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The Catalysis of the Ruff Oxidative Degradation of Aldonic Acids by Copper(II)-Containing Solids

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The catalysis of the Ruff oxidative degradation of calcium D-gluconate to D-arabinose by aqueous diluted hydrogen peroxide was investigated using copper(II)-containing solids: zeolites and resins. Among zeolites, copper(II)-exchanged Y faujasite has given good results, similar to homogeneous copper catalysts. Only minute amounts of soluble copper were detected at the end of the reaction and the recovered solid was recycled twice without diminution of efficiency. However, it was not true heterogeneous catalysis because the chelating gluconate anion leached copper right from the beginning of the reaction. So, the catalysis occurred in solution but the metal precipitated again at the end of the reaction, when all the gluconate was consumed. Copper (II) iminodiacetic resin, in which the metal cation is more strongly bound than in the gluconate complex, was not active. This demonstrates that copper(II) must be in solution in order to be active. © 2002 Elsevier Science (USA)

Key Words: **Ruff degradation; oxidative degradation; hydrogen peroxide; aqueous media; carbohydrates; gluconate; arabinose; copper(II)-exchanged zeolites; copper(II)-exchanged resins; leaching.**

INTRODUCTION

Aldopentoses are valuable starting materials for the production of xylitol (1), an important reduced-calorie, noncariogenic sugar substitute, or for the chemical synthesis of riboflavin (vitamin B_2) (2). Such monosaccharides, containing five carbon atoms, would be obtained by selective degradation of readily available aldohexoses. Among the various methods for shortening the carbon chain of sugars, the Ruff oxidative degradation reaction, known since 1898, seemed to be particularly appropriate (3). Starting from a salt of an aldonic acid, this reaction leads to an aldose with loss of one carbon atom (see Scheme 1). 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 calcium D-gluconate (4–8). The catalyst is always a soluble transition metal salt, but copper(II) proved to be more effective than iron(III) (7, 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.

Taking into account the fact that former authors classed the Ruff oxidation into the category of a Fenton-type reaction (10–12), we previously studied the catalysis of this reaction using titanium-containing zeolites. Such molecular sieves were known to be highly efficient for selective liquid-phase oxidation by hydrogen peroxide (13). Unfortunately, such solids were not effective in the heterogeneous catalysis of the Ruff oxidative degradation of calcium gluconate (14).

Then other redox solids were studied. The aim of this paper is to relate our attempts to perform heterogeneous catalysis of the Ruff degradation of calcium D-gluconate to D-arabinose, using copper-containing solids: copper(II)-exchanged zeolites and copper(II)-exchanged resins. Leaching of the transition metal was studied with the greatest care. From this study, a peculiar behavior of the reactive system is disclosed. Part of this work has already been published in a preliminary communication (15).

EXPERIMENTAL

Reactants

Hydrogen peroxide (30 wt% aqueous solution) was purchased from Prolabo. Calcium gluconate was a gift from Roquette Frères S.A. Peroxide tests were obtained from Merck. Copper(II) chloride and copper(II) sulfate were purchased from Aldrich.

Copper(II)-Exchanged Zeolites

$Cu(\tau)/XYZ(x)$ stands for a zeolite with XYZ structure, according to the recommendations of the International

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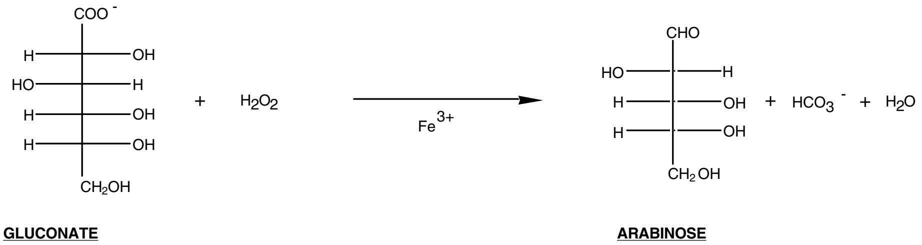

SCHEME 1. Ruff oxidative degradation of calcium D-gluconate.

Zeolite Association (16), with a Si/Al ratio equal to x, and τ% exchanged with copper(II).

Starting zeolites were commercial samples: Na/BEA from PQ Zeolites (CP 806), Na/FAU from Süd Chemie (CBV 100). K/LTL and H/MOR were provided by Zeocat.

Except for Cu(16)/MFI(26.9), which was obtained from IFP, copper–zeolites were prepared by ion exchange in solution. Zeolite (1 g) was stirred at room temperature for 24 h in 300 ml of a 0.03 M copper(II) chloride solution. 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 $\cdot$ min^{-1}) at 723 K for 6 h.

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. The chemical composition of solids was determined at the Service Central d'Analyse du CNRS (Solaize, France). Copper in solids was characterized by DR-UV–visible spectroscopy using a Perkin–Elmer Lambda 14 apparatus, equipped with a reflectance sphere, and by temperature-programmed reduction (TPR). The latter was performed using a Micromeritics Autochem 2910 apparatus, equipped with a katharometer. The temperature was programmed at a rate of 10 K $\cdot$ min^{-1} and the experiments were conducted in a flow of 30 ml $\cdot$ min^{-1} of an H_2/Ar (3% H_2) gas mixture. DRIFT spectra were obtained on a Bruker Equinox 55 instrument equipped with a Specac cell. Thermogravimetric analyses were carried out in a Setaram TGDSC-111 apparatus coupled with a Leybold Transpector SQX quadrupole mass spectrometer.

Copper(II)-Exchanged Resins

The starting resin was the commercial Lewatit TP 207, a gift from Bayer S.A.

Copper resin was obtained by exchange in solution. Resin (1 g) was stirred at room temperature for 24 h in an aqueous solution of 60 mg of copper(II) chloride in 20 ml of water. The solid was filtered, washed repeatedly with water until obtention of a neutral filtrate, and dried overnight at 333 K. The obtained resin contained 2.67 wt% copper.

Catalytic Tests

Using copper(II)-exchanged zeolites. The reactions were carried out in an open 50-ml glass reactor, thermostated at 293 K, and equipped with a magnetic stirrer. A mixture of calcium gluconate (2.30 g, 10.2 mmol of carboxylate) and catalyst (180 μmol of copper) was prepared in 20 ml of water. The pH of the solution was adjusted to 6.5 with a sodium hydroxide solution (0.5 M). Aqueous hydrogen peroxide (30%, 2.6 ml (25 mmol)) (Prolabo) was gradually added with a peristaltic pump over a period of 1 h. During oxidation, the pH was kept constant by adding sodium hydroxide solution, using an automatic burette (Metrohm 718 Stat-Titrino). After complete consumption of hydrogen peroxide, as determined by peroxide test, stirring was stopped and the reaction mixture was filtered and analyzed. After appropriate derivatization of the major reaction products, aldoses (arabinose, erythrose, and glyceraldehyde) and aldonic acids (gluconic, arabinonic, erythronic, and glyceric acids), the composition of the final solution was determined by GC equipped with a capillary DB-1 column (J & W Scientific). Neither carbon dioxide (or its hydrogenocarbonate form) nor as formic acid (or formiate), resulting from the oxidation of formed aldoses (17), were analyzed.

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

Copper in solution was determined by plasma atomic absorption spectroscopy (CIRAD Montpellier).

Using copper(II)-exchanged resins. Taking into account the mechanical fragility of the resin beads, an oscillating shaker was used instead of the usual magnetic stirrer. Consequently, considering the lower efficiency of the shaking, totally soluble sodium gluconate was used instead of partially soluble calcium gluconate.

RESULTS AND DISCUSSION

Catalysis by Copper(II)-Exchanged Zeolites

Screening of various zeolites. First of all, copper(II)-exchanged zeolites with various structures were tested in the Ruff degradation of calcium gluconate and compared,

$$H_2O_2 \xrightarrow{Cu^{2+}/Cu^{+}} 1/2\ O_2 + H_2O$$

SCHEME 2. Hydrogen peroxide decomposition.

in the same reaction conditions, with homogeneous catalysis by copper(II) sulfate. The amount of copper was the same in all cases. Hydrogen peroxide was used in large excess (×2.5). This amount was chosen because it gave the better arabinose yield in homogeneous catalysis (9). Excess of hydrogen peroxide was required in order to compensate for its competitive decomposition into oxygen and water, according to a mechanism similar to the Haber–Weiss cycle (18) (see Scheme 2).

The reactions were stopped when hydrogen peroxide was totally consumed. D-Arabinose and D-erythrose were the main products; glyceraldehyde was formed only as traces (<1% yield).

Results are given in Table 1. Calcium gluconate conversion, arabinose and erythrose yields, necessary time for complete consumption of hydrogen peroxide, and relative amount of copper in solution at the end of the reaction are reported for each experiment.

While no reaction occurred without catalyst, all copper-exchanged zeolites were proved more or less effective. In all cases, even in the case of homogeneous catalysis, the product balance was relatively low, between 60 and 80%. The loss of matter was attributed to a subsequent deep oxidation of the aldoses formed, producing carbon dioxide and untitrated formic acid as the ultimate product (17).

With mordenite Cu(72)/MOR(7.3), the time needed to fully consume hydrogen peroxide was quite large and the conversion was low. Both results are attributed to a slow oxidation of gluconate that, evidently, reduced the consumption of hydrogen peroxide, but that also increased the proportion of the competitive decomposition of the peroxide. So, the amount of hydrogen peroxide available for the conversion of gluconate was lower. The reason of the low oxidation rate could be the limitation of the diffusion rate of gluconate inside the monodirectional porosity of mordenite. The best results obtained with Cu(30)/LTL(2.8) and Cu(16)/BEA(11.3) were in agreement with the smallest crystal size in both cases and the largest pore aperture of the tridirectional structure of the BEA structure (19). According to these explanations, the good activity of Cu(16)/MFI(26.9), a zeolite with small pores, was surprising. In fact, with this solid, the copper leaching was so important that homogeneous catalysis might be involved. The low charge density in the MFI structure, due to the high Si/Al ratio, could explain the low stability of the divalent cupric cation inside this zeolite.

Peculiar behavior of a copper(II)-exchanged faujasite. Among all the solids, faujasite Cu(70)/FAU(2.4) has shown the better activity: the conversion was complete and the arabinose yield was equivalent to that obtained in homogeneous catalysis. Only the rate of the reaction was lower than in homogeneous catalysis, which could be explained by the diffusional restrictions for the reactant inside the solid, and/or by the inaccessibility of the part of the copper cations located in sodalite cages or in hexagonal prisms of the faujasite structure. Furthermore, the amount of copper in solution at the end of the reaction was very low.

More information about the activity of this copper(II)-exchanged faujasite is given in Table 2. A blank reaction, using the parent zeolite Na/FAU(2.4), has shown without ambiguity that the activity was due to the presence of copper in the solid. Morever, the copper(II)-containing solid recovered by filtration at the end of the reaction, then dried, was successively reused twice without loss of efficiency. These results were in agreement with a real heterogeneous catalytic activity of Cu(70)/FAU(2.4). However, they did not constitute absolute proof, since it was recently observed (20–23) that leaching of small amounts of transition metal (cobalt, chromium, or vanadium) could be

TABLE 1

Arabinose and Erythrose Yield in the Oxidative Degradation of Calcium Gluconate by Hydrogen Peroxide Catalyzed by Cu(II)-Exchanged Zeolites: Comparison with Homogeneous Catalysis[a]

Catalyst	Conversion (%)	Arabinose (%)	Erythrose (%)	Reaction time (h)	Leaching[b] (%)
None	0	0	0	7[c]	
Cu(72)/MOR(7.3)	37	19	2	5.8	8.1
Cu(30)/LTL(2.8)	60	38	5	1.5	16.8
Cu(16)/BEA(11.3)	77	45	5	1.0	16.6
Cu(16)/MFI(26.9)	87	60	8	2.0	32.7
Cu(70)/FAU(2.4)	100	63	9	3.5	0.23
$CuSO_4$	100	63	8	1.5	100

[a] Gluconate, 10.2 mmol; H_2O_2, 25.4 mmol; Cu(II), 180 μmol; H_2O, 20 ml; 293 K; pH 6.5.

[b] Relative amount of copper dissolved in the filtrate at the end of the reaction.

[c] The reaction was stopped after 7 h, though hydrogen peroxide was not totally consumed.

TABLE 2

Arabinose and Erythrose Yield in the Oxidative Degradation of Calcium Gluconate by Hydrogen Peroxide Catalyzed by Cu(II)-Exchanged Faujasite: Role of Copper and Recycling[a]

Catalyst	Conversion (%)	Arabinose (%)	Erythrose (%)	Reaction time (h)	Leaching[b] (%)
Na/FAU(2.4)	0	0	0	3.5[c]	0
Cu(70)/FAU(2.4)	100	62	9	3.5	0.23
Cu(70)/FAU(2.4)[d]	100	64	9	3.5	2
Cu(70)/FAU(2.4)[d]	100	63	9	4.5	0.15

[a] Gluconate, 10.2 mmol; H_2O_2, 25.4 mmol; Cu(II), 180 μmol; H_2O, 20 ml; 293 K; pH 6.5.

[b] Relative amount of copper dissolved in the filtrate at the end of the reaction.

[c] The reaction was stopped after 3.5 h, though hydrogen peroxide was not totally consumed.

[d] Successive reuses of the solid recovered at the end of the previous experiment.

responsible for the catalytic oxidative activity of some "redox molecular sieves." In fact, it was determined in some specific cases that the activity passed through a maximum at low metal concentration (20, 24). In order to determine if the dissolved copper could be responsible for the activity of Cu(70)/FAU(2.4), the homogeneous catalysis of the Ruff reaction by cupric salts was studied at low concentration. The reaction was stopped after 3.5 h, the reaction time required for the complete consumption of hydrogen peroxide when Cu(70)/FAU(2.4) was used. The obtained arabinose yield is shown in Fig. 1 as a function of the concentration of cupric sulfate. Catalytic activity varied monotonically with the amount of copper up to an amount of ca. 3.5 mmol/L. It was observed that concentrations of copper equivalent to those obtained in solution at the end of the reactions using copper faujasite (<0.15 mmol/L) gave arabinose yields lower than 3%. So, such amounts of dissolved copper could not be responsible for the catalytic activity of Cu(70)/FAU(2.4). The highest amount of copper used here (8.2 mmol/L) was that currently used in homogeneous catalysis (9). It must be observed that the yield had reached a plateau around 70%. The limitation in arabinose yield was explained by the formation of secondary products such as erythrose, glyceraldehyde, and indeterminate formic acid.

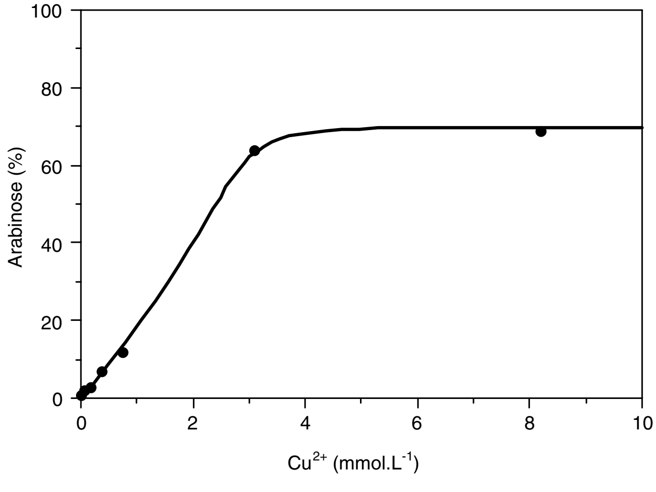

FIG. 1. Arabinose yield as a function of $CuSO_4$ concentration. Same conditions as in Table 1, except the reaction time was set to 3.5 h.

Though the previous result could constitute a new argument in favor of the heterogeneous nature of the catalysis, it could not be considered as absolute proof. Indeed, nothing ruled out the possibility of dissolution of copper during the reaction, followed by the precipitation of the metal at the end of the reaction. Such a phenomenon was recently reported concerning epoxidation of olefins with hydrogen peroxide, catalyzed by tungsten-containing solids (25). According to Sheldon *et al.* (26), "Rigorous proof of heterogeneity can be obtained by filtering the catalysts at the reaction temperature before completion of the reaction and testing the filtrate for activity." Unfortunately, in the present case, such a method was not possible because calcium gluconate is not totally soluble at the temperature of the reaction. In order to circumvent this difficulty, we have studied the variation of the amount of dissolved copper as a function of the reaction time. For that purpose, the reaction was stopped after various time periods and, each time, copper in solution was determined after filtration. The results were reported in Fig. 2. Zero time was set at the beginning of the addition of hydrogen peroxide. The mixture of calcium gluconate and copper exchanged zeolite in water was prepared 10 min before, a delay used for the adjustement of the pH. We can observe that copper leaching had already occurred before addition of hydrogen peroxide. Copper was completely dissolved during the reaction; then its concentration decreased and only traces of the soluble metal were present at the end of the reaction. Almost the whole amount of copper was back in the solid recovered after filtration, as shown by the copper-to-silicium ratio given in Table 3. The reaction behaved apparently like an heterogeneous catalysis but, in fact, the active species was in solution during the reaction, as for a homogeneous catalysis.

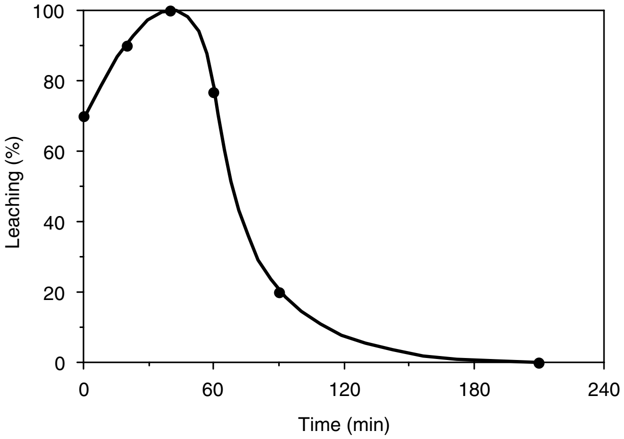

FIG. 2. Leaching of copper from Cu(70)/FAU(2.4) as a function of the reaction time. Same conditions as in Table 1.

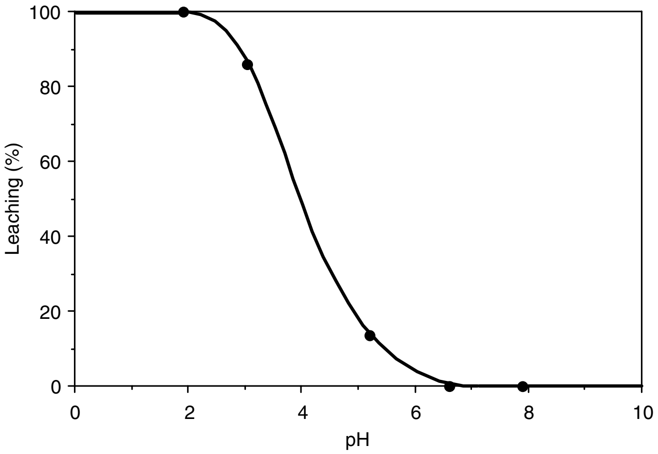

FIG. 3. Influence of pH on the leaching of copper from Cu(70)/FAU(2.4). Cu(70)/FAU(2.4), 175 mg (Cu(II), 180 μmol); H_2O, 20 ml; 293 K; 3.5 h.

In order to understand such behavior, it was necessary to determine the cause of copper leaching. Various reaction components (reagents and products) could be involved and their effects were tested under the conditions of the reaction (concentration, temperature, and time). First of all, the acidity could be a favorable factor for the leaching of copper from the solid, through exchange with protons. Figure 3 shows the dissolution of copper as a function of pH when the copper-exchanged faujasite was kept in water under stirring for 3.5 h at 293 K. Effectively, leaching of copper occurred in acidic conditions, but it was negligible ($<0.2\%$) at pH 6.5, the controlled pH of the Ruff reaction. Hydrogen peroxide was already claimed for promoting leaching in reactions using chromium molecular sieves (21). However, when the copper zeolite was kept in the presence of 25.4 mmol of oxidant agent, at pH 6.5, under the previous conditions, only traces of metal were detected in solution ($\leq 0.1\%$). A similar result was obtained when arabinose, the main product, was added in concentrations corresponding to 100% yield (10.2 mmol). On the contrary, in the same conditions (10.2 mmol), the reactant calcium gluconate caused the complete leaching of copper from the zeolite. This fact can be assigned to the high complexing power of gluconate anion toward multivalent transition metal cations (27, 28).

Thus, it is demonstrated that the dissolution of copper occurred upon mixing of Cu(70)/FAU(2.4) with the gluconate, and that copper precipitated again, at the end of the reaction, when the gluconate was completely consumed.

From these considerations, interpretation of the results given in Table 1 must be reviewed. Effectively, except for Cu(70)/FAU(2.4), for which the complete gluconate conversion led to the final precipitation of copper, the conversion and the yield in arabinose followed approximately the amount of dissolved copper. So, the limitation of activity was certainly dependent on the ability of the zeolite to release copper(II). Moreover, at the end of the reaction, copper(II) remained in solution because of the presence of unreacted gluconate.

In order to understand and eventually control the precipitation, efforts were then directed to the elucidation of the nature of the final solid.

TABLE 3

Mass and Chemical Composition of the Initial Catalyst and the Solid Recovered after Reaction, Filtration, and Calcination at 723 K

	Mass (g)	Si/Al	Cu/Si	C/Si	Ca/Si
Cu(70)/FAU(2.4)	175	2.50	0.15	0	0
Solid after reaction	378	2.51	0.14	0.54	0.42

Nature of the solid recovered at the end of the reaction. As shown in Table 3, the mass of the solid recovered at the end of the reaction was, after calcination at 723 K, twice the mass of the initial catalyst. Elemental analysis has shown the absence of dealumination and a low loss of copper ($<7\%$). The presence of carbon and calcium in great quantities could explain the increase in mass. One possibility could be a deposit of calcium gluconate on the external surface of the zeolite. However, the observed carbon-to-calcium ratio ($C/Ca = 1.28$) did not agree with the one of such a product ($C/Ca = 12$). Morever, the calcination performed before analysis should have eliminated all organic carbon.

X-ray powder diffraction patterns of the initial catalyst and of the recovered solid (noncalcinated) are given in Figs. 4a and 4b. The structure of the zeolite was retained, but new diffraction bands were observed. Four of these new signals, at $2\theta = 11.58, 14.72, 18.02$, and $19.72°$, identified in Fig. 4b by an asterisk, did correspond to the bands of calcium carbonate (Fig. 4c). The three other new bands, at

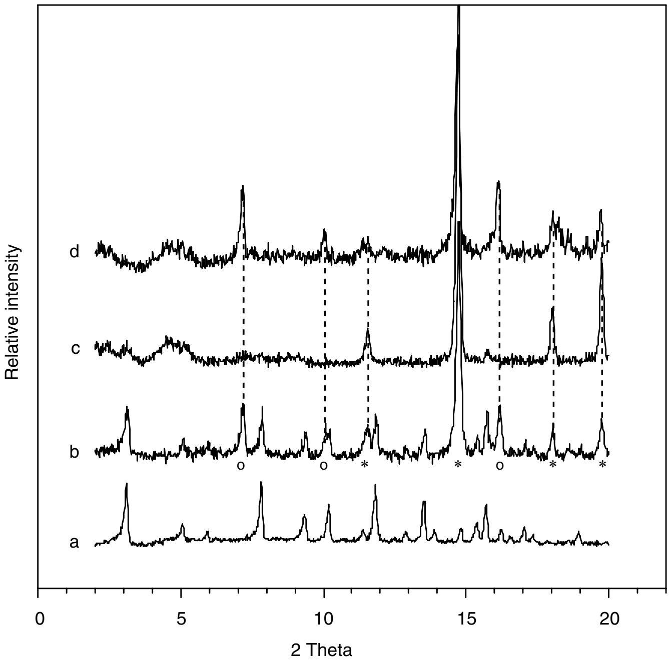

FIG. 4. XRD spectra of Cu(70)/FAU(2.4) before (a) and after (b) the Ruff reaction. (c) Calcium carbonate; (d) solid after homogeneous catalysis.

$2\theta = 7.20, 10.00$, and $16.14°$, identified in Fig. 4d by dotted lines up from the circles in Fig. 4b, were attributed to calcium oxalate according to ASTM tables (17-541). The presence of oxalate salt was confirmed, by infrared spectroscopy, by absorption bands at 786, 1319, and 1653 cm^{-1} (29). So, all the X-ray diffraction bands could be attributed, but this technique was unable to detect any species containing copper, certainly because of the low proportion of copper (<2 wt%) in the final solid.

A common method for copper characterization in solids is temperature-programmed reduction. As shown in Fig. 5a, copper(II) in exchanged faujasite exhibited two reduction steps (30). The group of peaks at low temperature was attributed to the reduction of Cu^{2+} into Cu^{+}. It was composed of two peaks, at ca. 450 and 555 K, and a shoulder at ca. 645 K, that were assigned to the reduction of Cu^{2+} in three different positions of the faujasite structure: supercage, sodalite cage, and hexagonal prism, respectively (30, 31). The high-temperature peak (ca. 1100 K) was attributed to the reduction of Cu^{+} into Cu^{0}, without position differentiation. Experimentally both massifs had equivalent surfaces, which was in accordance with the theory and proved the absence of other copper species as, for example, cupric oxide (CuO) aggregates. In contrast, the TPR profile of the final solid exhibited a single reduction peak at an intermediate temperature (ca. 975 K) (see Fig. 5b). In fact, a similar profile was observed when calcium carbonate, a component of the final solid, was analyzed in TPR. Since such a compound was certainly irreducible, the signal was ascribed to the decomposition of the carbonate into calcium oxide and carbon dioxide, this gas being detected by the katharometer of the apparatus. The decomposition of calcium carbonate at this temperature, with carbon dioxide emission, was actually confirmed by thermogravimetric analysis coupled with mass spectroscopy. Thus, TPR did not permit determination of the nature of copper in the final solid. The signal of this metal was certainly hidden by the signal of calcium carbonate. However, this technique has shown that the copper recovered at the end of the reaction was not in well-defined positions in the faujasite framework, as it was in the starting material.

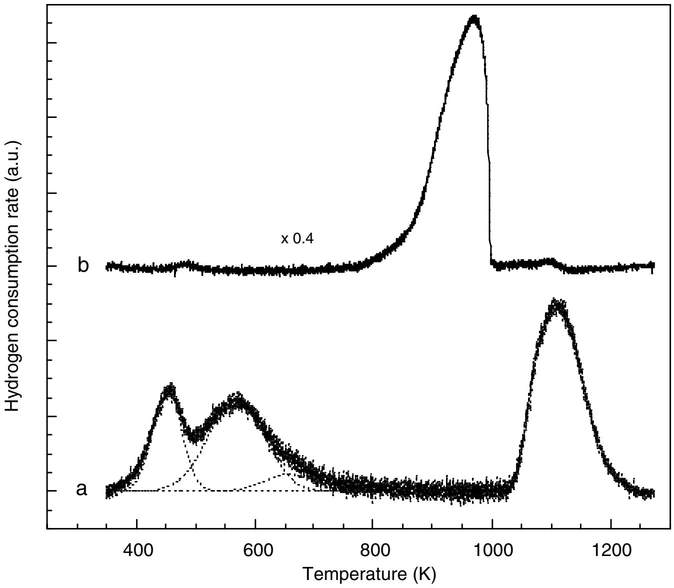

FIG. 5. Temperature-programmed reduction of Cu(70)/FAU(2.4) before (a) and after (b) the Ruff reaction.

Finally, the state of copper was probed by means of UV–visible diffuse reflectance spectroscopy. The position of the absorption band is a function of the coordination of the transition cation. Table 4 gives the wavelength of the maximum of absorption for the starting copper zeolite, the

TABLE 4

UV–Vis DRS λ_{max} of Cu(70)/FAU(2.4), of the Solid after Reaction, and of Various Copper(II)-Containing Solids

Solid	λ_{max} (nm)
Cu(70)/FAU(2.4)	830
Solid after reaction	732
Idem after calcination	445
$CuCO_3$	776
Cu gluconate	772
CuO	444
$Cu(OH)_2$	733

noncalcined final solid, and some possible species: $CuCO_3$, Cu gluconate, CuO, and $Cu(OH)_2$. First of all, UV–vis spectroscopy confirmed that copper in the solid recovered at the end of the reaction ($\lambda_{max} = 732$ nm) was different from the copper in Cu(70)/FAU(2.4) ($\lambda_{max} = 830$ nm). Then, the comparison with the spectrum of other copper(II) salts indicated that copper(II) hydroxide ($\lambda_{max} = 733$ nm) was the most probable copper-containing compound in the final solid. After calcination at 723 K, the final solid was brown and its absorption band had shifted to 445 nm, a wavelength corresponding to cupric oxide. We have confirmed, using thermogravimetric analysis, that copper(II) hydroxide was decomposed into CuO and water from 475 K. These results were in agreement with the presence of the hydroxide in the final product.

Now, according to the previous results, the possibility that the active species precipitates at the end of the reaction, even using homogeneous catalysis with calcium gluconate, must be examined.

Catalysis by copper(II) sulfate. An experiment was carried out with copper(II) sulfate, using the same conditions as in Table 1, but the reaction mixture was kept overnight under agitation. A green solid was obtained, containing carbon, calcium, and copper, in 1/0.7/0.05 relative molar proportion. Despite the poor crystallinity, the X-ray powder diffractogram (see Fig. 4d) exhibited the bands of calcium carbonate ($2\theta = 11.58, 14.72, 18.02$, and 19.72°) and calcium oxalate ($2\theta = 7.20, 10.00$, and 16.14°). Infrared spectroscopy confirmed the presence of oxalate (786, 1319, and 1653 cm^{-1}). As previously, the TPR signal at ca. 975 K was attributed to the decomposition of calcium carbonate, and the UV–visible absorption band at 728 nm was attributed to copper(II) hydroxide. Thus, this solid was a mixture of calcium carbonate, calcium oxalate, and copper(II) hydroxide, identical to the solid which had precipitated in addition to the zeolite, when Cu(70)/FAU(2.4) was used. However, the precipitation was slower than in heterogeneous catalysis, which means that the crystallization was assisted by the presence of the zeolite, according to a mechanism called "heterogeneous nucleation" (32).

The precipitation of copper salts at the end of the reaction can be advantageously used for easy separation and recycling of the catalyst (9).

Catalysis by Copper(II)-Exchanged Resins

We have previously demonstrated that gluconate was responsible for the leaching of the metal. This phenomenon was certainly due to a stronger interaction between the cupric cation and the chelating gluconate anion than between the divalent cation and the zeolite framework. So, a way to avoid the leaching could be to use a catalyst in which the cation would be more strongly bound to the solid. According to the literature (33), ethylenediaminetetraacetate anion (EDTA) is a better complexing agent than gluconate anion, at the pH of the Ruff reaction. So, we have used a macroporous polystyrenic resin, in which the complexing function was an iminodiacetate group, i.e., half a molecule of EDTA. Such an ion-exchange resin is selective for divalent cations and particularly for copper(II). Moreover, according to the technical information (from Bayer), it is able to extract copper(II) cations from aqueous solutions even in the presence of a chelating agent like gluconic acid, at the pH used for the Ruff reaction.

TABLE 5

Arabinose and Erythrose Yield in the Oxidative Degradation of Calcium Gluconate by Hydrogen Peroxide Catalyzed by Cu(II)-Exchanged Iminodiacetate Resin[a]

Catalyst	Conversion (%)	Arabinose (%)	Erythrose (%)	Leaching[b] (%)
Cu resin	20	8	3	16

[a] Gluconate, 10.2 mmol; H_2O_2, 25.4 mmol; Cu(II), 180 μmol; H_2O, 20 ml; 293 K; pH 6.5; time, 3.5 h.

[b] Relative amount of copper dissolved in the filtrate at the end of the reaction.

The result obtained with such a copper(II)-exchanged iminodiacetic resin is given in Table 5. The reaction was stopped after 3.5 h, as in Table 2, though hydrogen peroxide was not totally consumed.

Compared to the activity of Cu(70)/FAU(2.4), the activity of the copper(II) resin was very low. Moreover, a partial dissolution of copper was observed. It was also observed that some beads of resin had become opaque and some others were disintegrated. So, the dissolution of copper was certainly the result of a partial destruction of the polystyrene structure due to oxidation by hydrogen peroxide. Taking into account the amount of copper in solution and the results obtained in homogeneous catalysis, which are reported in Fig. 1, a yield in arabinose between 20 and 30% would be expected. The lower yield obtained (8%) was explained by the fact that the amount of copper in solution was determined at the end of the reaction, while the destruction of the resin and the concomitant dissolution of copper must be slow and progressive. In any case, it was evident that the activity observed was totally compatible with activity of the copper in solution. So, it must be considered that the solid copper(II)-exchanged iminodiacetic resin was inactive.

These results tend to demonstrate that copper(II) must be in solution in order to catalyze the Ruff reaction.

CONCLUSIONS

Considering a classical criterion like catalyst recycling, copper(II)-exchanged Y faujasite appeared as a good heterogeneous catalyst for the Ruff degradation of calcium D-gluconate into D-arabinose. However, this was an artifact.

Following the evolution of the concentration of copper in solution during the reaction, it was possible to show that gluconate leached the metal from the zeolite at the beginning of the reaction and then the dissolved copper disappeared from the solution at the end of the reaction. So, homogeneously dissolved copper salt was responsible for the reaction, but when the aldonic acid was completely consumed, copper precipitated as a hydroxide, helped by the the solid zeolite and the concomitant crystallization of calcium carbonate. As with a true heterogeneous catalysis, recycling was possible, but, opposite heterogeneous catalysis, such a behavior could not permit a continuous process. These results also constitute a new demonstration that recycling is not appropriate proof of the heterogeneity of catalysis in liquid-phase oxidation.

If the copper(II) cation was efficiently bound to the solid, as in an iminodiacetic resin, then the reaction was not catalyzed by the solid. So, it seems probable now that the metal must be in solution in order to be active. This point, which requires more detailed studies of the homogeneous system, will be the matter of a subsequent publication.

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