



Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: [www.elsevier.com/locate/electacta](http://www.elsevier.com/locate/electacta)



## Silver/ion exchanger nanocomposites as low-temperature redox-catalysts for methanal oxidation

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### ARTICLE INFO

#### Article history:

Received 23 December 2014

Received in revised form 31 March 2015

Accepted 31 March 2015

Available online xxx

#### Keywords:

catalytic oxidation  
silver nanoparticles  
formaldehyde (methanal)  
acetaldehyde (ethanal)  
pH effects  
anion-exchange matrix  
composite material  
redox-catalysis

### ABSTRACT

Metal/granulated ion exchanger materials composed of silver nanoparticles distributed near the external surface of anion- or cation-exchanger have been synthesized via redox deposition procedure, anion-exchanger composites being in its strongly basic ( $\text{OH}^-$ ) form while the cation-exchanger one being in its neutral ( $\text{Na}^+$ ) form. These composites have been applied as catalytic materials for room temperature oxidation of aldehyde pollutants (formaldehyde in water or acetaldehyde in ethanol) by dissolved oxygen. Conversion level of aldehyde is 80–95% with respect to its initial concentration for anion-exchange composites. Reaction rate depends on the oxidized surface state of silver nanoparticles. In the absence of dissolved oxygen the overall consumption of formaldehyde is limited by the amount of oxidation products on the silver surface, the redox process does not occur at all for reduced state of the silver surface. HCOH conversion in the presence of dissolved oxygen leads expectedly to formation of CO (gas) and  $\text{CO}_2/\text{CO}_3^{2-}$ . This conclusion follows from consumption of  $\text{OH}^-$  counter-ions inside strongly basic anion exchanger during kinetic or dynamic experiments. If this loss is compensated by the  $\text{OH}^-$  ion transport from the external solution into the ion-exchanger the composite is able to serve as efficient catalyst of HCOH oxidative removal from a series of its solutions. Otherwise, if the external solution is not sufficiently basic or  $\text{OH}^-$  ions are excluded from the exchanger because of its cation type the aldehyde oxidation process stops rapidly. These observations imply that hydroxide ions inside the matrix are consumed by their reaction with intermediate products of the oxidation reaction. Increase of the hydroxide-ion concentration inside matrix by means of its NaOH pretreatment returns the activity of the catalyst to its initial level. Thus, silver/anion-exchanger composites can be considered as renewable redox catalysts for oxidation of aldehyde impurities from water or ethanol.

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### 1. Introduction

Aldehyde pollutants in water and ethanol media are well known as toxic substances, especially harmful in the pharmaceutical area [1]. Thus, search for methods to remove them, especially formaldehyde (methanal), is an actually important problem. The catalytic oxidation of methanal is one of the prospective approaches. Numerous catalysts have been proposed for this

reaction. However, metal-oxide catalysts, such as  $\text{MnO}_x$ , CoO, CuO,  $\text{CeO}_2$ ,  $\text{La}_2\text{O}_3$ ,  $\text{ZnO}_2$ ,  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{SiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{WO}_3$ ,  $\text{MoO}_3$  and  $\text{ZnO}_2/\text{Al}_2\text{O}_3$  [2–7] are only efficient under high pressure and temperature  $\sim 200$ – $300^\circ\text{C}$ . Expensive noble metals such as Au, Pt and Pd have to be used at lower temperatures [8–15].

More effective and cheaper catalysts are provided by silver particles deposited on various carriers like  $\text{CeO}_2$  [1,16,17],  $\text{MnOx-CeO}_2$  [18,19], NaY, MCM-41, SBA-15 zeolites [20–24],  $\alpha\text{-Al}_2\text{O}_3$  and  $\text{SiO}_2$  [25,26]. Various forms of silver such as metallic silver particles ( $\text{Ag}^0$ ) with subsurface oxygen species, isolated  $\text{Ag}^+$  ions, well dispersed  $\text{Ag}_2\text{O}$  and  $\text{Ag}_n^{\delta+}$  clusters were found on the surface of these catalysts [20]. These species of different types on various carriers play an important role in surface reaction process

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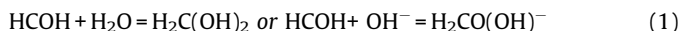
<sup>1</sup> ISE active members

of the formaldehyde oxidation. Formaldehyde adsorbed on silver sites was oxidized into dioxymethylene (DOM) and formate surface species, and they react with oxygen to form CO<sub>2</sub> at temperature about 100 °C. In some studies [22,27] it was mentioned that oxidation of formaldehyde became easier in the presence of OH-groups on the surface.

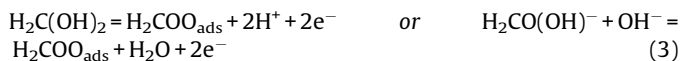
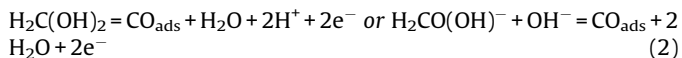
Silver-containing anion exchangers in OH-form represent materials with prospective properties for realizing this reaction. On the one hand, silver nanoparticles can be easily deposited in the surface region of the polymer matrix; on the other hand, the anion-exchange matrix behaves effectively like an intrinsically concentrated solution of OH<sup>-</sup> ions. The second advantage of such composites is their macroscopic size (since the dimension of their matrix is 0.5-1 mm in diameter) so the catalyst can be easily removed from solution after the reaction termination.

Therefore, such catalysts can be prospective for low-temperature formaldehyde oxidation. One should keep in mind that the mechanism of the methanal oxidation in aqueous solution may be essentially different from the gas-phase one (requiring an elevated temperature), which is mostly considered in literature [20,25].

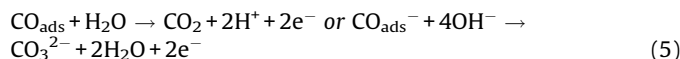
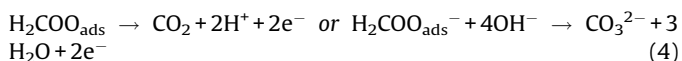
In this context it is worth to base such studies on results obtained for the electrochemical oxidation of HCOH with participation of primary products of its interaction with water. Reaction scheme of this process has been proposed in Refs [28–30]. It is known [28] that methanal reacts with water (or with hydroxide anion in alkali media) with formation of methylene glycol (or its deprotonated form):



Methylene glycol or its deprotonated anion is adsorbed on the surface of silver particles, with its further redox reaction with active forms of oxygen to generate intermediate products, adsorbed CO or formic acid species, Eqs. (2) and (3), respectively:



Interaction of these adsorbed species with OH-groups on the catalytic surface results in their complete oxidation till carbon dioxide:



This process is rapid for the adsorbed formic acid while this reaction is slow for adsorbed CO species.

One may expect that similar stages can also take place in the course of the low-temperature catalytic oxidation of formaldehyde by oxygen. Therefore, our results below for the non-electrochemical oxidation will be compared with the above mechanism of the electrochemical oxidation process.

The actual study is dealing with catalytic properties of a silver-containing strongly basic anion-exchanger matrix in the formaldehyde oxidation reaction. The possibility of employing such composites to the analogical reaction of ethanal (acetaldehyde) pollutant removal from ethanol has also been analyzed.

## 2. Experimental

### 2.1. Synthesis of silver-containing ion exchangers

Synthesis of silver/ion exchanger nanocomposites has been carried out via redox-reaction deposition procedure. Ion exchange matrices were commercial (Azot, Russia) granulated three-dimensional cross-linked polymers: anion exchangers (poly-N-threemethylstyreneamine with 8% divinylbenzene as cross-linking agent) and cation exchanger (sulfostyrene with 8% divinylbenzene as cross-linking agent). Two types of strongly basic anion exchangers were used: porous (PAE) and geleous (GAE) ones. Strongly acidic sulfocation exchanger was of geleous type (GCE).

Primary characteristics (type of fixed groups, counter ions, ion-exchange capacity) of these matrices are given in the Table 1.

Commercial ion exchangers were pretreated via conventional acid-base conditioning in dynamic mode until achieving the stability of the ion-exchange capacity [19]. This procedure was carried out in a special column where the 0.1 M solution of HCl or NaOH passed through the layer of polymer granules. Cation exchanger was treated first by NaOH, then by HCl, then again by NaOH, etc., to finish with HCl (resulting in the H<sup>+</sup> ionic form of its matrix), while the sequence was opposite (HCl, NaOH . . . NaOH) to transform anion exchangers into their OH<sup>-</sup> ionic form. Before each treatment with acidic or alkaline solution the layer was rinsed with distilled water. Stability in the ion-exchange capacity value was reached after 6–8 cycles of such conditioning.

After this conditioning procedure the cation exchanger was treated in dynamic mode with 0.1 M NaOH solution to transfer it from its H<sup>+</sup> ionic form into the Na<sup>+</sup> one. Similarly, anion exchangers were transformed from their OH<sup>-</sup> ionic form into the Cl<sup>-</sup> one via their contact with 0.1 M HCl solution.

**Table 1**  
Characteristics of the ion-exchange matrices.

Matrix type	Fixed ionogenic center type	Pore size, nm	Ion-exchange capacities: mmol OH <sup>-</sup> /H <sup>+</sup> , per 1 cm <sup>-3</sup> of matrix	Matrix density in dry state, g cm <sup>-3</sup>
GAE	–(CH <sub>3</sub> ) <sub>3</sub> N <sup>+</sup> OH <sup>-</sup>	1-10	1.12 ± 0.02	0.68
PAE	–(CH <sub>3</sub> ) <sub>3</sub> N <sup>+</sup> OH <sup>-</sup>	50-100	0.80 ± 0.02	0.69
GCE	–SO <sub>3</sub> H <sup>+</sup>	1-10	1.80 ± 0.01	1.43

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