Pt-zeolites as active catalysts for the removal of chlorate in water by hydrogenation reactions

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ABSTRACT

Catalytic hydrogenation is used to remove chlorate ions from water streams by using platinum catalysts supported on zeolites with different topologies (FAU, BEA, MWW, MFI and MOR), Si/Al ratio and compensating cation. It is observed that there is an important influence of the zeolite characteristics on the catalytic activity. The best results have been obtained with the catalyst supported on zeolites with a high number of acid centres, this is with a low Si/Al ratio and with protons, as counter-cation species compensating aluminium charge. The acid sites favour the interaction of the catalyst with the reactants and influence the neighbouring Pt species improving the redox properties of the catalyst. It is shown that with an adequate number of acid sites it is possible to decrease the metal content, keeping the same catalytic activity, by increasing the metal dispersion. The highest activity is obtained with an acidic FAU zeolite, with low Si/Al ratio and 1 wt% of Pt added by ion exchange. This catalyst is able to simultaneously reduce chlorate and chlorite ions and chlorate and bromate ions indicating that it is a multifunctional catalyst that can be utilized for removing different pollutants in water.

1. Introduction

Water is a fundamental resource for society and it is necessary to guarantee its quality mainly when used for human consumption [1]. Unfortunately, in many regions of the planet, the availability of safe drinking water is a challenge and it is calculated that pathogens in those regions cause about 1.7 million deaths a year, mainly through infectious diarrhea [2]. To avoid these problems, natural water quality should be improved in drinking water treatment plants according to international guidelines. The main process in this plant is the disinfection treatment, which usually is based on the addition of oxidative chlorine compounds, such as chlorine dioxide, that destroy the pathogen agents without the formation of toxic by-products such as trihalomethanes [3,4]. Nevertheless, in certain conditions, these compounds may produce chlorite and chlorate ions in water [5–9] that have negative effects on health as they are responsible for oxidative stress and size change of haemoglobin cells. The World Health Organization set a provisional limit of 0.7 mg L^{-1} for both pollutants in drinking water. In addition, the compounds used for disinfection may generate other toxic anions in the treated water as bromate due to the oxidation of bromide ions that are present in natural water. Bromate is considered as a mutagenic agent and European Union has established a reference value of 0.01 mg L^{-1} of bromate in drinking water.

Different techniques can be used for the control of these pollutants, such as adsorption with granular activated carbon [10] or with a Mg/Fe/Cl layered double hydroxide [11]. Other separation techniques such as ion exchange [12] or membranes may also be used, but all of them generate important wastes that must be treated. Another option is the chemical reduction with ferrous ions. In this reaction Fe^{2+} is oxidized to Fe^{3+} while ClO_2^- is reduced to Cl^-. The insoluble iron (III) oxide-hydroxide formed in the reaction, is easily removed by sedimentation and/or filtration. Nevertheless, to achieve high reaction rates, low pH values are required [13].

Therefore, the need for new sustainable technologies for the removal of oxo-anionic contaminants in water has risen in the last few years. Catalytic hydrogenation has been described as a possible solution for the treatment of some of these pollutants, such as NO_3^-, NO_2^-, BrO_3^-, ClO_4^-, ClO_3^- or ClO_2^- [14–16]. The catalytic reduction of nitrates is one of the most widely studied reaction and a combination of a noble and non-noble metal (mainly Pd, Pt, In, Cu and Sn) supported on different materials such as carbon, alumina, hydrotalcites or zeolites are used as catalysts [17–20]. It is established that the bimetallic sites catalyze the reduction of nitrates to nitrites, whilst nitrites are reduced on isolated noble metal sites. The main product is nitrogen but undesired

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ammonium is also formed, this depending on the reaction conditions and on the catalyst preparation [14,17]. The selectivity is the main drawback of the reaction, mostly when is applied in natural water [21].

Catalysts based on noble metals also catalyze the hydrogenation of bromates to bromide according to.

$$BrO_3^- + 3\ H_2 \rightarrow Br^- + 3\ H_2O$$
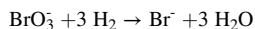
In this case, best results are obtained with Pd catalysts supported on alumina or carbon [22] observing a strong influence of the Pd precursor salt on the catalyst activity, as it has an effect on the Pd nanocrystal size. It is described that the highest TOF is obtained with catalysts prepared with a metal precursor that produces homogeneous and large Pd metallic crystallites [23]. Contrarily to what occurs with nitrate reduction, the catalysts used for this reaction are quite selective [24].

Similarly, the catalytic hydrogenation of chlorate may be considered as a tool for the treatment of this pollutant in water, as toxic chlorate would be reduced to innocuous chloride [15,16,25] according to:

$$ClO_3^- + 3H_2 \rightarrow Cl^- + 3H_2O$$
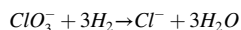
Nevertheless, only few works have studied this reaction even though a patent assigned to Solvay described the use of this method for removing halogen-oxygen compounds in water by using a supported precious metal catalyst [26]. Another patent assigned to the same company claims the use of this reaction for removing chlorate ions with Pt or Rh catalysts supported on a wettable material [27]. Other authors studied the reaction using noble metal catalysts supported on carbon materials. Kuznetsova et al. proposed the use of carbon-supported iridium catalysts for the reduction of chlorate in concentrated solutions of sodium chloride [28]. Recently Sikora et al. described the use of Pd [29] and Pt catalysts supported on granulated carbon nanotubes, improving the catalytic activity when the catalysts were promoted with transition metals [30,31]. Other authors studied the use of different nitrogen-doped carbon nanotubes with Pd obtaining a high chlorate conversion [32]. Liu et al. discussed the reduction of different oxyanions (chlorate and bromate) in water, observing that is possible to accelerate the oxyanion reduction with inert metal hydroxides as they alter the zeta potential enhancing the adsorption equilibrium [33]. The same authors reported the catalytic reduction of aqueous chlorate with MoO_x immobilized on Pd/C, observing that adding Mo to Pd/C enhances the catalytic activity and provides strong resistance to concentrated salts [34]. The catalytic reduction of oxyanion pollutants has also been explored with platinum group metal catalysts supported on alumina and carbon, observing significant advantages with Rh and Ru compared to Pd catalysts in terms of catalytic turnover frequency [35].

The main knowledge gaps, lessons learned and new opportunities for the catalytic reduction of water pollutants has been reviewed recently by Liu *et* Gao [36]. However, to the best of our knowledge, the use of zeolitic materials as catalysts for this reaction has not been reported despite the fact that zeolites are common catalysts or catalyst supports, due to their high surface area, ion exchange properties and topology [37–44]. Hereby, we study the performance of different Pt catalysts supported on zeolites for the hydrogenation of chlorate at room temperature and atmospheric pressure and evaluate the influence of the zeolite characteristics on the final activity. The optimized catalyst has been tested for the simultaneous removal of chlorate, chlorite and bromate ions in water phase.

2. Experimental

2.1. Catalyst preparation

Catalysts were prepared using commercial FAU, MFI and MOR zeolites supplied by Zeolyst, commercial BEA zeolite supplied by PQ Zeolites B.V and ITQ-2 zeolite prepared in the laboratory according to [45, 46]. Different aqueous solutions of a platinum precursor ($PtCl_4$) were

added by the wet impregnation method to obtain the desired platinum content in the final catalyst. After impregnation, catalysts were calcined at 350ºC, for 3 h and cooled down to room temperature. Another Pt-catalyst was prepared by ion exchange with an aqueous solution containing $PtCl_4$ with adequate concentration to achieve the desired amount of metal on the zeolite and with a solid/liquid ratio of 1/40. The metal exchange was made at room temperature. After 24 h under mechanical stirring, the solutions were washed, filtered, dried at 100 °C and calcined at 350ºC for 3 h. All the catalysts were activated with hydrogen at 200 °C for 4 h.

2.2. Catalytic tests

The polluted water was prepared by dissolving $NaClO_3$ in Milli-Q water. The experiments were conducted at room temperature and atmospheric pressure in a stirred batch reactor containing 0.6 L of water with 50 ppm of chlorate. The stirring velocity was 900 rpm. In specific experiments, 50 ppm of chlorite or bromate ions were added to the water. The experiments were made using 1 g of catalyst and before each test, the polluted water was hydrogenated for 2 h with a gas flow of 200 mL·min^{-1}. The same hydrogen flow was maintained throughout the reaction. Reactants and products were determined by an ionic chromatograph 883 Basic IC Plus (Metrohm®) equipped with a conductivity detector and a chemical suppressor. The anions were separated in a Metrosep A Supp 5–150/4.0 column.

2.3. Characterization studies

X-ray diffraction (XRD) patterns were recorded in a PANalytical CUBIX diffractometer equipped with a PANalytical X′Celerator detector. X-ray radiation of Cu Kα ($\lambda 1 = 1.5406$ Å, $\lambda 2 = 1.5444$ Å, $I2/I1 = 0.5$) was used with a tube voltage of 45 kV and with an intensity of 40 mA.

Textural properties of the catalysts were determined at -196 ºC by N_2 adsorption with a Micromeritics ASAP 2040 device. 0.2 g of the sample with a particle size between 0.4 and 0.6 mm was used for the analysis Surface areas of the catalysts were obtained by the BET method.

The chemical composition was measured by inductively coupled plasma (ICP-OES) in a Thermo Scientific™ iCAP PRO ICP-Optical Emission Spectrometer. Prior to analysis, 40 mg of each solid sample were digested with concentrated hydrofluoric and nitric acid for 24 h.

TPR profiles were obtained with a Micromeritics Autochem 2910 automated chemisorption analysis instrument. The reduction of the samples (10–20 mg) was conducted from 40° to 600°C with a thermal ramp of 10 °C·min^{-1} using an Ar:H_2 flow (10% H_2) of 50 mL·min^{-1}.

High resolution field emission scanning electron microscopy (HRFESEM) measurements were made in a ZEISS GeminiSEM 500. Micrographs were acquired at the same acceleration voltage (1.5 kV) at varying magnifications. Pt average particle size was obtained by measuring some particles of each catalyst in different micrographs and positions.

The acidity of the samples was measured by infrared spectroscopy in a Nicolet 710 FT IR spectrometer. Adsorption-desorption of pyridine experiments were measured on self-supported sample wafers. The wafers were activated at 350 °C under vacuum for 2 h. After activation, pyridine vapour was absorbed into the samples. Desorption of pyridine under vacuum was measured at 150, 250 and 350 °C, followed by an IR measurement at room temperature. The data were treated using Omnic™ Series software and normalised according to the sample weight. The concentration of Brønsted and Lewis acid sites was calculated from the integrated absorbance of the bands at 1545 and 1440 cm^{-1}, assigned respectively to Brønsted or Lewis acid sites, using the extinction coefficients of 1.88 and 1.42. [47].
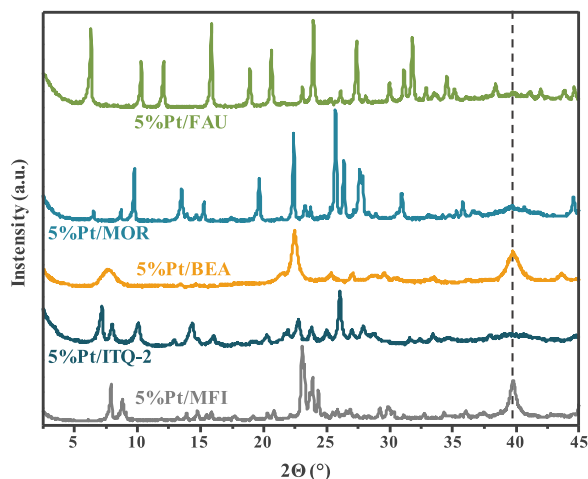
Fig. 1. XRD patterns of 5 wt% Pt-catalysts supported on different acid zeolites (FAU, MOR, BEA, ITQ-2 and MFI).

3. Results

3.1. Catalyst characterisation

The Fig. 1 shows the XRD patterns of some of the catalysts studied. The diffractograms feature the peaks associated with the crystal phase of the zeolites and the characteristic peak of Pt^0 that appear at $2\theta = 39.4°$ scattering from the (111) plane [30]. The different height and definition of this peak, depending on the zeolite, indicates the formation of Pt crystallites with diverse size in the different catalysts. XRD characterization of the materials after reaction was made observing the same XRD patterns, indicating that the zeolites are stable under the reaction conditions (water, room temperature and atmospheric pressure).

Table 1 shows the textural and chemical properties of some selected catalysts. Except for the ITQ-2, all the materials present type I isotherms typical of microporous materials. The BET surface area of all the samples is quite high and varies between 345 and 515 $m^2 \cdot g^{-1}$, depending on the type of zeolite. Compared with the surface area of the parent zeolites, the addition of the Pt precursor and subsequent calcination produces a decrease in the surface area of around 10%, probably due to the blockage of some zeolite pores. Nevertheless, as the XRD patterns show, the incorporation of the metal does not modify the zeolite structure.

TPR of some of the Pt catalysts are shown in Fig. 2. As it can be seen different peaks appear at different temperatures and with different intensities depending on the type of zeolite. These peaks correspond to the reduction of Pt^{2+} to Pt^0 in platinum species located in different positions of the zeolite and interacting with various strengths with the zeolite [48, 49]. This results in the formation of Pt sites with different H_2 reactivity and dissimilar redox properties.

3.2. Catalytic results

A blank reaction was previously carried out without any catalyst,

observing that the reduction of chlorate by hydrogen does not occur at room temperature and atmospheric pressure without a catalyst. After the addition of the Pt-zeolite catalyst, chlorate is reduced to chloride without the formation of any stable intermediate or by-products with a complete selectivity to the desired product. The activity for the chlorate reduction of the Pt catalysts supported on different types of zeolites was compared and the results are shown in Fig. 3. As it can be observed the best results were obtained with the Pt catalysts supported on FAU and MOR and the lowest activity was achieved with the Pt catalyst supported on ITQ-2. These results are quite suppressive as the best activity was obtained with two zeolites with quite a different topology, i.e. FAU that
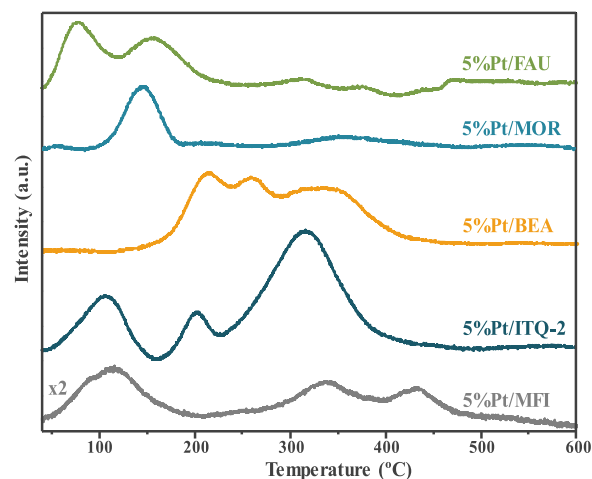

Fig. 2. TPR profiles of the calcined 5 wt% Pt-catalysts supported on different acid zeolites (FAU, MOR, BEA, ITQ-2 and MFI).
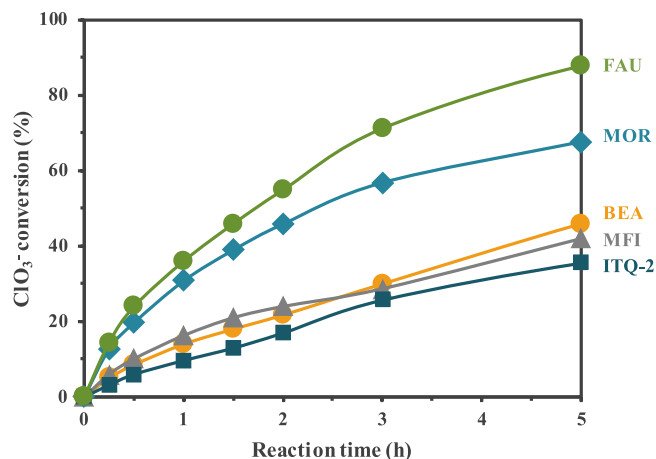

Fig. 3. Activity of 5 wt% Pt-catalysts supported on: (●) H^+-FAU, (◆) H^+-MOR, (●) H^+-BEA, (▲) H^+-MFI and (■) H^+-ITQ-2 (1 g. of catalyst, 0.6 L of water with 50 ppm of ClO_3^-, room temperature and atmospheric pressure).

Table 1
Chemical and textural properties of selected Pt-zeolite catalysts.

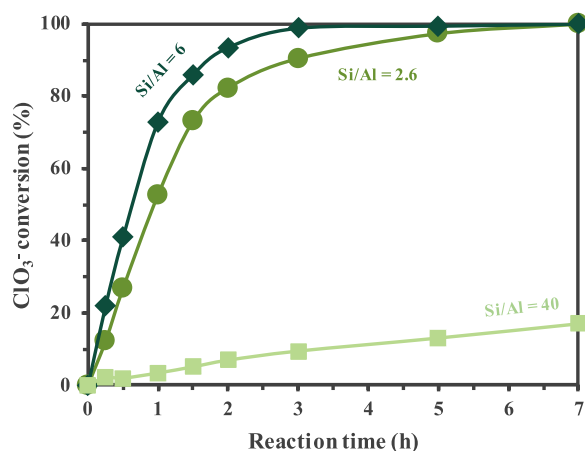| Catalyst	Surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})	Pore size (Å)	Chemical composition			
				Si/Al molar ratio	Na (wt%)	Nominal cation	Pt (wt%)
5%Pt/FAU	450	0.33	30	2.7	0.01	H^+	4.6
5%Pt/MOR	377	0.26	28	6	0.22	H^+	5.1
5%Pt/BEA	515	0.38	29	12	0.66	H^+	4.9
5%Pt/ITQ-2	477	0.42	35	17	0.02	H^+	4.6
5%Pt/MFI	346	0.27	31	15	0.02	H^+	4.7

Fig. 4. Activity of 5 wt% Pt-catalysts supported on FAU zeolites with different Si/Al ratio: (●) SiAl = 2.6, (♦) SiAl = 6 and (■) SiAl = 40 (1 g. of catalyst, 0.6 L of water with 50 ppm of ClO_3^-, room temperature and atmospheric pressure, former NH_4^+-zeolite).

Fig. 5. XRD patterns of 5 wt% Pt-catalysts supported FAU zeolites with different Si/Al ratio (former NH_4^+-zeolite).

Fig. 6. Activity of 5 wt% Pt-catalysts supported on FAU zeolite with a Si/Al ratio= 2.6 and with different sodium content: (●) 0 wt% Na, (♦) 2 wt% Na and (■) 8 wt% Na (1 g. of catalyst, 0.6 L of water with 50 ppm of ClO_3^-, room temperature and atmospheric pressure).

is a three-dimensional zeolite with large pores and MOR that is a bi-dimensional zeolite with 12 and 8-ring channels, indicating that zeolite structure is not the most important characteristic to have active catalysts for this reaction. The main similarity between these two zeolites is the low Si/Al ratio, implying that this parameter can be more important than zeolite topology for the design of an adequate catalyst.

In order to study this, catalysts with the same structure (FAU) but with different Si/Al ratios were prepared and the results are shown in Fig. 4. As can be seen, the best activity was obtained again with the catalysts with lower Si/Al ratio. Aluminium content can be related with zeolite acidity, then the Brønsted and Lewis acidity of the parent zeolites was determined by adsorbing pyridine and desorbing it at increasing temperatures [50]. The results are presented in Table 2, where is observed that an increase of the aluminium content, i.e a decrease of the Si/Al ratio, results in an increase of the number of Lewis and Brønsted sites. These results clearly indicate that the presence of acid sites is an important issue for this reaction.

XRD patterns of the catalysts are displayed in Fig. 5. It is observed that Pt-catalysts with higher aluminium content, feature larger and better-defined platinum peaks than the catalyst with low aluminium content. This is related to the formation of larger metal crystallites in the former catalysts, indicating a worse dispersion of the platinum on these zeolites. These results also provide evidence that acidity is more important than metal dispersion for the catalytic hydrogenation of chlorates with Pt-zeolites.

As acidity in zeolites, it is not only related with the aluminium content but also with the compensating cation, Pt catalysts supported on a FAU zeolite, with a Si/Al ratio of 2.6, but with different sodium content were prepared and the results obtained are shown in Fig. 6. As it can be seen, as the sodium content increases, the activity decreases, due to the less number of Brönsted acid sites in the zeolite.

These results confirm the necessity of the acid sites in the zeolites in order to have active catalysts for this reaction. Further research is necessary to clarify the role of the acid sites in the reaction, but they are
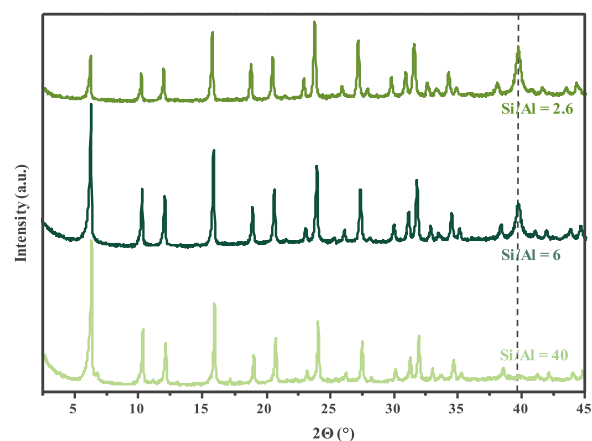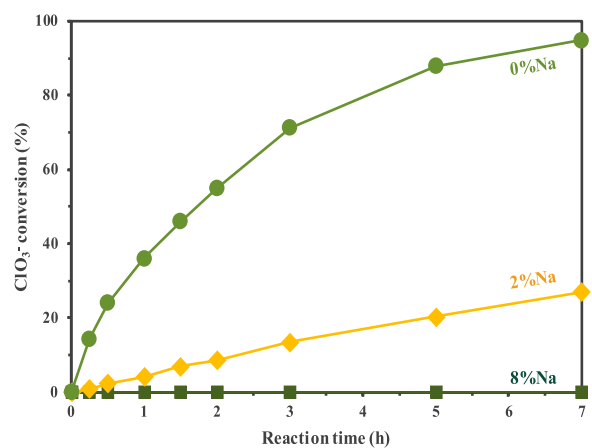
probably favouring the adsorption of the reactants and influencing the redox properties of the metallic active sites. The last is inferred by comparing the TPR of the Pt-catalysts supported on a sodic zeolite with the thermograms of the acidic zeolite (Fig. 7). It is observed that in the former one, the peaks assigned to the reduction of platinum appear at higher temperatures. This indicates that the interaction of the platinum species with the hydrogen is less favoured than in the acidic zeolites, forming less active metallic centres. The influence in the position of the platinum atoms of the zeolite acid sites has been previously studied by Sachtler *et al.* indicating that the different size of H^+ and Na^+ ions leads to different site preferences for platinum [48,51] and therefore to a diverse reactivity of the metal active centres.

The influence of the noble metal content on the catalyst activity was studied and the results are shown in Fig. 8. It is observed that in the

Table 2

Acidity of parent zeolites as determined by FT-IR combined with pyridine adsorption and desorption at increasing temperatures.

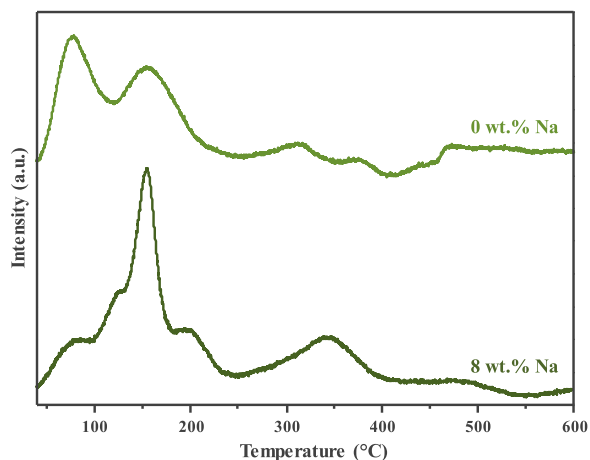| Samples	Concentration of acid sites (μmolPy g^{-1})					
	Brønsted			Lewis		
	T_1= 150 °C	T_2= 250 °C	T_3= 350 °C	T_1= 150 °C	T_2= 250 °C	T_3= 350 °C
NH_4^+-FAU, Si/Al= 2.6	367	287	160	170	128	96
NH_4^+-FAU, Si/Al= 6	210	167	95	78	58	45
NH_4^+-FAU, Si/Al= 40	130	120	55	30	22	35

Fig. 7. TPR profiles of the calcined 5 wt% Pt-catalysts supported on FAU zeolite with a Si/Al ratio= 2.6 and with different wt% Na: 0 wt% Na and 8 wt % Na.
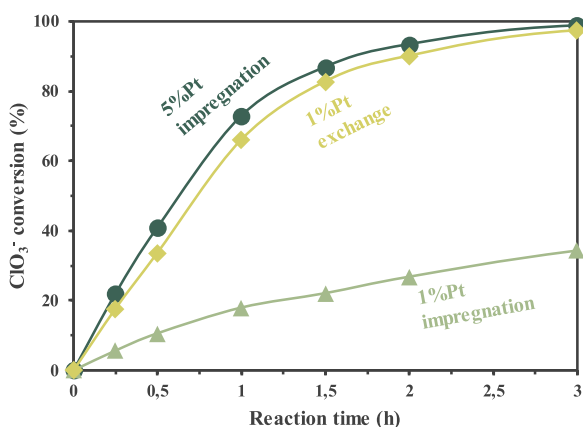

Fig. 8. Activity of Pt-catalysts supported on acid FAU zeolite (SiAl = 6) with different metal content: (●) 5 wt% Pt (prepared by wet impregnation), (◆) 1 wt % Pt (prepared by ion exchange) and (▲) 1 wt% Pt (prepared by wet impregnation).
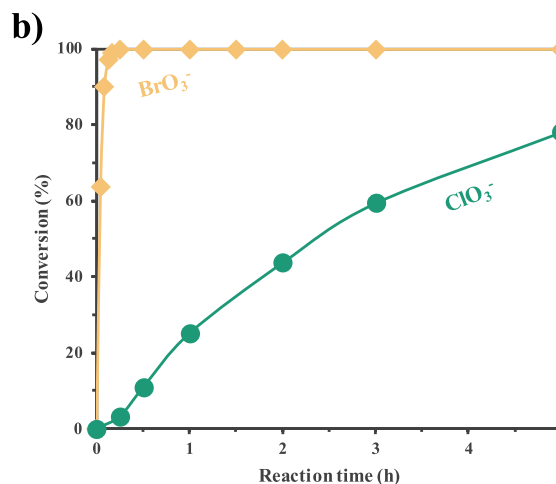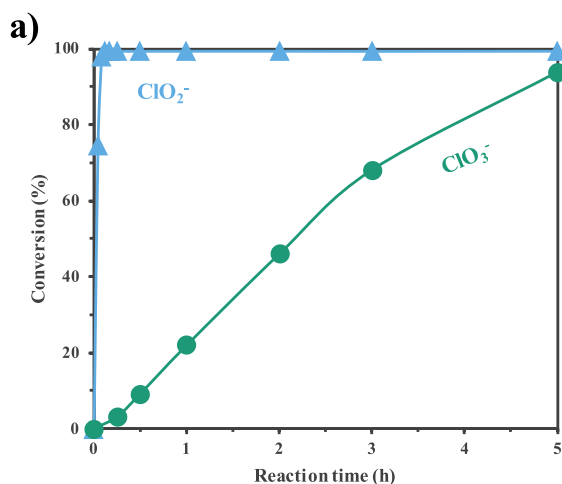
samples prepared by wet impregnation, a decrease of the metal content results in a proportional decrease of the catalyst activity. Nevertheless, if the catalyst is prepared by the ion exchange procedure, the activity of the catalyst containing 1 wt% of Pt is similar to the activity of the catalyst with 5 wt% of Pt prepared by wet impregnation. This has been related to a better dispersion of the platinum in the catalyst prepared by ion exchange, as the analysis of the Pt crystallites by electronic microscopy suggests. It was observed that in the catalyst prepared by ion exchange the distribution of the Pt crystallites is centred around 5–15 nm, whilst in the catalyst with the same platinum content but prepared by wet impregnation it is centred around 30–40 nm. These results demonstrate that with an adequate number of acid sites, the dispersion of the metal becomes an important aspect to be considered for the reaction.

The activity of the catalyst containing 1 wt% of Pt. prepared by ion exchange was studied for the simultaneous removal of chlorate and other anionic pollutants, i.e. chlorite and bromate. These anions were selected as they usually appear together with chlorate after disinfection treatments. The results obtained are shown in Fig. 9. It is observed that the catalyst is active for the reduction of both anions when they are simultaneously present in water. As can be seen in Fig. 9a, chlorite is first reduced and later on the chlorate reduction starts. This is probably related to the different geometry of the ions and to the easiest accessibility of the chlorine atom in the chlorite ion that favours the adsorption and reduction of the ClO_2 on the catalyst's active phase. The same trend is observed when bromates and chlorates are simultaneously present in water (Fig. 9b), in this case bromate is firstly reduced and then the reduction of chlorate starts even that both ions have a similar geometry. Similar results have been previously reported with other catalysts indicating that interaction between oxyanions substrates and metal active sites is an important factor to be considered. The activity of the catalyst for the removal of the different anions suggests that this is a multifunctional material that can be used for the removal of halogenated ionic pollutants in water phase.

4. Conclusions

Pt-zeolite catalysts are active materials for the hydrogenation of chlorate in water phase. Nevertheless, the activity of the materials depends on the characteristics of the zeolite being necessary the presence of acid sites that could participate in the adsorption of the reactants but that also affect to the redox properties of the platinum sites. It has been seen that with enough number of acid sites, metal dispersion becomes important, improving the activity when the platinum crystallites are

Fig. 9. Activity for the simultaneous removal of chlorate and other anions: a) ClO_3^- (●) and ClO_2^- (▲); b) ClO_3^- (●) and BrO_3^- (◆) (1 g of 1 wt% Pt-FAU prepared by ion exchange, 0.6 L of water with 50 ppm of each ion, room temperature and atmospheric pressure).

smaller and then the noble metal is better dispersed on the zeolite surface. We propose that the proper combination of metal dispersion, acid and redox properties is the key factor in order to design active catalysts for the chlorate reduction, nevertheless more studies are necessary to fully understand the reaction mechanism. The best activity has been obtained with an acidic FAU zeolite, with low Si/Al ratio and 1 wt% of Pt added by ion exchange. This catalyst is active for the simultaneous reduction of chlorate and chlorite as well as for the simultaneous reduction of chlorate and bromate, indicating that this is a multifunctional catalyst that can be utilized for removing different anionic pollutants in water.

CRediT authorship contribution statement

A. Plá-Hernández: Conceived and designed the analysis, Collected the data, Contributed data or analysis tools, Performed the analysis; F. Rey: Conceived and designed the analysis, Other contribution; A. E. Palomares: Conceived and designed the analysis, Contributed data or analysis tools, Wrote the paper, Other contribution.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Acknowledgements

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