Tetrahedron Vol. 43, No. 14, pp. 3303 to 3308, 1987
Printed in Great Britain.

0040-4020/87 $3.00+.00
Pergamon Journals Ltd.

INFLUENCE OF THE CHEMICAL AND TEXTURAL PROPERTIES OF $K_2Cr_2O_7$ SUPPORTED ON SOLIDS, IN THE OXIDATION OF CHOLESTEROL

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(*Received in UK* 15 *May* 1987)

Abastract. Several $K_2Cr_2O_7$ supported reagents on inert solids have been obtained by deposition of $K_2Cr_2O_7$ on different solids. $AlPO_4$, BPO_4 and solid mixtures BPO_4 -$AlPO_4$ are used as supports. The $K_2Cr_2O_7$ is deposited on solid as large crystals detected by an X-ray diagram in the Cr50 and Cr25 series giving solids with very low surface areas. The number of acid and oxidizing sites is dtermined. Solids supports with small surface areas and large pore diameter give $K_2Cr_2O_7$ supported reagents with higher activity than those obtained from solids with high surface areas and large pores.

Selective oxidation is one of the most important transformations. Many oxidants, however, remain too vigorous for such application. On the other hand, oxidant reagents are generally ionic compounds. therefore, they are insoluble in the organic media where organic compounds are soluble. Thus, the obtained yields are very poor in some cases.

Recently, the supported oxidants on solid matrix have been used to improve the selectivity and the yield in the oxidation process[1-3]. These works are focused on the synthetic aspects and meant to study the relatioship between the chemical and textural properties of solids and their oxidant activity. Nevertheless, solids control the process by the geometric, steric and electronic factors related to their active sites as has been proved with the $AlPO_4$ acid catalyst[4], with microcrystalline basic catalysts as activated $BA(OH)_2$[5,6] and with the $KMnO_4$ supported on solids[7]

In the present paper we discuss the influence of the chemical and textural properties of oxidant supported reagents in the oxidation of sterols.

The tested $K_2Cr_2O_7$ supported reagents were obtained by impregnation with aqueous $K_2Cr_2O_7$ solution of several acid solids (see Experimental). These solids were: pure $AlPO_4$-F and BPO_4-B and three $AlPO_4$ -BPO_4 solids: P14133 (P/(Al+B)=1.4; B/Al=1/3); P14313 (P/(Al+B)=1.4; B/Al=3/1); P10313 (P/(Al+B)=1; B/Al=3/1). The $K_2Cr_2O_7$ supported reagents were obtained at three different $K_2Cr_2O_7$/support ratios (w/w): 1/25 Cr25; 1/50 Cr50; 1/100 Cr100 series.

RESULTS AND DISCUSSION

1.-Chemical and textural properties of $K_2Cr_2O_7$ supported reagents

In order to relate the chemical and textural properties of $K_2Cr_2O_7$ supported reagents with their oxidizing activity, a general study of the textural properties (surface area=Sarea(m^2/g); pore diameter=dp(A); pore volume=ΣVp(mL/g)) and amount of acid oxidizing sites was carried out. The results obtained are shown in Table 1.

Table 1

Chemical and textural properties of $K_2Cr_2O_7$ supported reagents

Support	Oxidant reagent	Sarea (m^2/g)	dp(A)	ΣVp (mL/g)	acid sites v.s. Py(μmol/g.catg)[a]	oxidizing sites v.s PHTZ(μmol/g.cat)[a]
$AlPO_4$-F	-	109	82	0.45	115	1.0
BPO_4-B	-	11	810	0.47	300	0.4
P14133	-	23	2605	1.5	23	0.08
P14313	-	12	1723	0.53	19	0.35
P10313	-	11	6067	0.69	13	0.38
	FCr50	< 4[b]	-	-	65	14.1
	BCr50	< 4[b]	-	-	425	14.6
	P14133Cr25	< 4[b]	-	-	158	12.0
	P14133Cr50	< 4[b]	-	-	44	21.0
	P14133Cr100	< 4[b]	-	-	290	19.0
	P14313Cr50	< 4[b]	-	-	251	4.0
	P10313Cr50	< 4[b]	-	-	194	6.6

[a] Experimental error 10%

[b] The surface area values were lower than the lowest limit of the experimental method ($4m^2/g$). dp and ΣVp were no accessible due to the low surface area value of the solids.

If we analyze the solid supports, we can say that $AlPO_4$-F has the greatest surface area and smallest pore diameter. Boron orthophosphate, BPO_4-B and the other solids-mixtures of $AlPO_4$ and BPO_4-have similar surface area values. this is explained by the diminishing of the surface area of the solids due to the presence of BPO_4[8,9].

On the other hand, BPO_4 has higher number of acid and oxidizing sites as compared to $AlPO_4$-F. These magnitudes in the other solids show values lower than BPO_4, though higher than $AlPO_4$. P14313 and P10313 manifest higher densities of acid and reducing sites than P14133 which has an excess of Al and, therefore, of $AlPO_4$. This agress with the presence of an excess of BPO_4 versus $AlPO_4$ in these solids.

The nature of the acid sites of these solids has been related to superficial P-OH and the electron-acceptor sites to Al or B with defects in their coordination spheres[10,11].

The average pore diameter is large in all cases. therefore no diffusional problems could be observed with these solids. Nevertheless we must say the the solids $AlPO_4$-BPO_4 have very large pores. This is explained by the microcrystalline structure of these solids[12]. The X-ray analysis shows that they are a mixture of crystalline $AlPO_4$ and BPO_4.

When $K_2Cr_2O_7$ is deposited on these solids, supported reagents are obtained. FCr50 and BCr50 are $AlPO_4$-F and BPO_4-B with a ratio $K_2Cr_2O_7$/solid =1/50(w/w). The other solids are given the name of "solid support" and the ratio $K_2Cr_2O_7$/solid (1/25 series Cr25; 1/50 series cr50 and 1/100 series Cr100).

In all cases, the surface area of supported reagents were undetermined due to the fact tha the surface areas were lower thyan $4m^2/g$) (the lowest limit of BET method). Therefore we can say that the $K_2Cr_2O_7$ is on the solid in macrocrystalline form. These macrocrystalsover the pores of the solid and so, the surface area diminishes. It is well known that crystalline solids have a very low surface area. The presence of $K_2Cr_2O_7$ crystals on the solid surface was determined by X-ray diffraction diagrams in the Cr50 and cr25 series (These crystals are larger than the upper limit of X-ray analysis, 40A)[12]. On the other hand, all the chromium is Cr(VI) as has been proved by classical atomic adsorption experiments. This behaviour is

different than that observed in $KMnO_4$ supported on the same solids where an amount of Mn(VII) is transformed into Mn(IV) by a reaction with the reducing sites of the solids[7].

The addition of $K_2Cr_2O_7$ and H_2SO_4 to the solids produces the supported reagents. This increases the amount of acid and oxidizing sites versus the support (see Table 1).

As in the case of supports, BCr50 is the most acidic supported reagent. When the amount of B in the support is higher than the Al, the supported reagent (P14313Cr50 and P10313Cr50) are more acidic than P14133Cr50.

The amount of Cr(VI) does not influence the number and amount of acid sites. This can be explained by assuming that the $K_2Cr_2O_7$ is deposited on solids in large crystals where the cell lattice defects (related to the active sites titrated by the method described in the experimental part) are small.

The active sites of the supported reagents are related to very positive chromium ions on the edges of crystals, as in the case of supported metal catalysts where the cell lattice defects are the responsibles of the active stes of these catalysts.[13,14]

The acid sites must be H^+ from H_2SO_4 or non crystalline $H_2Cr\ O_4$ present on the surface (this species would not be detected by X-ray analysis).

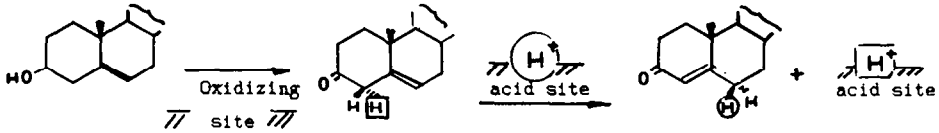
The X-ray analysis of solids gave $K_2Cr_2O_7$ crystalline on series Cr50 and Cr25 but not in the series Cr100. Therefore we can say tha the K Cr O_7 crystals in the former supported reagents are larger than 40A. In the case of the Series Cr100, the $K_2Cr_2O_7$ crystals could not be present or are lower than 40A. The $K_2Cr_2O_7$ has been detected by atomic absorption as the only Cr(VI) specie present in Cr100 Serie.

2.-Oxidizing activity

The oxidizing activity of the $K_2Cr_2O_7$ supported reagents was tested in the oxidation of cholesterol Δ^2-cholesten-3-one. This red-ox equation for the oxidation of an alcohol is:

$$8H^+ + Cr_2O_7^{=} + 3\ R_2CH\text{-}OH \rightarrow 2Cr(III) + 3\ R_2C{=}O + 7\ H_2O \quad [1]$$

The isomerization of $C_5 = C_6$ to $C_4 = C_5$ is favoured tehrmodinamically. It could be related to the acid sites of solids by a proton shift. So the rate cotrolling step will be the oxidation proces.



The results obtained are shown in Table 2. The yields were not optimized in order to determine the influence of the structure of the $K_2Cr_2O_7$ reagent in the yield. Therefore the results in Table 2 are lower than those described by Jone's or Collin's reagents.

From aquation [1] we can say that one mol of $K_2Cr_2O_7$ can transform three mols of alcohol. So, this molar ratio was used in all cases. From the results in Table 2 (entries 1-4) we can say that similar yields are obtained at reaction times over 45min. (±5% error).

The $AlPO_4/BPO_4$ ratio of the new inert solid of the $K_2Cr_2O_7$ supported reagent does not determine the oxidizing efficiency of the supported reagent because similar yields are obtained in the case of P14133Cr50, P14313Cr50 and P10313Cr50 (entries 5,7 and 8. Table). this is in accord with the presence of large $K_2Cr_2O_7$ crystals over the solid surface, in the

reagent. In this case, the support-$K_2Cr_2O_7$ crystal interaction is very poor which is well known in metal supported catalysts.[13,14]

Table 2

Oxidation of cholesterol to cholestenone. 1g. of $K_2Cr_2O_7$ supported reagent.
3.5mL of diethyl ether; reaction time 45min; room temperature

Entry	Supported reagent	amount of $K_2Cr_2O_7$ (mols)	t(min)	Yield (%molar in cholestenone)[a]
1	P14133Cr25	1.36 10	15	10
2	"	"	30	81
3	"	"	45	89
4	"	"	60	95
5	P14133Cr50	0.68 10	45	85
6	P14133Cr100	0.34 10	45	6
7	P14313Cr50	0.68 10	45	71
8	P10313Cr50	0.68 10	45	83
9	FCr50	0.68 10	45	20
10	BCr50[b]	0.68 10	45	58

[a] molar ratio cholesterol/$K_2Cr_2O_7$=3/1 in all cases

[b] unstable reagent

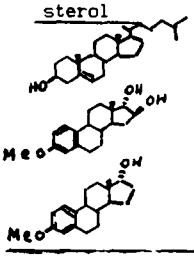
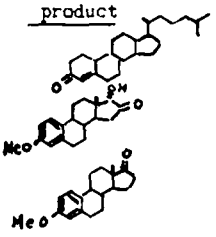
The amount of Cr(VI) affects the activity of IR supported reagent

P14133Cr25	89%
P14133Cr50	85%
P14133Cr100	6%

This is well explained by the crystal size of $K_2Cr_2O_7$. There are very large crystals in the Cr25 and Cr50 Series causing an absence of cell lattice defects and poor reactivity. In the case of Cr100, there are very small $K_2Cr_2O_7$ crystals and a great amount of acid sites (see Table 1). . This solid is more acid than oxidizing one. Therefore, poor yields are obtained such as we have observed.

Table 3

Influence of the nature of sterol on the yield.
2.04 10 mols of sterol; 3.5mL of ethylic ether; 1g of P14133Cr50; react. time=45min.;
room Temperature

sterol	product	yield (%molar)
		85
		51
		54

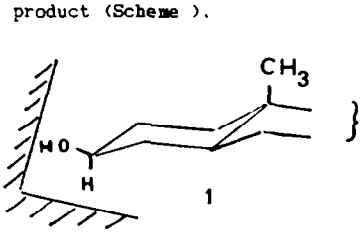
The supported reagents obtained from solids with small surface areas-B; P14133; P14313 and P10313- are better than the obtained from $AlPO_4$ -F with high surface areas.

This could be explained by analyzing the oxidation process. When the oxidation of cholesterol progresses, the large crystals of $K_2Cr_2O_7$ are slowly destroyed. Nevertheless, the $K_2Cr_2O_7$ deposited into th medium and small pores of $AlPO_4$-F will not be accessible for the large molecules of cholesterol. Therefore the reaction stops and the obtained yields are

lower than those obtained with supported reagents obtained from solid supports with large pores where all the Cr(VI) is accessible to cholesterol.

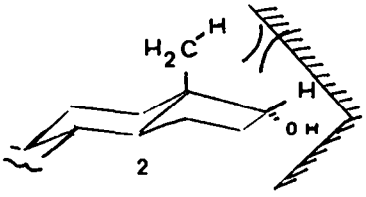
On the other hand we can say that our $K_2Cr_2O_7$ supported reagents are more regioselective versus the A-ring than versus the D-ring as can be observed in Table 3.

This can be explained by the nature of the adsorbed species that lead to the reaction product (Scheme).



1

less hindered



2

more hindered

The methyl group does not favour the adsorption of H_{17} and OH_{17} on the solid, 2, and, so, the reactions take place slowly in these cases. Therefore the yields obtained with striol and stradiol derivatives are lower than those obtained with cholesterol.

3.-Oxidation mechanism

The presence of active Cr(VI) and H^+ (oxidizing and acid sites) on the surface and the presence of Cr(III) at the end of the reaction let us propose an oxidative mechanism equal to that described in the literature for the oxidation of alcohols by Cr(VI). The process begins in two neighbouring acid and oxidizing sites.

$$R_2CHOH + \underset{\text{oxidizing site}}{\overset{}{/\!/}\,HCrO_4^-\,/\!/} + \underset{\text{acid site}}{\overset{}{/\!/}\,H^+\,/\!/} \longrightarrow \underset{\text{adsorbed}}{R_2CH\text{-}O\text{-}CrO_3H} + H_2O$$

$$R_2C{=}O + \underset{Cr(VI)}{HCrO_3^-} + \underset{\text{acid site}}{H^+}$$

slow

The unstable Cr(IV) can be transformed into Cr(III) by oxidation of the other alcohol molecule by a radical mechanism[15,16].

This reaction produces the alteration of the $K_2Cr_2O_7$ crystal giving new oxidizing and acid sites in the cell lattice defects. So the crystal is slowly consumed. If the solid support has large pores, all tyhe Cr(VI) will be accessible and nearly 100% yield will be obtained. If the solid is micro or mesoporous a part of Cr(VI) remains within the pores that are not accessible to the cholesterol molecule and no quantitative yields will be obtained.

EXPERIMENTAL

Solid supports

The solid support $AlPO_4$-F was obtained by the reaction of $AlCl_3.6H_2O$ and H_3PO_4 and gelified by the addition of NH_4OH according to a method described previously[17].

The BPO -B was obtained by heating a mixture of H_3BO_3 and H_3PO_4 at 90ºC for 3h.[18]

The other supports were obtained mixing $AlCL_3.6H_2O$, H_3BO_3 and H_3PO_4 according to the ratios:

P14133 (P/(Al+B)=1.4; B/Al=1/3)
P14313 (P/(Al+B)=1.4; B/Al=3/1)
P10313 (P/(Al+B)=1.0; B/Al=3/1)

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

Oxidizing sites

The $K_2Cr_2O_7$ supported reagents were obtained by mixing the solid with a solution of $K_2Cr_2O_7$ and H_2SO_4, followed by evaporation at vacuum in a rotatory evaporator. Then a yellowish powder is obtained.

Three oxidant/solid support ratios were obtained:

$K_2Cr_2O_7$/solid support=1/25 Cr25 Serie
" =1/50 Cr50 Serie
" =1/100 Cr100 Serie

Textural and chemical properties

The surface area (S area), pore diameter(dp) and pore volume (VVp) of the solids were determined by the B.E.T. method[19]

The nature and amount of active sites were determined by a spectrophotometric method described previously[20,21]. Pyridine (Py), pKa=5.3 and phenothiazine (PHTZ), I.P.=7.13 e.V. were used to titrate the acid and oxidizing sites of solids.

Oxidation of sterols

The oxidation of cholesterol was carried out mixing 3.5mL of diethylic ether ; 1g. of $K_2Cr_2O_7$ supported reagent and an amount of cholesterol three times greater than the added moles of $K_2Cr_2O_7$. The mixture was stirred for 45min. at room temperature. Then the reaction products were extracted with 2x3mL of 1,4-dioxane and analyzed by HPLC. All the products were Ega-Chemie.

A HPLC Perkin-Elmer serie 2 was used. UV-visible detector (λ=230nm). Eluent MeOH/Cl_2CH_2/H_2O (96/2/2; v/v/v). F=1.0mL/min. Anthracene was used as the internal standard.

The oxidation of stradiol-3-methyl-ether and estriol-3-methyl-ether were carried out in the same way.

Acknowledgments

WE thank the Comision asesora de Investigación Cientifica y Tecnica (CAICYT) from Spain, for a grant.

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