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Characterization and catalytic performance of a bimetallic Pt–Sn/HZSM-5 catalyst used in denitratation of drinking water

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Abstract

Removal of nitrates and nitrites from drinking water by catalytic hydrogenation over zeolite-supported Pt–Sn catalysts was studied. Bimetallic Pt–Sn/HZSM-5 catalysts were characterized by temperature-programmed reduction (TPR), H_2 chemisorption, X-ray photoelectron spectroscopy (XPS) and ^{119}Sn Mössbauer spectroscopy. The characterization techniques showed a significant decrease in the H/Pt ratio upon tin addition, tin surface enrichment, the formation of PtSn alloys and platinum catalysis of the tin reduction. The Pt–Sn/HZSM-5 catalyst clearly showed high catalytic activity for the reduction of nitrate to form N_2. In the bimetallic catalyst, the role of tin is to reduce nitrate or nitrite according to a redox process, while the platinum maintains tin in the metallic state.

Keywords: Nitrate/nitrite hydrogenation; Pt–Sn/ZSM-5; Pt–Sn alloy

1. Introduction

Nitrate is a widespread contaminant of ground and surface waters worldwide [1,2] and is a potential human health hazard, especially to infants, causing the condition known as methemoglobinemia, also called blue baby syndrome. Methemoglobin is probably formed in the intestinal tract of an infant when bacteria convert nitrate ions to nitrite ions [3]. This altered form of blood protein prevents blood cells from absorbing oxygen, leading to slow suffocation of the infant and possible death [4]. Chronic consumption of high levels of nitrate may also cause other health problems, for example some cancers and teratogenic effects; data are inconclusive, but remain a cause for concern [5,6].

Venezuelan environmental legislation has established a current drinking water standard and health advisory level of 10 mg/l nitrate-nitrogen (equivalent to 10 ppm nitrate-nitrogen or 45 ppm nitrate) based on the human health risks due to nitrate consumption. Standard water treatment practices, such as sedimentation, filtration, chlorination or pH adjustment with lime application, do not affect nitrate concentrations in water [7]. Nitrates from water can be removed by specialized water treatment technologies, such as ion exchange, biochemical denitrification, and reverse osmosis. Incorporation of these technologies for the removal of nitrates into a water treatment system could substantially increase the cost of water treatment. One decontamination method recently developed is the selective catalytic or electrocatalytic reduction of nitrate and nitrite to nitrogen. Different monometallic and bimetallic catalysts were found to be efficient for these reactions [8–27]. However, most of them are not selective enough and ammonia, a harmful contaminant, is obtained as a by-product. Humans and higher animals are less sensitive to ammonia in water, but long-term ingestion of water containing more than 1 mg/l (ppm) ammonia may be damaging to internal organ systems. Venezuelan legislation has established a drinking water standard of 0.5 mg/l (ppm). The rate of ammonia formation increases with increasing temperature and decreasing concentration of nitrate and H^+, i.e., selectivity for N_2 formation increases with decreasing pH. This points to the

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necessity of reliable control of the molar ratio of hydrogen to nitrate (nitrite) to achieve selective reduction to nitrogen. Improvement of the selectivity for nitrogen formation requires the solution of two problems: (i) an appropriate catalyst formulation and (ii) accessibility of catalytic sites. Based on these requirements, we considered it interesting to study Pt–Sn on HZSM-5 and to use such catalysts for the reduction of these substrates in aqueous solution.

2. Experimental

2.1. Preparation of the catalysts

The parent ZSM-5 zeolite was synthesized by an established hydrothermal procedure using tetrapropylammonium ions as template and subsequently ion-exchanged with an excess of 0.5 N HCl at 100 °C. Analysis of Na and Al contents, followed by the measurement of cation exchange capacity of the ammonium ions, allowed estimation of the chemical formula $Na_{0.1}H_{5.9}(AlO_2)_{6.0}(SiO_2)_{90.0}$. Tin- and platinum-modified ZSM-5 zeolite catalysts were prepared by ion exchange of platinum ($[Pt(NH_3)_4]Cl_2$) into the support, followed by tin ($SnCl_2{\cdot}2H_2O$) precipitation under basic conditions. Samples were calcined in air with stepwise increasing temperature at 1 °C/min and held at 300 °C for 1 h.

2.2. Elemental analysis

Elemental analysis was carried out by atomic absorption spectroscopy (Perkin-Elmer Analyst 100) after dissolution of suitable samples.

2.3. specific surface area

The BET specific surface areas were measured in a Micromeritics ASAP 2010 instrument. As pre-treatment, 100 mg of catalyst was placed in a quartz tube and evacuated for 1 h at 150 °C. The experimental error in the surface area measurement is approximately 10%.

2.4. X-ray diffraction

X-ray diffraction (XRD) patterns were collected at room temperature on a Siemens D5000 diffractometer using Ni-filtered Cu Kα ($\lambda = 1.5418$ Å) radiation at 40 kV and 30 mA. Diffraction intensities were collected in the 2θ range 5–90°. Qualitative phase analysis was carried out using the Siemens Diffrac AT software package.

2.5. Platinum dispersion

Hydrogen chemisorption experiments were performed in a conventional BET system similar to that used in by Betancourt et al. [28]. Catalyst samples of approximately 0.2 g were placed in a glass microreactor and reduced in situ with pure H_2 (60 cm^3/min) for 2 h at 500 °C. After evacuating the catalysts at the same temperature for 1 h, two adsorption isotherms were obtained at room temperature. The linear region of the first isotherm was extrapolated to zero to calculate the amount of physisorbed and chemisorbed H_2. The same procedure as for the first isotherm was used to calculate the amount of physisorbed species. The irreversibly held H_2 was calculated from the difference between both values. A 1:1 H/Pt stoichiometry was assumed to calculate the metallic dispersion (H/Pt). Blank experiments on the HZSM-5 support proved that there was no measurable uptake of hydrogen on the support itself or on the Sn/HZSM-5 sample.

2.6. Temperature-programmed reduction

The catalyst reducibility (after calcination) was probed by temperature-programmed reduction (TPR) using a Micromeritics 2900 TPR/TPD system, utilizing approximately 100 mg of catalyst in the quartz U-tube flow reactor. TPR was carried out by heating the sample from room temperature to 1000 °C (10 °C/min) under 5% H_2/Ar (vol.%) at a flow rate of 30 ml/min.

2.7. ^{119}Sn Mössbauer spectroscopy

^{119}Sn Mössbauer measurements were carried out in situ with a $^{119}Sn{:}CaSnO_3$ source (320 MBq) at 4.2 K using a liquid-helium-bath cryostat. The sample was treated in a special glass reactor and then transferred into a cylindrical glass ampoule attached to the reactor. Before sealing off the ampoule, the atmosphere was changed to helium, ensuring that temperature equilibrium was rapidly established when the samples were cooled down to 4.2 K for the Mössbauer measurement. The spectra were analyzed by a least-square fitting. Gaussian broadening into Voigt profiles was allowed for the Lorentzian lines by assuming a Gaussian distribution for the isomer shift. Thus, spectral parameters such as the electric quadrupole splitting (QS), the mean isomer shift (IS), and the relative resonance areas (Area) of the different spectral components were determined (Table 3). The Mössbauer spectrum of the reduced catalyst is shown in Fig. 2. Isomer shifts were referred to SnO_2.

2.8. X-ray photoelectron spectroscopy (XPS)

XPS spectra were recorded with a VG Instruments Escalab 200i spectrometer interfaced to a computer, using Mg Kα radiation (1253.6 eV). Spectral analysis involved smoothing, inelastic background removal using a linear integral profile, and curve-fitting by the least-squares method (using a mixed Gaussian–Lorentzian function). Atomic concentration ratios were calculated by correcting the intensity ratios with theoretical sensitivity factors based on the Scofield cross-section. The experimental error of XPS measurements for BE was considered to be approximately 0.2 eV.

Table 1
The operation conditions of catalytic nitrite reduction

Reaction temperature (K)	298
Operating pressure (bar)	1.0
Catalyst weight (g)	0.3
Initial nitrate/nitrite concentration (mg/l)	50
Reaction volume (l)	2
Hydrogen flow rate (ml/min)	60
Reaction time (min)	130

2.9. Catalytic testing

The catalytic reduction of nitrates and nitrites was carried out in an isothermal 2 l reactor made of Pyrex glass, equipped with a mechanical stirrer and temperature control. Hydrogen addition occurred via a glass frit. The temperature of the reaction mixture was set at 298 K, successfully controlled within ±0.1 K. In a typical run, a given amount of fresh (previously reduced) catalyst was suspended in the reactor containing distilled water, hydrogen was allowed to flow for 15 min and the reaction was started by adding an appropriate amount of KNO_3 or $NaNO_2$ solution to a final concentration of 50 mg/l. It was checked that the hydrogen flow and stirring were sufficient to ensure that the reaction was not rate-limited by reactant diffusion. The extent of the reaction was monitored by withdrawing samples periodically and analyzing them for nitrate and nitrite concentration. The reaction conditions used in this work are listed in Table 1. The pH values of samples were determined with a digital pH-meter (Orion model 710A). The reaction mixture was periodically sampled and the concentrations of NO_3^- and NO_2^- were analyzed with a Dionex DX-120 ion chromatograph. Ammonia was analyzed either spectrophotometrically (Standard Method 4500-NH_3 F) or by titration (Standard Method 4500-NH_3 C) [29].

3. Results and discussion

Table 2 shows the metal content and specific surface area (SSA) of the catalysts. It can be observed that there was no variation in SSA for the monometallic catalysts, with a value of ~380 $m^2\,g^{-1}$. The table also shows that the calcined bimetallic catalyst had a smaller area than the respective support (or monometallic catalyst).

The XRD pattern of the as-synthesized zeolite corresponds with the ZSM-5 phase (*Pnma*) with full crystallinity.

Results of H_2 chemisorption are reported in Table 2. The monometallic sample Pt/HZSM-5 shows an H/Pt ratio of 0.366. Addition of tin caused a strong decrease in the H/Pt ratio. This indicates that the availability of surface Pt atoms was markedly depressed by tin addition due to partial covering of the platinum surface by Sn species or/and by alloying of the particles. Several authors [30–32] have shown that for a bimetallic platinum–tin catalyst, alloy formation changes the hydrogen chemisorption. No adsorption of hydrogen was measured on the Sn/HZSM-5 sample.

Table 2
Main characteristics of the catalysts

Catalyst	Pt (%)	Sn (%)	SSA ($m^2\,g^{-1}$)	H/Pt
HZSM-5	–	–	380	0
Sn/HZSM-5	–	0.8	378	0
Pt/HZSM-5	0.5	–	380	0.366
Pt–Sn/HZSM-5	0.5	0.7	335	0.169

To investigate the reducibility of samples, a TPR study was carried out. Fig. 1 shows the TPR patterns for unreduced mono- and bimetallic catalysts. For the monometallic Pt/HZSM-5 catalyst, only a broad reduction peak centered at 250 °C was observed (Fig. 1a), which corresponds to the reduction of Pt(IV) to Pt^0. The temperatures are higher than those reported for bulk H_2PtCl_6 [33]. This indicates strong interaction of the metal with the support, which leads to different platinum species, as also suggested by the broad reduction peak. On the other hand, the TPR profile for the catalyst with 0.8% tin (Fig. 1c) shows one broad reduction peak starting at 400 °C with the maximum around 700 °C, probably indicating the presence of at least two different forms of tin. When the profiles of the two monometallic catalysts, Pt and Sn, are added, the sum does not match the profile of the bimetallic Pt–Sn catalyst (Fig. 1b). The profile obtained showed a double reduction peak with a maximum between 300 and 400 °C. This can be attributed to the reduction of Pt(IV) to Pt^0. The tin in the Pt–Sn catalyst was reduced at a lower temperature than in the Sn catalyst. This is most probably caused by platinum catalysis of the tin reduction [34–37]. This indicates that the two metals are in close contact.

X-ray photoelectron spectroscopy was carried out to obtain information on the oxidation state of both the noble metal and promoter. XPS data show that oxidized tin is the predominant form in the calcined bimetallic sample. Only small amounts of zero-valent tin have been identified. All or part of metallic tin could be alloyed with platinum to give PtSn alloys. The formation of PtSn alloys of different

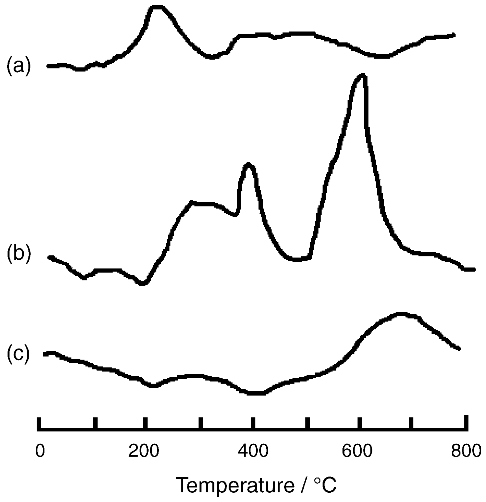

Fig. 1. TPR profiles of: (a) Pt/HZSM-5; (b) Pt–Sn/HZSM-5; (c) Sn/HZSM-5.

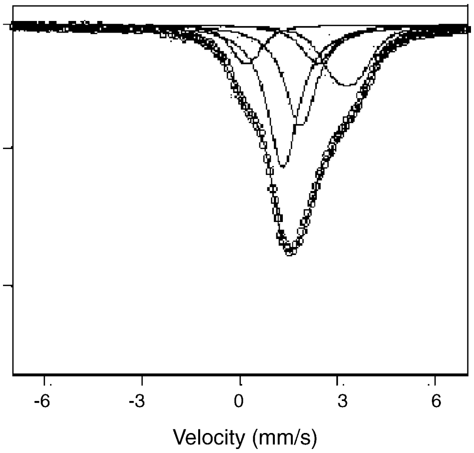

Fig. 2. ^{119}Sn Mössbauer spectra at 4.2 K of the Pt–Sn/HZSM-5 catalyst.

composition (PtSn, Pt_3Sn, Pt_2Sn_3, $PtSn_4$ and $PtSn_2$) has been reported by several authors [31,38]. However, no conclusion can be drawn regarding alloy formation in our bimetallic catalyst from the XPS data due to the limitations of this technique. The XPS data also show significant Sn surface enrichment in the bimetallic sample, with a surface Sn/Pt atomic ratio of 2.1.

The Mössbauer spectrum of Pt–Sn/HZSM-5 is rather complex, extending from approximately zero velocity to nearly 4 mm/s (Fig. 2) and revealing several components. These can be divided into three main groups of Sn-containing species: the shoulder at the left side of the spectrum, near zero velocity, is attributable to tetravalent tin, probably in the form of a tin(IV) oxide. This component accounts for <10% of the total resonance area, indicating that only a small part of the tin is completely oxidized (Table 3). The central part of the spectrum has isomer shifts typical for intermetallic compounds of Pt and Sn. In fact, in bimetallic Pt–Sn compounds, the isomer shift changes linearly with the composition, from 2.56 mm/s in β-Sn to approximately 1.2 mm/s in diluted solid solutions of Sn in Pt [39]. The corresponding part of the spectrum can be fitted with between three and five single lines without a notable change in the accuracy of the fit. The result of such fits yields Mössbauer parameters corresponding to practically the whole range of compositions. Since the choice of the number of components is arbitrary, their attribution to specific Pt–Sn species is ambiguous. In Table 3, the results obtained by fitting the smallest possible number of lines are given without attributing these lines to specific bimetallic alloys. In any case, the data suggest that almost all of the possible intermetallic compounds may form, in agreement with previous investigations of Pt–Sn/Al_2O_3 catalysts in which several different species, namely Pt metal (which may contain up to approx. 12% Sn), Pt_3Sn, PtSn, $PtSn_2$ and $PtSn_4$ were identified [39–41]. It should be noted, however, that components with smaller isomer shifts, i.e., those attributable to species with a low Sn content, are more intense than those at more positive velocities (Table 3), indicating that zero-valent tin is mostly contained in Pt-rich species. Finally, together with the components typical for Pt–Sn intermetallic compounds, in this portion of the spectrum the presence of components due to surface Sn atoms on Pt cannot be ruled out. In fact, Bowles and Cranshaw [42], in a study on monolayers of Sn on Pt, found that the Mössbauer spectrum of Sn monoatomic layers on Pt is a quadrupole doublet, having an isomer shift slightly smaller than that of β-Sn. Such a spectral feature could therefore be hidden by those attributed to the intermetallic compounds.

Table 3
^{119}Sn Mössbauer parameters at 4.2 K of the Pt–Sn/HZSM-5 catalyst

QS (mm/s)	IS[a] (mm/s)	Area (%)	Chemical state of tin
0.4(1)	0.19	9	Sn(IV)
0	1.32	36	Sn(0)
0	1.86	26	Sn(0)
0	2.36	10	Sn(0)
0.70(5)	3.26	19	Sn(II)

[a] Isomer shift referred to the $CaSnO_3$ source.

The third region of the spectrum at the most positive velocities can be fitted with a broadened quadrupole doublet. The average parameters of this doublet fall in the typical range for divalent tin compounds, although they are different from those of Sn(II) oxides and hydroxides [43] and from those obtained for oxidic Sn(II) in previous studies of Pt–Sn catalysts [44–48], which were mainly prepared by impregnation. The difference lies mainly in the value of the quadrupole splitting, which is smaller than the values obtained in previous studies, while the values of the isomer shift are comparable. Components with a quadrupole splitting smaller than that of Sn(II) oxides were attributed to surface Sn(II) by Kuznetsov et al. [45]. However, although it is not improbable that this component is due to the presence of Sn(II), it appears to be different from the oxidic Sn(II) usually formed in Pt–Sn catalysts prepared by impregnation.

The catalytic behavior of the samples was tested in the hydrogenation of nitrate/nitrite solutions. During the reduction experiments, the solution pH was measured. The pH of the solution increased sharply at the start of the reaction and then increased slowly and tended to a value near 10. This evolution of pH is due to reactions involved in the reduction process leading to the formation of OH^-. Table 4 gives a summary of the reactivity features of the different catalysts. It can be observed that Pt–Sn/HZSM-5 was the most active catalyst for nitrate reduction, but also produced the highest amount of ammonia (7 ppm). The use of tin as promoter yields high activity and poor selectivity. The level of ammonium ion formation was determined for the three catalysts. Results are reported in Table 4. According this table, the bimetallic catalyst shows important selectivity towards ammonium ions, although this is lower than that obtained for the Pt/HZSM-5 catalyst. This result implies that tin addition modulates the formation of ammonium ions on the bimetallic catalyst. Parameters such as particle size,

Table 4
Reactivity features of the different catalysts in the hydrogenation of nitrate and nitrite

Catalyst	Nitrate			Nitrite	
	Activity (mg g_{cat}^{-1} h^{-1})	NO_2^- (ppm)	NH_4^+ (ppm)	Activity (mg g_{cat}^{-1} h^{-1})	NH_4^+ (ppm)
Sn/HZSM-5	54.1	0.0	0	64.5	0.1
Pt/HZSM-5	0	0.4	11	301.1	3.0
Pt–Sn/HZSM-5	304.1	0.2	7	92.8	0.7

electronic, and/or geometric effects induced by the tin could explain these changes. On the other hand, the formation of a certain quantity of ammonia over catalysts based on HZSM-5 could trap this component on acid sites of the support.

It should be noted that the nitrite concentration formed as a reaction intermediate after complete conversion of the nitrate is lower than the limit allowed by legislation.

The Pt/HZSM-5 catalyst showed no activity towards the removal of NO_3^-, while showing considerable activity for the removal of NO_2^- ions. The Sn/HZSM-5 solid showed low but comparable catalytic activity towards the removal of the aforementioned ions. When tin was incorporated into the Pt/HZSM-5 catalyst, an increase in catalytic activity for nitrate reduction was observed. The latter catalyst shows nitrate removal activity five-fold higher than the monometallic tin catalyst.

If Pt and Sn exist as separate entities on zeolite, the nitrate hydrogenation activity of the bimetallic catalyst would be expected to be similar to that corresponding to Pt and Sn contributions separately. The bimetallic catalyst exhibits activity showing a synergistic effect from the addition of tin to the Pt catalyst, since the catalytic activity is greater than that expected from the individual contributions of the separate platinum and tin entities.

In contrast to the nitrate reduction results, the catalytic activity of platinum for nitrite hydrogenation decreased with the addition of tin (Table 4). It is important to point out that the catalytic activity for nitrite removal follows the same trend as for hydrogen chemisorption, suggesting a surface arrangement responsible for the behavior in nitrite hydrogenation. The possibility that tin concentrates strongly on the surface of the Pt–Sn/HZSM-5 catalyst (vide supra XPS data) would imply a much greater change in catalytic properties in the surface region (formation of composites such as PtSn alloys).

In the present study, it was shown that the monometallic platinum catalyst is inactive for nitrate reduction, while metallic-state tin is able to reduce nitrate according to a redox reaction. Therefore, we can infer that the first step in the nitrate reduction is probably a redox reaction between Sn(0) (or alloy PtSn centers) and nitrate ions, leading to nitrite intermediates or directly to N_2 or ammonium ions, and to an oxidized form of tin. Subsequently, the role of the platinum is to activate hydrogen, allowing the reduction of tin. With regard to nitrite intermediates, they could be reduced either on tin, according to a similar redox process similar to that described above, or on the platinum by catalytic reduction. Similar proposals for the Pt–Cu/Al_2O_3 system have been published [11].

4. Conclusion

The investigation of the catalytic properties of Pt–Sn/HZSM-5 for the catalytic reduction of nitrate (nitrite) ions in water can be summarized as follows:

1. The characterization results are: (a) a significant decrease in the H/Pt ratio upon addition of tin; (b) tin surface enrichment revealed by XPS; (c) the observation that the catalyst contains bimetallic PtSn alloys; (d) platinum catalyzes the reduction of tin.
2. Tin can reduce nitrates and nitrites according to a redox process. Monometallic platinum catalysts are inactive for nitrate reduction.
3. The Pt–Sn/HZSM-5 catalyst clearly showed catalytic activity for the decomposition of nitrate to form N_2. In the bimetallic catalyst, the role of tin is to reduce nitrate or nitrite according to a redox process. In this step, the interaction between tin and platinum is of major importance, maintaining tin in the metallic state. The Pt–Sn/HZSM-5 sample reported here appears to be valuable catalyst from the viewpoint of the environmental protection of water.

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