Electrocatalytic properties of $CuCl_2$ or FeO doped polyaniline composites in electrohydrogenation of aromatic nitro-compounds

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Introduction

Metal-polymer composites on the base of conductive polymer polyaniline (PAni) have a number of practically valuable properties. In particular, they are actively used as catalysts in catalytic reactions and as electrode coatings in electrocatalytic systems.

Aims

The aim of the present work was to investigate the electrocatalytic activity of copper- and iron-containing PAni composites obtained by chemical methods in the processes of electrocatalytic hydrogenation of aromatic nitro-compounds, such as *p*-nitroaniline and *p*-nitrobenzoic acid .

Methods

Copper- and iron-PAni composites were prepared by incorporating copper chloride (II) or iron oxide (FeO) in the reaction medium of oxidative polymerization of aniline (oxidizer – ammonium peroxydisulfate).

The experiments on electrocatalytic hydrogenation were carried out in a diaphragm electrochemical cell in an alcohol–aqueous alkali catholyte. The anode was a Pt-gauze, the cathode was a Cu-plate, which closely contacted the bottom of the electrolyzer and served as a substrate for the PAni composite catalyst. The experiments were performed at a current of 1.5 A and a temperature of 30°C.

Discussion

PAni+$CuCl_2$

The electrohydrogenation reaction of *p*-nitroaniline (*p*-NA) :

$$NH_2–C_6H_4–NO_2 + 6H \rightarrow NH_2–C_6H_4–NH_2$$

Table 1. Electrocatalytic hydrogenation of *p*-NA on PAni+$CuCl_2$ composites obtained by *in situ* method

Composites	Copper content in 1 g of composites	W, ml H_2/min (α= 0.25)	η, % (α= 0.25)	α, %
Cu-cathode	-	6.6	64.6	89.5
PAni	-	4.6	45.0	75.6
PAni + $CuCl_2$ (1:0.5)	0.007	6.0	56.3	80.7
PAni + $CuCl_2$ (1:1)	0.057	6.8	66.7	93.3
PAni + $CuCl_2$ (1:1) with evaporation procedure	0.105	8.1	79.2	97.2
PAni + $CuCl_2$ (1:1.5)	0.101	7.0	66.7	91.5
PAni + $CuCl_2$ (1:2)	0.145	7.0	68.8	92.0

Rate of *p*-NA hydrogenation increases when the copper content grows up in the composites with ratios of 1:0.5, 1:1, 1:1.5 and 1:2 (relative to aniline).

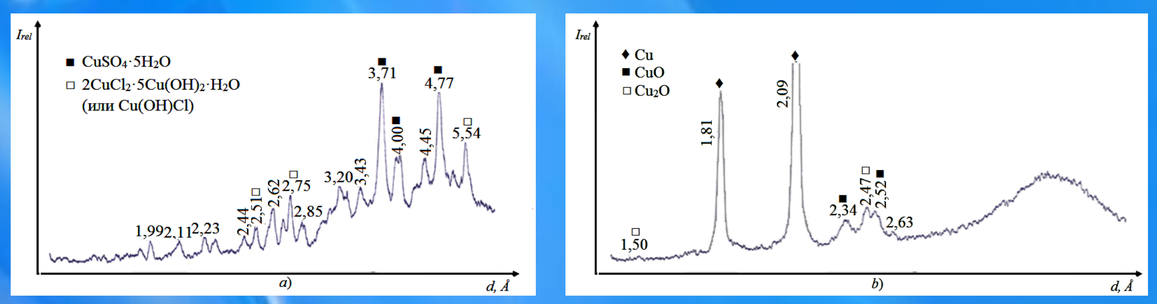


Figure 1. XRD patterns for PAni+ $CuCl_2$ (1:1) composite with solvent evaporation procedure before (*a*) and after (*b*) electrohydrogenation of *p*-NA

By X-ray analysis it is determined that in the constitution of PAni+$CuCl_2$ composites synthesized with and without solvent evaporation procedure after applying them to activate the cathode in electrohydrogenation of *p*-NA there are the crystalline phases of Cu^0 and copper oxides (Figure 1, b).

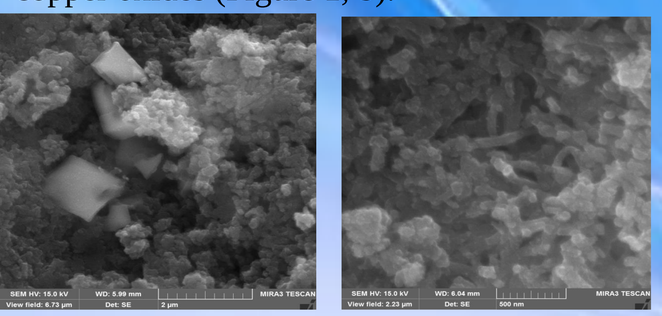


Figure 2. Micrographs of PAni+ $CuCl_2$ (1:1) composite with solvent evaporation procedure before electrohydrogenation of *p*-NA

PAni+FeO

The electrohydrogenation reaction of *p*-nitrobenzoic acid (*p*-NBA):

$$HOOC–C_6H_4–NO_2 + 6H \rightarrow HOOC–C_6H_4–NH_2$$

Table 2. Electrocatalytic hydrogenation of *p*-NBA on PAni+ FeO composites obtained by *in situ* method

Composites	Iron content in 1 g of composites	W, ml H_2/min (α= 0.25)	η, % (α= 0.25)	α, %
Cu-cathode	-	3.7	34.6	70.1
PAni + FeO (1:0.2)	0.134	4.6	41.4	67.4
PAni + FeO (1:0.4)	0.284	4.3	38.0	73.1
PAni + FeO (1:0.6)	0.291	6.4	47.0	96.0
PAni + FeO (1:0.8)	0.344	3.9	37.6	78.8
PAni + FeO (1:1)	0.410	6.0	52.2	87.4
PAni + FeO (1:1.5)	0.486	3.6	30.4	90.3

The electrochemical reduction of nitro group in *p*-NBA to amino group in *p*-ABA on the Cu-cathode is performed with average reaction rate and quite high conversion of *p*-NBA (70.1%). Electrohydrogenation of *p*-NBA in the presence of PAni+FeO (1:0.6) and PAni+FeO (1:1) composite occurs with higher reaction rate than in the electrochemical process.

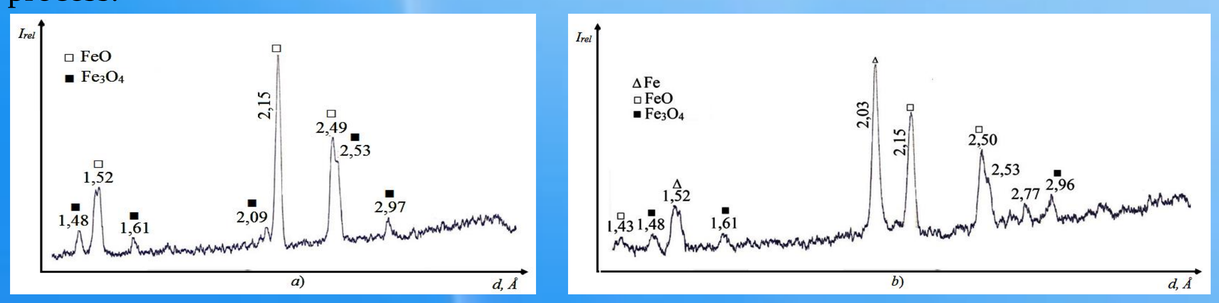
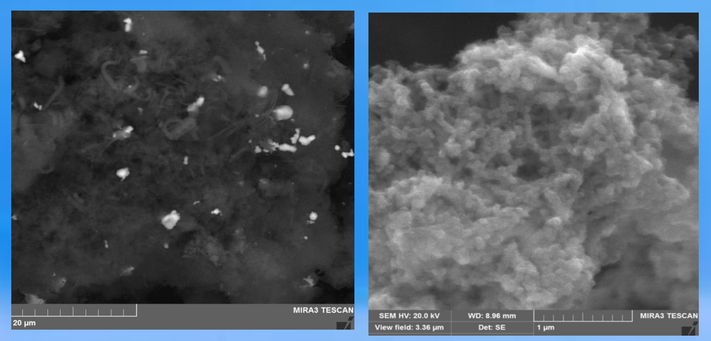


Figure 3. XRD patterns for PAni+ FeO (1:1) composite before (*a*) and after (*b*) electrohydrogenation of *p*-NBA

In the constitution of PAni+FeO composites after hydrogenation of *p*-NBA there are crystalline phases of Fe^0, FeO and Fe_3O_4 (Figure 3, b).

Figure 4. Micrographs of PAni+FeO (1:1) composite after electrohydrogenation of *p*-NBA



Conclusions

1. Copper- and iron-PAni composites were synthesized by incorporating copper chloride (II) or iron oxide (FeO) into polyaniline matrix.
2. The electrocatalytic activity of copper- and iron-containing PAni composites was investigated in the processes of electrocatalytic hydrogenation of aromatic nitro-compounds, such as *p*-nitroaniline and *p*-nitrobenzoic acid.
3. XRD and SEM of PAni+$CuCl_2$ and PAni+FeO composites revealed that the appearance of copper and iron particles in zero-valence state in the composites indicates the passage of electrochemical reduction of metal cations from their compounds present in these composites before the hydrogenation processes. In the case, the hydrogenation rates and conversion of hydrogenated compounds increase in comparison with their electrochemical reduction on Cu-cathode.