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The catalysis of the Ruff oxidative degradation of aldonic acids by titanium-containing zeolites

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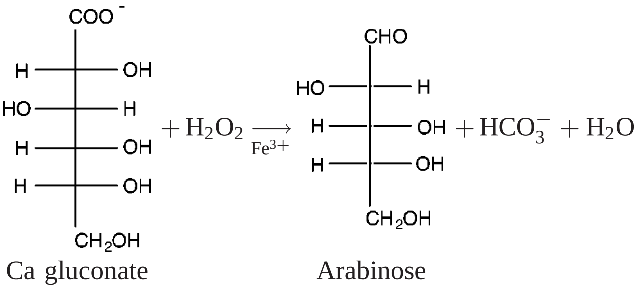
Ti-BEA and Ti-FAU, obtained by post-synthesis treatment, and TS-1, obtained by direct hydrothermal synthesis, have been tested as catalysts for the Ruff oxidative degradation of calcium D-gluconate to D-arabinose using diluted hydrogen peroxide as oxidant. Only large-pore zeolites Ti-BEA and Ti-FAU were found to be active. It was shown, in particular, that a very rapid leaching of titanium occurred and that the titanium species present in the solution were responsible for the catalytic activity observed.

Keywords: Ruff degradation, carbohydrates, oxidative degradation, hydrogen peroxide, microporous titanium-containing molecular sieves

1. Introduction

Although there is an increasing demand for pharmaceutical and industrial applications, sugar alcohols, generally referred to as polyols, are mainly used in food industry as reduced calorie, non-cariogenic sweeteners and sugar substitutes in a number of food products [1–3]. Among others, polyols produced on an industrial scale [4], may contain six (sorbitol, mannitol), five (xylitol) or four carbon atoms (erythritol).

In order to produce pentoses from hexoses, in particular from a readily accessible and cheap material such as glucose, the Ruff oxidative degradation reaction, known since 1898, seemed to be particularly appropriate [5]. Starting from a salt of an aldonic acid, this reaction leads to an aldose with loss of one carbon atom. The original process used aqueous hydrogen peroxide as oxidant, in the presence of catalytic amounts of ferric salts. Such a method has received some improvements, particularly in connection with the preparation of D-arabinose from D-gluconate [6–10].



Scheme 1. Reaction scheme for the Ruff's oxidative degradation of calcium D-gluconate.

The catalyst is always a soluble transition metal salt, but copper(II) proved to be more effective than iron(III) [9]. However, in spite of the well-known complexant character of the D-gluconate anion for multivalent cations, it was an interesting challenge to investigate this reaction in the presence of heterogeneous catalysts with respect to the possible technical, economical and environmental advantages due to the utilization of such solid catalysts.

Regarding the mechanism of the reaction, the site of attack of the oxidant agent on the aldonic acid (abstraction of an alcoholic hydrogen or abstraction of hydrogen on the α- or β-carbon) has been the subject of discussions [11–13]. In particular, the formation of an hydroxyl radical and its effective role as active intermediate have never been disputed. So, the Ruff reaction showed some similarities with the Fenton system. Taking into account the efficiency of microporous titanosilicates for selective partial oxidations of organic compounds by hydrogen peroxide [14], we have considered such molecular sieves as possible catalysts for the Ruff reaction.

The aim of this paper is to relate our attempts to perform heterogeneous catalysis of Ruff degradation of calcium D-gluconate to D-arabinose, using various microporous titanosilicates. From the obtained results, the presently accepted mechanism will be discussed.

2. Experimental

2.1. Reactants

Hydrogen peroxide (30 wt% aqueous solution) was purchased from Prolabo. Calcium gluconate was a gift from Roquette Frères SA. Titanium(IV) isopropoxide, ti-

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tanium(IV) fluoride and copper(II) sulfate were obtained from Aldrich.

2.2. Catalysts

The EUROTS-1 sample, a Ti-silicalite with MFI structure [15], obtained by direct hydrothermal synthesis, was a gift from Rhodia.

Ti-BEA and Ti-FAU, respectively Ti-beta and Ti-faujasite, were prepared by post-synthetic treatment of commercial Na/BEA (Si/Al = 12.5) (PQ CP 806) and H/FAU (Si/Al = 21) (PQ CBV 740). According to Di Renzo et al. [16], isomorphic substitution of aluminium by titanium was carried out by treating 2.5 g of starting zeolites simultaneously with 250 ml of 65% nitric acid (Merck) and 32 mg of titanium tetrafluoride, under overnight reflux. The solid was filtered, washed repeatedly with water until a neutral filtrate was obtained, dried overnight at 353 K and calcined under flowing dry air (250 ml min^{-1}) at 723 K for 6 h.

Table 1
Chemical composition of catalysts in molar fraction (%).

	Si	Al	Ti
TS-1 (EUROTS-1)	97.22	0.00	2.78
Ti-BEA	99.14	0.12	0.74
Ti-FAU	97.64	2.21	0.15

Preservation of the zeolite structure was verified by X-ray power diffraction (XRD) patterns recorded on a CGR Theta 60 instrument using Cu $K\alpha_1$ filtered radiation. Incorporation of titanium in the framework was ascertained by DR-UV-visible spectroscopy (Perkin–Elmer Lambda 14, equipped with a reflectance sphere) and infrared spectroscopy (FTIR Nicolet 320), using self-supported wafers of pure zeolite. The chemical composition of solids, obtained by chemical analyses performed at the Service Central d'Analyse du CNRS (Solaize, France), is given in table 1.

2.3. Catalytic tests

The catalytic tests were carried out in an open 50 ml thermostated glass reactor, equipped with a magnetic stirrer. A mixture of calcium gluconate (2.30 g, 10.2 mmol of carboxylate) and catalyst (variable amounts) was prepared in 20 ml of water and heated to 313 K. The pH of the solution was adjusted to 6.5 with a sodium hydroxide solution (0.5 M). 30% aqueous hydrogen peroxide (2.6 ml, 25 mmol) was gradually added with a peristaltic pump over a period of 1 h. During the oxidation, the pH was kept constant by adding sodium hydroxide solution, using an automatic burette (Metrohm 718 Stat-Titrino). After 7 h, the stirring was stopped and the mixture was filtered at 298 K and analysed. After appropriate derivatization of the major reaction products, aldoses (arabinose, erythrose, glyceraldehyde) and aldonic acids (gluconic, arabinonic, erythronic, glyceric acids), the composition (aldonic acids and aldoses) of the final solution was determined by GC equipped with a capillary DB-1 column (J&W Scientific). Titanium in solution was determined by plasma atomic absorption spectroscopy (CIRAD Montpellier).

In fact, under the operating conditions used, the only detectable products were arabinose and erythrose. Carbon dioxide (or its hydrogenocarbonate form), as well as formic acid, resulting from the deep oxidation reaction, were not analysed. Analysis in terms of conversion and selectivity as a function of time was not possible. Calcium D-gluconate is only slightly soluble in water so that, at low gluconate conversion, the mass balance is poor since unreacted gluconate is filtered together with the catalyst before derivatization of the filtered solution and GC analysis. Experimental results are then given as yields in arabinose and erythrose. However, in other experiments where the gluconate conversion is complete, mass balances around 90% are found.

Blank experiments were performed under the same conditions, without addition of catalyst.

In order to compare titanium(IV) and copper(II) in homogeneous catalysis, reactions were carried out as above, except for the amount of metal used (180 μmol), the temperature (293 K) and the duration of the reaction (1.5 h), which are the usual conditions for homogeneous cupric catalysis of the Ruff reaction.

3. Results and discussion

Three types of titanium-containing zeolites have been tested. The first one was a TS-1 sample (EuroTS-1), a titanium-silicalite having MFI structure with tridirectional channels with small-pore (0.53 × 0.56 nm) apertures [17]. It was synthesized by direct hydrothermal reaction and did not contain aluminium. The two other zeolites were Ti-BEA and Ti-FAU, classified as large-pore (0.76 × 0.64 nm and 0.74 nm, respectively [17]), with twelve-membered ring aperture and tridirectional porosity. As hydrothermal synthesis of Ti-BEA required the presence of aluminium (or trivalent metal), and as Ti-FAU was never obtained by direct hydrothermal treatment, these two large-pore Ti-zeolites were prepared by post-synthesis treatments. According to a procedure elaborated in the laboratory [16], aluminium atoms of the corresponding zeolites were substituted by titanium atoms in oxidizing acid solutions. The incorporation of tetrahedrally coordinated titanium in the framework was confirmed by the observation of an infrared adsorption band at 960 cm^{-1} and a single band at 205–210 nm in UV absorption spectra [18,19]. No band corresponding to segregated TiO_2 particules or octahedral titanium was found. However, as shown in table 1, from chemical analysis, the replacement of Al by Ti was incomplete, particularly with FAU. In the case of Ti-BEA, the absence of the vibration characteristic of acid hydroxyl in the infrared spectrum, was indicative of the absence of aluminium in the framework. So, the remaining aluminium was certainly present as extraframework species in Ti-BEA.

Table 2

Yield of arabinose in the oxidative degradation of calcium gluconate by hydrogen peroxide catalysed by titanium zeolites. Comparison with homogeneous titanium catalysis.[a]

Catalyst	Weight (mg)	Ti[b] (μmol)	Arabinose (%)	Erythrose (%)	Leaching[c] (%)
None	0	0	0	0	
TS-1	200	83	<1	0	1
Ti-BEA	200	21	12	<1	60
Ti-FAU	500	11	17	1	99
Ti(iPrO)$_4$	6.75	20	11	2	[d]
TiF$_4$	1.24	10	18	2	100

[a] Reaction conditions: 10.2 mmol gluconate, 25.4 mmol H_2O_2, 20 ml H_2O, 313 K, 7 h.

[b] Amount of titanium introduced by the Ti-zeolites.

[c] Relative amount of titanium dissolved in the filtrate at the end of the reaction.

[d] Incomplete dissolution of Ti(iPrO)$_4$.

Table 3

Comparison between titanium(IV) and copper(II) in the homogeneous catalysis of the degradation of calcium gluconate by hydrogen peroxide.[a]

Catalyst	Metal amount (μmol)	Arabinose (%)	Erythrose (%)	Unreacted gluconate (%)
TiF$_4$	180	2	3	66
Cu(SO$_4$)$_2$	180	63	8	0

[a] Reaction conditions: 10.5 mmol gluconate, 25.4 mmol H_2O_2, 20 ml H_2O, 293 K, 1.5 h.

Table 2 reports the catalytic activity of the three Ti-zeolites and compares the results with those obtained using homogeneous titanium catalysts. TS-1 was practically inactive. In contrast, large-pore Ti-BEA and Ti-FAU zeolites gave arabinose in low yield (12–17%), and the only detectable secondary product was erythrose. The difference in reactivity between the zeolite catalysts could be the result of the difference in pore size; the pores of TS-1 would be too small to admit gluconate and then the catalytic reaction could not occur. The formation of traces of product with this zeolite could be the effect of titanium at the outer surface of the crystals. However, two other phenomena must be taken into account: the first one could be related to the lower stability towards hydrogen peroxide of titanium in large-pore Ti-zeolites, as determined with Ti-BEA, which could lead to extraframework Ti-species [20]; the other one could be the high complexing power of the gluconate anion towards transition metal cations [21,22], which could promote the dissolution of titanium. So, the question arose whether the reaction is truly heterogeneous or not. Therefore, we have measured the amount of titanium dissolved at the end of the reaction. As given in table 2, the results obtained with Ti-BEA and Ti-FAU show a very important leaching of titanium, practically quantitative in the case of the FAU structure. In contrast, TS-1 has released only traces of titanium in solution. The difference in the extent of leaching between large-pore molecular sieves and TS-1 can be explained by the higher stability of titanium(IV) in the MFI framework of TS-1 but, also, by the impossibility for the carbohydrate carboxylate to penetrate TS-1 in order to extract, by complexation, titanium from the zeolite lattice. By now, nothing allows one to distinguish between these two assumptions, but the conjunction of both phenomena is quite likely.

In order to confirm that the dissolved titanium is actually the active catalytic species, soluble Ti(IV) salts were tested in conditions close to those reported for Ti-zeolites, using equivalent amounts of titanium in solution. Titanium(IV) isopropoxide and titanium tetrafluoride led to yields in arabinose nearly similar to those observed with large-pore molecular sieves Ti-BEA and Ti-FAU at equivalent Ti content. From such results, there was no doubt that the oxidative degradation of calcium D-gluconate to D-arabinose, using Ti-BEA and Ti-FAU, was the result from the presence of titanium in solution. This is in accordance with recent related work which showed that hydrogen peroxide oxidation of glucopyranoside with Ti-MCM-41, occurred only when titanium was leached [23].

Titanium(IV) in solution was thus able to catalyse the oxidative degradation of calcium D-gluconate, but the experimental conditions, particularly the amount of metal salt, the temperature and the reaction time, were far from those generally used with copper(II). Table 3 compares the activity of homogeneous titanium(IV) with that of homogeneous copper(II), in the typical conditions used with the latter metal. While cupric salts allowed the total transformation of gluconate and the formation of arabinose with a yield of 63% yield, Ti(IV) salt led only to very small amounts of arabinose, and the conversion was low because 66% of gluconate was recovered. The activity of titanium was much lower than the activity of copper, despite the fact that titanium is usually considered as a good generator of hydroxyl radicals from hydrogen peroxide [24]. Such a result conflicts with a mechanism related to that of the Fenton reaction, involving the formation and the reactivity of hydroxyl radicals. This is confirmed by the recent observation of formation of D-erythrose with high selectivity when the oxidative degradation of calcium D-gluconate is catalysed by cobalt salts [25]. Actually, if hydroxyl radical was the effective oxidizing intermediate, the nature of the product ought to be independent of the nature of the catalytic metal salt. Therefore, the mechanism involved in the oxidative degradation of gluconate cannot be classified as a Fenton type reaction and is certainly dependent on the metal salt used as catalyst.

It is noteworthy that, using titanium(IV) fluoride in a similar conversion range (30–40%), a larger amount of catalyst used at a lower temperature and for a shorter time has given a lower yield in arabinose, but a similar yield in erythrose. This fact means that a larger amount of titanium(IV) leads to the consumption of arabinose. In the absence of other detectable carbohydrates, the total degradation of arabinose into small molecules such as carbon dioxide and formic acid is likely.

4. Conclusions

Depending on their porous structure, titanium-containing zeolites exhibit two different behaviours for the catalysis of the Ruff oxidative degradation of calcium gluconate: small-pore TS-1 prove inactive, while large-pore zeolites – Ti-BEA and Ti-FAU – are active. In the latter cases, leaching of titanium is responsible for the catalytic activity. It is concluded that titanium-containing zeolites cannot be used as genuine heterogeneous catalysts for the Ruff reaction. Following the conclusions already reached in the case of chromium-substituted molecular sieves (CrAPO and Cr-ZSM-5) [26] and cobalt-containing molecular sieves (CoAPO and Co-beta) [27–29], it is demonstrated here that titanium-substituted zeolites also behave as precursors for homogeneous catalysis: the solid, like the Trojan horse [30], releasing the active agents. Furthermore, titanium(IV) in solution is not as effective as copper(II) for oxidative degradation of gluconate. From these results, the classification of the Ruff reaction into the class of Fenton-type reactions, in which hydroxyl radicals play an important role, could be questioned. The mechanism of the Ruff reaction, catalysed by copper(II) salts, will be the subject of further publications.

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References

[1] M. Elseviers, B. de Wannemaeker and H. Röper, Agro-Food-Industry Hi-Tech 10 (1999) 15.
[2] B. Nidetzky, W. Neuhauseur, D. Haltrich and K.D. Kulbe, in: *Carbohydrates as Organic Raw Materials*, Vol. IV, eds. W. Praznik and A. Huber (WUV-Universitätsverlag, Wien, 1998) p. 190.
[3] J.B. Park, C. Yook and Y.K. Park, Starch/Stärke 50 (1998) 120.
[4] F. Lichtenthaler, Carbohydr. Res. 313 (1998) 69.
[5] O. Ruff, Berichte 31 (1898) 1573.
[6] R.C. Hockett and C.S. Hudson, J. Am. Chem. Soc. 56 (1934) 1632.
[7] H.G. Fletcher, H.W. Diehl and C.S. Hudson, J. Am. Chem. Soc. 72 (1950) 4546.
[8] R.G.P. Walon, US Patent 3 755 294 (1973).
[9] V. Bilik, CZ Patent 6749-83 (1986).
[10] M. Rosenberg, J. Svitel, E. Sturdik, J. Kocan, P. Magdolen and J. Kubala, CZ Patent 4458-90 (1990).
[11] K.J. Buchanan, A. Goosen and J.D. Lovelock, S. Afr. J. Chem. 30 (1977) 191.
[12] H.S. Isbell and M.A. Salam, Carbohydr. Res. 90 (1981) 123.
[13] L. Lukac, A. Krihova, M. Matulova and L. Petrus, Chem. Papers 47 (1993) 124.
[14] B. Notari, Catal. Today 18 (1993) 163.
[15] J.A. Martens, P. Buskens, P.A. Jacobs, A. van der Pol, J.H.C. van Hooff, C. Ferrini, H.W. Kouwenhoven, P.J. Kooyman and H. van Bekkum, Appl. Catal. A 99 (1993) 71.
[16] F. Di Renzo, S. Gomez, F. Fajula and R. Teissier, Fr. Patent 95 09436 (1995).
[17] W.M. Meier, D.H. Olson and C. Baerlocher, *Atlas of Zeolite Structure Types*, 4th Ed. (Elsevier, London, 1996).
[18] A. Zecchina, G. Spoto, S. Bordiga, A. Ferrero, G. Petrini, G. Leofanti and M. Padovan, Stud. Surf. Sci. Catal. 69 (1991) 251.
[19] F. Geobaldo, S. Bordiga, A. Zecchina, E. Giamello, G. Leofanti and G. Petrini, Catal. Lett. 16 (1992) 109.
[20] A. Carati, C. Flego, E.P. Massara, R. Millini, L. Carluccio, W.O. Parker and G. Bellussi, Micropor. Mesopor. Mater. 30 (1999) 137.
[21] Y.E. Alekseev, A.D. Garnovskii and Y.A. Zhdanov, Usp. Khim. 67 (1998) 723.
[22] D.T. Sawyer, Chem. Rev. 64 (1964) 633.
[23] E.J.M. Mombarg, S.J.M. Osnabrug, F. van Rantwijk and H. van Bekkum, Stud. Surf. Sci. Catal. 108 (1997) 385.
[24] W.T. Dixon and R.O.C. Norman, J. Chem. Soc. (1963) 3119.
[25] G. Flèche and R. Tamion, Eur. Patent 0 829 485 (1998).
[26] R.A. Sheldon, Stud. Surf. Sci. Catal. 110 (1997) 567.
[27] B. Kraushaar-Czarnetzki, W.G.M. Hoogervorst and W.H.J. Stork, Stud. Surf. Sci. Catal. 84 (1994) 1869.
[28] D.L. Vanoppen, D.E. de Vos, M.J. Genet, P.G. Rouxhet and P.A. Jacobs, Angew. Chem. Int. Ed. Engl. 34 (1995) 560.
[29] I. Belkhir, A. Germain, F. Fajula and E. Fache, J. Chem. Soc. Faraday Trans. 94 (1998) 1761.
[30] R.A. Sheldon, M. Wallau, I.W.C.E. Arends and U. Schuchardt, Acc. Chem. Res. 31 (1998) 485.