Highly efficient reduction of bromate to bromide over mono and bimetallic ZSM5 catalysts

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The reduction of bromate to bromide was successfully catalyzed by mono and bimetallic catalysts based on ZSM5 zeolite. This reaction is important since the presence of bromate in water is potentially carcinogen to humans. The catalysts were prepared by ion-exchange and incipient wetness methods with different metals (copper, palladium, rhodium and thorium) using ZSM5. Several analytical techniques (N_2 adsorption, TPR experiments, NH_3-TPD, FTIR, XRD, SEM/EDX and TEM/EDX were used to characterize the mono and bimetallic catalysts prepared by the two methods. The catalytic tests were carried out in a semi-batch reactor under hydrogen, working at room temperature and pressure. All catalysts prepared are undeniably effective in achieving the complete conversion of bromate into bromide. The most promising among the catalysts tested in this work are the palladium bimetallic catalysts.

Introduction

Bromate is obtained in the treatment processes involving ozonation or chlorination of bromide-containing waters.[1] Considering that the ion is potentially carcinogenic to humans, its presence in water has been attracting attention. Since the World Health Organization (WHO) and the United States Environmental Protection Agency (EPA) began to regulate the levels of bromate in water (maximum of 10 μg/L), it has become very important to develop an effective treatment method for its removal.

There are different processes for bromate removal or to prevent their production in water like electrochemical reduction, photocatalytic processes, bioreactors, reduction with the Fe^{2+}/Fe^{0} pair and heterogeneous catalysis.[2-10] Most of these technologies concentrate contaminates in a secondary waste stream, which requires additional treatment.[11] The use of hydrogenation catalysts has been widely studied for the reduction of a large number of priority water contaminants as nitrate, nitrite, chlorate, perchlorate, N-nitrosamines and a number of halogenated alkanes, alkenes and aromatics.[12] However, in the case of bromate only a few studies regarding the catalytic reduction with hydrogen have been reported. The reduction can be described by consecutive and parallel reactions where the ions are reduced over metal supported catalysts in the presence of hydrogen. The support selected is also important in the reduction reactions.

Recently, zeolites have been explored as supports or even as catalysts for reduction reactions.[13] Zeolites are crystalline microporous aluminosilicates with a defined three-dimensional structure composed by silicon, aluminium and oxygen. The aluminium ion is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms and the isomorphs replacement of Si^{4+} by Al^{3+} produces a negative charge on the network that needs to be balanced by the presence of cationic species.[14-18] These cationic species are not directly bonded to the inorganic network, but are retained by steric effects and electrostatic interactions, and hence can be exchanged by other cations, triggering one of the main applications of zeolites in industry as cation-exchangers.[15-17]

In this study, the preparation and characterization of the mono and bimetallic catalysts based on ZSM5 zeolite and their activity in the catalytic reduction of bromate in water was investigated. ZSM5 zeolite (MFI-type structure) is a high silica zeolite that is composed of several pentasil units linked together by oxygen bridges to form pentasil chains. ZSM5 is a medium pore zeolite with pore diameters of 5.4-5.6 Å that are defined by these 10 member oxygen rings.[19] The mono and bimetallic catalysts based on ZSM5 with different metals (copper, palladium, rhodium and thorium) were prepared using two methods: ion-exchange and incipient wetness. The prepared catalysts were selected for the study of bromate reduction under hydrogen. To the best of our knowledge, this is the first systematic study for testing a wide range of mono and bimetallic catalysts based on ZSM5 zeolite for the bromate reduction to bromide in water.

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Experimental

Preparation of mono and bimetallic catalysts

The mono and bimetallic catalysts were prepared by two different methods reported by us elsewhere.[18,20,21] The zeolite ZSM5 (CBV 3024E, Zeolyst International, Si/Al=15.0), available in the ammonium form, was modified by these methods with aqueous solutions of palladium ($Pd(NO_3)_2.2H_2O$, Aldrich), copper ($Cu(NO_3)_2.3H_2O$, Riedel de Haen) and thorium ($Th(NO_3)_4.6H_2O$, Analar) nitrates and rhodium chloride hydrate ($RhCl_3.xH_2O$, Fluka). After the preparation, the resulting catalysts were calcined at 500 °C during 4 h under a dry air flow rate of 45 cm^3(STP) min^{-1}. Finally the catalysts were reduced at 200 °C in hydrogen with a flow rate of 50 cm^3(STP) min^{-1} during 3 h.

The monometallic catalysts (Cu-ZSM5, Pd-ZSM5, Th-ZSM5 and Rh-ZSM5) were prepared by the ion-exchange method, with 50 mL of aqueous solutions 0.01 M of the corresponding metal.[18,20] The catalysts were dried at 90 °C for 12 h, calcined under a dry air flow and finally reduced under a hydrogen flow. The bimetallic (CuPd-ZSM5, PdCu-ZSM5, ThCu-ZSM5 and RhCu-ZSM5) catalysts were prepared by the introduction of the second metal (0.01 M) into the monometallic catalyst by ion-exchange after the calcination step. Finally, the bimetallic catalysts were once more calcined and reduced at the same experimental conditions of the monometallic catalysts.

In the incipient wetness method,[21] only the aqueous solutions of palladium and copper salts were used for the preparation of the four bimetallic catalysts, Pd3%Cu3%-ZSM5, Pd1.5%Cu3%-ZSM5, Cu3%Pd3%-ZSM5 and Cu1.5%Pd3%-ZSM5, where the amount of metal is expressed in wt%, and the order of the metals corresponds to the respective order of impregnation. These samples were dried at 100 °C for 24 h, calcined under dry air (flow rate = 45 cm^3(STP) min^{-1}) at 500 °C for 4 h and reduced at 200 °C in hydrogen with a flow rate of 50 cm^3(STP) min^{-1} during 3 h.

Characterization methods

The textural characterization of the catalysts was based on the corresponding N_2 adsorption isotherms, determined at -196 °C with a Nova 4200e (Quantachrome Instruments) equipment. The micropore volumes (V_{micro}) and mesopore surface areas (S_{meso}) were calculated by the t-method. Surface areas were calculated by applying the BET equation. Mesopore size distributions were determined from the desorption branch of the isotherm using the Barrett, Joyner and Halenda (BJH) method. TPR experiments were carried out in an AMI-200 (Altamira Instruments) apparatus. The sample (about 100 mg) was placed in a U-shaped quartz tube located inside an electrical furnace and heated at 5 °C min^{-1} up to 600 °C under a flow of 5% (v/v) H_2 diluted with He (total flow rate of 30 cm^3(STP) min^{-1}). The H_2 consumption was followed by a thermal conductivity detector (TCD). NH_3-TPD spectra were obtained with a fully automated AMI-200 (Altamira Instruments) apparatus. The sample (circa 100 mg) was placed in a U-shaped quartz tube located inside an electrical furnace and heated at 10 °C min^{-1} using a constant flow rate of helium equal to 25 cm^3(STP) min^{-1} until 550 °C, in order to remove adsorbed impurities. Next, the sample was cooled to 100 °C and saturated for 90 min using 25 cm^3(STP) min^{-1} of 5 % NH_3/He (Air Liquid). The excess of ammonia was flushed out with helium (25 cm^3(STP) min^{-1}) during 40 min. Therefore, the temperature was increased to 700 °C at a rate of 10 °C min^{-1} in a 25 cm^3(STP) min^{-1} helium flow. A thermal conductivity detector (TCD) was used to measure ammonia. Room temperature Fourier Transform Infrared (FTIR) spectra of the samples in KBr pellets (2 mg of sample was mixed in a mortar with 200 mg of KBr) were measured using a Bomem MB104 spectrometer in the range 4000-500 cm^{-1} by averaging 32 scans at a maximum resolution of 8 cm^{-1}. Scanning electron micrographs (SEM) were collected on a LEICA Cambridge S360 Scanning Microscope equipped with an Energy-dispersive X-ray spectroscopy (EDX) system. In order to avoid surface charging, samples were coated with gold in vacuum prior to analysis, by using a Fisons Instruments SC502 sputter coater. Powder X-ray diffraction patterns (XRD) were recorded using a Philips Analytical X-ray model PW1710 BASED diffractometer system. Scans were taken at room temperature, using Cu Kα radiation in a 2θ range between 5° and 70°.The determination of the pH_{PZC} of the ZSM5 was carried out as follows: 50 mL of NaCl 0.01 M solution was placed in closed Erlenmeyer flasks; the pH was adjusted to values between 2 and 10 by adding HCl 0.10 M or NaOH 0.10 M; then, 50 mg of the sample was added and the final pH measured after 24 h under stirring at room temperature. For each pH, a blank experiment (without the zeolite) was carried out in order to subtract the variation of pH caused by the effect of CO_2 present in head space ($pH_{initial}$). The pH_{PZC} is the point where the curve pH_{final} *vs.* $pH_{initial}$ crosses the line pHinitial = pHfinal. High Resolution Transmission Electron Microscopy (HRTEM) measurements were performed on a JEOL2010F instrument; with 0.19 nm spatial resolution at Scherzer defocus conditions.

Catalytic tests

Reduction of bromate was performed using a semi-batch reactor, equipped with a magnetic stirrer and a thermostatic jacket, at room temperature and atmospheric pressure. In all experiments, the reactor was filled with 290 mL of ultrapure water and 150 mg of catalyst; then the magnetic stirrer was adjusted to 700 rpm and hydrogen as a reducing agent (flow rate = 50 cm^3(STP) min^{-1}) was passed through the reactor during 15 min to remove air. After that period, 10 mL of a bromate solution, prepared from $NaBrO_3$, was added to the reactor, in order to obtain an initial concentration of BrO_3^- equal to 10 mg L^{-1}. Small samples were taken from the reactor after defined periods for quantification of bromate and bromide ions. The ions were followed by ionic chromatography using an 881 Compact IC Pro of Metrohm apparatus equipped with anion exchange column Metrosep A Supp 7 250/4.01 of Metrohm.

Results and Discussion

Characterization of catalysts

ZSM5 zeolite and mono and bimetallic catalysts were studied as heterogeneous catalysts for the bromate reduction in water. Prior the catalytic tests, the physicochemical properties of the parent zeolite and the catalysts prepared were investigated by different analytical techniques.

In hydrogenation reactions, the acidity of the support plays an important role on the activity of the catalysts. The pH_{pzc} value obtained for ZSM5 was 4.4, which confirms the acidic properties of the zeolite. This result was obtained after the calcination of the parent zeolite, NH_4ZSM5. In this step, the ammonium present in the framework is transformed into NH_3 and H^+. NH_3 desorbs and the presence of protons increases the number of acid sites, enhancing the catalytic properties of the zeolite. The mono and bimetallic catalysts were prepared with the zeolite ZSM5 in ammonium form. After introduction of the metals and subsequent calcinations, the acid nature of the zeolite is preserved.

Ammonia temperature-programmed desorption (NH_3-TPD) was carried out to characterized the parent zeolite acidity after calcination. Fig. 1 shows the typical NH_3-TPD profile obtained for ZSM5. The total acidity and acid strength distribution can be obtained from the total peak area and relative area of NH_3-TPD peaks at lower and higher temperatures. The zeolite exhibits two well resolved NH_3 desorption peaks, one around 250 ^oC and the other around 450 ^oC. The low temperature peak corresponds to NH_3 desorption from the weaker acid sites and the high temperature peak is assigned to the stronger acidic sites.[22-24] The total amount of NH_3 desorbed from weak and strong acid sites for ZSM5 was 1.56 mmol g^{-1}. The value determined for total acidity in ZSM5 zeolite is due to the low aluminium content (2.25 wt%).

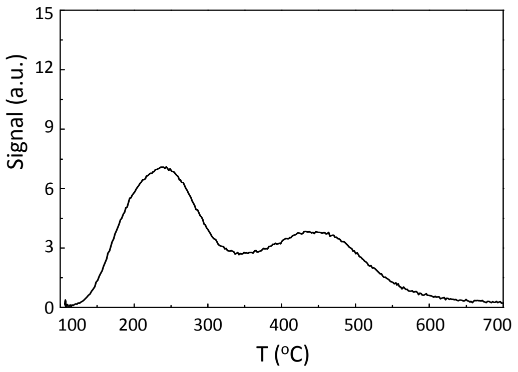

Fig. 1 Temperature programmed desorption profile of NH_3 from ZSM5 after calcination.

Characterization of the catalysts by XRD, N_2 adsorption, SEM/EDX and FTIR helps to understand the effect of the preparation methods used in the catalytic properties of the catalysts. XRD patterns obtained for all catalysts are in agreement with the characteristic diffraction pattern of the zeolite ZSM5, in terms of peak positions and their relative intensities. All catalysts exhibited the typical and similar patterns of highly crystalline MFI zeolite structure.[25] Fig. 2 shows the diffraction patterns of ZSM5 and mono and bimetallic catalysts with palladium prepared by the ion exchange method.

As expected, calcined ZSM5, Pd-ZSM5 and PdCu-ZSM5 display the same characteristic XRD patterns of the zeolite structure. These patterns show a well crystallized framework and a low background that is an indication of the absence of amorphous phase in these catalysts. No diffraction peaks assigned to metal species is observed for any of the catalysts. This absence suggests the successful incorporation of palladium and copper in the framework of ZSM5. Besides, the zeolite framework has not undergone any significant structural change during the preparation of these catalysts by the ion exchange method.

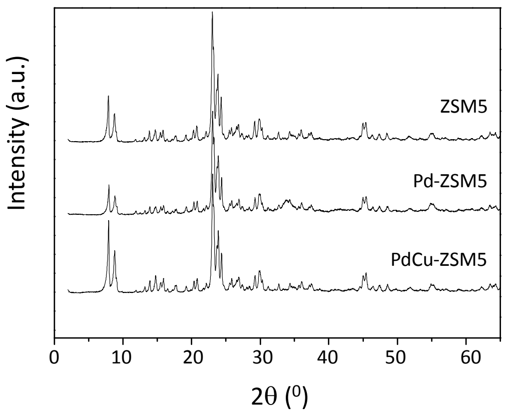

Fig. 2 XRD patterns of ZSM5, Pd-ZSM5 and PdCu-ZSM5 catalysts.

However, in the bimetallic catalysts prepared by the incipient wetness method there is a marked decrease in the intensity of the characteristic peaks of zeolite, showing the influence on the crystallinity of the catalysts. The relative crystallinity of catalysts was estimated by comparing the peak intensities of the samples with ZSM5, used as a standard (100 % crystalline), according to the standard method ASTM D-5758. For Pd-ZSM5 and PdCu-ZSM5, the crystallinities observed were 79% and 82%, respectively. This reduction of the crystallinity became more significant when the catalysts were prepared by the incipient wetness method. Values around 50% were calculated for these catalysts.

Textural properties obtained from the N_2 adsorption isotherms at -196 ºC for the parent zeolite and for all catalysts confirm that the incipient wetness method has a higher impact in the zeolite texture than the ion exchange method. The results are presented in Table 1.

As can be seen, the surface areas of the catalysts prepared by the ion exchange method are not significantly different from the parent zeolite. The decrease in the mesopore surface area was observed after the introduction of the second metal especially for the bimetallic catalysts ThCu-ZSM5. For the catalysts prepared by the incipient wetness method, there are severe decreases in both BET surface and mesopore surface areas concluding that this method caused a blockage of the pores of the zeolite. The occurrence of this obstruction causes a loss of ZSM5 acids sites, which will be affecting the catalytic activity.

Fourier Transformed Infrared spectroscopy confirms that the incipient wetness method causes damages in the structure of the zeolite. Fig. 3 displays the FTIR spectra of ZSM5 and the bimetallic catalysts with Pd and Cu prepared by the two methods.

FTIR spectra of the bimetallic catalysts are dominated by the strong bands assigned to the vibrational modes arising from the ZSM5 structure.

Table 1 Textural characterization and chemical analysis (wt%) of the parent zeolite and catalysts.

Catalysts	S_{BET} (m^2 g^{-1})	S_{meso} (m /g^{-1})	V_{micro} (cm^3 g^{-1})	M (wt%)^a
ZSM5	395	182	0.096	-
Pd-ZSM5	344	116	0.099	1.50
Cu-ZSM5	346	131	0.094	0.85
Th-ZSM5	382	180	0.091	0.40
Rh-ZSM5	377	153	0.098	0.45
PdCu-ZSM5	343	133	0.095	1.40 (Pd) 1.00 (Cu)
CuPd-ZSM5	374	174	0.089	0.55 (Cu) 1.90 (Pd)
RhCu-ZSM5	295	111	0.096	0.30 (Rh) 1.60 (Cu)
ThCu-ZSM5	377	27	0.194	0.35 (Th) 1.30 (Cu)
Pd3%Cu3%-ZSM5	86	0	0.072	1.20 (Pd) 1.70 (Cu)
Cu3%Pd3%-ZSM5	275	31	0.133	2.10 (Cu) 1.80 (Pd)
Pd3%Cu1.5%-ZSM5	250	56	0.101	-
Cu1.5%Pd3%-ZSM5	191	63	0.066	-

^{a}Loading of metals obtained by EDX

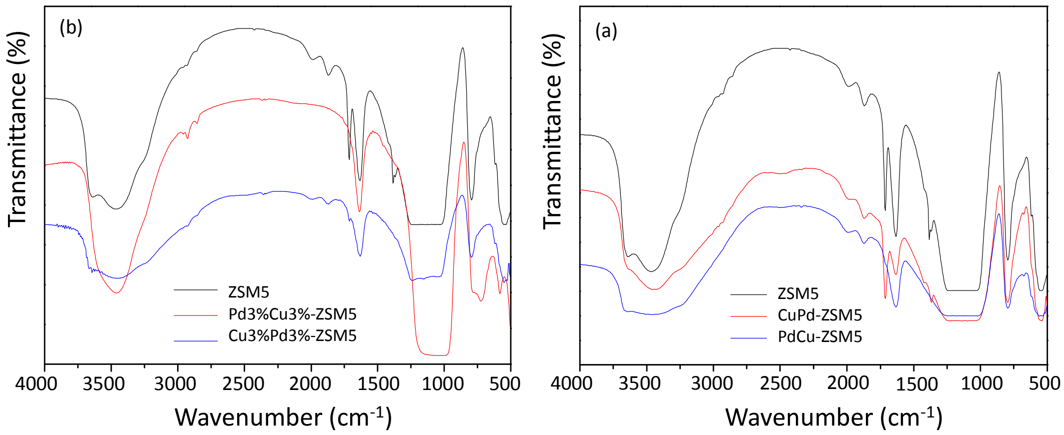

Fig. 3 FTIR spectra of the zeolite ZSM5 and bimetallic catalysts prepared by the ion exchange method (a) and by the incipient wetness impregnation method (b).

For ZSM5, the presence of physisorbed water is detected by the ν(O-H) stretching vibration at 3500 cm^{-1} and the δ(O-H) deformation band at 1650 cm^{-1}. The bands corresponding to the lattice vibrations are observed in the spectral region between 1250 and 500 cm^{-1}.[26] In all bimetallic catalysts, no new bands appear where the parent zeolite does not absorb. Also, no shift of the bands characteristic for vibration of zeolite framework was observed in spectra of the bimetallic catalysts, especially in the catalysts prepared by ion-exchange method. However for the catalysts prepared by the incipient wetness impregnation method, the intensity of the characteristic bands decreases. This implies that the zeolite structure is affect by this preparation method in agreement with XRD and N_2 adsorption analyses.

The morphology of the zeolite and catalysts was further confirmed by SEM analysis. Fig. 4 shows the SEM micrographs obtained for ZSM5 and the bimetallic catalysts PdCu-ZSM5, CuPd-ZSM5 and Cu3%Pd3%-ZSM5.

Analysis of the SEM micrographs of the ZSM5 and bimetallic catalysts show the typical morphology of the zeolite with the individual particles forming larger and irregular aggregates and no significant differences were found in the bimetallic catalysts prepared by the different methods. Therefore, the preparation of the catalysts by both methods does not cause any apparent modification on the morphology of the zeolite.

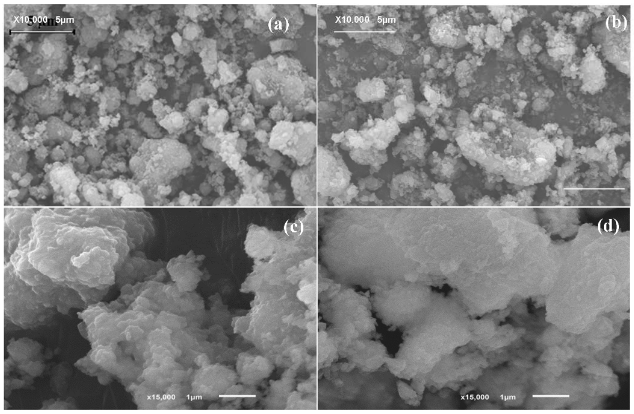

Fig. 4 SEM micrographs of (a) ZSM5, (b) PdCu-ZSM5 (c) CuPd-ZSM5 (d) Cu3%Pd3%-ZSM5 catalysts with different resolutions.

In order to have information about the dispersion of the metal particles in the bimetallic catalysts prepared by different methods, TEM analysis was carried out with PdCu-ZSM5 and Pd3%Cu3%-ZSM5. Fig. 5 displays the selected micrographs of the bimetallic catalysts with 100, 50 and 20 nm scale.

The typical morphology of the parent zeolite was preserved after the preparation of the catalysts by both methods,[27,28] in agreement with SEM analysis. Also, the presence of the metals in both bimetallic catalysts can be observed. The catalyst prepared by the ion exchange method shows a good dispersion of the metals, especially for palladium, which was the first metal ion exchanged. Cu particles are detected by TEM analysis and suggest that this metal is more available at the surface of zeolite particle. However, Pd particles are not detected by TEM probably because they have a diameter lower than 2 nm (detection limit of the equipment used). As expected, the distribution of the metal particles is different for the bimetallic catalyst prepared by impregnation method, where large particles are clearly seen. The presence of both metal particles is clearer in the micrographs and was confirmed by EDX analysis. The periphery of the zeolite particles was richer in both metals than the interior and both metals are accessible to the surface of the zeolite.

The chemical analysis of the mono and bimetallic catalysts prepared the by the ion exchange method was obtained by Energy-dispersive X-ray (EDX) analysis and the results are present in Table 1.

From chemical analysis, the amount of copper was shifting between 0.55 and 1.60 wt% and palladium content ranges from 1.40 to 1.90 wt% for the catalysts prepared by ion exchange method. As expected, the decrease observed in the mesopore surface was more pronounced in the bimetallic catalysts than in the monometallic catalysts. For the bimetallic catalysts prepared by the incipient wetness impregnation method, the amount of copper or palladium is higher (the amount of each metal ranges from 1.5 to 3.0 wt%) than the same catalysts prepared by the ion exchange method. Also the metal atoms in these catalysts are preferentially located on the surface and, thus, more likely accessible to the reagents. In the catalysts prepared by the ion exchange method, the metals are probably located within the mesopores.

Temperature Programmed Reduction (TPR) profiles of the monometallic catalysts is shown in Fig. 6. All catalysts exhibit identical profiles.

Considering that the range of temperature reduction of these catalysts was 100-200 °C, the temperature of 200 °C was selected to perform the reduction of the catalysts. In the case of Pd-ZSM5, the reduction peak observed at 60 °C is attributed to the decomposition of Pd β-hydride.[29,30] The bimetallic PdCu-ZSM5 catalyst (profile not shown) presented a single reduction peak around 150 °C that can be assigned to the reduction of Cu oxides, promoted by the presence of the noble metal.[31,32] The decrease in the reduction temperature of supported copper in bimetallic catalysts induced by the presence of palladium indicates that a close proximity between copper and palladium species was achieved.[30]

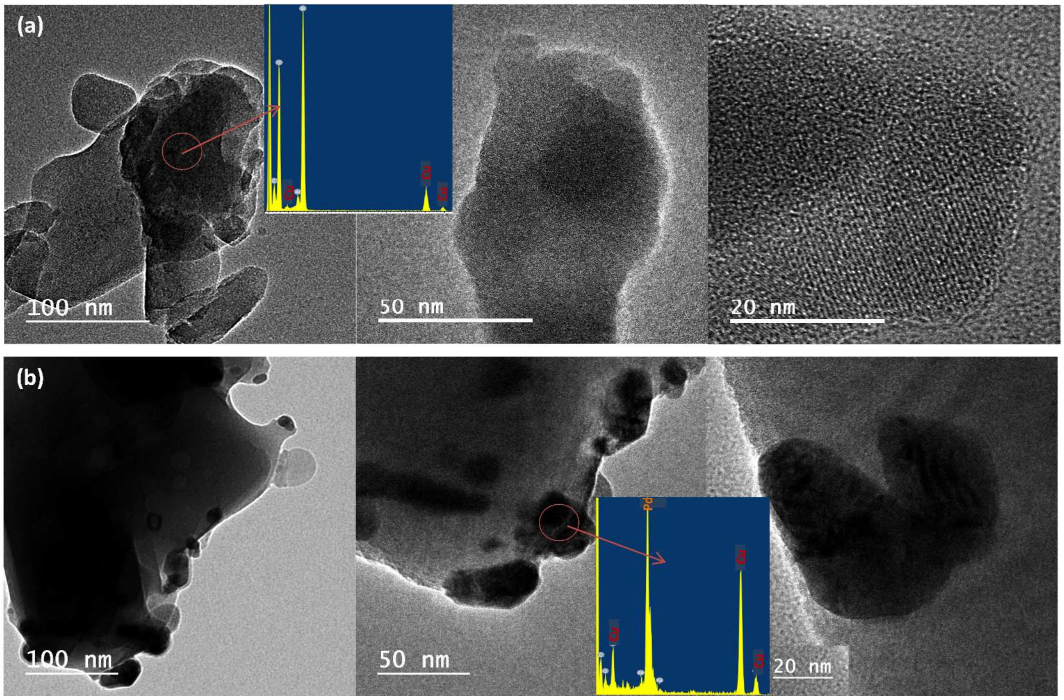

Fig. 5 TEM micrographs of (a) PdCu-ZSM5 and (b) Pd3%Cu3%-ZSM5 catalysts.

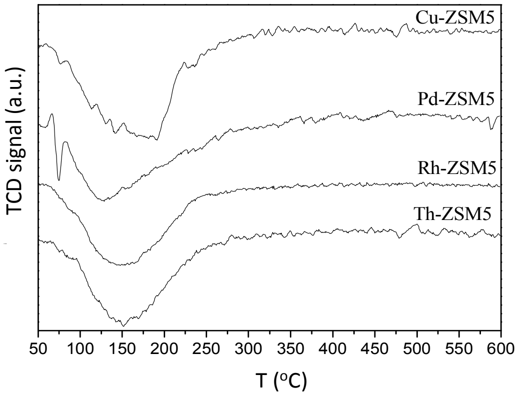

Fig. 6 TPR profiles of the monometallic catalysts.

Catalytic tests

Fig. 7 shows the evolution of bromate concentration, over the mono and bimetallic catalysts prepared by ion exchange method.

Blank tests using only the zeolite (ZSM5) and hydrogen were also carried out. It was observed that the reduction of bromate into bromide ion occurs in the blank tests. All the experiments were carried out in the presence of hydrogen and in all cases it was observed that bromate is being completely converted. The distributions of bromate and bromide concentrations during the reaction time show that the removal of bromate over the ZSM5 and catalysts completely corresponds to the conversion into bromide. This fact eliminates the possibility of bromate removal by adsorption on the ZSM5 surface. Hydrogen by itself resulted in a bromate removal of approximately 70% after 120 min of reaction, but in the presence of ZSM5 almost complete conversion is achieved at the same reaction time. The presence of metals improved significantly the conversion of bromate. Through these results Pd appears as the ideal metal to be used in this catalytic reduction, as suggested in the literature[33,34] once the Pd-ZSM5 catalyst shows faster removal when compared with the other metals. These results are probably due to the hydrogen activation properties of Pd[12] and to the structural properties of this metal on the zeolite surface, where Pd metal with large particle size has high activity.[33,34] 100% conversion was achieved after 10 min of reaction for the bimetallic catalysts prepared by ion exchange method.

The catalysts prepared with the metals Th and Rh (Fig. 8) exhibit different catalytic activity from discussed for the previous catalysts. In this group of catalysts, those with better performance are ThCu-ZSM5, Th-ZSM5 and Rh-ZSM5 completely converting bromate to bromide at the end of 20, 60 and 90 min, respectively. Comparing the bimetallic catalysts, copper and palladium demonstrated to be the most promising catalysts in the reduction of bromate into bromide. In the bimetallic catalysts the incorporation of a promoter metal (copper) improves the performance of all catalysts with the exception of the rhodium catalyst.

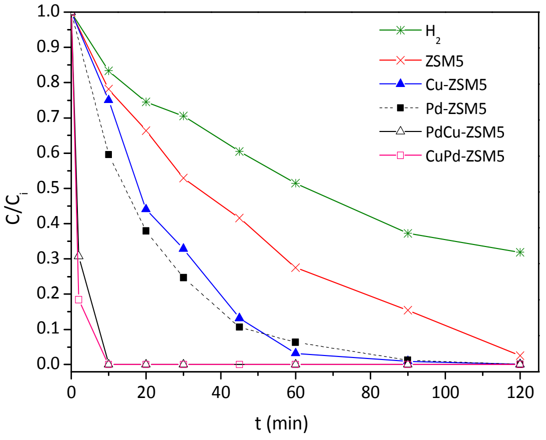

Fig. 7 Dimensionless concentration of bromate as a function of time in the presence of hydrogen, the zeolite ZSM5 and over the mono and bimetallic catalysts with Pd and Cu prepared by the ion exchange method ($C_{BrO_3^-}$ = 10 mg L^{-1}, catalyst = 0.5 g L^{-1}, Q_{H_2} = 50 cm^3(STP) min^{-1}, T = 25 °C).

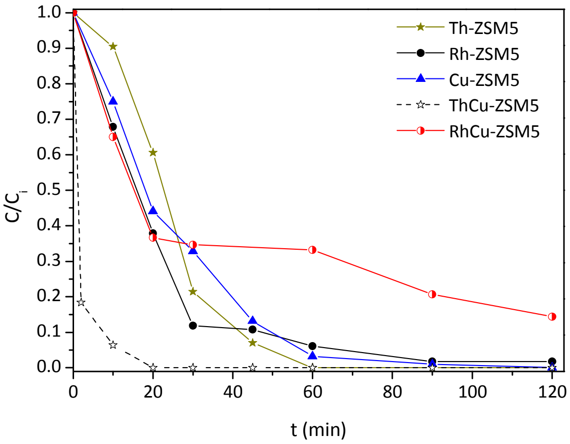

Fig. 8 Dimensionless concentration of bromate as a function of time over the mono and bimetallic catalysts with Th, Rh and Cu prepared by the ion exchange method ($C_{BrO_3^-}$ = 10 mg L^{-1}, catalyst = 0.5 g L^{-1}, Q_{H_2} = 50 cm^3(STP) min^{-1}, T = 25 °C).

For heterogeneous catalysis, the catalytic reaction essentially occurs on the catalyst surface and reactant adsorption is a prerequisite step.[34] In order to test the influence of the preparation method in the reaction, the bromate reduction was evaluated over Pd and Cu catalysts prepared by the incipient wetness impregnation method with different contents of promoter metal. The results obtained are shown in Fig. 9.

As it can be observed, these bimetallic catalysts show activity in the reduction of bromate; however, the best results are obtained for the catalysts with lower amount of Cu. Effectively, in this group, the catalysts with the best results are Cu1.5%Pd3%-ZSM5 and Pd3%Cu1.5%-ZSM5, followed by Cu3%Pd3%-ZSM5.

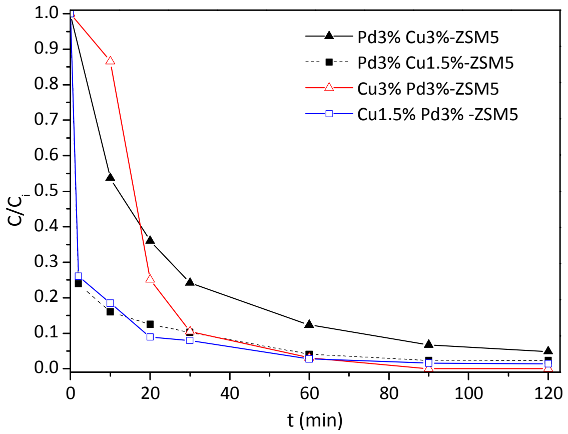

Fig. 9 Dimensionless concentration of bromate as a function of time over the catalysts with Pd and Cu supported on ZSM5 prepared by the incipient wetness method ($C_{BrO_3^-}$ = 10 mg L^{-1}, catalyst = 0.5 g L^{-1}, Q_{H_2} = 50 cm^3(STP) min^{-1}, T = 25 °C.

Comparing the performance of the bimetallic catalysts prepared by the impregnation method (Fig. 9) with the catalysts prepared by ion exchange (Fig. 7), it can be stated that the ion exchanged catalysts have better outcomes. The performance of these catalysts is related to the excess of metal impregnated on structures resulting in pores obstruction, as determined by the amount of surface area shown in Table 1. It can be observed that the impregnated catalysts with the lowest percentage of Cu have higher surface areas and therefore allow better conversion rates.

The occurrence of obstruction causes a loss of the ZSM5 acid sites and affects its microporosity, preventing the access of the reactants to the internal structure; the ion exchange catalysts became more promising because they have a more free structure to promote bromate reduction.

The results obtained in the present study are in line with those obtained in previous works using activated carbon as support,[35, 36] where the catalysts based on Pd and Pd-Cu demonstrated to be the most efficient in the bromate removal from water. The main difference observed is related to the absence of bromate adsorption when the zeolite is used as support. For similar operation conditions, the bromate removal is faster for the Pd-Cu catalysts prepared by the ion exchange method in the ZSM5 zeolite. Nevertheless, when the metals are supported by the incipient impregnation method, the catalysts supported on the activated carbon present better performances[36] than those supported on the zeolite allowing faster bromate reduction into bromide.

An additional experiment was carried out using sample Cu1.5%Pd3%-ZSM5 to investigate the stability of the catalysts. After a first typical experiment, the catalyst was dried and used again under the same experimental conditions. The results obtained (Fig. 10) demonstrated that the catalyst has the same activity in the three consecutive runs.

Considering the practical application of these catalysts in water treatment, it is important to find catalysts not only active for bromate reduction but also stable, without metal leaching, in order to avoid the increase of effluent toxicity. Therefore, after each reaction test, the amount of leached metals was measured. No dissolution of Pd was detected (within the experimental error) in all the experiments, whereas Cu is leached in different amounts; however the obtained results are lower than 1% of the initial amount.

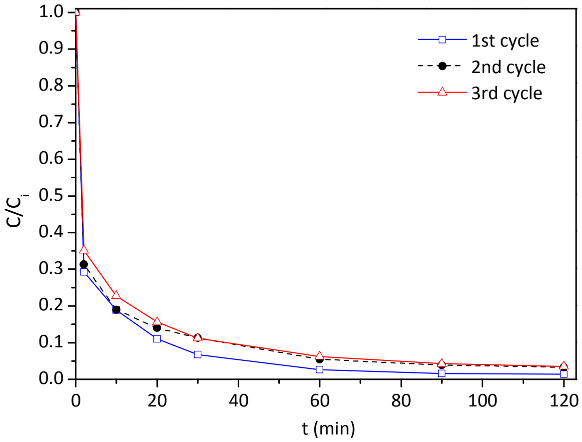

Fig. 10 Dimensionless concentration of bromate as a function of time for Cu1.5%Pd3%-ZSM5 after 1, 2 and 3 consecutive runs. ($C_{BrO_3^-}$ = 10 mg L^{-1}, catalyst = 0.5 g L^{-1}, Q_{H_2} = 50 cm^3 (STP) min^{-1}, T = 25 °C.

Taking into account the results obtained here and those shown in a previous work,[35] the reaction can occur by different pathways. Bromate can be reduced by direct reaction with hydrogen in solution, by adsorption and reduction by hydrogen on the surface of the zeolite and also by adsorption and reduction by hydrogen on the surface of the metallic particles. Then, bromide is released in the solution and the metal becomes oxidized. To complete the cycle, hydrogen also reduces the metal phases, which are available again to further interaction with bromate and hydrogen.[37]

Conclusions

The mono and bimetallic ZSM5 catalysts are very active in the reduction of bromate to bromide. The presence of metals in the zeolite structure improve significantly the conversion of bromate. 100% conversion was achieved after 10 min of reaction for the bimetallic catalysts containing Pd and Cu, obtained by the ion exchange method. Comparing the bimetallic catalysts, copper and palladium demonstrated to be the most promising catalysts in the reduction of bromate into bromide. The leaching of the metals in the active catalysts was not noteworthy and can be efficiently reused in sequential catalytic cycles. These results clearly show that the mono and bimetallic catalysts based on zeolites have plenty of potential in the removal of bromate from water sources.

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ARTICLE

Graphical Abstract

Reduction of bromate to bromide over mono and bimetallic ZSM5 catalysts was efficiently achieved and PdCu-ZSM5 is the best catalyst.