

CELLULOSE AS A PRECURSOR OF CATALYST SUPPORT : NEW ASPECTS OF THERMOLYSIS AND OXIDATION – A DRIFT, XPS AND TGA STUDY

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Introduction

Catalysts supported on carbonaceous materials are very promising systems in which the adsorbent support provides a high concentration environment of pollutant around the catalyst [1]. Moreover, physico-chemical properties of the support seem to play a major role towards catalytic activity.

The optimization of some thermal treatment parameters allows us to obtain carbonaceous supports with various properties from microcrystalline cellulose [2]. After impregnation with a copper nitrate solution, the ability of the prepared supports towards catalytic oxidation of methanol was evaluated.

Experimental

Microcrystalline cellulose was carbonized at 450 °C and then oxidized under air at different temperatures (from 200 to 280 °C) in order to improve the hydrophilic character of the support. Weight evolutions were followed by thermogravimetric analysis (Setaram TGA 92). The evolution of functional groups was monitored by DRIFT spectroscopy (Bio-Rad FTS 185 spectrometer equipped with the Graseby Specac Selector accessory), and XPS (Riber Mac 2). Specific surface area measurements (BET method) were obtained on a Sorptomatic 1900 apparatus by adsorption of N₂ at 77 K.

Before catalytic tests, the impregnated samples were thermally treated at 400 °C during 2 hours under N₂ or H₂ in order to obtain several different copper oxidation states. In situ DRIFT spectroscopy allows us to investigate both the degradation of methanol on the support and the possible reaction pathways. Catalytic tests were performed by contacting the catalyst support with methanol vapor at 350 °C. DRIFT spectra of both the adsorbed species and the evolved gases were recorded at ambient temperature.

Results and discussion

I. Carbonization. Table 1 shows how the carbonization parameters influence the specific surface areas and the char yield. A pretreatment is found to be necessary in

order to enhance the porosity of the sample (492 m²/g when the pretreatment is carried out under air at 250 °C) even if the char yield is slightly decreased. During the isotherm at 250 °C, reticulation reactions have the time to take place and thus many oxygen bridges are formed between active cellulose chains. Then, when carbonization is carried out at 450 °C, some of these oxygenated structures leave the solid and porosity appears.

II. Oxidation. The oxidation of the cellulose chars in air allows to the creation of new functional groups with a maximal weight gain of 5 % after 30 min at 280 °C (table 2). DRIFTS and XPS analyses seem to show the progressive conversion of carboxyles into anhydrides (figure 1). The weight loss that occurs at the end of oxidation must be related to the consumption of carbon into gasification reactions. The comparison of the O/C ratio with infrared and ultimate analysis results establishes that the oxidation occurs into bulk layers of the powdered samples and not only at the surface (table 2 and figure 2).

III. Catalytic tests. Catalytic tests were performed either on the sample oxidized 30 min at 280 °C loaded at 1.8 % wt with copper (OxI) and the non-impregnated sample (OxNI). When adsorption of methanol is carried out at 30 °C, bands appear in IR spectrum at 2940, 2828, 1714 and 1025 cm⁻¹ for both samples. The band at 1031 cm⁻¹ can be assigned to the C-O stretch of methoxy species. After heating at 350 °C, the spectrum of the gaseous phase (figure 3) shows that the emission of CO₂, CO, H₂O and CH₄ resulting from the degradation of methanol seem more important for sample OxI than for OxNI. After evacuation with N₂, IR spectra indicate that chemisorbed species are mainly formaldehyde (916 and 1719 cm⁻¹). The band at 2100 cm⁻¹ for sample OxI can be attributed to CO chemisorbed on copper species.

Conclusions

It has been demonstrated that catalysts support can be easily obtained from microcrystalline cellulose. The environmental device seem to be a powerful means to study the degradation of methanol on our support and it can be also extended to other systems. Quantitative

aspects of catalytic tests will be investigated now by coupling our chamber with a gas chromatograph.

[1] T. Ibusuki, K. Takeuchi, Journal of molecular Catalysis 88 (1994) 93

[2] J. Zawadzi, Chemistry & Physics of Carbon 21, P.A. Throver, Marcel Dekker Inc., New York and Basel, 1988

References

Table 1: optimization of the charring process

experimental conditions	mi (mg)	char yield (%)	S _{BET} (m ² /g)
carbonization under N ₂ atmosphere in an open crucible	20	10.5	
carbonization in a sealed crucible	15.4	30.5	
carbonization in a sealed crucible	20	33	28
pretreatment at 250 °C during 3 hours in a sealed crucible + carbonization	20	30	320
pretreatment under air at 250 °C during 6 hours in an open crucible + carbonization under N ₂ atmosphere	20	20	492

Table 2: TGA, XPS and ultimate analysis results on the oxidized samples

sample	oxidation conditions	ultimate analysis			total weight evolution (%)	O/C ratio
		% C	% H	% O		
1	no oxidation	82.1	4.1	11.5	-1.4	0.34
2	200 °C 0 min				-0.32	0.42
3	250 °C 0 min				2.19	0.48
4	265 °C 0min				3.07	0.57
5	280 °C 0min				4.19	0.62
6	280 °C 40 min	70.7	2.6	26.2	5.14	0.8
7	280 °C 3 h				2.69	0.91
8	280 °C 6 h	65	2.2	32.6	0.93	1.04

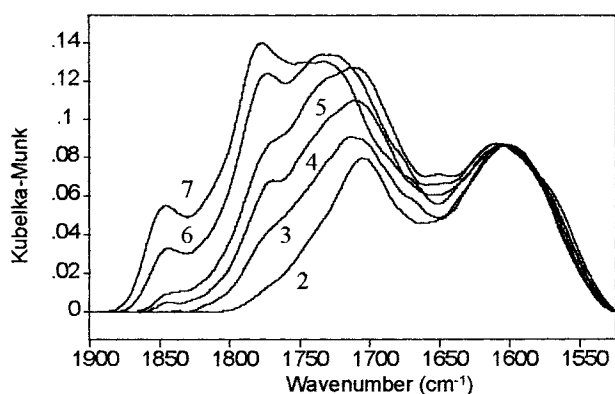


Figure 1 : Kubelka-Munk spectra of the oxidized samples for the 1520-1900 cm⁻¹ region. Numbers on the figure corresponds to those from table 2.

Figure 3 : DRIFT spectra after catalytic tests on OxI.

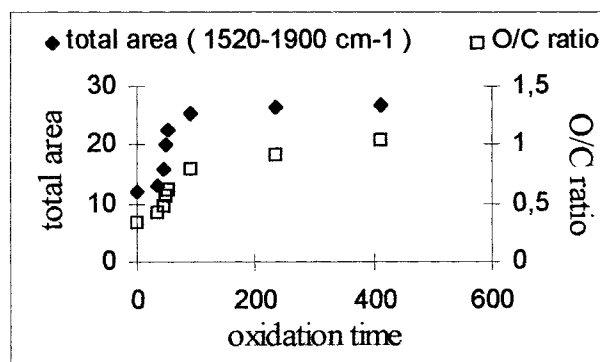


Figure 2 : Comparison between DRIFT and XPS results versus the oxidation time. The total area means the area of IR bands after curve-fitting between 1520 and 1900 cm⁻¹.

