I**), 1.8 mL of the Rh(0)-CMCNa solution (prepared as described above, Substrate/ Rh = 500) and 23.5 mg (0.15 mmol, CMCNa/M 1/100 mol/mol, COONa/M 3.2 mol/mol) of *n*-undecane as internal standard. Then, the vial was placed in a pre-purged 150 mL autoclave and 10 atm of H_2 were added. The autoclave was then heated at 60 °C and kept under constant magnetic stirring for 4 h, then the autoclave was cooled to room temperature and the residual gas vented off. The reaction mixture was extracted with 5 mL × 2 aliquots of diethyl ether, and the organic phase dried with $MgSO_4$, filtered, and analysed by GC. Further the organic solvent was evaporated, and products characterized by GC–MS, FT-IR and ^1H, ^{13}C NMR and data compared to literature data [22,89–94]. The water solution was kept under nitrogen and used for recycling experiments. All experiments were performed in triplicate. All recycling experiments were carried out in the same reaction conditions as first run, unless otherwise specified.

Scheme 1. Hydrogenation of the substrates tested in the work.

Table 1
Hydrogenation of Cinnamaldehyde (**I**) in the presence of MNP(0)s-CMCNa.

Entry[a]	MNPs-CMCNa	T (°C)	p(H$_2$) (atm)	t (h)	Conv. (%)[b]	(II) (%)[b]	(IV) (%)[b]
1[c]	Rh(0)-CMCNa	80	10	24	100	98	2
2[d]	Rh(0)-CMCNa	80	10	24	100	97	3
3[c]	Ru(0)-CMCNa	80	10	24	62[e]	44	11
4[d]	Ru(0)-CMCNa	80	10	24	64[e]	43	13
5	Rh(0)-CMCNa	80	10	24	100	98	2
5$_{r1}$[f]					100	100	0
6	Ru(0)-CMCNa	80	10	24	63[e]	44	11
7	Rh(0)-CMCNa	80	5	1	96	96	0
7$_{r1}$[f]					38	38	0
8	Rh(0)-CMCNa	60	10	4	100	98	2
8$_{r1}$[f]					74	67	7
8$_{r2}$				24	100	96	4
8$_{r3}$				24	100	97	3

[a] Reaction conditions: Substrate (**I**) 4.0×10^{-5} mol; Solvent: H$_2$O/THF 1/1 v/v (4 mL); Rh or Ru: 8×10^{-7} mol; CMCNa/M 1/100 (mol/mol); COONa/M 3.2 (mol/mol); 23.5 mg (0.15 mmol) n-undecane.

[b] Data determined by GC–MS (%) using n-undecane internal standard.

[c] COONa/M 0.8 (mol/mol).

[d] COONa/M 1.6 (mol/mol).

[e] 7 % of (**III**) was also formed.

[f] r = recycling experiment.
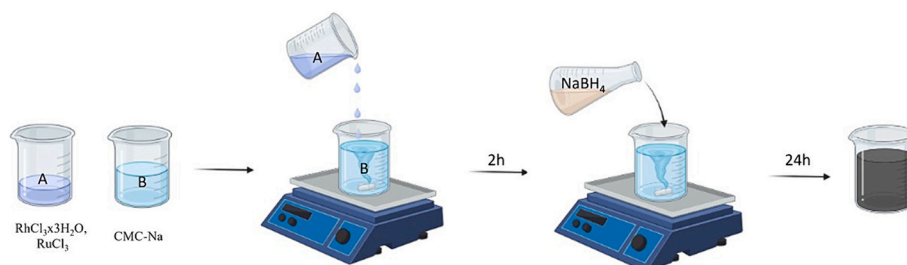
3. Results and discussion

3.1. Preparation of MNP(0)s-CMCNa

The MNP(0)s-CMCNa nanoparticles were easily prepared by adding, at room temperature, RhCl$_3$x3H$_2$O or RuCl$_3$ catalyst precursor (Scheme 2, A) to an aqueous solution of CMCNa, followed by reduction with NaBH$_4$ (Scheme 2) [72,75,95]. The resulting dark colour solution containing the nanoparticles was stored under nitrogen and used for hydrogenation reactions without further purification (see Table 1).

This approach appears particularly appealing also for industrial applications since very mild conditions are employed to prepare the catalyst solution which is used without any work up.

Different batches of Rh(0) and Ru(0)-CMCNa were prepared at variable CMCNa/M wt/wt ratios (0.20, 0.40, 0.80, 1.2, 1.6 g/L) was investigated since, according to the literature, the stability of MNP(0)-CMCNa nanoparticles is influenced by the concentration of the CMCNa solution [72–75]. Interestingly, previous literature works neglect to study the influence of the COONa/M mol/mol ratio between the metal and the -COONa functional groups present in CMCNa [72–75]. Since, metal complexation is known to be assisted by carboxylic functional groups present in CMCNa [74] (Scheme 3), in this paper the influence of both CMCNa/M wt/wt and COONa/M mol/mol ratios was investigated (see below).

COONa/M mol/mol ratios were calculated as follows: molecular formula of the carboxymethyl cellulose monosaccharide units is [C$_6$H$_7$O(OH)$_{3-x}$(OCH$_2$COONa)$_x$]$_n$ where x is the substitution degree and n the polymerisation degree. Consequently, the average molecular weight of CMCNa used in this work (c = 0.7) is PMm = 202. This implies that CMCNa contains approximately 446 monosaccharide units (90.000/202), 312 of which are carboxylated and 134 are not. This in mind, different quantities of metal precursors were used in order to prepare nanocatalysts with CMCNa/M mol/mol ratios of 1/400, 1/200 and 1/100 corresponding respectively to a COONa/M mol/mol ratio of 0.8, 1.6 and 3.2 respectively (see Table S1). These ratios were selected in order to verify metal stability in the presence of -COONa mmoles above and below stoichiometric ratio as compared to the mmoles of transition metal catalyst precursor used.

3.2. Characterization of MNP(0)s-CMC by FT-IR, XRD and TEM

3.2.1. FT-IR analysis

The Ru(0) and Rh(0) MNP(0)s-CMCNa nanoparticles were characterized by FT-IR before and after reduction with NaBH$_4$. The FT-IR spectra of RhCl$_3$ + CMCNa and Rh(0)-CMCNa catalysts are shown in Fig. 1(a,b). In the FT-IR spectrum, characteristic absorptions of −COOH and − COONa of CMCNa were observed at 1600–1640 cm^{-1} and 1400–450 cm^{-1} [62,96], while adsorptions at approximately 2920 cm^{-1} are attributed to the −CH stretching of the −CH$_2$ and − CH$_3$ groups. At 1325 cm^{-1} a sharp band corresponds to the −OH bending vibration while the broad absorption band between 3200 cm^{-1} and 3600 cm^{-1} is characteristic of the stretching frequency of the −OH groups. Observing the position of the maxima of the bands corresponding to the stretching vibrations of the residual non-carboxylated hydroxyl groups for Rh containing species, a shift from 3440 cm^{-1} to lower values can be seen upon reduction with NaBH$_4$. This suggests that the Rh^{3+} cation is initially complexed with −OH functional groups while after reduction the shift to lower values indicates the absence of Rh^{3+} complexes. Absorption at 1030 cm^{-1} is characteristic of the carboxymethyl ether.

Analogous patterns were observed in the RuCl$_3$ + CMCNa and Ru(0)-CMCNa (Fig. 1c,d), except for the fact that in this case the shift around 3400 cm^{-1} was not appreciable. Since FT-IR analysis were insufficient to give exhaustive evidence of MNPs formation, further characterizations were carried out in order to gain evidence of MNP(0)s-CMCNa formation.

3.2.2. XRD analysis

The XRD patterns of Rh(0) and Ru(0)-CMCNa nanoparticles after reduction with NaBH$_4$ are reported in Fig. 2. In particular, XRD patterns show the characteristic peaks of Rh(0): 40°, 46° and 54° (JCPDS No. 88-2334) and Ru(0): 38.3°, 42.1°, 44.0° and 58.3° (JCPDS No. 70-0274) respectively, confirming complete reduction of the MNPs. Moreover, the intensity of the peaks both of the Rh(0) and Ru(0)-CMCNa nanoparticles, reflect the high dispersion and the nanostructure of metal particles formed, in agreement with the literature [75,97,98].

3.2.3. TEM analysis

It is with TEM images that the formation of Rh(0)-CMCNa and Ru(0)-

Scheme 2. Preparation of MNP(0)s-CMCNa, M = Ru(0) or Rh(0).
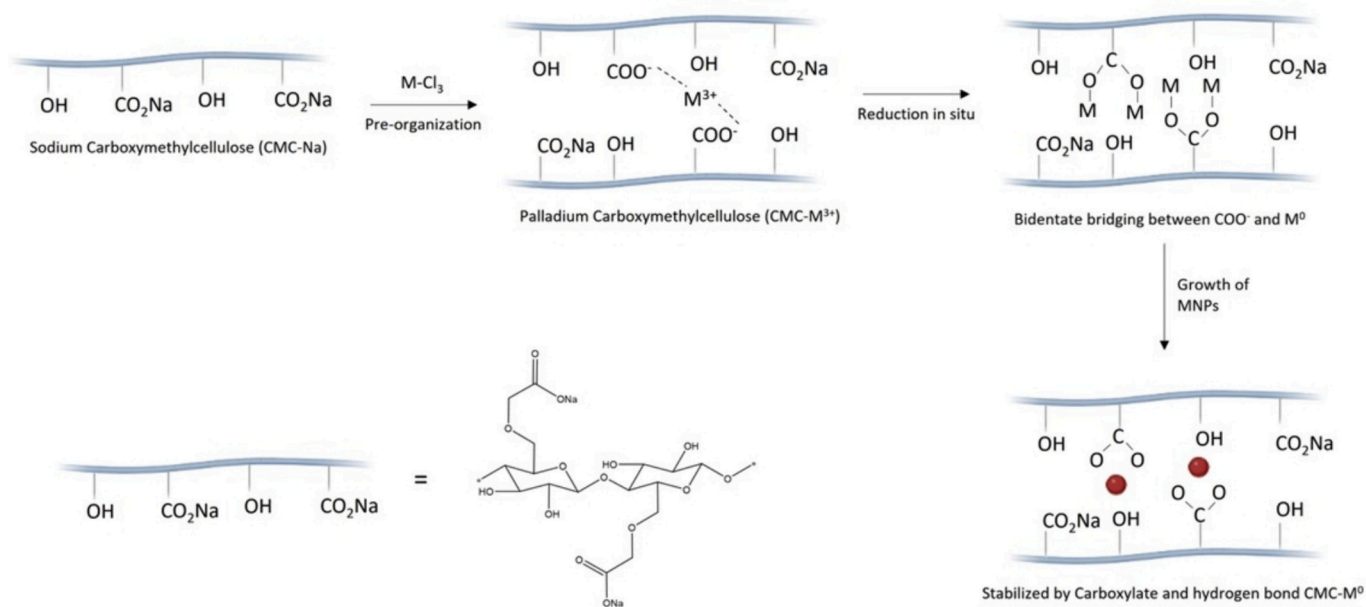
Scheme 3. Proposed scheme of MNPs formation by coordination of the Metal to -COONa groups.
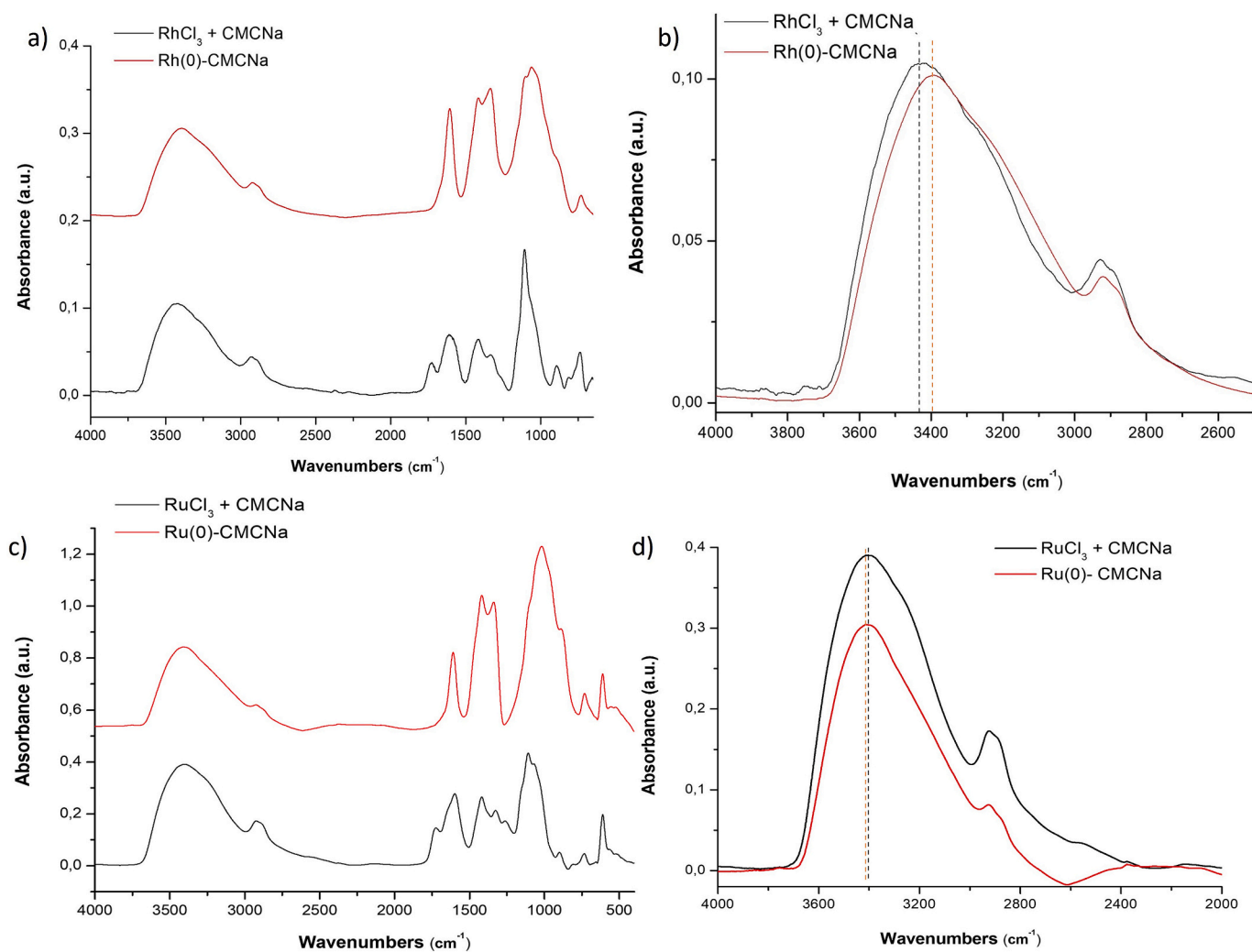

Fig. 1. Comparison between FT-IR spectra of Rh catalyst before and after reduction (a, b), and Ru catalyst before and after reduction (c, d).
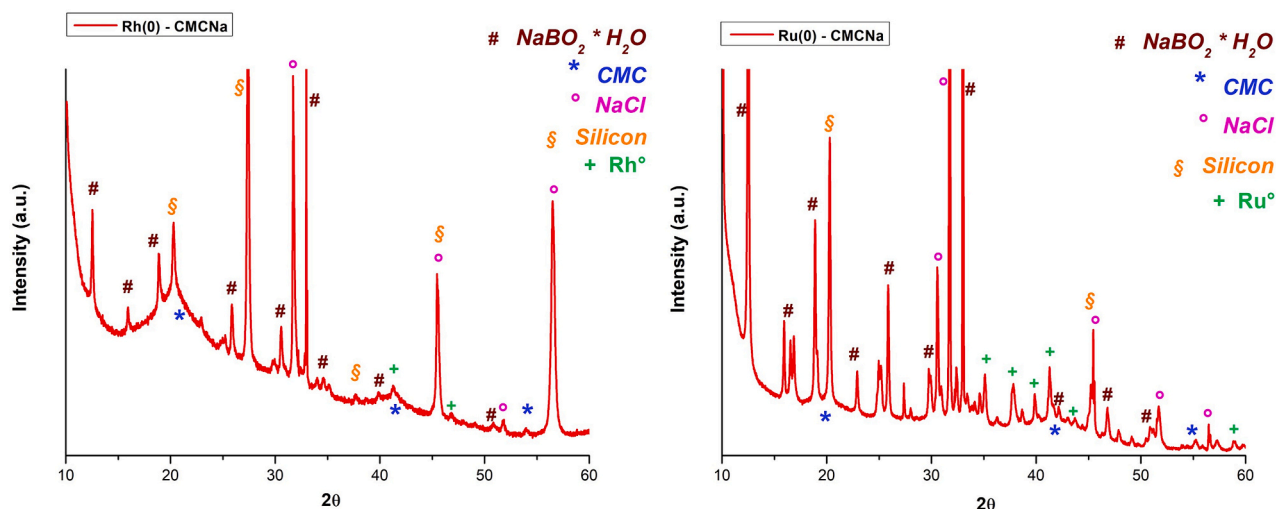
Fig. 2. XRD diffraction pattern of (a) Rh(0)-CMCNa and (b) Ru(0)-CMCNa.

CMCNa nanoparticles after the reduction was evident. The size of Rh(0)-CMCNa was estimated to be around 2.2 nm (Fig. 3a) while Ru(0)-CMCNa gave smaller nanoparticles of an average size of 1.5 nm (Fig. 3c). Comparison of TEM images of Rh(0)-CMCNa nanoparticles registered before and after the hydrogenation of (**I**), show that no aggregation phenomena occur during the catalytic reaction as the size of the nanoparticles is unaffected (Fig. 3a,b). On the contrary, TEM images of Ru(0)-CMCNa before and after the hydrogenation of (**V**) show that the distribution of the size of the nanoparticles is spread over a wider size range after the reaction (Fig. 3d) and aggregation of MNPs is evidenced by the increase in size of the Ru(0)-CMCNa nanoparticles from 1.5 to 2.5 nm due to aggregation phenomena (compare Fig. 3c and 3d). This aggregation phenomena, as shown by the hydrogenation experiments reported below (Table 2), does not have any consequences on the performance of Ru(0)-CMCNa upon recycling.

3.3. Catalytic hydrogenation in the presence of MNP(0)s-CMCNa

To study the activity of MNP(0)s-CMCNa and optimize hydrogenation reaction conditions, preliminary experiments were carried out using (*E*)-cinnamaldehyde (**I**) as model substrate in reaction conditions comparable with the literature (80 °C, p(H$_2$) 10 atm, (**I**)/Rh 500, for 24 h) [16,72,75], at different CMCNa concentrations (between 0.2 and 1.6 g/L).

The presence of a C=C double bond and a C=O double bond in (**I**) allows to evaluate both the activity and the selectivity of the Rh(0) and Ru(0) catalytic systems under study. In fact, hydrogenation of cinnamaldehyde (**I**) for the production of either hydro cinnamaldehyde (**II**) or cinnamyl alcohol (**III**) is challenging due to the possible formation of several products [99–102] (Scheme 1), thus selective hydrogenation of (**I**) is often chosen as model reaction considering both its scientific and industrial relevance [103–107].

Preliminary experiments, as mentioned above, were devoted to verifying the influence on the activity and selectivity of Rh(0) and Ru(0)-CMCNa prepared employing variable concentrations of CMCNa. From these experiments CMCNa concentrations of 0.40 g/L appeared to be sufficient in both cases (from RhCl$_3$x3H$_2$O or RuCl$_3$) to achieve stable and recyclable MNP(0)s-CMCNa nanoparticles. In agreement with the literature, concentrations <0.40 g/L led to catalyst precipitation after the reaction, whereas CMCNa concentrations >0.4 g/L gave no significant advantages, thus 0.4 g/L was chosen for further hydrogenation experiments under aqueous conditions [72,74,95,108].

Then, the influence of the reduction by NaBH$_4$ on Rh and Ru nanoparticles was investigated. Thus, a set of experiments were performed employing metal/CMCNa solutions prepared with and without the use of NaBH$_4$, referred to as Rh(0)-CMCNa, Rh(II)-CMCNa, Ru(0)-CMCNa, Ru(II)-CMCNa respectively. At 80 °C and p(H$_2$) 10 atm in the presence of Rh(0)-CMCNa total conversion of (**I**) was achieved in 24 h (entry 1, Table 1) and 98 % in (**II**), while Rh(II)-CMCNa gave lower substrate conversions (<75 %) and reduced selectivities in (**II**) (<50 %). A similar reduction of activity and selectivity was observed also employing Ru(0)-CMCNa and Ru(II)-CMCNa. Interestingly, recycling experiments showed that nanoparticles prepared without pre-reduction with NaBH$_4$ totally lost catalytic activity, adversely to pre-reduced MNPs-CMCNa (see below). Although it could be summoned that hydrogen employed during the catalytic reaction would reduce the metal and thus generate "*in situ*" the MNPs(0)-CMCNa, recycling experiments clearly show that this is not the case and that pre-reduction with NaBH$_4$ is determinant to achieve highly active MNPs(0)-CMCNa nanocatalysts.

Further experiments were devoted to study the influence of COONa/M mol/mol ratio on the efficacy and stability of MNP(0)s-CMCNa nanoparticles. Hydrogenation of (**I**) at 80 °C and p(H$_2$) 10 atm, was performed with a COONa/M mol/mol ratio of 0.8, 1.6 and 3.2 for 24 h (entries 1–6, Table 1). Although conversions of (**I**) and selectivity in (**II**) were not affected by the different COONa/M mol/mol ratio, catalyst precipitation was observed after the reaction when COONa/M of 0.8 and 1.6 mol/mol ratios were used, probably due to an insufficient amount of COO$^-$ functional groups stabilizing the catalyst and negatively influencing the stability of the nanoparticles. It is interesting to note that these results clearly confirm the role of the COO$^-$ groups in stabilizing the nanoparticles and underline the importance of the COONa/M mol/mol ratio, generally not considered in previous literature work [74,75,109]. Further experiments were thus carried out with COONa/M 3.2 mol/mol corresponding to CMCNa/M 1/100 mol/mol.

Data reported in Table 1 (compare entries 5 and 6) clearly highlight a strong difference in the activity and selectivity of the two nanocatalysts for the hydrogenation of (**I**). In fact, at 80 °C and p(H$_2$) 10 atm in the presence of Rh(0)-CMCNa total conversion of (**I**) was achieved in 24 h with very high selectivities towards carbon-carbon double bond hydrogenation (entry 5, Table 1). On the contrary, when Ru(0)-CMCNa was used in the same reaction conditions both conversion of (**I**) (63 %) and selectivity in (**II**) were significantly depressed since together with cinnamaldehyde (**II**) also (**III**) and hydrocinnamyl alcohol (**IV**) were formed respectively in 11 % and 7 % (entry 6, Table 1).

Additional experiments to optimize reaction conditions were carried out only with best performing Rh(0)-CMC, at different temperatures, p(H$_2$) and times (entries 7, 8, Table 1). At 60 °C and p(H$_2$) 10 atm by 4 h Rh(0)-CMCNa allowed to achieve total substrate conversion and 97 %
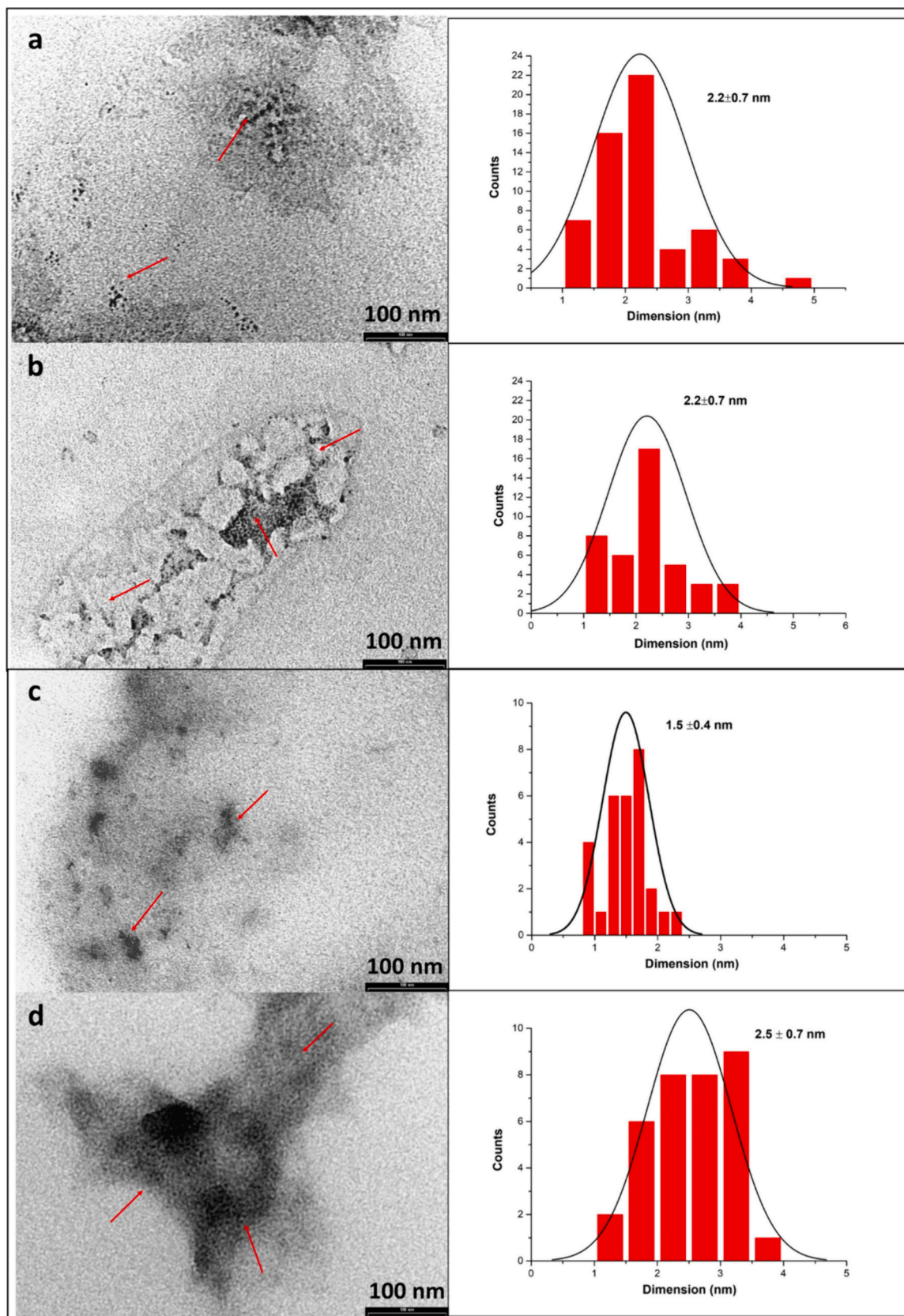
Fig. 3. TEM images of Rh(0)-CMCNa and Ru(0)-CMCNa nanoparticles, (a, c) before and (b, d) after hydrogenation.

Table 2
Hydrogenation of **V** and **VII** substrates in the presence of MNP(0)s-CMCNa.

Entry[a]	MNP(0)s-CMCNa	S	M/S (mol/mol)	T(°C)	p(H$_2$) (atm)	t(h)	Conv.(%)[b]	Product
		(V)						(VI) (%)[b]
1	Rh(0)-CMCNa		1/100	80	20	24	75	75
1$_{r1}$[c]							72	72
1$_{r2}$							79	79
2	Rh(0)-CMCNa		1/100	100	60	24	95	95
2$_{r1}$[c]							96	96
2$_{r2}$							95	95
3	Ru(0)-CMCNa		1/100	80	20	24	71	71
3$_{r1}$[c]							65	65
3$_{r2}$							55	55
4	Ru(0)-CMCNa		1/100	100	60	24	92	92
4$_{r1}$[c]							91	91
4$_{r2}$							92	92
		(VII)						(VIII) (%)[b]
5	Ru(0)-CMCNa		1/100	60	10	24	100	100
5$_{r1}$[c]							100	100
6	Ru(0)-CMCNa		1/100	60	20	2	100	100
6$_{r1}$							88	88
7	Ru(0)-CMCNa		1/100	40	20	4	100	100
7$_{r1}$[c]							84	84
8	Ru(0)-CMCNa		1/100	30	20	6	100	100
8$_{r1}$[c]							100	100
9	Ru(0)-CMCNa		1/500	60	20	2	72	72
9$_{r1}$[c]							50	50
10	Ru(0)-CMCNa		1/500	40	20	4	65	65
10$_{r1}$[c]							60	60

[a] Reaction conditions: Substrate (**V**) or (**VII**) 4.0×10^{-5} mol; Solvent: H$_2$O (4 mL). Rh or Ru: 8×10^{-7} mol; CMCNa/M 1/100 (mol/mol); COONa/M 3.2 (mol/mol); 23.5 mg (0.15 mmol) *n*-undecane.

[b] Data determined by GC–MS (%) using *n*-undecane internal standard.

[c] r = recycling experiment.

selectivity in (**II**) after three recycling experiments.

Recycling experiments were carried out as follows at the end of the reaction the product was separated from the catalyst phase by extraction with diethyl ether, fresh (*E*)-cinnamaldehyde was added to the catalytic aqueous solution and hydrogenation repeated under the same reaction conditions as entry 8 of Table 1. Activity of Rh(0)-CMCNa moderately decreases upon recycling (entry 8$_{r1}$, Table 1), but prolonging reaction times to 24 h, total conversion of (**I**) and high selectivity in (**II**) (96–97 %) could be achieved after two more recycling experiments (entries 8$_{r2}$ and 8$_{r3}$, Table 1).

Since no data are available in the literature on the hydrogenation of (**I**) with CMCNa nanoparticles, in order to evaluate the efficiency of Rh (0)-CMCNa tested in this work, comparison with heterogeneous Rh(0) catalysts supported on carbon reported in the literature has been carried out. According to a very recent work by Patil and co-workers [99], results achieved with Rh(0)-CMCNa for the hydrogenation of (**I**) with Rh (0)-CMCNa emerge to be particularly interesting since in most cases heterogeneous catalysts reported in the literature have modest activity and selectivity, requiring harsh conditions [99] (100 °C, 20 atm pH $_2$) and environmentally unfriendly organic solvents [44,110]. For example, Liu reported the use of Rh@MIL-101 (Cr) a metal–organic framework (MOF) with high surface area and porosity, for the hydrogenation of (I). At 30 °C, p(H2) 10 atm, with a (I)/Rh molar ratio of 400, in ethanol as solvent conversions of up to 98 % of (**I**) were achieved by 5 h, with selectivity in (**II**) of 99 %. In analogous reaction conditions Rh/C gave significantly lower conversions (53 %) and selectivity in (**II**) (89 %). Although Rh@MIL-101 (Cr) can be recycled up to two times with almost no change in activity and selectivity, its sustainability is low considering that MIL is synthesized using toxic chemicals such as *N, N*-dimethylformamide (DMF) or hydrofluoric acid (HF) [111]. Alternatively Rh porphyrins have been used for the hydrogenation of (**I**), but with modest selectivities in (**II**) ($\leq$ 80 %). Additionally, toluene was used together with water as reaction solvent and NEt$_3$ had to be added to promote the solubility in water of the Rh porphyrin complex [110].

To widen the scope of the reaction, further hydrogenation reactions of furfural (**V**) and levulinic acid (**VII**) (Scheme 1) were performed with Rh(0)-CMCNa and Ru(0)-CMCNa and results reported in Table 2. The development of efficient protocols for the valorisation of bio-based feedstocks is gaining increasing interest to produce sustainable building blocks in alternative to fossil-based ones. In fact, in the last decade scientists and the industry have developed many alternative methodologies for the valorisation of biobased platform chemicals such as furfural and to produce polymers, fine chemicals, plasticizers, diols, green solvents, among others [16,79–87]. Specifically, many different homogeneous and heterogeneous catalysts have been tested, using noble and non-noble metals for the selective hydrogenation of (**V**) to produce furfuryl alcohol (**VI**) [112–116] and levulinic acid (**VII**) for the synthesis of γ-valerolactone (**VIII**) [48,117–121].

Hydrogenation of (**V**) and (**VII**) with Rh(0)-CMCNa and Ru(0)-CMCNa were initially carried out in best reaction conditions defined for (**I**) (entry 8, Table 1), but gave modest to no conversion. Thus, hydrogenation of (**V**) was replicated at moderately higher p(H$_2$) or temperature (entries 1 and 2, Table 2) and good conversions and total selectivity in (**VI**) was obtained both with Rh(0)-CMCNa and Ru(0)-CMCNa. It is interesting to note that at 100 °C, p(H$_2$) 60 atm by 24 h with a M/S mol/mol ratio of 500, higher conversions of (**V**) (92–95 %, entries 2 and 4, Table 2) and total selectivity were achieved with both Rh (0)-CMCNa and Ru(0)-CMCNa nanoparticles.

Hydrogenation of (**VII**) carried out in the presence of Rh(0)-CMCNa gave very unsatisfying results, while with Ru(0)-CMCNa at optimised conditions for (**I**), allowed to recover (**VIII**) with total yields and selectivity in (**VIII**) also after recycling (entries 5, 5$_{r1}$, Table 2). Moreover, at p(H$_2$) 20 atm, temperature could be lowered down to 30 °C reaching total conversion of (**VII**) and selectivity in (**VIII**) by 6 h, also after recycling (entries 8 and 8$_{r1}$, Table 2).

As for (**V**) data achieved for the hydrogenation of levulinic acid (**VII**)

with Ru(0)-CMCNa are extremely interesting. Recently Ndolomingo and coworkers reported a comparison between the efficiency of different MNP employed for the hydrogenation of (VII) has been reported [21]. From this work it emerges that Ru@Meso-SiO$_2$ nanoparticles are highly efficient for the hydrogenation of (VII) at moderate p(H2) (10 atm) and short times (5 h), yet very high temperatures are required (150 °C) and dioxane is used as solvent [122]. Also, Ru/SiO$_2$, Ru/Al$_2$O$_3$, Ru/ZnO$_2$ and Ru/TiO2 have been reported by Tan for the hydrogenation of (**VII**) but also in this case high temperatures are required [78].

4. Conclusions

In conclusion, in this work, an easy protocol for the preparation of highly active Rh(0) and Ru(0)-CMCNa nanoparticles for the hydrogenation of important platform chemicals, has been reported. MNP(0)s-CMCNa prepared simply by mixing a metal precursor (RhCl$_3$x3H$_2$O or RuCl$_3$) and CMCNa in aqueous solution, followed by NaBH$_4$ reduction, were characterized before and after reduction by FT-IR, XRD to verify formation of the nanoparticles. The influence on the stability of the nanocatalysts was investigated at different CMCNa g/L concentration and COONa/M mol/mol ratio for the hydrogenation of cinnamaldehyde and other platform chemicals such as furfural and levulinic acid [76–78]. TEM analysis allowed to determine their size (of the order of nanometres) and monitor possible aggregation phenomena after recycling experiments. In fact, TEM analysis showed that the metal nanoparticles have a random distribution within the CMCNa, also confirmed by XRD analysis and undergo gradual aggregation after recycling experiment which nevertheless does not deplete their activity upon recycling, up to three times in best reaction conditions. Rh(0)-CMCNa allowed to achieve complete conversions of (**I**) at 60 °C and p(H$_2$) 10 atm by 4 h, with total selectivity in (**II**). On the contrary Ru(0)-CMCNa was less active for the hydrogenation of (**I**), but interestingly, this catalyst was highly efficient in the selective hydrogenation of (**V**) and (**VII**) to produce (**VI**) and (**VIII**) respectively. Comparison with literature data further highlights that MNP(0)s-CMCNa have very high performance as compared to best heterogeneous catalysis known for the hydrogenation of (*E*)-cinnamaldehyde, furfural and levulinic acid [48,112–121].

Further studies implementing chitosan and other water soluble bio-derived substrates bearing suitable functional groups for the anchoring of MNPs are in progress, in order to evaluate and compare their performances in hydrogenation reactions to those of MNPs(0)-CMCNa reported in this work.

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CRediT authorship contribution statement

Stefano Paganelli: Supervision, Formal analysis, Data curation. **Nicola Massimi:** Formal analysis, Data curation. **Alessandro Di Michele:** Formal analysis, Data curation. **Oreste Piccolo:** Writing – review & editing, Formal analysis. **Rachele Rampazzo:** Writing – review & editing, Data curation. **Manuela Facchin:** Writing – review & editing, Data curation. **Valentina Beghetto:** Writing – review & editing, Writing – original draft, Supervision, Investigation, Formal analysis, Conceptualization.

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.

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