OXIDISING   SUPPORTED   REAGENTS-II-INFLUENCE   OF   THE   CHEMICAL
AND TEXTURAL PROPERTIES OF THE $K_2Cr_2O_7$ SUPPORTED REAGENTS
ON THE OXIDATION OF MENTHOL.

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ABSTRACT – We have analyzed the influence of the chemical and
textural properties of the solid supports as well as the
oxidising $K_2Cr_2O_7$supported reagent on the oxidation of menthol
to menthone –as a reaction test– . The most active $K_2Cr_2O_7$
supported reagents are obtained with amorphous solid supports
with large surface areas or with microcrystalline solids, with
great amounts of oxidising sites titrated by phenothiazine.

Oxidising supported reagents are used more and more in organic synthesis
due to the high selectivities obtained[1-4].These reagents are easily obtained,
permit simple synthetic procedures and avoid the problems produced by the
limited solubility of pure oxidants in organic media. Therefore a lot of
research is being done in this area although it is not focused is not on the
analysis of the relationship between the, textural properties of the supported
reagents and their oxidising activity.

Recently we have reported that physisorbed $KMnO_4$ on a solid is the active
species in $KMnO_4$ supported reagent[5]. On the other hand, no basic or redusing
sites can be present in the solid because these sites react with $KMnO_4$ giving
MnO_2 (unreactive form)[5]. In the present paper we analyze the influence of the
chemical and textural properties of $K_2Cr_2O_7$ supported on several solids, in the
oxidation of menthol, 1 , to menthone, 2.
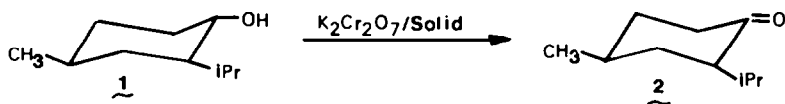
The supported reagents were obtained by impregnation of several
acidic/solids with aqueous $K_2Cr_2O_7/H_2SO_4$ solution. The solids were silica (S)
pure $AlPO_4$–F and BPO_4–B and three $AlPO_4$– BPO_4 mixture solids; P1413(P/(Al+B) –
1.4; B/Al – 3); P1431(P/(Al+B) – 1.4; B/Al – 3/1) and P1031 (P/(Al+B) – 1; B/Al
– 3/1. The $K_2Cr_2O_7$ /solid ratios were: series Cr25 (w/w – 1/25) and Series Cr100
(w/w – 1/100).

RESULTS AND DISCUSSION.

1.– Chemical and textural properties of supports and supported reagents.

In order to relate the structure of supported oxidising reagents with their
oxidising activity, a general survey was carried out to verify the textural
properties of the pure support and of the $K_2Cr_2O_7$ supported reagents (Surface
area – Sarea (m^2/g); pore average diameter – dp (Å) and accumulated pore volumen

ΣVp (mL/g)). Furthermore, the number of active sites in the supports and oxidising reagents was measured by a method described previously[6]. Pyridine Py (pka - 5.3); phenotiazine; PNTZ (I.P 7.13 eV); benzoic acid, BA (pKa -4.2) and 1,3-dinitrobenzene, DNB (E.A -2.21 eV) were used to titrate the acid, oxidising, basic and reducing sites, respectively. The results obtained are shown in Table

Table 1

Chemical and textural properties of solid supports and $K_2Cr_2O_7$ supported reagents.

SUPPORT	OXIDANT RAGENT	Sarea (m^2/g)	dp (Å)	ΣVp (mL/g)	acids v.s.Py	oxidising v.s.PNTZ	basic v.s.BA	reducing v.s.DNB
					active sites ($\mu mol/g$ solid)[a]			
S	___	395	32	0.55	290	44.3	66.5	7.5
F	___	109	82	0.45	115	1.0	91	1.9
F-72	___	280	35	0.46	290	65.8	72.7	7.5
B	___	11	810	0.47	300	0.4	0.5	0.5
P1413	___	23	2605	1.50	23	0.08	2.2	1.4
P1431	___	12	1723	0.53	19	0.35	1.5	__e
P1031	___	11	6067	0.69	13	0.38	3.2	__e
	SCr25	254	__d	__d	265	86	13	5.6
	FCr25	23	__d	__d	128	28	26	0.7
	BCr25	__b	__c	__c	485	18	0.6	__e
	F-72Cr25	165	__d	__d	310	43	28	1.2
	P1413Cr25	__b	__c	__c	158	12	3.9	__e
	P1413Cr100	__b	__c	__c	290	19	7.2	0.7
	P1431Cr100	__b	__c	__c	576	7	0.6	0.3
	P1031Cr100	__b	__c	__c	530	2	0.8	__e

[a]Experimental error±10%
[b]Lower than 4 m^2/g (experimental limit of the B.E.T method).
[c]Not accessible due to the low surface area value of the solid.
[d]Not determined.
[e]No adsorption was detecte.

The amorphous solids S,F, and F-72, have greater surface area values than the microcrystalline solids B, P1413, P1431 and P1031, as was predictable. Therefore, these latter solids have a greater average pore diameter (dp) than amorphous solids do and are more recommendable than amorphous ones for use in solid-liquid conditions where the organic molecules are solvated by solvents. Therefore the diffusional restrictions are not observed.

Support B has a higher number of acid and oxidizing sites than pure $AlPO_4$; P1413; P1431 and P1031 (mixture $AlPO_4$- and BPO_4) have intermediate values.

When $K_2Cr_2O_7$ is deposited on these solids, the surface area diminishes versus the area of pure supports e.g; S v.s SCr25; F vs FCr25 etc. In the case of microcrystalline supports (B, P1413, P1431 and P1031), this fact produces a strong diminution in surface area ($<4m^2$ /g) and cannot be determined by the B.E.T. method. The decrease in surface area is explained by the deposition of large $K_2Cr_2O_7$ microcrystals on the solid surface which are detected by X-ray diffraction.

On the other hand, when the supported reagent is washed with water the $K_2Cr_2O_7$ (yellow) is removed from the surface. The white solid has no Cr, although all Cr(VI) is in the solution according to the atomic absorption experiments.

This bahaviour is different than that observed in $KMnO_4$ supported on the same solids. In this case, the basic-reducing sites of the solid react with Mn(VII) to give non active[5] Mn(IV).

The addition of $K_2Cr_2O_7$ and H_2SO_4 to the supports to produce the supported reagents increases the number of acid and oxidising sites as could be expected. As the amount of $K_2Cr_2O_7$ supported on the same amount of solid increases, the

number of acid and oxidising sites goes down (P1413Cr25)($K_2Cr_2O_7$/solid = 1/25) versus P1413Cr100 ($K_2Cr_2O_7$/solids =1/100)). This is related to the increase in the amount of $K_2Cr_2O_7$ which hinders crystal defects and, so, the formation of active sites.

The oxidising sites of the supported reagents might be related to very positive chromium ions on the edges of crystals, as in the case of the supported metal catalyst where cell lattice defects are responsible for the active catalyst sites[8,9].

The acid sites might be related to the physisorbed H_2SO_4.

2- Oxidation of menthol.

The optimation of the oxidation process was carried out using the supported reagents on the new solids -P1413, P1431 and P1031.- with a $K_2Cr_2O_7$/solid ratio = 1/100 (w/w).

The influence of the reaction time is shown in Figure 1 where we can observe that the yield is constant for reaction times over 45 min.

The P1413Cr100 reagent that has the greatest number of oxidising sites (Table 1) is the most active oxidising reagent. Therefore the oxidising activity is related to the number of oxidising sites in the supported reagent.

P1413Cr100 > P1431Cr100 > P1031Cr100

Oxidising activity

The solid/$K_2Cr_2O_7$ (w/w) ratio is not important whenever the molar ratio, $K_2Cr_2O_7$/menthol is 1/3, according to the re-dox process (Figure 2).

$$3CH_3 \text{—} \overbrace{}^{} \text{—OH} + K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow 3CH_3 \text{—} \overbrace{}^{} =O + Cr_2(SO_4)_3 + 7H_2O + K_2SO_4$$
(iPr)   (iPr)

Diffusional problems related to the amount of solvent are shown in Figure 3 The optimum yield is reached at 10 mL of solvent equivalent to a solvent/solids ratio = 3.33 (w/w).

From the red-ox equation we can observe that the H_2SO_4/$K_2Cr_2O_7$ molar ratio is 4. In order to learn if the acid sites of the solid support can give protons to carry out the process, several reactions were carried out at H_2SO_4 /$K_2Cr_2O_7$ <4 (Figure 4). We can observe that the acid sites of the solid do not seem to be active because the presence of H_2SO_4 is necessary to carry out the process. (The reaction does not take place without H_2SO_4 (Figure 4)). This can only be explained by assuming that $K_2Cr_2O_7$ is deposited as large crystals - detected by an X-ray diffraction power diagram - covering the solid surface. Then the H_2SO_4 is physisorbed on these crystals when the solvent evaporates during the preparation of the supported reagent giving the acid sites of the $K_2Cr_2O_7$ supported reagent. Therefore, the solid support acid sites are not accessible to the reagents. Nevertheless, the solid support active sites of the seem to control the deposition of $K_2Cr_2O_7$ on the solid by geometric and electrical factors as can be deduced from Figure 1. In this figure, we can observe that the more acidic the solid support, the more active the $K_2Cr_2O_7$ supported reagent (molar ratios $K_2Cr_2O_7$/ menthol = 1/3 and H_2SO_4/$K_2Cr_2O_7$ = 4). Therefore, a more detailed study of the interaction between $K_2Cr_2O_7$ microcrystals and solids must be carried out by inorganic chemists specialized in solid state chemistry in order to explain these experimental data.
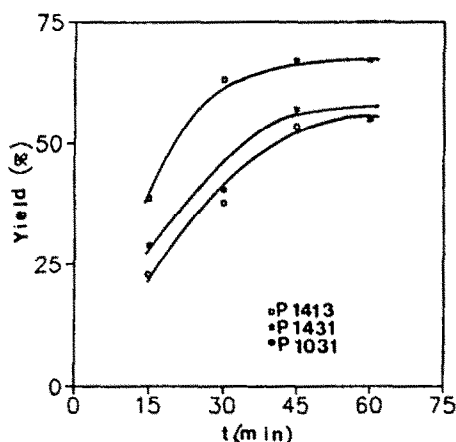
Figure 1

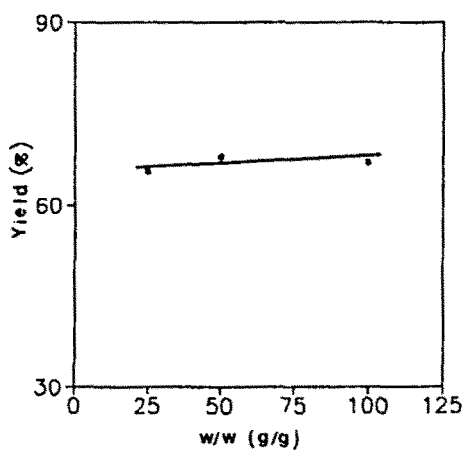

Figure 2
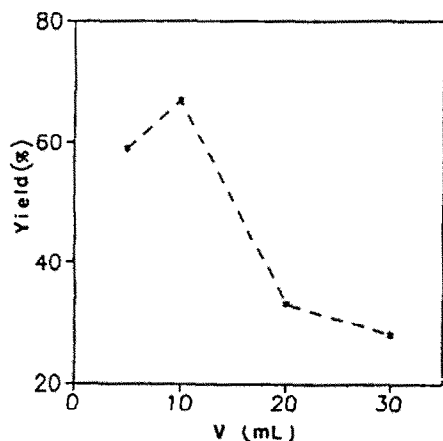

Figure 3.
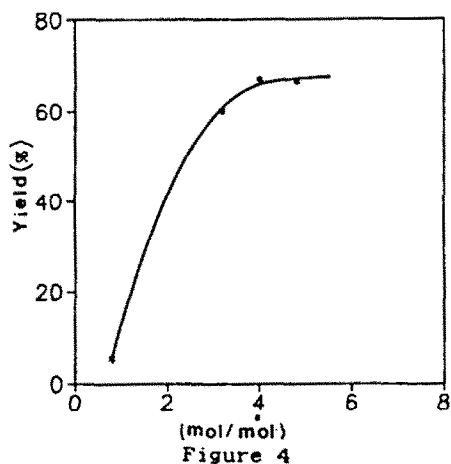

Figure 4

Figure 1.–Influence of the reaction times in the oxidation to menthone. 2.95 10^4 moles of menthol;10mL diethyl ether; 3g supported reagent;T = room temperature; menthol/$K_2Cr_2O_7$= 3; H_2SO_4/$K_2Cr_2O_7$= 4(mole/mole);supports P1413, P1431 and P1031.

Figure 2.–Influence of ratio solid support/$K_2Cr_2O_7$(w/w) on the oxidation of menthol diethyl ether; 2.95 10^{-4} ; 3g supported reagent; reaction times = 45 min;T = room temperature; menthol/$K_2Cr_2O_7$= 3; H_2SO_4/$K_2Cr_2O_7$ = 4 (mole/mole). support P1413.

Figure 3.– Influence of the amount of solvent on the yield: 3g of supported reagents; 2.95 10^{-4} moles of menthol reaction times = 45 min;T = room temperature; menthol/$K_2Cr_2O_7$= 3; H_2SO_4 /$K_2Cr_2O_7$ = 4 (mole/mole); support P1413.

Figure 4.– Influence of the molar ratio H_2SO_4 / $K_2Cr_2O_7$on the oxidation of menthol to menthone. 1.17 10^{-3} moles of menthol;reaction times =45'; 10mL diethyl ether; 3g supported reagent; T = room temperature; menthol/$K_2Cr_2O_7$ = 3; support P14133.

3.- Influence of the structure of solid support on the oxidation process.

Several solids were tested to learn more about the influence of the structure of solid supports on the process. Amorphous silica(S), $AlPO_4$ (F) and mixture $AlPO_4-SiO_2$ (F-72) were chosen to analyze the influence of the amorphous structure versus the microcrystalline structure of the $AlPO_4-BPO_4$ solids on the reaction process. On the other hand, pure BPO_4(B) and $AlPO_4$(F) were tested to analyze the influence of the chemical structure on the oxidant activity. The results obtained using the constant molar ratio $K_2Cr_2O_7$/solid = 25 are shown in Table 2.

Table 2
Influence of the support structure in the oxidation of menthol.
$1.17 \cdot 10^{-3}$ moles of menthol; 3g of supported reagent; 10mL of diethylether
T = room temperature;Reaction time = 45 min.

Supported reagent	Yield (%) molar) in menthone
SCr25	96
FCr25	19
F-72Cr25	37
BCr25	95
P1413Cr25	67

According to the chemical composition and the structure of solids we have two kinds of solids:

$$SCr25 \quad > \quad F-72Cr25 \quad > \quad FCr25$$
$$(SiO_2) \qquad \left(\begin{array}{c} AlPO_4 20\% \\ SiO_2 80\% \end{array}\right) \qquad (AlPO_4)$$
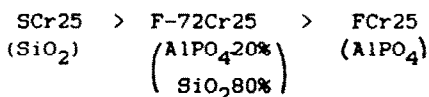
$\longleftarrow$
yield in menthone

In these amorphous solids, the surface area (see Table 1) seems to be the most important factors explaining the oxidant activity of the suppoted reagent. The other group is:

$$BCr25 \quad > \quad P1413Cr25 \quad > \quad FCr25$$
$$(BPO_4) \qquad (BPO_4-AlPO_4) \qquad (AlPO_4)$$
microcrystalline   microcrystalline   amorphous
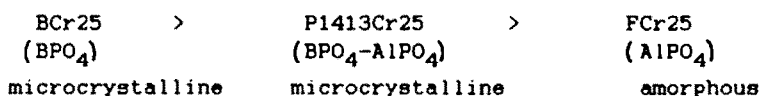
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yield in menthone.

We can observe that the microcrystalline solid yields better conversions than the amorphous one. Therefore the solid surface does not seem to be determinant because the surface area of FCr25 is greater than that of the other solids. In the microcrystalline solids Br25 and P1413Cr25, the number of oxidant sites seems to be the determining factor in oxidising activity.

Therefore we can say that if amorphous solids are used, a large surface area is needed to obtain active oxidant reagents. Nevertheless, if microcrystalline solids with a small surface area are used, a greater number of oxidising sites results in a more active oxidising supported reagent obtained.

EXPERIMENTAL

Solid supports

The solid supports were: silica (Kiselgel 60 MercK(70-230 mesh)) S; BPO_4 (B)[10];SiO_2-AlPO_4 (F-72)[11]; $AlPO_4$ (F)[12] obtained according to the methods described previously.
The other supports were obtained mixing $AlCl_3.6H_2O$, H_3BO_3 and H_3PO_4 (Probus S.A) to the ratios

P1413 (P/(Al+B) =1.4; B/Al = 1/3)
P1431 (P/(Al+B) =1.4; B/Al = 3/1)
P1031 (P/(Al+B) =1.0; B/Al = 3/1)

The mixture was heated at 90°C for 1h and calcinated at 300°C for 3h. The white powder was sifted to a particle size of 70-230 mesh.

Oxidising reagents.

The $K_2Cr_2O_7$ supported reagents were obtained by mixing the solids with aqueous solutions of $K_2Cr_2O_7$ and H_2SO_4, followed by evaporation at vacumm in a rotatory evaporator. A yellowish powder is obtained.

Two oxidant/solid support ratios were obtained

$$K_2Cr_2O_7 \text{ /solid} = 1/25 \qquad = Cr25 \text{ Serie}$$
$$\text{"} \qquad = 1/100 \qquad = Cr100 \text{ Serie}$$

Textural and chemical properties.

The surface area (S area); pore average diameter (dp) and pore volume (ΣVp) of the solids and supported reagents were determined by the B.E.T. method[13]

The nature and number of active sites were determined by the spectrometric method described previously[6,14]. Pyridine, Py (pKa = 5.3); phenothiazine, PNTZ (I.P = 7.13 e.V); benzoic acid, BA (pKa = 4.2) and 1,3-dinitrobencene, DNB (E.A. = 2.21 eV) were used to titrate the acid, oxidant, basic and reducing sites, respectively.

Oxidations of menthol.

The oxidation of menthol was carried out mixing 10 mL diethylether; $1.17.10^3$ moles of menthol and 3g. of $K_2Cr_2O_7$ supported reagent. The mixture was stirre during the reaction time at room temperature.

Then the mixture was filtered. The solid was washed with 3_x5 mL of diethylether and analyzed by G.C. using a 2 m 18" column of 0.65% EGA on (80/100) chromosorb w.aW. Carrier gas flow (N_2) = 30mL/min; initial Temperature = 20°C, end temperature = 150°C.

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