Catalytic Activity and Magnetic Properties of Co-ZSM-5 zeolites prepared by different methods

Liliana B. Pierella[1,3*], Clara Saux[1,3], Silvana C. Caglieri[1], Héctor R. Bertorello[2,3] and Paula G. Bercoff [2,3]

[1] *Grupo Zeolitas - CITeQ (Centro de Investigación y Tecnología Química), Facultad Córdoba, Universidad Tecnológica Nacional. Córdoba-Argentina.*

Email: lpierella@scdt.frc.utn.edu.ar

[2] *Facultad de Matemática, Astronomía y Física, Universidad Nacional de Córdoba. Córdoba-Argentina.*

[3] *Conicet (Consejo Nacional de Investigaciones Científicas y Técnicas), Argentina.*

Abstract

The selective catalytic oxidation of styrene with hydrogen peroxide was studied over Co-ZSM-5 catalysts which differ in the preparation methods. The catalysts were obtained from NH_4^+-ZSM-5 by wetness impregnation and ion-exchange techniques followed by different post-thermal treatments: oxidation and reduction. The characterization of acidic properties by FTIR of adsorbed pyridine revealed that new and strong Lewis sites (1452 cm^{-1}), different from those characteristics of aluminum in the matrix (1456 cm^{-1}) were generated by cobalt introduction. Styrene conversion shows an important increment over the exchanged samples as compared to the impregnated ones. This behavior may be explained by the high Lewis acid sites concentration. Benzaldehyde was the main product in all the samples under study. The samples' magnetic properties were improved with the cobalt incorporation and the applied thermal treatments. The catalytic and magnetic properties of Co-ZSM-5 samples are discussed.

Keywords: Co-ZSM-5; Lewis and Brönsted acidity; Styrene oxidation; Magnetic Properties

*****To whom correspondence should be addressed

1. Introduction

Metal containing zeolites have been used as catalysts for a wide range of chemical reactions, such as hydrogenation, oxidation, isomerization and cracking of various feed stocks [1-6]. In particular, transition metal ion-containing molecular sieves are extensively investigated in academic and industrial laboratories taking into account their promising catalytic behavior in the removal of NO_x and in the oxidation of organic compounds under mild conditions [7, 8].

Catalytic selective oxidation is widely employed in the manufacture of bulk chemicals from aromatics and more recently, as an environmentally attractive method for the production of fine chemicals. The catalytic epoxidation of olefins has been a subject of growing interest in the production of chemicals and fine chemicals, since epoxides are the key starting materials for a wide variety of products [9]. So, the development of effective catalysts for these reactions is an important, but difficult task in catalysis. Despite the success in homogeneous catalysis, there is a clear demand for solid materials that catalyze the epoxidations with easily available oxidants such as molecular oxygen or H_2O_2 [10]. Styrene oxidation at side chains is of considerable interest for academic research and utilization in the industry [11].

From an ecological standpoint, the exclusion of pollutants from unselective preparation methods is always preferable to subsequent treatment. In this context, the goal of modern organic synthesis is to develop efficient catalytic methods that can produce compounds with atom economy and environmental advantages. Considering oxidation reactions with oxygen donors, one of the preferred methods involves using technology based on catalytic oxygen transfer from *clean* oxygen donors, such as hydrogen peroxide. This choice is motivated by its ease of handling and high active oxygen content, as well as the fact that water is the sole by-product [12].

Cobalt-containing zeolites have drawn a great deal of attention in recent years. These materials may contain at least two different kinds of cobalt species in cationic ion-exchange positions in ZSM-5 and cobalt oxide particles [13] in the zeolite channels or over the external surface of the zeolite microcrystals when the samples are heated in an oxidant atmosphere. These cobalt species may exhibit different catalytic [14-17] and magnetic [18] properties.

Micro and/or nanosized Co particles and/or species in the zeolite would have different effects on the electronic, optical and magnetic properties. Magnetic nanoparticles can be widely used in many important areas of high technology such as ferrofluids, catalysts, ultra-high-density magnetic storage media, biomedical and medical treatments and analyses, high-frequency soft magnetic materials, microwave absorbing materials, etc. and are currently attracting much attention [19]. In previous articles we presented novel results of similar Co-materials where a complete characterization study was done and their magnetic behavior was evaluated [18, 20].

In the present paper, we compare Co-ZSM-5 materials prepared via different routes, which are similar in their cobalt content but markedly differ in their acidity, catalytic activity and magnetic behavior. The effect of the different cobalt incorporation methods and the post-activation process on the matrix is analyzed. We then correlate this effect with the catalytic activity in the selective styrene oxidation and the magnetic properties of the samples.

2. Experimental

2.1 Catalysts preparation

ZSM-5 zeolite (Si/Al=17) was obtained by hydrothermal crystallization in the Na_2O-Al_2O_3-SiO_2 system, using TPAOH (Tetrapropylammonium Hydroxide) as a structure directing agent by known methods [21]. The obtained gel reached a pH > 9 and was maintained at 120-160 °C for 10-12 days under self-generated pressure on autoclave. Afterwards, the reaction product was extracted, washed and dried at 110 °C for 12 h. The structure directing agent (TPA) was desorbed in N_2 atmosphere (20 ml/min) at programmed temperature (10 °C/min) from room temperature to 500 °C and then it was calcined in air at 500 °C for 12 h to obtain Na-HZSM-5.

The NH_4^+-form of the catalyst was prepared by ion-exchange of Na-zeolite with NH_4Cl (1 M) for 40 h at 80ºC. In order to obtain H-ZSM-5 the ammonium form was desorbed for 16 h in N_2 (10 ml/min) at 500ºC and later calcined in air at 500ºC for 8 h.

Cobalt containing zeolites were prepared following the next procedures:

a) By ion-exchange (samples denoted E) of NH_4- ZSM-5 with $CoCl_2.6H_2O$ 0.5 M aqueous solution at 80 ºC for 24 h.

b) By wetness impregnation (samples denoted I) of NH_4- ZSM-5, which was suspended in a solution of $CoCl_2.6H_2O$ with known concentration in the least amount of distilled water. The water was evaporated using a rotator–evaporator at 80°C under vacuum until complete dryness.

Afterwards, samples E and I were dried at 110 °C and desorbed in N_2 flow at 500 ºC for 12 h, followed by calcination in air at 500 ºC for 8 h to obtain Co-ZSM-5 oxidized samples (EO and IO).

In order to carry out a complete study, calcined Co-samples were reduced from room temperature to 500 ºC at 5 ºC/min and holding at 500 °C for 5 h in 10 ml/min of H_2 flow, to obtain Co-ZSM-5 reduced samples (ER and IR).

2.2 Catalysts characterization

The cobalt effective percentage of all the samples under study was determined by Atomic Absorption in a Perkin Elmer AAnalyst 800 spectrometer after the digestion of the samples by microwave in a Milestone ETHOS 900 digester.

BET surface area determinations were carried out with an ASAP 2000 equipment.

Infrared measurements of H-zeolites and Co-zeolites were performed on a JASCO 5300 FTIR spectrometer. The samples were pressed into self-supporting wafers (8-10 mg/cm^2). Spectral scanning was done from 4600 to 400 cm^{-1} in 16 consecutive registers of 4 cm^{-1} resolution each one. In order to evaluate the OH$^-$ groups absorption zone, the wafers were heated at 400 ºC in vacuum (10^{-4} Torr) for 6 h. Afterwards, in order to determine the concentration of Lewis and Brönsted acidic sites, pyridine (Py) (3 Torr) was adsorbed at room temperature for 12 h and desorbed for an hour at 250, 350 and 400 ºC at 10^{-4} Torr. The experiments were carried out using a thermostatized cell with CaF_2 windows connected to a vacuum line. The numbers of Brönsted and Lewis acid sites were calculated from the maximum intensity of the adsorption bands at 1545 cm^{-1} and 1450-1460 cm^{-1}, respectively, and then quantified using the literature data of the integrated molar extinction coefficients [22], which are independent of-the catalysts or strength of the sites. The FTIR spectra in the lattice vibration region (400-1800 cm^{-1}) were performed using KBr 0.05% wafer technique.

Temperature programmed reduction (TPR) experiments were performed on an Okhura TP 2002 S instrument equipped with a TCD detector. The reducing gas system was 5% H_2 on Ar, at 30 ml/min and a heating rate of 10 ºC/min from room temperature to 900 ºC was used.

2.3 Catalytic activity

Catalytic partial oxidation of styrene (99.5 % Fluka) with H_2O_2 (aqueous solution 30 wt%) as oxidant agent was carried out in a glass flask reactor (25 cm^3) with magnetic stirring immersed in a thermostatized bath, equipped with a reflux condenser. The catalytic tests were performed at 60°C using 0.2 g of the catalyst and three molar ratios of styrene/hydrogen peroxide (R= 0.9, 1.7 and 3). Several solvents with different dielectric constants were tested for the reaction: acetonitrile (99.5 % Cicarelli), acetone (analytical grade, Aldrich), ethyl methyl ketone (analytical grade, Aldrich) and secbutyl alcohol (99.5%, Merck). The reaction was monitored by taking aliquots of the reaction mixture at different reaction times. Prior to analysis, the catalyst was separated by filtration. Organic compounds were analyzed quantitatively by gas chromatography (Hewlett Packard HP-5890) with a Methyl Silicone capillary column (30m x 0.32 mm id) and a flame ionization detector (FID), and qualitatively, by mass spectrometry GC- Mass (Shimadzu QP 5050 GC-17 A), using a HP-S (25 m x 0.2 mm i.d) capillary column. The substrate conversion was measured as a function of reaction time and the values observed are reported as mol %. It is to be noted here that no leaching of cobalt was observed in randomly selected catalytic runs by analyzing the reaction solution.

2.4 Magnetic Measurements

Magnetic measurements were performed on the samples at room temperature using a Vibrating Sample Magnetometer Lakeshore 7300 which can reach a maximum magnetic field of 15 000 Oe. The powders were shaped into disks of 6 mm diameter and 1 mm height using an organic binder and compacted with the aid of a uniaxial press. Magnetization (M) as function of the applied field (H) was measured from H= -15 000 Oe to H= 15 000 Oe.

3. Results and Discussion

The analyses performed by Atomic Absorption revealed that a 0.63 Co wt% was effectively incorporated in sample I and a 0.64 Co wt% in sample E. XRD and FTIR on the fingerprint zone results (not shown here) presented 98% and 97% of crystallinity for both cobalt samples, respectively. Structure MFI and orthorhombic symmetry were confirmed. According with BET results the ZSM-5 zeolite showed a 382 m^2/g of surface area. It is noticeable that surface areas of the catalysts in this study did not significantly change after the various pretreatments.

The IR spectra on the OH^- absorption zone (3800-3500 cm^{-1}) of the parent H-ZSM-5 zeolite and the Co-ZSM-5 catalysts (samples EC, ER, IC and IR) are compared in Figure 1. The spectrum of the parent H-ZSM-5 zeolite shows the following bands: 3730 cm^{-1}, assigned to the O-H stretching vibrations of terminal silanols groups [23] (located on the external surface and weakly acidic) and the band at 3610 cm^{-1} attributed to strong Brönsted acid sites Si-(OH)-Al [24, 25]. Although the peak at 3610 cm^{-1} can also be seen in the spectra of Cobalt-samples, its intensity is greatly reduced, especially in the case of exchanged samples (~ 76%). This result suggests that the Co^{2+} ions are mainly located at the bridging oxygen of Si-OH-Al groups. Also the band of the silanols groups - absorbing at 3730 cm^{-1}- is lowered, suggesting that some cobalt may stay at the external surface [26]. These cations at exchange positions are balancing the negative charge of AlO_4^- tetrahedra, wich is facilitated by the fact that in a zeolite of Si/Al= 17, distances between AlO_4^- tetrahedra are relatively short, so divalent Co^{2+} ions may be neutralized by two neighbouring tetrahedra [27]. In the case of impregnated samples, the band at 3610 cm^{-1} is also reduced in intensity (~ 31%), as compared to the Co-free sample, but not when compared to the exchanged ones. According to Góra-

Marek et al. [27], this result suggests that some Co ions do not neutralize negative framework charge of the Si-OH-Al, but have their own anions (probably in the form of CoO and "oxide-type clusters").

Figure 1

Pyridine adsorption over acid materials is a common technique to characterize the acid sites nature and strength by FTIR spectroscopy based on the observation of the vibrational perturbation that is undergone when this kind of probe-molecules adsorb on them [28]. Acid strength of the sites is determined according to the ability to retain pyridine as temperature is increased. Pyridine was adsorbed at room temperature over the samples and desorbed at 250, 350 and 400°C under vacuum for an hour.

IR spectra of pyridine adsorbed on H-ZSM-5 and Co-ZSM-5 (both samples E and I) and desorbed at 400 ºC and 10^{-4} Torr for an hour are shown in Figure 2. Bands at 1452-1456 cm^{-1} (? 19B mode) and 1612 cm^{-1} (? 8A mode), corresponding to pyridine ~~Py~~ interaction with Lewis acid sites (L-Py) could be observed, as well as bands at 1547 cm^{-1}(? 19B mode) and a shoulder at 1635 cm^{-1} (? 8A mode), indicative of the interaction with Brönsted acid sites (PyH^+) [28]. The band at 1490-1495 cm^{-1} corresponds to the vibration of adsorbed pyridine over both Brönsted and Lewis acid sites [29, 30]. Bands corresponding to hydrogen-bonded pyridine (1440-1447 cm^{-1} and 1580-1600 cm^{-1}) and physically adsorbed pyridine (1439 and 1580 cm^{-1}) [31] are not present since the spectra shown were taken after desorption at 400 ºC.

Figure 2

H-ZSM-5 spectrum presents an important signal of Brönsted sites and some L-Py resulting from Al^{3+}. The introduction of Co, especially in the case of exchanged samples, caused a decrease in the intensity of the Brönsted sites band (1547 cm^{-1}), in accordance with the results obtained for the OH absorption zone (Figure 1), confirming that some of the zeolite protons are consumed during the exchange process [32]. The formation of a new, strong Electron-Donor-Acceptor (EDA) adduct of Pyridine-Lewis sites at 1452 cm^{-1} is clear, probably due to an interaction between a Co unoccupied molecular orbital and the probe molecule, different from the well-known Lewis Aluminium sites of the zeolite framework (1456 cm^{-1}). This shift of the band to lower wavenumbers upon introduction of cobalt is indicative of the weakness of the surface acid site [33, 34].

Upon cobalt introduction, the Brönsted to Lewis ratio is significantly reduced (6.41 for H-ZSM-5, 1.03 for IO and 0.63 for EO). This arises not so much from a disappearance of Brönsted acidity but predominantly from a strong enhancement of the L-Py band [33]. The fact that the concentration of Py over Brönsted sites did not substantially change for impregnated samples indicates that a part of Co had its own anion, which agrees with the conclusion drawn by comparing the intensities of Si-OH-Al groups. This conclusion does also agree with the earlier results of Góra-Marek et al. [27] who did also find that in CoZSM-5 zeolite an important amount of Co was not at exchange positions.

When reduction treatments were applied to the exchanged and impregnated samples (ER and IR), the number of total acidic sites decreased from 0.0445 mmol Py/mg to 0.0312 mmol Py/mg in the exchanged samples and from 0.0424 mmol Py/mg to 0.0329 mmol Py/mg in the case of the impregnated ones. According with the results obtained from TPR analyses, which are presented in Figure 3, cobalt oxide species in oxidized samples (EO and IO) would be reduced during the reduction treatment to Co^0. So, the decrease of the total density of acid sites (the sum of total Brönsted and Lewis acid sites) may be due to a "blocking" effect of metallic cobalt over the acid sites.

An interesting way to discriminate between Lewis sites ought to framework aluminium and those due to cobalt species is to study the 1630-1610 cm^{-1} zone. The assignment of the band at 1624 cm^{-1} is controversial. Buzzoni *et al.* [35] and Schwidder *et al.* [33] assigned it to Brönsted acidity in zeolites, whereas Busca et al. [28] and Mohamed et al. [34] attributed it to Lewis acid sites. According with our results we consider this band as Al^{3+} Lewis sites. When cobalt is incorporated this band turns secondary and a new one appears at a lower wavenumber (1612 cm^{-1}), particularly in exchanged samples. The new signal becomes more intense as cobalt content is increased in the samples [36] confirming the assignment of the band to the presence of new Lewis acid sites from cobalt ions in the channels of the zeolite and to Co oxide clusters [20, 37], since the intensity of the signal is diminished for the reduced samples (ER and IR).

H_2-TPR profiles of oxidized catalysts are shown in Figure 3. Even when no cobalt-species peaks were detected by XRD, Co oxide reduction signals are clearly visible, indicating the fine dispersion of cobalt oxides with mean particle size that must be smaller than 4 nm [38-40]. There are two regions in the TPR profiles. The first region between 300-550 ºC consists of two peaks, one at lower temperature due to Co oxo-ions and the other to very finely dispersed Co_3O_4. It is possible that reduction of Co_3O_4 clusters results in CoO as a primary product, which is then further reduced to Co^0. The second TPR region, with a peak around 850 ºC indicates reduction of isolated Co^{2+} ions in exchange positions [39, 41].

Figure 3

This results are in accordance with those obtained by FTIR, since Co^{2+} in exchange positions is confirmed by the presence of the last reduction peak in the TPR profiles and in the important decrease in intensity of Brönsted sites bands (3610 cm^{-1} in the OH absorption zone and 1547 cm^{-1} in the Py absorbed analysis). The presence of Co oxide species also confirms that part of the Co incorporated in the samples is not in exchanged positions but is present as clusters of some Co oxide, which are also the responsible for the generation of new Lewis acid sites (1612 cm^{-1}).

The materials so far characterized from their structural characteristics and acidic properties were then used as catalysts for styrene selective oxidation, as model reaction, to evaluate their catalytic efficiency. The catalytic reactions were carried out varying time, styrene to H_2O_2 molar ratio and using various solvents over the samples under study (EO, ER, IO and IR). Induction period of *ca.* 1 h in Figures 4-6 plots suggests that either formation of the reactive intermediate takes longer time itself or intermediate formed takes longer time to transfer oxygen to the substrate.

The effect of hydrogen peroxide concentration on the oxidation of styrene is illustrated in Figure 4, at a temperature of 60 ºC, 7 h of reaction time, acetonitrile as solvent and 0.2 g of catalyst. The results show an improvement of the styrene conversion from 18.5 mol% to 26.7 mol% when styrene/H_2O_2 molar ratio decreases from 3 to 1.7 over ion-exchanged calcined Co-ZSM-5 (EO), but finally a decreasing trend is observed at R= 0.9. The reason for the decreasing trend may be due to dilution of the reaction mixture by the presence of larger amount of water molecules in H_2O_2 solution [42]. In the presence of water, the Lewis acid sites of the catalyst are expected to be blocked by the strongly adsorbed water molecules, which may also hinder the performance of the catalyst for the styrene conversion [43, 44]. Thus, it is clear that the 1.7 molar ratio is the best one to obtain the optimum styrene conversion of 26.7% in 7 h reaction time.

Figure 4

The results of styrene conversion over EO, ER, IO and IR at R= 1.7 are given in Figure 5. The catalysts were apparently active for the reaction with benzaldehyde as the main product (Table 1), even though others could still be found, such as styrene oxide, phenylacetaldehyde, 1-phenyl, 1,2-ethanediol and benzoic acid. According to the results shown in Figure 5, styrene conversion exhibits an important increment over the exchanged Co-ZSM-5 samples when compared to the impregnated ones, at constant molar ratio (R=1.7). This behavior may be explained by the greater Lewis acidity of the cobalt ion-exchanged samples than that of the impregnated ones. These results allow us to consider Lewis acid sites as the catalyst's active sites for this reaction. On the other hand, a better catalytic activity is observed in the calcined catalysts when comparing to the reduced ones. This behavior may be explained by the smaller Brönsted/Lewis ratio of the cobalt oxidized samples (Table 1).

Figure 5

Table 1

The nature of the solvent has an important effect on the outcome of the reaction so its choice has a crucial effect on the activity [45, 46]. In order to investigate the solvent effect in the styrene oxidation, we have used both aprotic and protic solvents such as: acetonitrile, acetone, ethyl methyl ketone and secbutyl alcohol. Table 2 reports the principal properties of the solvents used.

Table 2

Figure 6

The results reported in Figure 6 indicate an increment of styrene conversion with aprotic solvents. This behavior may be explained by the increase of substrate concentration over Co-ZSM-5 surface, as the polarity of the solvent increases. Indeed, the higher the solvent polarity, the higher the concentration of the substrate in the vicinity of the active sites and the higher the styrene conversion will be, as indicated by the experimental results. The hydrophilic character of Co-ZSM-5 would act forming stable complexes between alcohols (as solvents) with active sites in detriment of organic substrate adsorption over the surface of the zeolite, decreasing the activity for the reaction. New Brönsted acid sites could be generated by the adsorption of protic molecules over Lewis acid sites of the Co-HZSM-5 samples [47]. Acetonitrile (aprotic solvent with the highest dielectric constant) reveals to be the best solvent in terms of activity for the reaction [48]. This behavior could be associated with the poisoning of Brönsted acid sites by the basic acetonitrile molecules.

It has been confirmed that no leaching of Co^{2+} from Co-ZSM-5 samples occurs during the reaction. The cobalt content in the sample after several reaction cycles did not change, and cobalt could not be detected in the filtrate after the reaction. No significant conversion of styrene was observed when the liquid filtrate was used instead of the solid catalyst for further reaction. Furthermore, the repeated use of the catalysts did not show any decrease in the catalytic activity. These observations strongly suggest that the reaction proceeds heterogeneously over the catalyst.

The magnetic behavior of the ZSM-5 zeolite matrix (previous to cobalt incorporation) and the cobalt incorporated samples are quite different. The ZSM-5 matrix behavior is clearly diamagnetic with a susceptibility of $\chi = -1.06 \times 10^{-6}$ emu/g Oe (see Figure 7), in agreement with other authors' results [49, 50]. The values of magnetizacion *M* are very low, as expected for this type of material, reaching a maximum value of 1.6×10^{-2} emu/g with the maximum applied field of 15 000 Oe.

Figure 7

The *M* vs *H* curves for samples IO and IR are shown in Figure 8 and the corresponding ones for samples EO and ER are shown in Figure 9. The units of magnetization are emu per gram of cobalt, since it is Co the only possible source of a para/ferromagnetic signal.

Figure 8

Figure 9

In every case a hysteresis loop is obtained, with coercivities around 300 Oe, indicating a ferromagnetic contribution. The results also show a paramagnetic contribution, since the curves do not saturate. Samples IO and IR have the same susceptibility of 1.6×10^{-4} emu/gCo Oe and the exchanged samples have lower values (1.2×10^{-4} emu/gCo Oe for EO and 0.7×10^{-4} emu/gCo Oe for ER). The diamagnetic matrix has a two orders of magnitude lower susceptibility and does not add significantly to the total χ.

Substracting the paramagnetic contribution from the hysteresis loops evidences more clearly the ferromagnetic behaviors. This is shown in Figure 10, where it is possible to observe that the calcined samples (IO and EO) have a lower ferromagnetic content than the reduced samples (IR and ER). The larger magnetic signal in the reduced samples is mainly due to the presence of fine particles of metallic Co [20] while in the calcined samples the ferromagnetic contribution is due to the presence of Co_3O_4 which was detected by TPR analysis (Figure 3) and confirmed with FTIR of pyridine adsorbed results, since the number of Lewis acid sites from Co oxide clusters diminished after reduction in H_2 (Figure 2).

Figure 10

The paramagnetic contribution cannot be accounted for by only isolated Co ions, and some contribution from small Co clusters has to be invoked. This type of behavior has already been seen in a similar zeolite with higher Co content [18]. In that system, small clusters of approximately 20 Co ions were the responsible for the observed magnetic behavior as a function of temperature.

Figure 11 shows a summary of the results obtained from catalytic activity, magnetic properties and acid characteristics of the materials under study. It is clear that sample EO presents the best catalytic activity, since Lewis acid site concentration (owed to Co^{2+} ions in the channels of the zeolite and to Co oxide clusters) is the highest of the group. The catalytic activity of the samples under study is enhanced with the number of Lewis acidic sites, but decreases as Brönsted acidity is increased. This conjugated effect is clear when analysing sample IO. Even when Lewis acidity is higher than in sample ER, Brönsted acidity is also higher, resulting in a less active catalyst. This negative effect from Brönsted acidity is confirmed by the solvents study, where acetonitrile resulted as the best one. It was associated with the poisoning of Brönsted acid sites by the basic acetonitrile molecules.

Figure 11

Cobalt cation incorporation by ion exchange seems to be better than by wet impregnation, from styrene conversion and higher magnetization values. According to previous results for impregnated samples with higher cobalt content [20], wet impregnation mainly generates Co_3O_4 over the matrix, while ion exchange favours the incorporation of cobalt cations at exchanged positions.

Reduction post-treatment improves the magnetic behavior due to the presence of Co^0, but does not benefit the catalytic properties of the material for the studied reaction, since the number of Lewis sites from cobalt oxide species decreased.

4. Conclusions

Co-containing molecular sieve with MFI structure was synthesized by the hydrothermal crystallization method and cobalt was incorporated in it by ion exchange or wet impregnation techniques. Thermal post-treatments were applied to Co-ZSM-5: calcination and reduction.

According with de FTIR results, we can conclude that after modification of the zeolite by cobalt, a major part of Co^{2+} ions were exchanged with strongly acidic sites (3610 cm^{-1} IR band) but others formed their own anions in the form of oxide-type clusters, especially in the case of IO sample. New and stronger Lewis acidic sites were created after cobalt loading since pyridine was retained after desorption at 400 ºC [51].

The exchanged and oxidized sample (EO) presented the highest Lewis acid sites concentration. This result is in accordance with the highest activity for the selective styrene oxidation. No evidence of the Brönsted acidity importance for catalyzing the reaction was found. What is more, a formal inverse correlation was discovered. In all the cases, benzaldehyde was the principal product of the reaction. The study with different styrene/ H_2O_2 molar ratios revealed that the best results were obtained at R=1.7, a major concentration of H_2O_2 in the reaction system increased the presence of water molecules in H_2O_2 solution, which favours the blocking of Lewis sites by the water molecules decreasing styrene conversion.

The magnetic behavior of the materials was evaluated varying the applied magnetic field at room temperature. The ZSM-5 matrix showed a diamagnetic behavior. When cobalt was incorporated, a hysteresis loop was obtained, indicating a ferromagnetic contribution. The results also showed a paramagnetic contribution, since the curves did not saturate. The larger magnetic signal in the reduced samples was due to the presence of fine particles of metallic Co while in the calcined samples the ferromagnetic contribution was due to Co_3O_4. TPR results confirmed the presence of cobalt-oxide species on samples EO and IO which are reduced to Co^0 during the post-thermal reduction treatment applied (samples ER and IR).

Analyzing each of the cobalt incorporation techniques to the zeolitic matrix, an improvement on the catalytic behaviour for styrene selective oxidation as Brönsted / Lewis ratio decrease is observed while the magnetic behaviour is disfavored. Since vibrating sample magnetometry is a fast, easy and not expensive characterization techique, we believe that a magnetic/catalytic correlation is useful as a first step for selecting possible materials with a good catalytic performance.

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Figures captions

Figure 1: FTIR spectra in the region of OH groups of Co-ZSM-5 (EO, ER, IO and IR) and the parent H-ZSM-5zeolite after evacuation at 400ºC and 10^{-4} Torr for 6 h

Figure 2: FTIR spectra of pyridine adsorbed on Co-ZSM-5 (EO, ER, IO and IR) and the parent H-ZSM-5zeolite after evacuation at 400ºC and 10^{-4} Torr for 1 h

Figure 3: H_2-TPR profiles of oxidized Co-ZSM-5 prepared by different methods (EO and IO)

Figure 4: Effect of styrene:H_2O_2 molar ratio (R) on styrene oxidation over Co-ZSM-5 (EO) at 60 ºC using acetonitrile as solvent

Figure 5: Catalytic activity of EO, ER, IO and IR Co-ZSM-5 samples for the oxidation of styrene at 60 ºC using acetonitrile as solvent at R= 1.7

Figure 6: Influence of solvent on the catalytic activity for the styrene oxidation using Co-ZSM-5 (EO) as catalyst at 60 ºC and R= 1.7

Figure 7: Magnetization as a function of applied field for H-ZSM-5. The negative slope is inherent to diamagnetic materials

Figure 8: Hysteresis loops for samples IO and IR

Figure 9: Hysteresis loops for samples EO and ER

Figure 10: Ferromagnetic contribution of all the studied samples, obtained by substracting the paramagnetic contribution to the measured loops

Figure 11: Correlation between Catalytic, Acidic and Magnetic properties of Co-ZSM-5 samples (EO, ER, IO and IR)

Table 1: Catalytic activity and acidic characteristics of the samples

Samples[*]	Conv.[a]	S_{Benz}[a]	Brönsted[b]	Lewis[b]	Total [b]	B/L[c]
EO	26.7	89.4	0.0172	0.0273	0.0445	0.629
ER	23.9	81.4	0.0156	0.0156	0.0312	0.996
IO	16.35	99.87	0.0215	0.0209	0.0424	1.03
IR	13.97	81.7	0.0186	0.0143	0.0329	1.305

Reaction conditions: Temperature 60 °C; styrene:H_2O_2 molar ratio= 1.7; time 7 h; solvent: Acetonitrile; catalyst 0.2 g

[*] Co-ZSM-5 samples: EO) Exchanged and Oxidized; ER) Exchanged and Reduced; IO) Impregnated and Oxidized; IR) Impregnated and Reduced

[a] (mol %); [b] Acidity (mmol Py/mg); [c] Brönsted/Lewis ratio

Table 2: Characteristics of solvents used in the styrene oxidation reactions

Solvents	Dielectric Constant	Boiling point (°C)
Acetonitrile[a]	37.5	81.6
Acetone[a]	20.7	56.3
Ethyl methyl ketone[a]	18.5	79.6
Sec-Butyl alcohol[p]	16.5	99.5

[a] aprotic; [p] protic

Figure 1

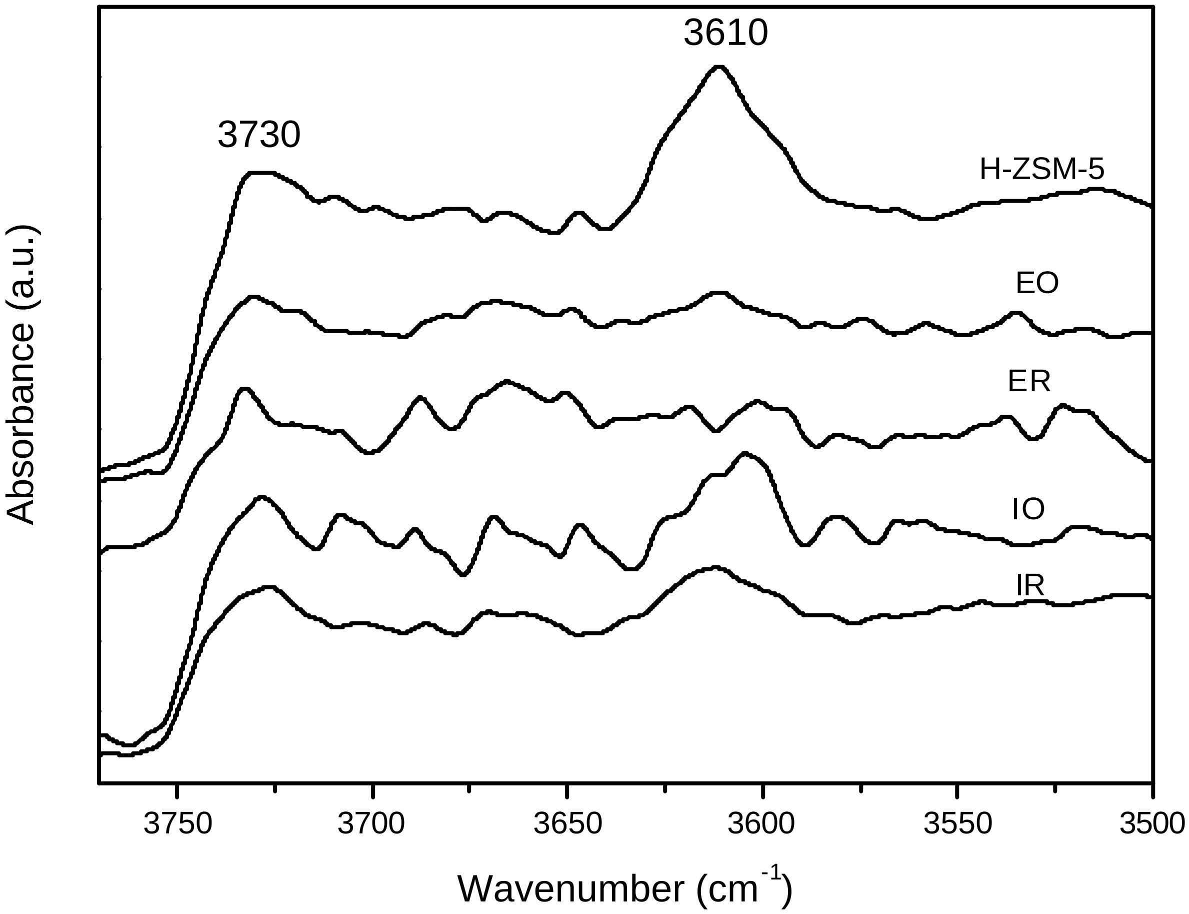

3610
3730
H-ZSM-5
EO
ER
IO
IR
Absorbance (a.u.)
3750
3700
3650
3600
3550
3500
Wavenumber (cm^{-1})

Figure 2

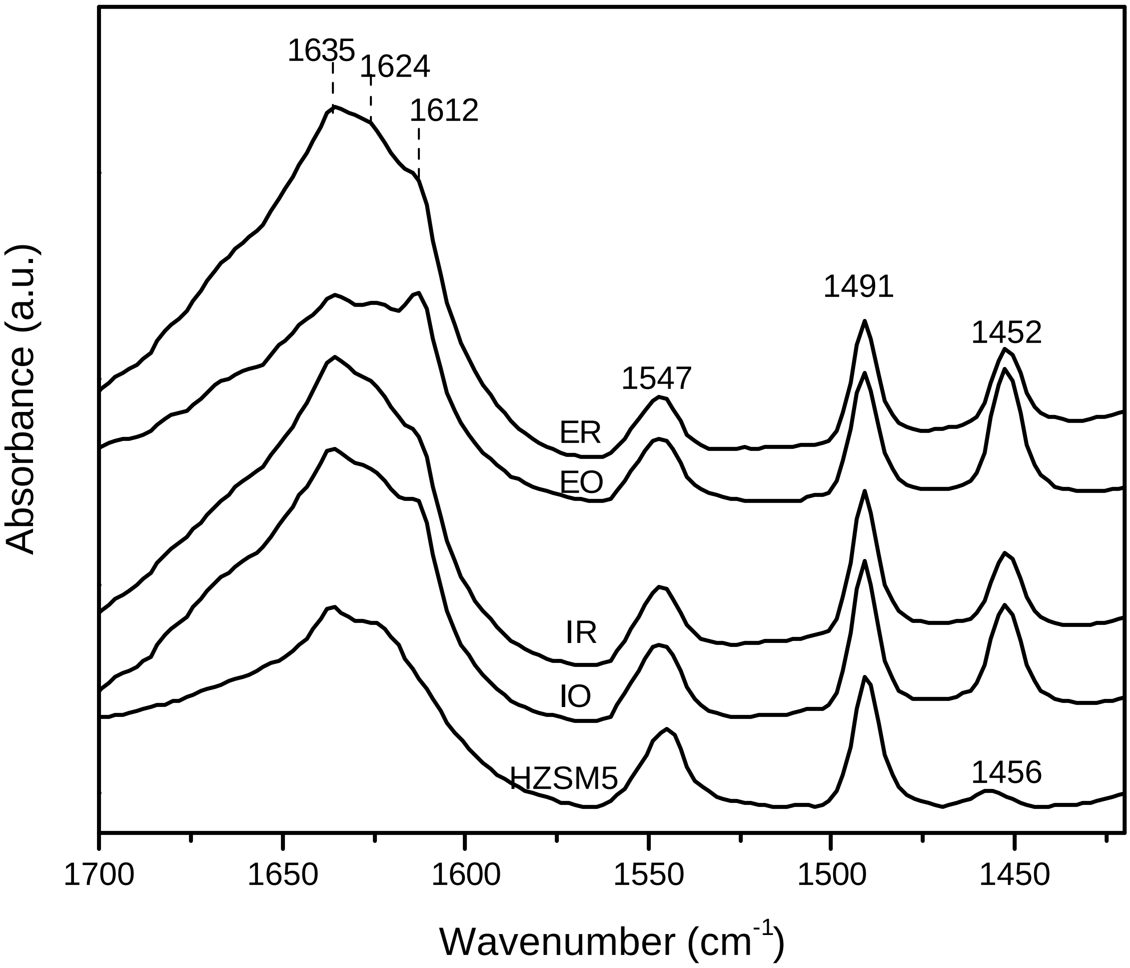

1635
1624
1612
1491
1452
1547
ER
EO
IR
IO
HZSM5
1456
Absorbance (a.u.)
1700
1650
1600
1550
1500
1450
Wavenumber (cm^{-1})

Figure 3

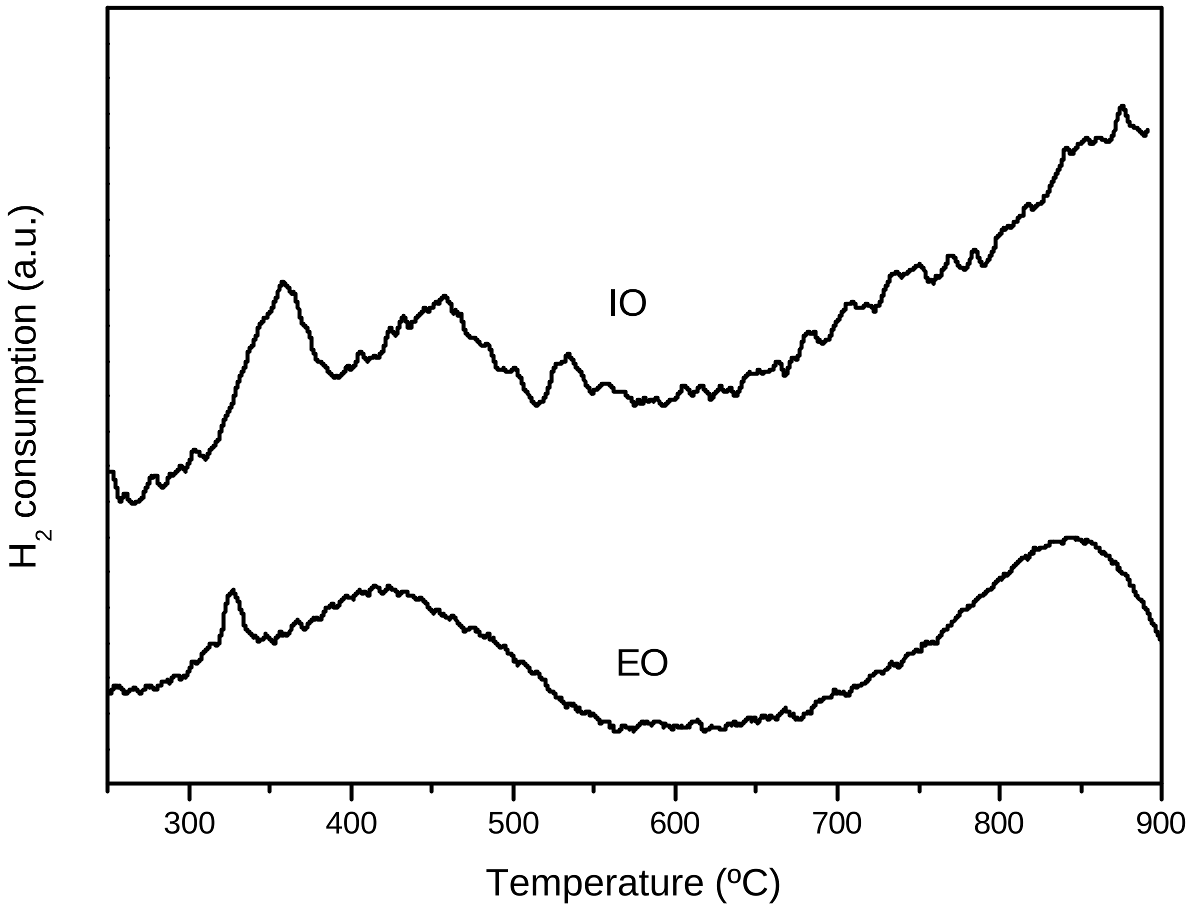

IO
EO
H_2 consumption (a.u.)
300
400
500
600
700
800
900
Temperature (ºC)

Figure 4

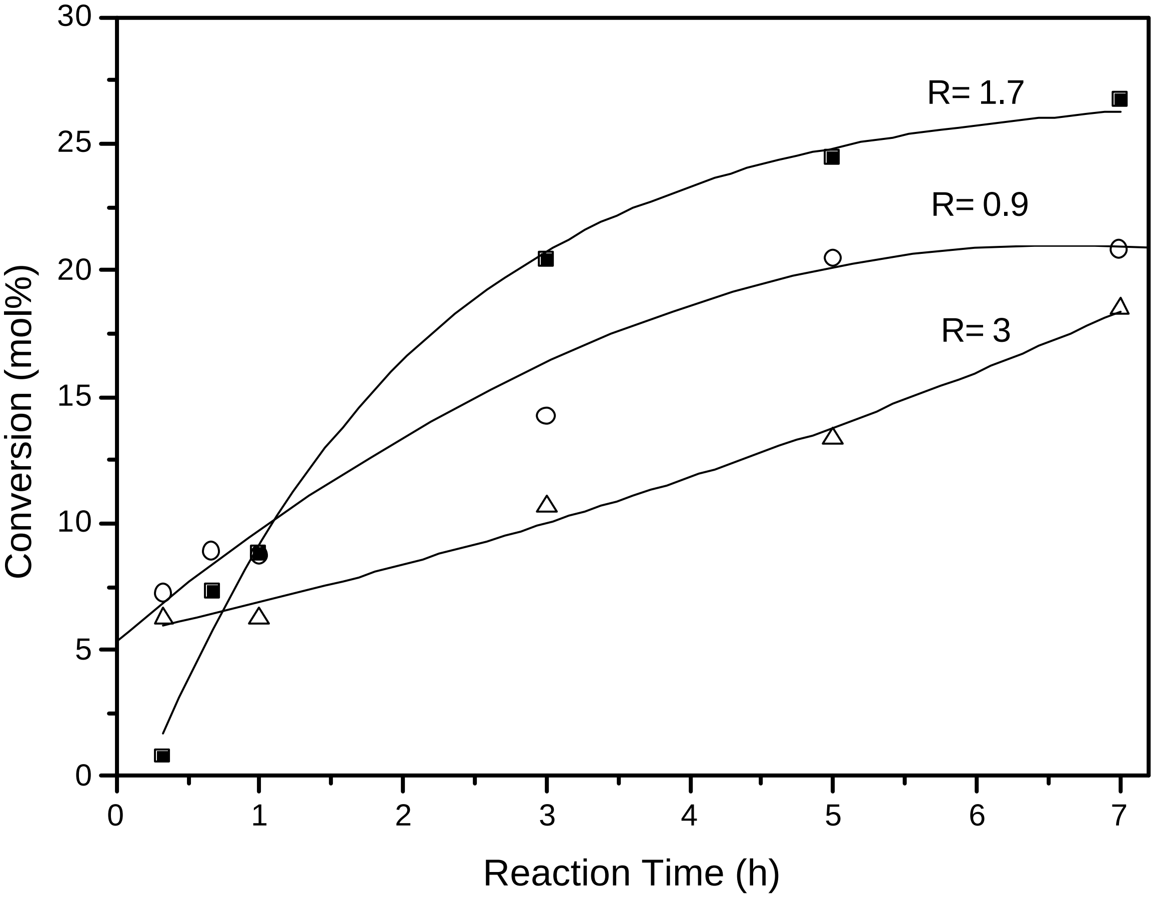

Conversion (mol%)
Reaction Time (h)
0
5
10
15
20
25
30
0
1
2
3
4
5
6
7
R= 1.7
R= 0.9
R= 3

Figure 5

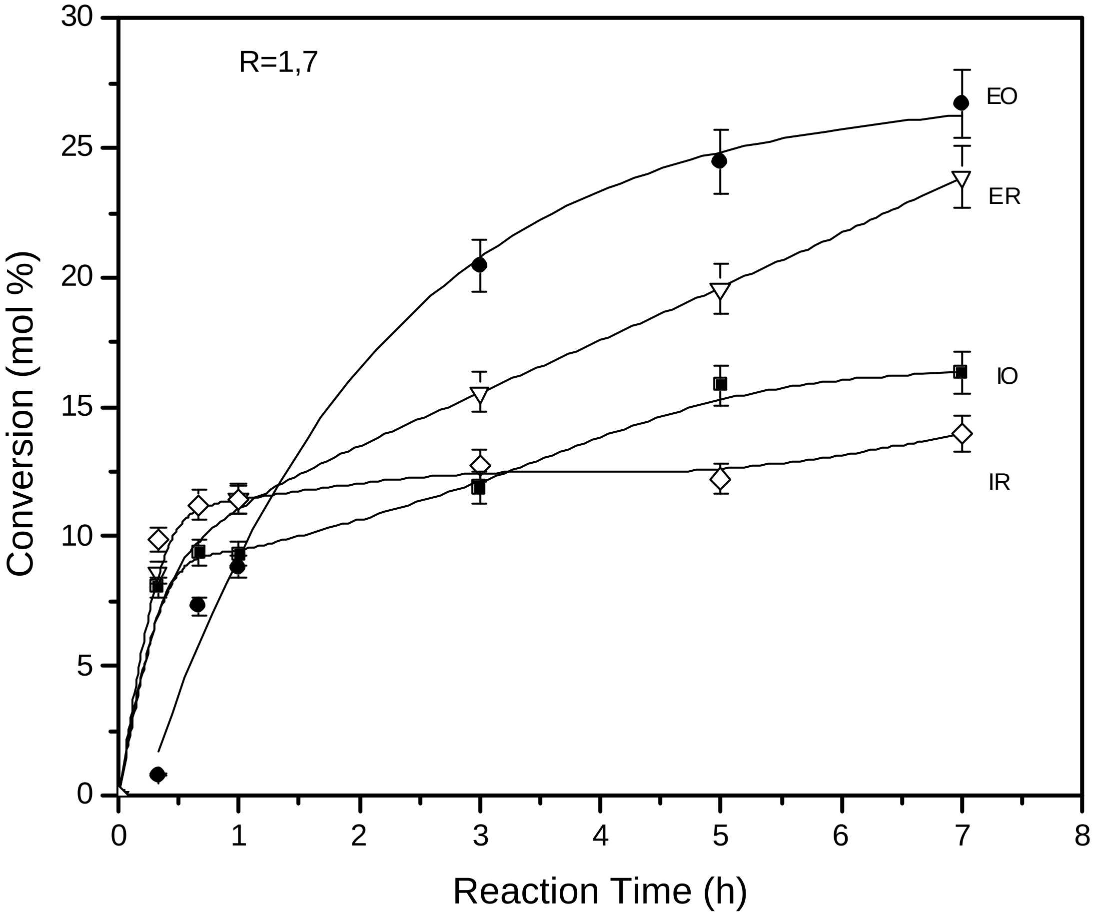

R=1,7
EO
ER
IO
IR
Conversion (mol %)
Reaction Time (h)
0
5
10
15
20
25
30
0
1
2
3
4
5
6
7
8

Figure 6

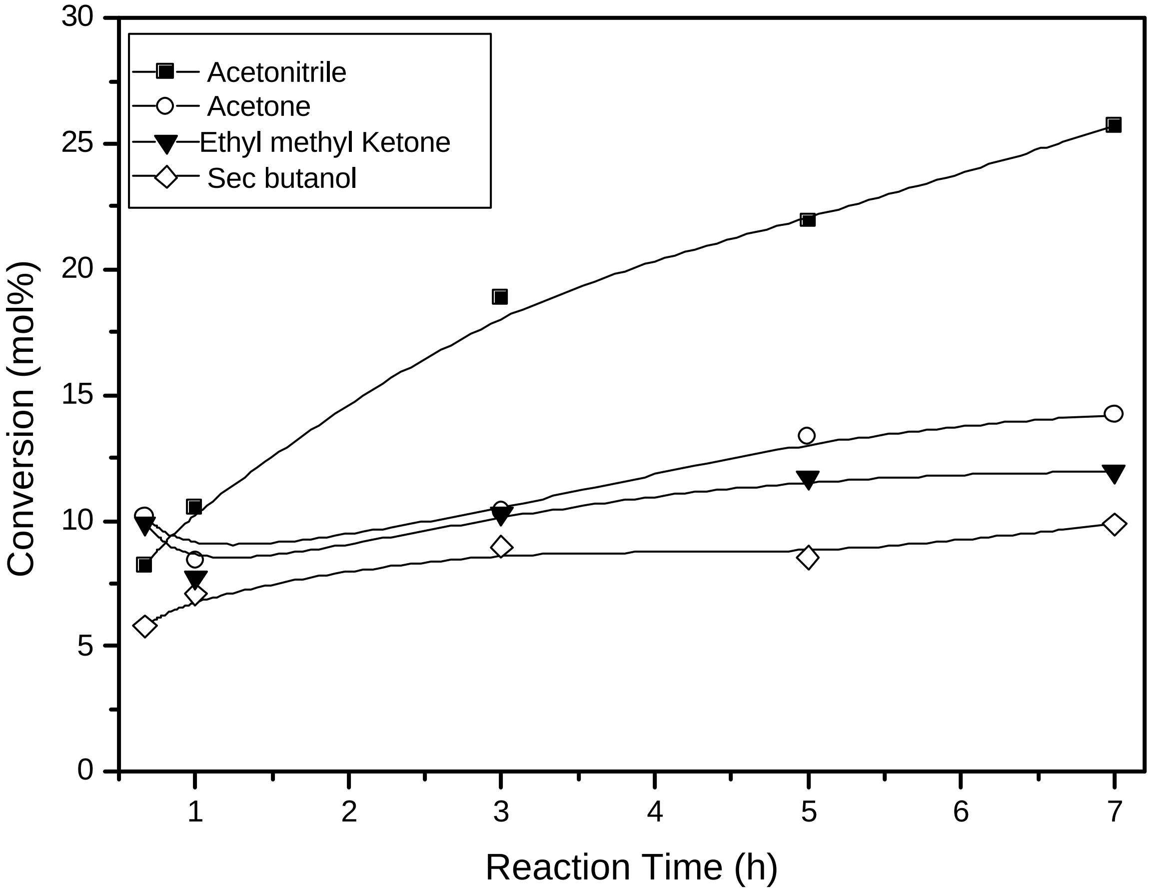
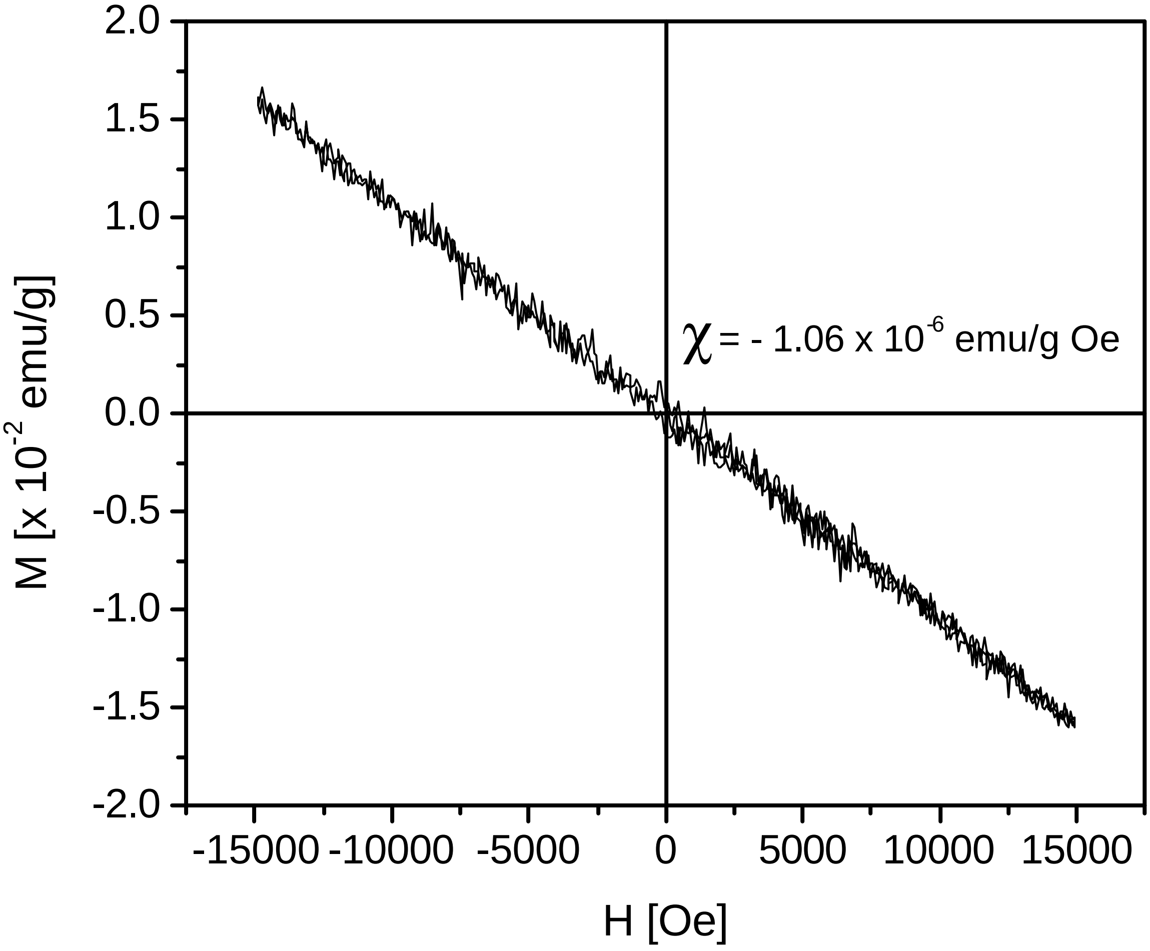

30
25
20
15
10
5
0
Conversion (mol%)
1
2
3
4
5
6
7
Reaction Time (h)
Acetonitrile
Acetone
Ethyl methyl Ketone
Sec butanol

Figure 7



2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
M [x 10^{-2} emu/g]
-15000
-10000
-5000
0
5000
10000
15000
H [Oe]
χ = - 1.06 x 10^{-6} emu/g Oe

Figure 8

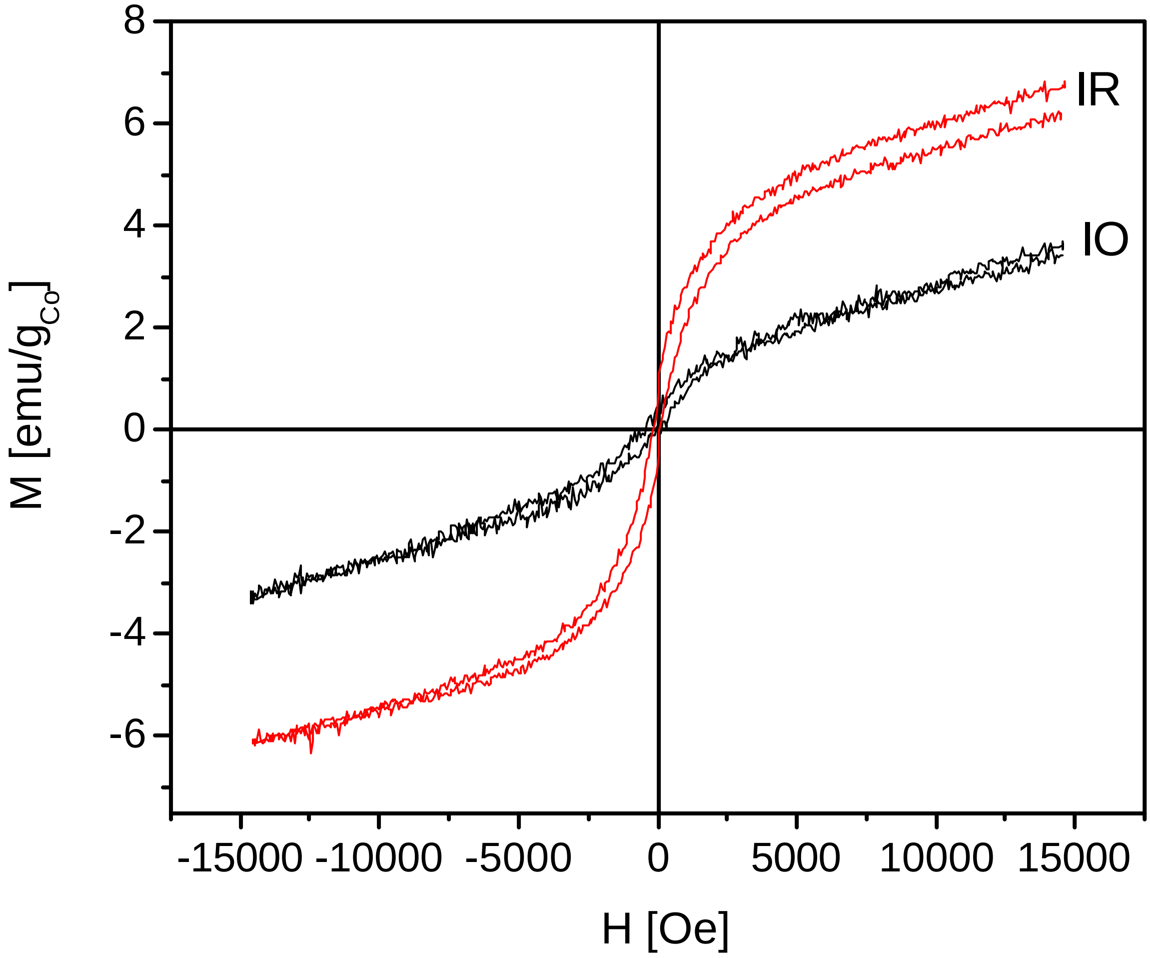

8
6
4
2
0
-2
-4
-6
M [emu/g$_{Co}$]
-15000
-10000
-5000
0
5000
10000
15000
H [Oe]
IR
IO

Figure 9

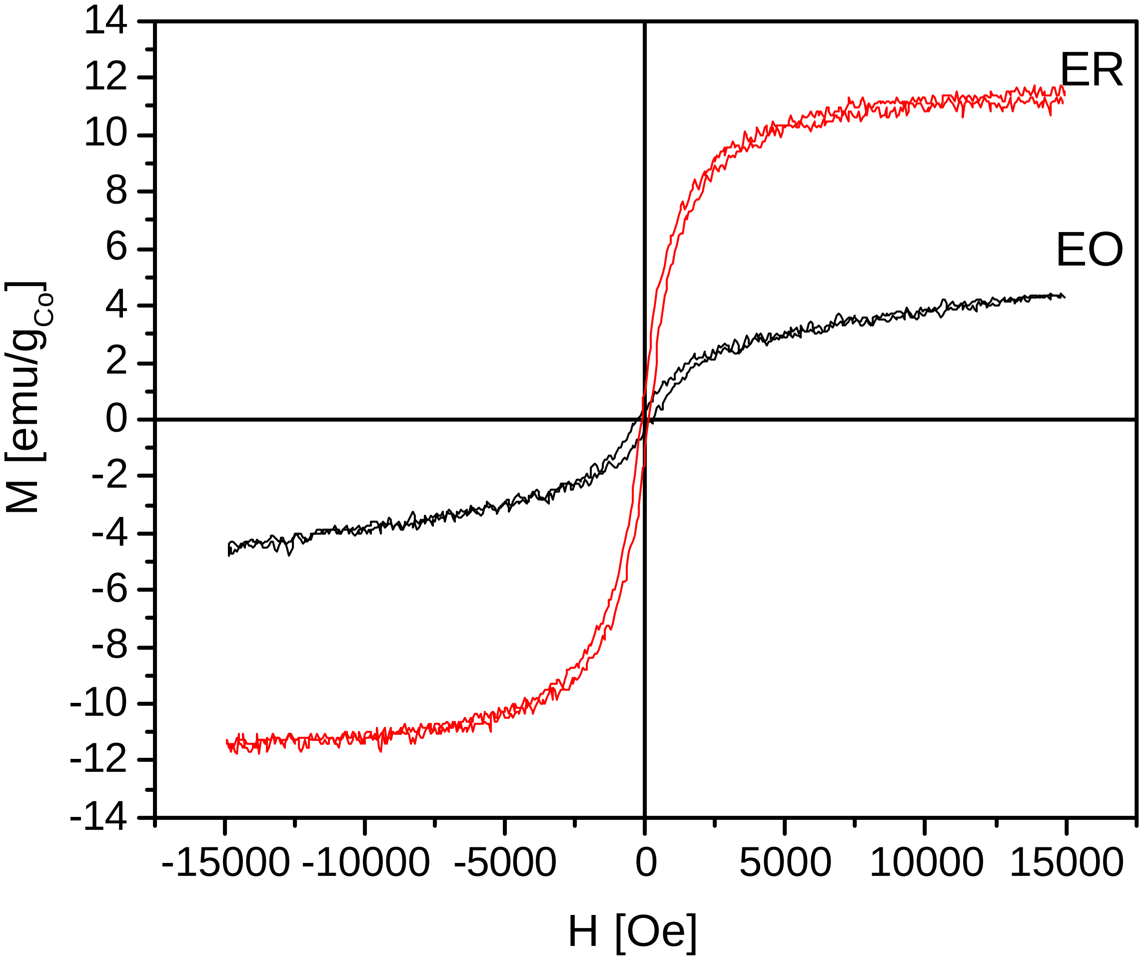

ER
EO
M [emu/g$_{Co}$]
H [Oe]
14
12
10
8
6
4
2
0
-2
-4
-6
-8
-10
-12
-14
-15000
-10000
-5000
0
5000
10000
15000

Figure 10

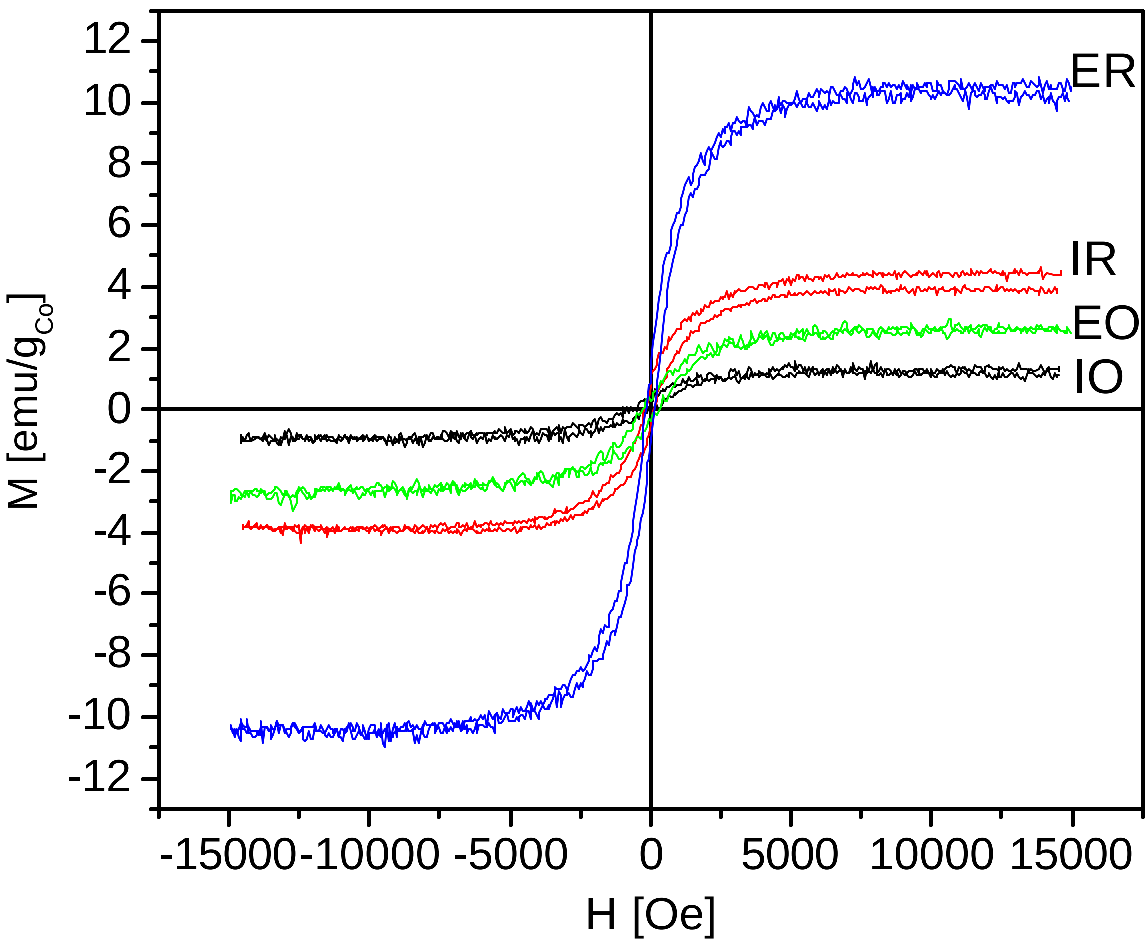
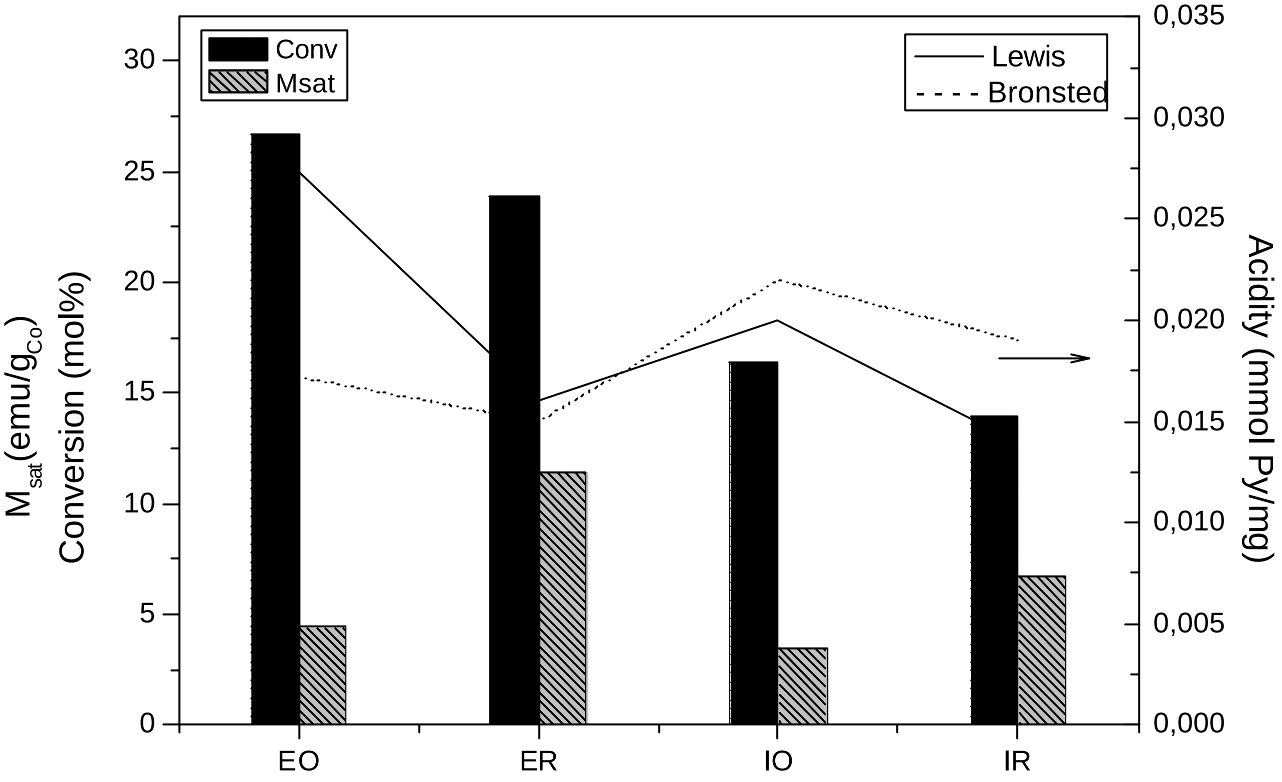

ER
IR
EO
IO
M [emu/g_{Co}]
12
10
8
6
4
2
0
-2
-4
-6
-8
-10
-12
-15000
-10000
-5000
0
5000
10000
15000
H [Oe]

Figure 11



Conv
Msat
Lewis
Bronsted
30
25
20
15
10
5
0
0,035
0,030
0,025
0,020
0,015
0,010
0,005
0,000
M_{sat}(emu/g_{Co})
Conversion (mol%)
Acidity (mmol Py/mg)
EO
ER
IO
IR