A new, cheap and reproducible microwave method for large scale preparation of uniform and efficient nanocatalysts

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Introduction

Nanostructured metal catalysts are of great interest because of their marked catalytic performances. Consequently, different synthetic methods have been reported in literature but, up to now, all these methods present several drawbacks for their application on industrial scale. Today microwave chemistry is experiencing an exponential growth because it is a powerful energy source and it is generally performed using a closed metal cavity, i.e. a microwave oven. However, the current commercial systems present a number of relevant limitations. In fact, ordinary chemical reactors connected with auxiliary components cannot be introduced in an oven and the majority of useful auxiliary devices are not permitted for safety reasons. Local heating in the oven occurs in an unpredictable way and the results are not always reproducible. Openings in the walls of the microwave oven are severely limited and visual control and manual access during the process are forbidden. Multi-disciplinary applications are complicated or even impossible. Therefore industrial scale-up is not straightforward at all and requires very high project and investment costs. Now we have applied [1,2] a new microwave method enabling the possibility of working without the above constraints, enabling to obtain ruthenium, palladium and silver nanocatalysts. Ruthenium systems were employed in the selective hydrogenation of phenol to cyclohexanone [2] while palladium ones in the selective hydrogenation of cinnamaldehyde to hydrocinnamaldehyde.

Materials and Methods

The new arrangement comprises a 2450 MHz microwave source operatively connected to an insulated coaxial antenna irradiating in situ the reacting material and unlimited microwave power can be applied by simply using a number of independent microwave probes [3]. The preparation of nanocatalysts is very simple: a quantity of a metal precursor, the stabilizing polymer and if necessary the support were all dissolved in ethylene glycol at room temperature and under magnetic stirring. The resulting mixture was irradiated by microwave radiation for a selected time and after the removal of the solvent, the nanocatalysts were washed and finally dried. All the hydrogenation reactions were carried out in a 300 ml mechanically stirred autoclave. In a typical procedure the amount of catalysts was inserted in the autoclave under inert atmosphere. Then the autoclave was closed, evacuated up to 0.5 mm Hg and then the reagent with the solvent were introduced inside by suction. Then the autoclave was pressurized with hydrogen and heated. The hydrogenation of phenol was carried out at 160 °C and 50 atm of H_2 while the hydrogenation of cinnamaldehyde at 100°C and 20 atm of H_2

Results and Discussion

Our microwave method is safe and cheap, it enables to obtain the utmost efficiency and control also for industrial applications, without resorting to an ordinary oven. We have successfully adopted our procedure for the synthesis "in situ" of ruthenium, palladium and silver nanocatalysts on different supports that present little average diameters (from 1 to 4 nm), good morphology and very narrow sizes distribution with an absolute reproducibility. The reduction of the metal was also confirmed by XPS measurements. Our ruthenium nanocatalysts resulted particularly efficient, in terms of activity and selectivity, in different selective catalytic reactions such as the hydrogenation of phenol to cyclohexanone while palladium ones in the hydrogenation of cinnamaldehyde to idrocinnamaldehyde. Only few selected results obtained in the first reaction are reported in Table 1.

Table 1. Phenol hydrogenation: (phenol: 10 g; solvent: cyclohexane 50 ml; T: 160°C; P_{H_2}:50 atm)

Run Ru	Ru catalyst, synthesis solvent, (polymer used), mg Ru	D nm	Phenol Conv. (mol %)			Sel. to cyclo-hexanone (mol %)		
			30'	1 h	2 h	30'	1 h	2 h
1	Commercial Aldrich 5 % on γ-Al_2O_3, 2.14	-	4.3	7.0	11.7	79.1	76.9	72.2
2	0.5 % on γ-Al_2O_3,ethylen glycol, (PVP), 2.47	1.96	13.7	25.8	64.7	94.5	91.1	86.4
3	0.5 % on γ-Al_2O_3, ethylene glycol (without PVP) 2,52	2.00	26.8	38.1	81.5	95.0	92	86.7
4	0.5 % on γ-Al_2O_3,benzyl alcohol, (PVP), 2.28	2.12	-	19	35.2	-	95.3	92.8

The above results highlight the remarkable performances of our nanocatalysts prepared with our microwave method and show the high selectivity towards the formation of cyclohexanone in comparison with catalytic performances of the commercial system. Run Ru 3 is particularly promising because in this case the stabilizing polymer (poly-N-vinyl-2-pyrrolidone) used for the other nanocatalysts preparation, is absent and this aspect should affect its catalytic behaviour.

Significance

Our results are very important because they underline the possibility of preparing efficient nanocatalysts with a simple, cheap and reproducible microwave method in the perspective of the development of green and sustainable chemical process [4].

References

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