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Insight into the mechanism of base free furfural oxidation using Raman spectroscopy

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PURPOSE OF THE ABSTRACT

Introduction

Catalyst today plays the role of a technology lock. The demand for catalyst continues to rise especially in the green chemistry field. Furfural (Fur) is a natural product which is easily obtained by dehydration of xylose, a monosaccharide found in large quantities in the hemicellulose fraction of lignocellulosic biomass. It is considered as one of the most attractive platform molecules due to the possibility to upgrade it to numerous molecules with application as bio-fuels or as monomers for the polymer industry. Furoic acid (FA) is the first down-line oxidation derivative of furfural. Currently the industrial route involves the Cannizaro reaction of furfural in a base solution1. The addition of base is a serious drawback for the environmental sustainability of the process. This work focuses on the development of an efficient catalytic process to produce furoic acid from the selective oxidation of furfural liquid phase, without the use of basic. Besides, it highlights the mechanism of Fur to FA that is studied using Raman spectroscopy.

Experimental

Gold (Au) supported on Hydrotalcite (HT) material was used. Different molar ratios between MgO and Al2O3 were prepared in order to study the acidbase properties of the supports (Molar Ratio Mg :Al 4:1; 2:1; 1:1; 1:5). Two % wt of gold nanoparticles were deposited on the supports using the solid immobilization method2-3. All synthesized catalysts were characterized using different techniques: X-ray diffraction (XRD), Inductively coupled plasma (ICP-OES) and Brunauer-Emmett-Teller theory (BET). Catalysis were tested in a base free oxidation condition and by adding H2O2 to the reaction medium using (i) Batch Multi-Reactor that allows to set up 11 reactions in parallel (ii) Screening Pressure Reactor (SPR) that allows to conduct 24 tests in parallel under high pressure and temperature. The reaction mixtures were analyzed using High Performance Liquid Chromatography (HPLC). The mechanism of the reaction was studied using on a quasi in-situ Raman spectroscopy.

Results

ICP analysis confirmed that the Au content varies between 1.5 and 1.9 wt%. BET results showed that all materials have high specific surface of about 150 m2/g. In order to evaluate the mechanism, several Raman spectra were collected from different experimentation MR &SPR (performed in the same conditions) but different reaction time (Fig. 1). Fig. 2 shows two peaks displacement: 1st between 1100 -1190 cm-1 and 2nd between 1350-1450 cm-1. These two Raman shift zones correspond to the transformation of aldehyde to acid vibration. No other chemical intermediates appear in the experimental medium analyzed. As expected the leaching of Mg ions from the HT support was observed. The presence of in situ formed base originated from the Mg leaching strongly affected the catalytic activity. Indeed, higher rates could be observed for the reaction performed at higher pH. It is well known that H2O2 could attack randomly both, the furan ring and carbonyl group resulting in side reaction (such as degradation and Baeyer?Villiger reaction). In our case any products formed by the ring opening or ring oxidation reactions was not observed (maleic or succinic acids, furanone). It could be postulated that the dissolved Mg ions suppress the side reactions on furan ring. The first step in the mechanism will be the reaction between dissolved

Mg(OH)2 with hydrogen peroxide, to produce hydroperoxide (OOH-) species in aqueous solution. These OOH-species will extract hydrogen from aldehyde group. As formed intermediate diol will adsorb on gold surface and undergo a hydride elimination to form carboxylic acid. Gold nanoparticles permit to improve the selectivity to furoic acid while the dissolved Mg(OH)2 is responsible for the high rates2-4.

Conclusion

This study has shown that the green synthesis (without using NaOH) lead to a very performing catalyst. The Raman has permitted to highlights the mechanism of Fur to FA transformation.

FIGURES

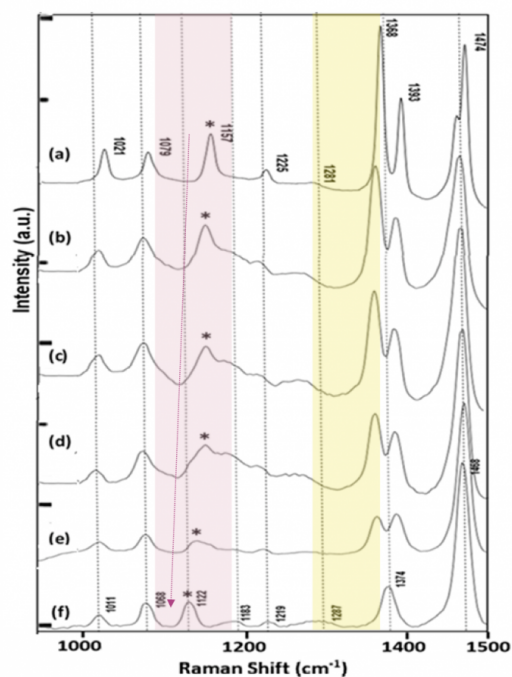| Time (min)	%conv	%selec.	%Yield	carbon balance
10 (b)	12%	37%	4%	93%
90	19%	48%	9%	90%
150	24%	67%	16%	92%
270 (c)	32%	79%	26%	93%
520	48%	80%	39%	90%
600 (d)	55%	83%	46%	91%
SPR (e)	95%	100%	100%	100%

FIGURE 1

Table of %conversion, %selectivity, %yield and carbon balance for the 6 reaction times. (b), (c), (d), (e) corresponds to spectra in figure 2

Catalyst 4:1 was split into 6 parallel reactors and SPR. Condition MR : H2O2/Fur =4; Fur/Au =100; T=90°C, P=1 bar; Condition SPR: H2O2/Fur =4; Fur/Au =100; T=110°C, P=15 bar;

FIGURE 2

Raman spectrum of reactional medium from MR and SPR

(a) correspond to 0% of conversion (t0) or Pure Fur, (b) to 12%Conv. (10min), (c) to 32%Conv. (270min), (d) to 55%Conv (600min), (e) to 95%Conv (reactional liquid of SPR test with HT- 4:1 and H2O2 as oxidant), (f) to 100% furoic acid.

KEYWORDS

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