



# METAL AND METAL-SULPHIDE CONTAINING CARBONS FROM SULPHONATED STYRENE-DIVINYLBENZENE COPOLYMER BASED ION-EXCHANGERS

László Kótai<sup>[a]\*</sup>, Tibor Pasinszki<sup>[b]</sup>, Zsuzsanna Czégény<sup>[a]</sup>, Szabolcs Bálint<sup>[a]</sup>,  
István Sajó<sup>[a]</sup>, Zoltán May<sup>[a]</sup>, Péter Németh<sup>[a]</sup>, Zoltán Károly<sup>[a]</sup>, Pradeep K. Sharma<sup>[c]</sup>,  
Vinita Sharma and Kalyan K. Banerji<sup>[d]</sup>

**Keywords:** metal-containing activated carbons; waste ion-exchangers; carbonization; metal/metal compound-carbon composites; sulphonated styrene-divinylbenzene copolymers

A temperature controlled carbonization process (5-800 °C for 1-4 h) of metal forms of various types of partially or completely saturated sulphonated styrene-divinylbenzene copolymer based ion-exchangers loaded with various valence state metal ions has been evaluated. The effect of temperature, nature and valence of metal ions, cross-linking and other parameters on the composition and properties of the synthesised composites have been evaluated. Depending on the ionic form and the degree of saturation of the ion exchangers the sulphur content of the ion-exchangers can partially transform into metal sulphides, SO<sub>3</sub> or SO<sub>2</sub>. Ni(II), Mn(II) and Zn(II) forms of the ion-exchangers resulted the appropriate M<sup>II</sup>S type metal sulphides (NiS, MnS or ZnS), while copper(II) resulted metallic copper formation at 500 °C in 2 h. Both iron(II) and iron(III) forms of sulphonated styrene-divinylbenzene copolymers resulted Fe<sub>0.95</sub>S and α-Fe formation at 800 °C for 2 h, however, the ratio of these compounds depended on the valence state of iron and were found to be 8:1 and 7:2 in the case of Fe(III) and Fe(II)-forms, respectively. The shape of the so formed carbon particles are bead-like and the hardness of the formed carbon beads proportional with the divinylbenzene content of the starting polymer. The higher divinylbenzene content the harder beads of carbon forms. All the beads have a leakage path due to evolution of gases which emitted at the weakest part of ball-like bead. The ball-like metal-containing activated carbon beads have low hydrodynamic resistance towards fluid streams and this carbonisation method can be used as an environmentally friendly way for processing of waste ion-exchangers into industrially usable carbon based metallic containing composites.

\* Corresponding Authors

Tel: 00-36-70-2440001

E-Mail: kotail@chemres.hu

- [a] Research Centre for Natural Sciences, Hungarian Academy of Sciences, Budapest, H-1025, Pusztaszeri u. 59-67.;
- [b] Department of Inorganic Chemistry, Institute of Chemistry, Eötvös Loránd University of Sciences, Budapest, Pázmány Péter sétány 1/A, H-1117, Hungary
- [c] Department of Chemistry, J. N. V. University, Jodhpur, Rajasthan, 342005, India.
- [d] Faculty of Science, National Law University, Mandore, Jodhpur 342304, India
- [e] Axial-Chem Ltd., Sajóbáony, Gyártelep.

performed with sulphonic acid type active group containing styrene-divinylbenzene copolymers loaded with various valence state metal ions and containing different amount of cross-linking agent (divinylbenzene) are presented.

## Experimental

Synthesis of metal-loaded ion-exchangers was performed in column experiments with H<sup>+</sup>-forms of the sulphonic acid type ion-exchangers (Varion KS, Varion KSM, Varion KS660 and Lewatit P100). The columns were filled with 100 g of the ion-exchangers and activated with the saturated aqueous solutions of zin(II) sulphate, manganese(II) nitrate, iron(II) chloride, iron(III)-chloride, zinc(II) sulphate, nickel(II) sulphate and copper(II) sulphate until complete saturation. All saturation experiments were performed at room temperature. The activated resins contained homogeneously distributed metal loading at the active groups were washed with distilled water and dried in open air and overnight. The partially saturated ion-exchangers were prepared by using method of Somogyi et al.<sup>3</sup>

The carbonisation experiments were performed between 500 and 800 °C for 1-4 h under flowing N<sub>2</sub> in an 50 cm long quartz tube. Metal content of the composites were determined by inductively coupled plasma (ICP) emission spectrometric measurements with a Spectro Genesis (Thermo Scientific) ICP-OES spectrometer after digestion of carbonized samples in 3:1 cc. HCl:HNO<sub>3</sub> mixture for 24 h.

X-ray powder diffraction measurements were performed by means of a Philips PW-1050 Bragg-Brentano parafocusing goniometer, equipped with a secondary beam graphite monochromator and proportional counter; scans

## Introduction

Numerous metal or metal-compound loaded with carbon composites have already been synthesized, and studied in various chemical processes such as catalysts, chemosorbents or reactive materials<sup>1</sup> etc. The preparation of these composites generally based on adsorption/chemisorption of a particular metal compounds which is transformed into the active ingredients on the surface of the carbon, or a mixture of carbon precursors and metal compounds are carbonized together. These processes generally give heterogeneous composites whose properties hardly controlled or can be adjusted only in separate processes. In order to solve these problems a simple method has been introduced to prepare metal-loaded activated carbons with unique features and homogeneous metal/metal compound loading.

We have developed a simple method for preparation of iron(II) oxide containing carbon supported catalysts of paracetamol production<sup>2</sup> based on the temperature controlled carbonization of iron form of a carboxylate type iron(III)-ion saturated ion-exchanger polymer. In this article, the preliminary results obtained in the analogous experiments

were recorded in step mode by using  $\text{CuK}_\alpha$  radiation at 40 kV and 35 mA tube power. Evaluation of the diffraction patterns have been obtained by full profile fitting techniques.

TG-MS measurements were accomplished by a modified Perkin-Elmer TGS-2 thermobalance and a HIDEN HAL 2/301 PIC quadrupole mass spectrometer with 5 °C heating rate in Ar flow.

SEM measurements were performed with a Hitachi S-570 scanning electron microscope equipped with a Rontec EDR 288 detector.

BET surface areas were determined from  $\text{N}_2$  adsorption-desorption isotherms with using a Quantachrome AUTOSORB-1 instrument.

## Results and Discussions

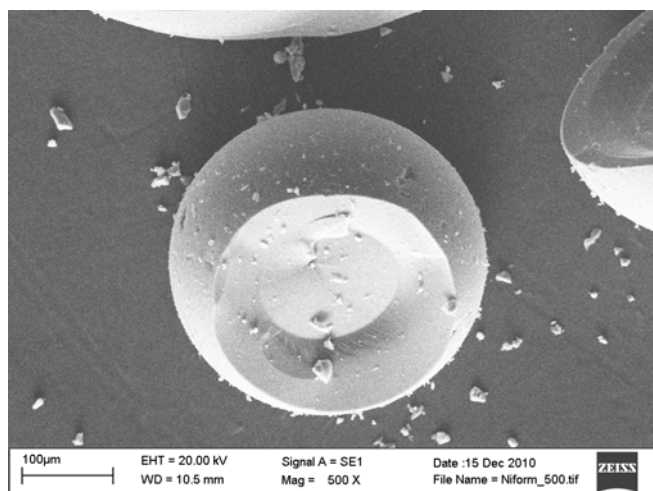
Preparation of metal-containing ion-exchangers were performed in an usual way with loading of hydrogen forms of sulphonated ion exchangers with using saturated aqueous metal salt solutions.<sup>3</sup> The carbon composites were prepared by controlled temperature carbonization (5-800 °C for 1-4 h) of the metal forms of various styrene-based ion exchangers. The carbonization temperatures were adjusted on the basis of the TG-MS results, and the optimal carbonisation time was found to be about 2 h. Depending on the ionic form and the degree of saturation of the ion exchanger the sulphur content of the ion-exchangers can partially transform into metal sulphides,  $\text{SO}_3$  or  $\text{SO}_2$  which could be detected by TG-MS unambiguously. The yield of metal/metal sulphide containing carbon composites strongly depends on the nature of metal, ion-exchanger and the carbonisation conditions as well.

The sulphonated styrene-divinylbenzene copolymers are the most frequently used cation exchangers used which results a large amount of waste ion-exchangers. Completely (100 %) and partially saturated forms (25 and 50 % of their capacity) of Varion KS and Varion KSM resins were carbonised at 500 °C for 2 h. Depending on the nature of metal, sulphide ( $\text{MnS}$ ,  $\text{NiS}$  and  $\text{ZnS}$ ,  $\text{FeS}_{0.95}$ ) species or elemental metal ( $\text{Cu}$ ,  $\alpha\text{-Fe}$ ) were formed. In case of iron,  $\text{Fe}_{0.95}\text{S}$  and  $\alpha\text{-Fe}$  were formed together at 800 °C, the sulphide component was the major product, however the ratio of  $\text{Fe}_{0.95}\text{S}:\alpha\text{-Fe}$  depended on the valence form ( $\text{Fe}^{\text{II}}$  or  $\text{Fe}^{\text{III}}$ ) of the iron loaded onto the ion exchanger resin.

The saturation degree has no important effect on the chemical form of the metal in the composites formed at the studied temperature range. The shape of the formed carbon particles is bead-like (Fig.1.), and the hardness of the formed carbon beads proportional with the divinylbenzene content of the starting polymer, the higher divinylbenzene content the harder the beads of carbon formed. All the beads have a leakage path due to evolution of gases which are emitted at the weakest part of ball-like bead causing leakage. Due to evolution of large amount of gases within the structure of beads which evolve at the time when the resistance of the resin material becomes lesser than the inner pressure, an "explosion-like" evolution of gases ( $\text{SO}_2$ ,  $\text{H}_2\text{O}$ , hydrocarbon crack gases) could be observed, and the resin beads "jump" during the carbonization. The formed ball-like metal-containing activated carbon beads have low

hydrodynamic resistance towards fluid streams and these materials are potential candidates for treatment of liquid flows.

The SEM picture of the nickel-carbon composite with ca. 30 % nickel content can be seen in Fig.1.



**Figure 1.** SEM picture of the nickel sulphide containing carbon composite bead prepared from Lewatit S100 (8 % divinylbenzene content) loaded fully with  $\text{Ni}(\text{II})$  at 500 °C for 2 h

The bead-like resins formed in the pyrolysis of Lewatit S100 resin contained 2.3 mekv  $\text{g}^{-1}$  nickel(II) resulted a carbon composite of  $\text{NiS}$  with 35 % nickel content. The specific surface area was found to be 371  $\text{m}^2\text{g}^{-1}$ , but the specific surface area strongly depends on the pyrolysis temperature and the divinylbenzene content (porosity) of the starting ion exchanger. The specific surface areas of nickel sulphide containing carbons formed at 500 °C in 2 h in the case of Varion KS and KS660 resins were found to be 172 and 341  $\text{m}^2\text{g}^{-1}$ , respectively.

Two kinds of iron form ( $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  loaded) of Varion KSM resins were carbonised at 800 °C for 2 h. The same products were formed,  $\text{Fe}_{0.95}\text{S}$  and metallic iron ( $\alpha\text{-Fe}$ ), however, the ratio of these products depended on the valence of the iron loaded on the ion-exchanger. The approximate ratio of iron sulphide/ $\alpha\text{-Fe}$  were found to be 8:1 and 7:2 in the case of  $\text{Fe}^{\text{III}}$  and  $\text{Fe}^{\text{II}}$  forms of the Varion KSM ion exchanger, respectively. It can be the consequence of the oxidizing nature of  $\text{Fe}^{\text{III}}$  which partially prevents the complete reduction of sulphonic acid group into sulphide.

The metal or metal-compound containing activated carbons can be activated with vapour or other methods and their metal content can also be removed by acidic treatment, e.g. with digestion in dilute  $\text{HCl}$  or  $\text{HNO}_3$ . The formed metallic salt solutions can be recycled into loading new ion exchangers into metallic forms, and the formed carbons can be utilized as simple activated carbons as well.

This method can be a good example as an environmentally friendly way to transform the waste ion-exchangers into useful materials. The acidic or oxidative acidic leaching of the metal-containing species formed during the chemisorption leads to activated carbons with acidic and oxidized surface characteristics.

## Conclusion

Ion-exchanger materials, particularly sulphonated styrene-divinylbenzene copolymers can be transformed into metal/metal sulphide composites at 500-800 °C in 1-4 h. These composite materials can be used as catalyst or chemisorbents (with or without further activation) in various technological processes. The systematic investigation of the effect of functional groups, divinylbenzene content, and the composition of polymer chain, temperature, reaction time and other factors are in progress. Further studies on the utilization of various metal-containing activated carbon composites prepared in this way, and their transformation with acidic or oxidative acidic leaching into activated carbons are in progress.

## Acknowledgement

We express our thanks to the National Development Agency and MAG Zrt. (Magyar Gazdaságfejlesztési Központ Zrt., 1139 Budapest, Váci út 81-83.) who supplied the “Activated Carbon Production from Waste Ion Exchangers at the Axial Chem Ltd .” project (GOP 1.1.1.- 09/1-2009-0081) of Axial Chem Ltd. (Sajóbábony, 3792,024/73 hrsz. ). The project is supported by the European Union and co- financed by the European Regional Development Fund.

## References

- <sup>1</sup>Cui, H., Turn, S. Q. *Appl. Catal. B: Environmental* **2009**, 88(1-2), 25-31; Marban, G., Antuna, R., Fuertes, A. B., *Appl. Catal. B: Environmental*, **2003**, 41(3), 323-338; St. Tsoncheva, T., Nickolov, R. N., Neinska, Y. G., Minchev, C. I., Mehandjiev, D. R., *Bulg. Chem. Comm.* **2000**, 32(2), 218-229; Yamamoto, O., Sawai, J., *Bull. Chem. Soc. Japan* **2001**, 74(9), 1761-1765; Mondal, P., Mohanty, B., Majumder, C. B. *Can. J. Chem. Eng.* **2009**, 87(5), 766-778; Chiang, H.-L., Huang, C. P., Chiang, P. C., You, J. H., *Carbon* **1999**, 37(12), 1919-1928; Lee, J.-J., Suh, J.-K., Hong, J.-S., Lee, J.-M., Lee, Y.-S., Park, J.-W., *Carbon* **2008**, 46(13), 1648-1655.
- <sup>2</sup>Sreedhar, B., Bhaskar, V., Sridhar, C., Srinivas, T., Kotai, L., Szentmihályi, K., *J. Mol. Catal. A-Chem.*, **2003**, 191(1) 141-147.
- <sup>3</sup>Somogyi, I., Kótai, L., Angyal, A. Report **2012**, *Activated Carbon Production from Waste Ion Exchangers at the Axial Chem Ltd*, GOP 1.1.1.-09/1-2009-0081.

Received: 10.10.2012

Accepted 20.10.2012.