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Mixed (Fe²⁺ and Cu²⁺) double metal hexacyanocobaltates as solid catalyst for the aerobic oxidation of oximes to carbonyl compounds

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ABSTRACT

Mixed Iron and copper hexacyanocolbatate was found to be a suitable heterogeneous and recoverable catalyst for the aerobic oxidation of oximes to the corresponding ketone. The reaction can be conveniently carried out in water-ethanol 1-1 mixture as solvent. The tinme-conversion plots shows the presence of an induction period that do not correspond to the leaching of metal ions or to the damage of the crystal structure of the material. The proposed reaction mechanism is based on the cooperation of the Lewis acidity of iron with the ability of copper to interact with oxygen. Given the remarkable stability of metal hexacyanocobaltates and the large diversity of metals that can contain, our reports opens the way for the general use of these affordable and accessible solids as heterogeneous catalysts.

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1. Introduction

Double metal cyanides have a crystal structure constituted by octahedral building units in which a divalent, trivalent or tetravalent transition metal is octahedrally coordinated by the C atom to six cyanide ligands. These hexacyanometallate building blocks are spatially arranged and held in the lattice by a second divalent transition metal cation that also coordinates octahedrally through the N atoms of the cyanide ligands of the building units [1]. Fig. 1 illustrates the porous structure of double metal cyanides and the cubic arrangement of their lattice where the larger pores can be formed by systematic vacancies for the building block. The crystal structures of double metal hexacyanide usually belong to the Fm3m and Pm3m space group where the metals linked to the N end of CN ligands are randomly distributed in their structural position to form solid solution [1a,1b,2].

Double metal cyanides are obtained through a simple synthetic procedure consisting in the precipitation of solutions of hexacyanometallate by addition of an aqueous solution of the appropriate mixture of divalent metals [2b,3]. Besides affordable starting materials, double metal cyanides show considerably versatility in the inner and outer metals, even allowing the presence of a third divalent metal cation in various proportions [3]. In addition, these solids can be prepared in multigram scale in scalable and reproducible manner. The main structural characteristic of double metal cyanides is that they have high content in two or more transition metals together with a high thermal and chemical stability [2c]. For this reason double metal cyanides are used as heterogeneous catalysis for the industrial ring epoxide aperture with alcohols leading to polyetherols [4]. However, double metal cyanides offer many other possibilities that still have to be realized [5]. Recently de Vos and coworkers have reported the use of these materials as solid catalyst for hydroaminacion of alkenes and alkynes [1c,6]. It was found that this reaction occurs exclusively on the external surface on the catalyst particles, since the pore opening of the cubic lattice (about 0.5 nm in Fig. 1) does not allow the internal diffusion of reagents. Nevertheless, high catalytic activities comparable or higher than those achieved by using other conventional solid catalyst were obtained [7].

Continuing with the exploitation of the opportunities that double metal cyanides offer as solid catalysts and considering that transition metals have excellent activity for oxidation reactions, in the present contribution we describe the use of metal hexacyanocobaltates for the aerobic oxidation of oximes to the corresponding carbonyl compounds. One topic with high industrial relevance in green chemistry is the use of molecular oxygen in combination with a catalyst to produce oxidation of organic substrates [7,8]. Classically, stoichiometric amounts of transition metal oxidation reagents have been used to perform oxidation of oximes and other organic compounds and although this type of reaction does not require catalysts, they generated a considerable amount of, frequently, toxic wastes. In contrast, oxidation with oxygen is characterized by high activation barriers and poor selectivity toward as single product. These two limitations can be overcome by using catalysts that should decrease the activation energies and direct the process toward a single product. Catalytic oxidative deoximation is a well-established method to obtain the corresponding

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Fig. 1. Crystal structure of double metal hexacyanocobaltate showing the lattice and the dimensions of cubic pores; the larger pores arise from vacancies in the framework.

ketone [9]. In the present case, we will show that mixed-metal, Cucontaining metal hexacyanocobaltates are stable and reusable solids promoting the oxidation of oximes by molecular oxygen.

2. Results and discussion

For the present study, we have prepared a series of twelve metal hexacyanocobaltates that were obtained by precipitation of a solution of hexacyanocobaltate and aqueous solution of a divalent metal (Mn²⁺, Co²⁺, Ni²⁺ and Cu²⁺) as well as mixtures of two of these divalent metals. The selection of these materials was made on purpose in order to have present in the solid hexacyanocobaltate ions that can provide the structural integrity and other two transition metal ions that can interact with oxygen and introduce Lewis acidity to bind hydroxylamine functionalities of the oximes. These two transition metals may also participate in other elementary steps occurring during oxidations such as decomposition of hydroperoxide intermediate and radical trapping. In the selection of the double metal hexacyanocobaltate, we have used previous information in the field of metal organic frameworks as catalysts that have shown that mixtures of cobalt and copper imidazolate MOFs are active and selective to perform the aerobic oxidation of tetrahydronaphthalene to the corresponding ol/one mixtures containing a minimal amount of the correspond hydroperoxide [10]. This information has shown that the efficiencies of catalyst containing two metals, such copper and cobalt, are the best performing materials. The list of the materials prepared and the most relevant physicochemical properties and infrared vibration wavenumber for v(CN)and δ (CoCN) [11] are summarized in Table 1 (see Figs. S1–S11 in

Table 1

Physicochemical properties and infrared vibration wavenumber for the twelve materials prepared.

Structural formula (X ^a)	BET surface area $(m^2 g^{-1})$	Pore volume (cm ³ g ⁻¹)	IR bands v (CN)/ δ (CoCN) (cm ⁻¹)
$Cu_3[Co(CN)_6]_2(5)$	773	0.32	2181/475
$MnCu_{2}[Co(CN)_{6}]_{2}(8)$	787	0.34	2171/465
$Ni_{1,3}Cu_{1,7}[Co(CN)_6]_2(8)$	808	0.36	2191/465
$FeCu_2[Co(CN)_6]_2$ (7.5)	782	0.33	2181/475
$Ni_3[Co(CN)_6]_2(7)$	834	0.36	2181/454
$Co_3[Co(CN)_6]_2(8)$	795	0.39	2171/450
Mn _{1.2} Fe _{1.8} [Co(CN) ₆] (8)	769	0.37	2173/462
Fe _{1.4} Ni _{1.6} [Co(CN) ₆] ₂ (7.5)	781	0.35	2170/454
$Mn_3[Co(CN)_6]_2(8)$	803	0.39	2171/454
$Co_{1.5}Ni_{1.5}(Co(CN)_6)_2$ (8)	811	0.38	2181/454
$Co_{1.4}Cu_{1.6}(Co(CN)_6)$ (8)	797	0.36	2181/465
$Fe_{1.4}Co_{1.6}(Co(CN)_6)_2$ (8)	783	0.40	2171/465

^a X: molecules of water present in the formula calculated with TG curves.



Fig. 2. Typical morphology of double metal cyanide microcrystals. The obtained powder is formed by small cubic crystals of about 1 μ m of size.



Fig. 3. HR-TEM image of Cu₃[Co(CN)₆]₂.

the Supporting Information for details). Figs. S12–S23 and S25–S36 in the Supporting Information provide a collection of XRD and thermogravimetric curves, respectively. In addition, representative SEM and HR-TEM images of double metal cyanides are shown in Figs. 2 and 3 in which the high crystallinity of these materials are observed. Fig. 4, on the other hand, presents an example of CO_2 adsorption isotherm indicating that double metal cyanides exhibit significant micro-/nanoporosity [1c].

In the initial stage of our work, we screened the catalytic activity of the series of metal hexacyanocobaltates for the oxidation of cyclohexanone oxime and oxygen at low pressure in a mixture of ethanol/water as solvent. The results showing the oxime conversion and cyclohexanone yield at final reaction times are presented in Table 2. Reaction times were screened from 1 to 30.5 h. From this preliminary screening, we can conclude that, in agreement with our initial hypothesis, those cobaltates containing Cu were the most efficient ones and, therefore, they were selected for additional studies.

Considering that the organic reaction takes place on the external surface due to the small pore size of double metal



Fig. 4. CO_2 adsorption isotherms for the mixed series $Co_{3-x}Ni_x[Co(CN)_6]_2$. Inset: the region of low coverage (low pressures) for the same isotherms. No significant modification for the pore volume is observed when solid solutions involving different metals are formed.

Table 2

Results of the cyclohexanone oxime oxidation by molecular oxygen in the presence of double metal hexacyanocobaltates as catalysts. Reaction conditions: Cyclohexanone oxime: 0.5 mmol, catalyst/substrate ratio: 5 mol%, solvent: 2 ml EtOH/H₂O 1:1, temperature: 100 °C, oxygen pressure: 5 bar.

Catalyst	Time (h)	Conv. (%)	Yield (%)
$Cu_3[Co(CN)_6]_2$	1	94	82
$MnCu_2[Co(CN)_6]_2$	2	55	42
Ni _{1.3} Cu _{1.7} [Co(CN) ₆] ₂	1	100	82 ^a
FeCu ₂ [Co(CN) ₆] ₂	2	96	77 ^a
$Ni_3[Co(CN)_6]_2$	30.5	20	28
$Co_3[Co(CN)_6]_2$	30.5	39	37
$Mn_{1,2}Fe_{1,8}[Co(CN)_6]_2$	23	38	30
$Fe_{1.4}Ni_{1.6}[Co(CN)_6]_2$	23	17	36
$Mn_3[Co(CN)_6]_2$	18	20	13
Co _{1.5} Ni _{1.5} (Co(CN) ₆) ₂	3	5	7
Co _{1.4} Cu _{1.6} (Co(CN) ₆) ₂	3	100	100
Fe _{1.4} Co _{1.6} (Co(CN) ₆) ₂	23	33	36

^a Formation of 1,1-diethoxycyclohexanone was observed.

hexacyanometallate [1c,2c] and that as a general observation in heterogeneous catalysis, the solvent should play a role in the process by reversible adsorption on the metal sites competing with the substrate modulating the reaction rate, several solvents were tested as reaction medium. In fact, as can be seen in Table 3 using $Cu_3[Co(CN)_6]_2$ as catalyst, cyclohexanone oxime conversion and ketone selectivity were lower when the reaction is carried out in toluene or in pure ethanol than in mixtures ethanol/water. Reaction times from 1 to 22 h were screened. It was found that a convenient reaction media is a mixture of ethanol/water in appropriate proportions 1:1.

After the initial screening, further work was pursued using acetophenone oxime as substrate, the mixture of ethanol–water 1:1 as a solvent and a series of hexacyanocobaltates at 5 mol% as catalysts. Also in these tests, almost complete conversions with high selectivity toward acetophenone were observed for Cu-containing hexacyanocobaltates. The results are presented in Table 4. Although hexacyanocolbatates exhibit high conversion at final reaction times, the temporal profile of the reaction was remarkably different depending on the catalyst. Thus, for the FeCu₂[Co(CN)₆]₂ catalyst, no induction period was observed, while, in contrast, for Ni_{1.3}Cu_{1.7}[Co(CN)₆]₂ and Co_{1.4}Cu_{1.6}[Co(CN)₆]₂ the reaction in the first hour occurred in a very low extent, indicating the existence of an induction period for the process. Fig. 5 shows the temporal profiles for acetophenone formation catalyzed by the set of Cu-containing hexacyanocobaltates.

Conversion of acetophenone oxime into acetophenone can also be carried out both with air and with pure oxygen. The reaction rate estimated using air was as 0.48 mmol h^{-1} . This reaction rate is essentially the same as that found for the same system in pure oxygen, indicating that the reaction is under their present conditions of zero order with respect to the oxygen pressure. However, at long reaction time, we noted that the final conversion of acetophenone oxime under air is lower (about 80%, 25 h) than for the reaction carried out under oxygen suggesting that the catalyst undergoes some deactivation when air is used.

In order to gain understanding on the origin of the induction period observed for some Cu-containing hexacyanocobaltate catalysts, we performed some additional experimental work. In the first control, the solvent was contacted with de catalyst under the experimental reaction conditions, but in the absence of acetophenone oxime and the liquid phase analyzed by ICP-OES for the presence of dissolved metal ions, while simultaneously the solid was submitted to ICP-OES analysis and X-ray diffraction. The results show that the solid catalyst maintains its crystal structure and chemical composition under these conditions and very low amounts of Cu or Co were found in the liquid phase (below 1% of metal content present in the solid catalyst). These measurements rule out the possibility that the induction period could be due to the leaching of metal ions from the solid to the solution or to the partial dissolution of the solid.

In a second experiment, the reaction was initiated under the typical reaction conditions but in the absence of acetophenone oxime and the substrate was added after 90 min and the mixture surveyed for conversion and selectivity. It was observed that under these conditions, an induction period similar to that shown in Fig. 5 takes place. Therefore, the induction period observed in the time-conversion plot for Ni_{1.3}Cu_{1.7}(Co(CN)₆)₂ and Co_{1.4}Cu_{1.6} (Co(CN)₆)₂ catalysts should reflect probably changes on the surface of the crystal, probably by coordination of the alcohol or by the interaction with molecular oxygen forming peroxo species. This surface conditioning would not take place or would be much faster in the case of FeCu₂[Co(CN)₆]₂ catalyst and for this reason this catalyst was selected for further studies.

Fig. 6 shows the time-conversion plot for the reaction of acetophenone oxime in the presence of $FeCu_2[Co(CN)_6]_2$ catalyst. The plot shows a pseudo first-order kinetics for the disappearance for the acetophenone oxime and that acetophenone is the only and stable product accounting completely for the disappearance of the starting material.

Fig. 7 shows, on the other hand, the kinetics of two consecutive reuses of the same $FeCu_2[Co(CN)_6]_2$ catalyst with an accumulated 9 h use of the solid. After one run, the solid catalyst was recovered by filtration, washed with pure ethanol and reused for a consecutive reaction without further treatment. As can be seen in Fig. 7, the temporal profiles of the fresh and reused catalyst differ at short reaction times, where an induction period of about 15 min was observed. However, the initial reaction rate after the induction period and final conversion of the fresh and first and second reuses are almost coincident, indicating the stability and recyclability of the $FeCu_2[Co(CN)_6]_2$ as catalyst. Since the appearance of the induction period could be a sign of deactivation, the catalyst was surveyed for crystallinity by XRD after its third consecutive use. The same diffraction pattern as the fresh material was recorded indicating the stability of the FeCu₂[Co(CN)₆]₂ material under the present reaction conditions (see Fig. S24 in the Supporting Information). Further understanding of the origin of the induction period is needed to rationalize its appearance upon reuse (vide supra for the data on the induction period).

Besides cyclohexanone and acetophenone oximes, the scope of the $FeCu_2[Co(CN)_6]_2$ catalyst activity was further expanded by using benzophenone and carvone oximes as substrates. It should

Table 3

Influence of the solvent on the performance of $Cu_3[Co(CN)_6]_2$ as catalyst. Reaction conditions: Cyclohexanone oxime: 0.5 mmol, solvent: 2 ml, temperature: 100 °C, oxygen pressure: 5 bar.

HO.N	O ₂ / solvent			
Entry	Catalyst (mol%)	Solvent time (h)	Conv. (%)	Yield (%)
1	10	Toluene 22	79	49
2	10	EtOH 5	48	31 ^a
3	5	EtOH/H ₂ O 1:1 ^b	94	82
4 ^c	5	H ₂ O/EtOH 1:1 ^d 21	46	35
5	5	H ₂ O/EtOH 1:1 6	74	59
6	5	EtOH/H ₂ O 1.5:0.5 2	82	63 ^a
7	3	H ₂ O/EtOH 1:1 16	76	62
8	3	EtOH/H ₂ O 1:1 23	70	55
9	1	EtOH/H ₂ O 1:1 28	48	43

^a Formation of 1,1-dietoxycyclohexanone was observed.

^b Ethanol was added before that water.

^c Air at 5 bar.

^d Water was added before Ethanol.

Table 4

Catalytic activity for the conversion of acetophenone oxime to acetophenone. Reaction conditions: Acetophenone oxime: 0.5 mmol, catalyst/substrate ratio: 5 mol%, solvent: EtOH/H₂O 1:1; 2 ml, temperature: 100 °C, oxygen pressure: 5 bar. Selectivity to acetophenone <99% in all cases.







Fig. 5. Time-yield plots for the oxidation of acetophenone oxime to acetophenone catalyzed by $FeCu_2[Co(CN)_6]_2(\times)$, $Co_{1.4}Cu_{1.6}[Co(CN)_6]_2(\blacktriangle)$, $Ni_{1.3}Cu_{1.7}[Co(CN)_6]_2(\blacklozenge)$, $Cu_3[Co(CN)_6]_2(\blacksquare)$, $FeCu_2[Co(CN)_6]_2(^*)$. Reaction conditions: Acetophenone oxime: 0.5 mmol, catalyst/substrate ratio: 5 mol%, solvent: 2 ml of EtOH/H₂O 1:1, temperature: 100 °C, oxygen pressure: 5 bar.

be noted that carvone is used in the fragrance industry and one of the commercial synthetic routes is based on deoximation of carvone oxime. In spite of the larger molecular dimension of these

Fig. 6. Time-percentage plot for the oxidation of acetophenone oxime by molecular oxygen using $\text{FeCu}_2[\text{Co}(\text{CN})_6]_2$ as catalyst. Conversion of acetophenone oxime (\blacklozenge); Yield of acetophenone (\blacksquare). Reaction conditions: Acetophenone oxime: 0.5 mmol, catalyst/substrate ratio: 5 mol%, solvent: 2 ml of EtOH/H₂O 1:1; temperature: 100 °C, oxygen pressure: 5 bar.

substrates also almost a full conversion to benzophenone and carvone were achieved indicating that $FeCu_2[Co(CN)_6]_2$ catalyst is also efficient for the oxidation of bulk aromatic oximes. This reactivity



Fig. 7. Time-yield plot for the consecutive runs using the same $\text{FeCu}_2[\text{Co}(\text{CN})_6]_2$ sample as catalyst; (a) first run: \blacklozenge ; (b) second run: \blacksquare ; (c) third run \blacktriangle . Reaction conditions: Acetophenone oxime: 0.25 mmol, catalyst/substrate ratio: 5 mol%, solvent: 1 ml of EtOH/H₂O 1:1; temperature: 100 °C, oxygen pressure: 5 bar.



Fig. 8. Time-yield plots for the oxidation of acetophenone oxime in the presence of hydroquinone 10 mol% (\times), ascorbic acid 10 mol% (\blacklozenge), benzoic acid 5 mol% (*), NaAcO 1 mol% (\blacktriangle) and without any additive (\blacksquare). Reaction conditions: Acetophenone oxime: 0.25 mmol, catalyst/substrate ratio: 5 mol%, solvent: EtOH/H₂O 1:1; 1 ml, temperature: 100 °C, oxygen pressure: 5 bar. Amount of additive: hydroquinone, 2.8 mg; ascorbic acid, 4.5 mg; benzoic acid, 3 mg; NaAcO, 0.4 mg.

of benzophenone and carvone oxime strongly suggests that the reaction take places exclusively on the external surface of the hexacyanocobaltates, since both oximes are absolutely excluded from intracrystalline diffusion.

Information about the reaction mechanism using $FeCu_2$ [Co(CN)₆]₂ as catalyst was obtained by performing acetophenone oxime oxidation in the presence of small percentages of radical

quenchers (hydroquinone and ascorbic acid), carboxylic acids (ascorbic and benzoic acid), and carboxylate anion (NaAcO). Fig. 8 shows time-conversion plots for the acetophenone oxime oxidation in the presence of these additives. Thus, it was found that the hydroquinone leads to the appearance of an induction period that can be interpreted as the time required to produce the oxidation of hydroquinone. According to this, the reaction mechanism is likely to involve some radical species that will be quenched by hydroquinone. The presence of carboxylic acids, on the other hand, increases the reaction rate, suggesting that protonation of acetophenone oxime or a possible intermediate accelerates the reaction. On the contrary, addition of acetate (1%) leads to a complete quenching of the reaction that can be interpreted as arising from the strong adsorption to the acetate on the Lewis acid sites of the catalyst.

We also considered that possibility that the mechanism involves partially acid-catalyzed hydrolysis of oxime, particularly taking into account that oxime conversion and ketone selectivity in the presence of water is higher than in pure ethanol and that acids increase the reaction rate. To address this issue, we performed controls using HCl (1 mol%) or H₂SO₄ (5 mol%) in ethanol/water mixtures under the same conditions as those indicated in Table 2. It was observed that using HCl or H₂SO₄ as Brönsted acid catalysts cyclohexanone conversion at 1 h reaction time was 8% and 24%, with ketone yields of 7% and 21%, respectively. These values contrast with the 94% oxime conversion and 82% cyclohexanone yield achieved under the same conditions with Cu₃[Co(CN)₆]₂ and indicate that the relative contribution of acid hydrolysis to deoximation should be relatively minor.

Considering the relative acidity of the Fe²⁺ with respect to Cu²⁺, the Fe²⁺ ion will be the most likely binding site for interaction with the oxime. Accordingly, Scheme 1 presents a mechanistic proposal to rationalize the catalytic activity of double metal hexacyanocobaltates as solid catalysts in the aerobic oxidation of oximes.

According to this proposal, the oxime will bind to the most acidic metal ion Fe^{2+} , while Cu^{2+} will interact with oxygen and the combination of these two metal sites adsorbing the oxime (Fe^{2+}) and the oxidizing reagent (Cu^{2+}) will result in the formation of the carbonyl compound by the oxidative cleavage of C=N. It could be that the corresponding oxazyridine could be the reaction intermediate. The role of the internal hexacyanocobaltate units in this mechanism will be just structural, maintaining the crystallinity of the material. In agreement with our proposal, other double



Scheme 1. Proposed mechanism for the aerobic oxidation of oximes to carboxylic compound in the presence of mixed double metal cyanides.

metal hexacyanocobaltates less efficient to interact with the oxime will exhibit lower catalytic activity and the solid containing exclusively copper ions will also be almost inactive due to the low affinity to bind the oxime. However, on the other hand, the ability of Cu^{2+} ions to bind molecular O_2 will be reflected in the need for this transition metal to have a high active catalyst.

3. Conclusions

The present study constitutes one of the few examples illustrating the remarkable catalytic activity of (mixed) double metal hexacyanocobaltates to promote oxidations with molecular oxygen. Due to the narrow pore size, only the external surface of the solid crystallites will be catalytically relevant. The potential of these solid hexacyanocobaltates in heterogeneous catalysis is demonstrated by the proposed reaction mechanism that is based on the cooperation of two different metal sites to interact one preferentially with the oxime and the other preferentially with molecular oxygen. Also, we propose that the presence of functional groups on the substrate able to bind with the external double metal hexacyanides ions such as OH groups is a necessary prerequisite for a substrate to undergo a catalytic reaction in the presence of these solids. Considering the easy synthesis of (mixed) double metal hexacyanocobaltates and the large variety of transition metals that can be incorporated in a wide range of proportions as well as the interest in the developing oxidations using molecular oxygen, our report opens the way for the general use of this type of materials in aerobic oxidations of appropriate organic compounds.

4. Experimental

4.1. Materials and apparatus

The nature of the hexacyanocobaltates (III) was corroborated by their IR spectra. The atomic metal ratio (T:Co) was estimated by energy dispersive X-ray spectroscopy (EDS) analyses and the expected formula unit, $T_x^A T_{3-x}^B$ [Co(CN)₆]₂ × H₂O was established. The hydration degree (*x*) was calculated from thermogravimetric (TG) curves.

The structural characterization was carried out from X-ray diffraction (XRD) data (see Supporting Informations for the patterns Figs. S12–24).

IR spectra were recorded in an FT-IR spectrophotometer Nicolet 710. XRD powder patterns were obtained with Cu K α radiation in an HZG-4 diffractometer (from Carl Zeiss) and their evaluation carried out using Dicvol program [12].

TG curves were analyzed in a METTLER TOLEDO TGA/SDTA851 and the specific surface area and porosity of the materials under study was in a Micromeritics ASAP 2010 by N_2 at 77 K after exhaustive outgassing until constant weight.

Elemental analyses of metals in the liquid phase were performed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) in a Varian 715-ES, after solid dissolution in HNO₃/HCl/HF aqueous solution. Gas chromatography (GC) was performed using He as carrier gas with a Varian 3900 apparatus equipped with an TRB-5MS column (5% phenyl, 95% polymethylsiloxane, 30 m, 0.25 mm \times 0.25 µm, Teknokroma). GC/MS analyses were performed on an Agilent spectrometer equipped with the same column as the GC and operated under the same conditions.

4.2. Catalyst preparation

The materials under study were prepared mixing aqueous solutions (0.05 M) of $K_3[Co(CN)_6]$ and of sulfate (0.063 M) of the

involved metals (Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺ y Cu²⁺). The resulting precipitates were aged for 24 h within the mother liquor, followed by its separation by centrifugation. The solid fraction was repeatedly washed with distilled water to remove all the accompanying ions and then air-dried until constant weight.

The crystal structure, thermal stability, and information on the electronic structure for the materials under consideration are available from previous studies [2c,13] and XRD powder patterns and TG curves of the studied samples are provided in the Supporting Information Figs. S12–S36.

4.3. Catalytic experiments

Catalytic experiments were performed in reinforced glass semi continuous reactors equipped with temperature and pressure controllers. For each reaction, a 2-ml mixture of reactants and solvent was placed into the reactor (3 ml capacity) together with appropriate amount of catalyst.

The reaction conditions for acid (HCl or H_2SO_4)-catalyzed hydrolysis of cyclohexanone oxime (0..5 mmol) employed a catalyst (HCl or H_2SO_4)/substrate ratio: 1 or 5 mol%, respectively, in 2 ml EtOH/ H_2O 1:1 as solvent at 100 °C under 5 bar oxygen pressure.

In the cases in which no water was used as a solvent, conversion and yields were estimated using dodecane as internal standard. After sealing the reactor, air was purged by filling the reactor with oxygen (5 bar) and pumping out three times before final pressurization of the reactor with O_2 or air at 5 bar. The reactor was deeply introduced into a stirring and temperature controller that was preheated at the reaction temperature. During the experiment, the pressure was maintained constant and the reaction mixture was magnetically stirred at 1200 rpm. Aliquots were taken from the reactor at different reaction times. Once the catalyst particles were removed from the solution by centrifuging at 8000 rpm the sample were analyzed by GC. The products were identified by GC-MS and also by comparing their retention time with that of commercial pure samples when available. When mixtures of water-ethanol were used as a solvent, quantification was performed adding a known weight of dodecane as external standard to aliquots of the reaction mixtures diluted in ethanol. Only experiments with mass balances further than 95% were considered.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2013.12.011.

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