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FT-IR/PAS study of surface EDTA-ZnO interactions

Marcin Kuśmierz^a and Sylwia Pasieczna-Patkowska^b

^a*Department of Environmental Chemistry,*

^b*Department of Chemical Technology,*

Faculty of Chemistry, Maria Curie-Skłodowska University,

pl. M. Curie-Skłodowskiej 3, 20-031 Lublin, Poland

marcin.kusmierz@poczta.umcs.lublin.pl

The interaction of EDTA disodium salt with zinc oxide was investigated by photoacoustic (PA) FT-IR. It was demonstrated that EDTA-III adsorbs on ZnO, and the process mimics behaviour of EDTA-oxide systems, in which IEPS of oxide catalytic supports is higher than 9. Model of the interaction, described in literature, was discussed.

1. INTRODUCTION

Ethylenediaminetetraacetic acid (EDTA) and its sodium salts are often used in preparation of catalysts by double impregnation method (DIM). In the first stage of the preparation a chelating compound (usually disodium EDTA salt) is deposited on a surface of metal oxide, which serves as a support. After drying, so-called "activated carrier" is impregnated with a solution of a catalyst precursor. This method is well suited for preparing supported catalysts characterized with high metallic phase dispersion [1].

Understanding the interactions between EDTA and support oxides is essential for obtaining catalysts with desired properties. Most of the literature data devoted to this preparation technique is focused on EDTA–Al₂O₃ [2–5], EDTA–AlPO₄ [6] and EDTA–MgO/Al₂O₃ systems [7].

Contrary to SiO_2 or Al_2O_3 , zinc oxide is a partially reducible support [8–10] and therefore reduced Zn may form alloys with main metallic phase. In some cases such binary catalyst performs better than a single-phase one: Iwasa [11] reported that in the reaction of CO_2 hydrogenation on Pd-Zn/ZnO catalysts showed higher activities and selectivities towards methanol than pure palladium based ones.

The DIM method facilitates high dispersion of catalyst metallic phase, thus forming alloys is easier. This study focuses on phenomena occurring during the first stage of the process: interactions between EDTA and ZnO.

2. EXPERIMENTAL

Two samples of ZnO (supplied by INS Puławy, Poland) were calcined in air at 823 K using muffle furnace for 8 hours (sample S8) and 4 hours (sample S4). According to calcination curve supplied by producer this thermal treatment lowered their surface areas to about $5 \text{ m}^2/\text{g}$ and $15 \text{ m}^2/\text{g}$, respectively. EDTA and its salts strongly chelates metal ions (which charge is at least +2). It even may leach them from oxide and hydroxide solids [12–15]. High surface area of metal oxides facilitates this phenomena and in consequence may hinder investigations of EDTA adsorption. In the case when this phenomena would have been observed for S4 samples, strongly calcined S8 samples have been prepared.

Both S8 and S4 samples were divided into subsamples S8H, S8E and S4H, S4E, respectively. Subsamples S8E and S4E were impregnated with 0.1M EDTA-III (EDTA disodium salt, $\text{Na}_2\text{H}_2\text{Y}$, supplied by POCh, Gliwice) solution at 343 K for 20 minutes. For the reference purposes subsamples S8H and S4H were treated in the same manner with distilled water. All the subsamples were then dried at 391 K overnight.

FT-IR/PAS spectra of investigated materials (S8H, S4H, S8E, S4E) were recorded using Bio-Rad spectrometer equipped with MTEC300 photoacoustic detector, over the $4000\text{--}400 \text{ cm}^{-1}$ range. The spectra were measured at RT at 4 cm^{-1} resolution and normalized by computing the ratio of a sample spectrum to the spectrum of a MTEC carbon black standard. Prior to measurements the PA cell was purged with dry helium for 5 minutes. Interferograms of 512 scans were average for each spectrum. Spectra of untreated ZnO samples (S8 and S4) were also recorded.

3. RESULTS AND DISCUSSION

Spectra of S8, S8H and S8E samples are presented in Figure 1. Peaks at 3065, 2957, 2922 and 2854 cm^{-1} (small chart) are characteristic for surface carbon species [18]. Their presence is caused by incomplete removal of graphite, which is used as a grease during production of ZnO pellets. This implies that flow furnace and oxygen atmosphere should be used, rather than muffle one and air.

Band at 1640 cm^{-1} , present in spectra S8 and S8H is ascribed to oxide surface hydroxyl groups. In spectrum S8E this peak is covered by features at 1626 and 1670 cm^{-1} (very weak shoulder), which can be assigned to $\nu_{\text{as}}\text{-COO}^-$ and -COOH vibrations of EDTA-III carboxyl groups, respectively [16–18]. Bands associated with strong symmetric vibrations of -COO^- groups appear at 1400 and 1323 cm^{-1} , and the peak at 1280 cm^{-1} corresponds to vibrations of $\text{-CH}_2\text{COOH}$ chains [16–18].

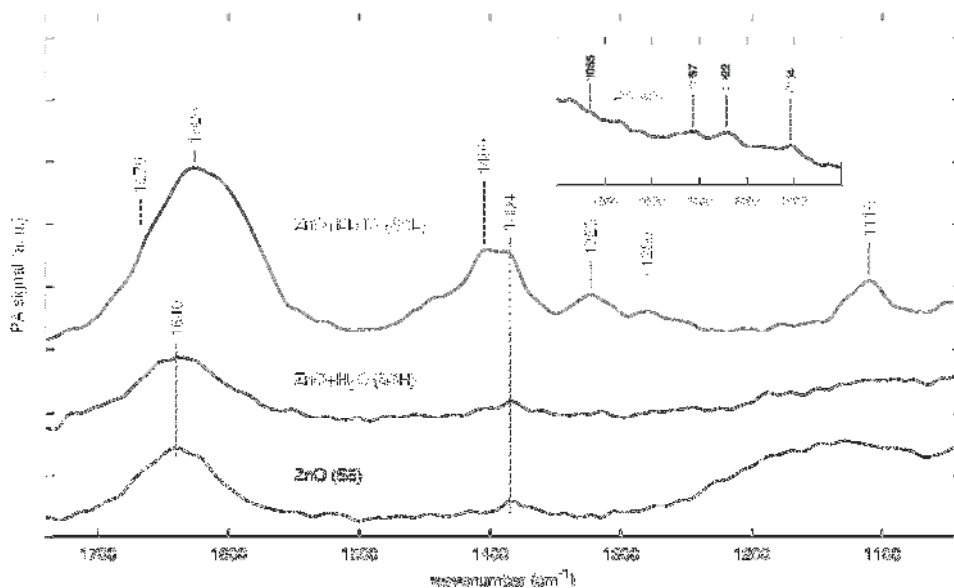


Fig 1. FT-IR/PAS spectra of S8E, S8H and S8 samples.

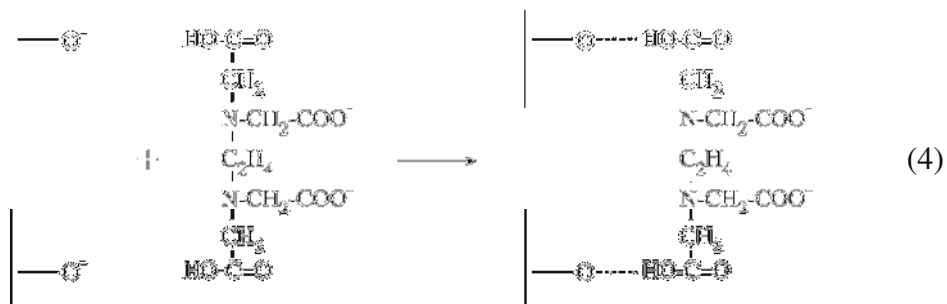
The presence of EDTA adsorbed on the ZnO surface is confirmed by relatively intensive band at 1110 cm^{-1} , which is attributed to stretching of C–N bond [16–18]. Spectra of S4, S4H and S4E samples were almost identical to those described above, and therefore they are not shown.

Interactions between adsorbates and metal oxides strongly depends on surface composition of the latter. Hydroxyl groups and their

distribution are of special importance. In the case of impregnation from water solutions, the population of these species depends on isoelectric point of solid surface (IEPS) and pH of the solution [19]. Equations describing protonation, deprotonation and state of the oxide surface in water solution are included in papers [20,21]. Their more general form is presented in paper [5], and can be applied to various oxides:



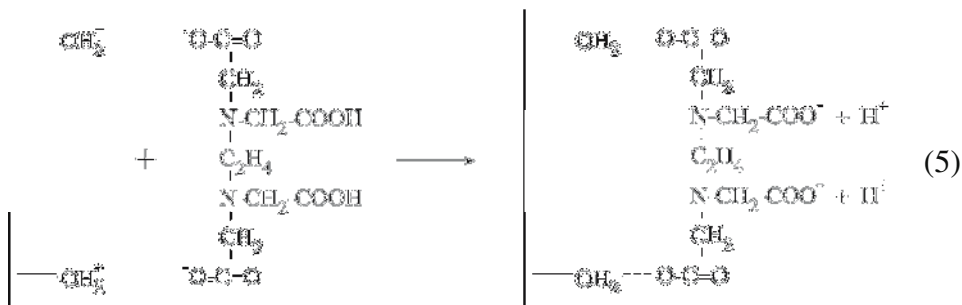
In publication [5] models of interactions between EDTA disodium salt and various inorganic oxides are shown. For magnesium oxide the proposed reaction is as follows:



According to scheme (4) EDTA salt interacts with surface $\text{M}-\text{O}^-$ species via undissociated carboxyl groups. This view is supported by relative intensity of bands in spectrum included in cited work: peak corresponding to $-\text{COO}^-$ groups is more intensive than one associated with $-\text{COOH}$ groups.

IEPS values for MgO and ZnO are in similar, alkaline range: ≈ 12 . Because pH of impregnation solution used (≈ 6) was far below this value, according to equation (3) the most numerous surface species were $\text{M}-\text{OH}$ and $\text{M}-\text{OH}^+_2$ groups. Moreover, if the oxide surface is positively charged it is more likely to happen that EDTA salt will contact with surface via dissociated carboxyl groups, due to electrostatic forces. Higher intensity of the peak at 1626 cm^{-1} , corresponding to asymmetric vibrations of $-\text{COO}^-$, in comparison to the peak at 1670 cm^{-1} ($-\text{COOH}$ groups) can be explained by dissociation of adsorbed EDTA carboxyl groups. Scheme

(5) describes proposed model of EDTA salt adsorption from weakly acidic solution.



4. CONCLUSIONS

It was demonstrated that EDTA-III is adsorbed on zinc oxide surface and it can be assumed, that application of double impregnation method for preparing catalysts supported on ZnO is possible.

Low pH (c.a. 6) of impregnation solution in combination with high IEPs of ZnO suggest, that during the impregnation $-\text{OH}^+$ groups were most numerous surface species. This suggestion is supported by relatively high intensity of bands at 1640 cm^{-1} and 1384 cm^{-1} , corresponding to oxide surface hydroxyl groups.

The foregoing statement indicates that EDTA-III adsorbs on surface of zinc oxide mainly via dissociated carboxyl groups. Strong peaks at 1626 cm^{-1} corresponding to asymmetric vibrations of $-\text{COO}^-$ groups are probably caused by deprotonation of hitherto undissociated EDTA-III carboxyl groups.

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CURRICULA VITAE



Marcin Kuśmierz born in Lublin (1971). Graduated from Maria Curie-Skłodowska University in Lublin (1997). Received his Ph. D. degree in physical chemistry (2005) from the Maria Curie-Skłodowska University. His main fields of interest are environmental impacts of biochars use and fate and bioavailability of hydrophobic organic pollutants in environment (especially PAHs and o-PAHs).



Sylwia Pasieczna-Patkowska was born in Lublin, Poland in 1974. She studied chemistry at the Maria Curie-Skłodowska University, graduated in 1998. Received her Ph.D. (2006) in physical chemistry from the UMCS in Lublin. Since 2007 she is an adjunct at UMCS. She is an author and co-author of 73 articles in science-technical press, the author and co-author of 126 papers and posters at domestic and foreign conferences. Scientific interests: infrared spectroscopy, chemical technology. She is member of Polish Chemical Society (1998-) and Polish Catalysis Club (1998-).