Selective hydrogenation of biomass-derived compounds by metallic colloidal suspensions stabilized by water-soluble protective agents

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Introduction

Since the beginning of the 2000, the transformation of non-food biomass into (petro)chemicals is an important sustainability issue [1,2]. The catalytic hydrogenation of the dehydration sugars products (C5 and C6) is mainly interesting because reaction products as 2-methylfuran, furfuryl alcohol (C5), 2,5-bis(hydroxymethyl)tetrahydrofuran and 2,5 dimethylfuran are very useful for industrial applications such as polymer synthesis, solvents and production of petroleum [3,4]. Most of the catalytic systems reported in the literature for these conversions are heterogeneous catalysts [5,6], only one nanoheterogeneous system in liquid phase has been reported for the hydrogenation of biomass-derived compounds [7]. Indeed, colloids can give very interesting results in terms of activity and selectivity under mild reaction conditions in organic and aqueous solvents [8]. In water, the most common polymer used for the stabilization of nanoparticles is polyvinylpyrrolidone (PVP). This water-soluble polymer is known to have strong interactions with Ru nanoparticles [9,10,11]. Moreover, previous works in our laboratory reported the use of cyclodextrins (CD) for the stabilization of Ru@NPs [12,13]. We report hereby the first use of metallic nanoparticles stabilized by PVP:cyclodextrin mixture dispersed in aqueous medium for the hydrogenation of furfural.

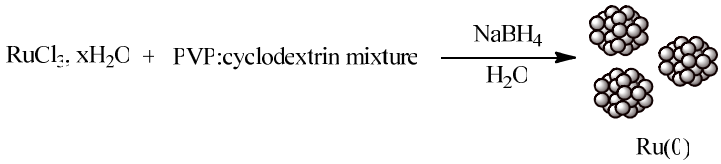
Experimental

Colloidal suspension synthesis

Colloidal suspension was prepared at ambient temperature. The desired quantities of PVP and cyclodextrin were dissolved in 5 mL of deionized water under vigorous stirring during 24h. $RuCl_3$, xH_2O was dispersed in 5 mL of deionized water. The two solutions were mixed together under stirring during 30 min. Then, $NaBH_4$ was quickly added to the mixture under vigorous stirring.

Results and Discussion

For the synthesis of the catalytic system, Ru(0) nanoparticles (noted Ru@NPs) were prepared by reducing ruthenium trichloride with sodium borohydride in presence of PVP:cyclodextrin mixture in aqueous solution (Scheme 1).

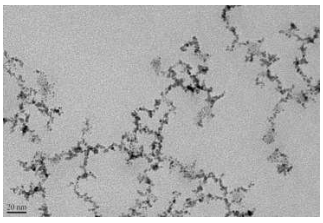


Scheme 1. Synthesis of Ru(0) nanoparticles stabilized by PVP:cyclodextrin mixture

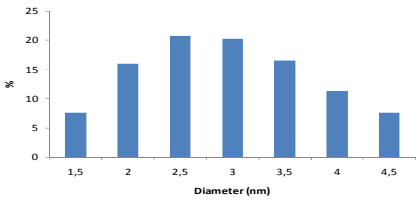
PVP-K30 was used as standard water-soluble protective agent. Randomly methylated and native cyclodextrins have been tested for the synthesis of Ru@NPs. Preliminary tests have been realized with a standard PVP-K30 monomer unit/CD molar ratio of 4. Whatever the CD, very stable colloidal suspensions are obtained without any agglomeration during several months.

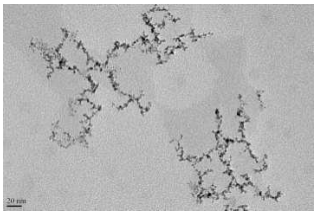
The colloidal suspensions with 8:0 and 8:2 PVP:RaMe-β-CD molar ratio have been characterized by Transmission Electron Microscopy (Figure 1).

The average diameters of Ru@PVP and Ru@PVP:RaMe-β-CD (8:2) are respectively 2.75 nm and 2 nm. No aggregation of the colloids is observed in both cases, showing the ability of PVP and PVP:RaMe-β-CD mixture to stabilize Ru@NPs. When the reduction step is realized in presence of RaMe-β-CD, a decrease in the average diameter is observed without any modification of their shape.



Ru@PVP





Ru@PVP:RaMe-β-CD (8:2)

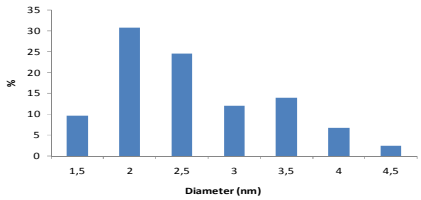


Figure 1: TEM image and size distribution of Ru@NPs

After these characterizations, the influence of the nature of the cyclodextrin on catalytic activity and selectivity has been studied. These colloidal suspensions have been tested for the furfural hydrogenation under 1 MPa of H_2 and at 303K. Catalytic results are summarized in table 1.

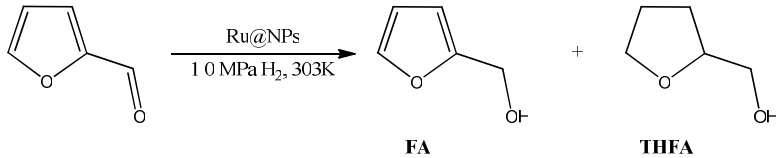


Table 1. Influence of the nature of the cyclodextrin on catalytic activity and selectivity for furfural hydrogenation with Ru@NPs[a]

Entry	CD	Conversion[b] (%)	Selectivity (%)[b]	
			FA	THFA
1	No CD	30	94	6
2	α-OH	30	95	5
3	β-OH	25	93	7
4	γ-OH	38	94	6
5	RaMe-α-CD	31	97	3
6	RaMe-β-CD	53	90	10
7	RaMe-γ-CD	61	95	5

[a] Reaction conditions : Ru(0) (3.8×10^{-5} mol), PVP-K30 (3.0×10^{-4} mol), CD (7.6×10^{-5} mol), Substrate/Ru(0) (mol/mol)= 50, Water (10 mL), Hydrogen pressure (1.0 MPa), Temperature (303K), t = 1.5h, stirred at 750 rpm [b] Determined by GC analysis

The nature of the cyclodextrin has no significant influence on the selectivity of the reaction with 90-95% of furfuryl alcohol in each case. Without cyclodextrin, 30% of furfural is converted within 90 min (Entry 1). No enhancement of activity is observed for native cyclodextrins (Entry 2, 3, 4) and RaMe-α-CD (Entry 5). The best results are obtained with RaMe-β-CD and RaMe-γ-CD with respectively 53 and 61% of conversion. This hypothesis is correlated with the TEM analysis of Ru@PVP and Ru@PVP:RaMe-β-CD (8:2) colloidal suspensions (Figure 1). Indeed, when RaMe-β-CD is used during the synthesis of colloidal suspensions, a decrease in the diameter of the nanoparticles is observed involving an increase in the active surface area.

Conclusions

To conclude, we have developed a new Ru(0) nanoheterogeneous catalytic system stabilized by PVP:cyclodextrin mixture in aqueous media. Ru@NPs in a size range of 2 to 2.75 nm have been easily synthesized by chemical reduction. These nanoparticles have shown interesting activities in the hydrogenation of furfural under mild experimental conditions. These colloidal suspensions are very stable and could be reused several times. Moreover, this study has clearly shown the beneficial effect of cyclodextrins such as RaMe-β-CD and RaMe-γ-CD for the enhancement of catalytic activity. The crucial role of cyclodextrin has not been clearly elucidated. Supplementary experiments are in course for the understanding of mechanistic role of CD, especially during the nucleation step of colloids.

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