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Synthesis and Characterization of Co-Mo Bimetallic Carbides

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Abstract:

Co-Mo carbides were prepared by impregnation with aqueous solution of metal salts and sucrose into ordered mesoporous SBA-15 silica template using carbothermal hydrogen reduction. Bimetallic Co-Mo carbide obtained by using carbothermal hydrogen reduction of Co-Mo precursors is formed when the Co-Mo molar ratio is 1.0. The obtained samples were characterized by X-ray diffraction, scanning electron microscopy and energy dispersive X-ray analysis. Electrochemical characterization of obtained materials were performed by cyclic voltammetry in acid solution.

Keywords: *Co-Mo carbides; SBA-15; Impregnation; Carbothermal-hydrogen reduction; Cyclic voltammetry.*

1. Introduction

Alternative power sources such as PEMFCs (proton exchanged membrane fuel cells) commonly use carbon as catalyst support for platinum nanoparticles. Anodic materials of PEMFCs compacted carbon has several disadvantages, electrochemical oxidation leading to agglomeration or even loss of platinum decreasing the catalyst electroactive surface area and consequently lowering the performance of PEMFCs.

Trasiton Metal Carbides (TMCs) possess unique physical and chemical properties of three different classes of materials: covalent solids, ionic crystals, and transition metals [1, 2]. As a result, they display high electrical conductivity and chemical stability as well. Therefore, the major challenge in fuel cell research is to reduce the cost of the electrocatalyst either by reduced Pt loading or by developing a non-noble catalyst [3]. Since transition metal carbides, typically of group 6, have been reported to have Pt-like chemical activities and electronic properties [3-9], there have been many studies related to the development of transition metal carbides for use as hydrogen fuel cell electrocatalyst. One of the very important advantages of transition metal carbides is that they have a good resistance to very strong catalytic poisons as carbon monoxide, hydrocarbons and hydrogen sulfide [9].

There have been many studies related to the development of transition metal carbides for use as hydrogen fuel cell electrocatalysts. Wang and coworkers [11] successfully synthesized two phases of cobalt-molybdenum bimetallic carbides, $\text{Co}_3\text{Mo}_3\text{C}$ and $\text{Co}_6\text{Mo}_6\text{C}$, both prepared by the hexamethylenetetramine based one-step thermal decomposition method. Newsam et al. [12] synthesized $\text{Co}_6\text{Mo}_6\text{C}_2$ ($\text{Co}_3\text{Mo}_3\text{C}$) by a two-stage reaction method. Ma and colleagues synthesized nanocomposite $\text{Co}_6\text{Mo}_6\text{C}_2$ on graphitized carbon using an ion-

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exchange method [13]. Bussell's group synthesized the bulk and alumina supported $\text{Co}_3\text{Mo}_3\text{C}$ through a temperature-programmed nitridation and subsequent topotactic carburization route [14]. Xiao et al. used oxide precursor instead of nitride and operated the carburization under the flow of $\text{C}_2\text{H}_6/\text{H}_2$ mixture [15]. On the other hand, Lang et al. developed a carbothermal hydrogen reduction method for the preparation of Co-Mo carbide [16] as well as nanostructure $\beta\text{-Mo}_2\text{C}$ [17] and W_2C [18].

In the current study, ordered mesoporous silica (SBA-15) silica SBA-15 employed as a hard template was infiltrated with aqueous solution of metal salts (Co-Mo) and sucrose (as carbon source) followed by its carbonization, and subsequent template removal in order to obtain Co-Mo carbides. The obtained catalyst support inherited well preserved microstructure and satisfactory electronic conductivity.

2. Materials and Experimental Procedures

2.1. Synthesis of Co-Mo carbide

The parent SBA-15 template was synthesized according to Ref. [19]. Commercially available solvents and reagents were used in the whole procedure. Sample referred to as 1 was synthesized according to following procedure. Mesoporous silica SBA-15 material (0.5 g) was first impregnated with 4.1 ml of $0.01 \text{ mol L}^{-1}(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (Merck) aqueous solution under stirring. The obtained material was dried at 140°C for 24 h and then crushed to get a fine powder. The resulting material was then impregnated again with 2.8 ml of $0.01 \text{ mol L}^{-1}(\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O})$ (Merck) aqueous solution, under stirring, dried at 50°C for 24 h and crushed to get a fine powder. The atomic ratio of Co-Mo = 1 was fixed, while the $(\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O})$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ were mixed with a mole ratio of 7:1 for both prepared samples. Finally, 0.5 g of obtained material was impregnated with aqueous solution obtained by dissolving 0.8 g of sucrose (BDH Prolabo) and 0.1 g of H_2SO_4 (p.a., Centrohem) in 4 cm^3 of distilled water. The mixtures were heated for 6 h at 100°C and for 6 h at 160°C . The material was impregnated again with aqueous solution obtained by dissolving 0.5 g of sucrose, 0.05 g of H_2SO_4 and 2.5 cm^3 of distilled water. The sample was treated for 6 h at 100°C and then for 6 h at 160°C .

Similar procedure was applied to prepare Sample referred to as 2. The oxide precursors of the Co-Mo carbides were prepared by the mixture of aqueous solutions of cobalt nitrate 6-hydrate ($\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, and ammonium heptamolybdate 4-hydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$). The solid hydroxide products were dissolved in water at 30°C under stirring, dried overnight at 140°C , and then crushed to get a fine powder. Precursors $(\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O})$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ were mixed with a mole ratio of 7:1. The atomic ratio of Co-Mo = 1 was fixed. Mesoporous silica SBA-15 material (0.5 g) was impregnated with 6.9 ml of above mentioned 0.01 mol L^{-1} solution, under stirring at 30°C . The obtained material was dried at 45°C and then at 140°C for 48 h. After the calcination at 500°C for 3 h in air resulting material was crushed to get a fine powder. Impregnation procedure of obtained material with solution obtained by dissolving of sucrose and H_2SO_4 in distilled water was done in the same manner as described previously. Obtained Sample 1 was heated in a conventional furnace, at 500°C held for 2h in hydrogen flow. Samples 1 and 2, underwent carbothermal reduction at 900°C held for 2h in argon flow. After the heat treatment, the samples were cooled to room temperature under argon atmosphere.

The SBA-15 template was removed by mixing 1 g of the obtained powders with 20 cm^3 of HF (p.a. 40 %, Merck) for 20 h and washing in 200 cm^3 of ethanol and distilled water, until the neutral pH reaction. Obtained powders were dried on air at 120°C for 24 h.

2.2. Characterization methods

X-ray diffraction (XRD) data were collected on a Philips PW 1050 diffractometer with Cu-K $\alpha_{1,2}$ radiation (Ni filter) at the room temperature. Measurements were done in 2θ range of 5-60° with a scanning step width of 0.05° and 1s times per step.

Microstructure analysis is performed by scanning electron microscope (SEM, VEGA TS 5130 MM, Tescan). X-ray microanalysis (EDS) was carried out with INCA PentaFET-x3, Oxford Instruments.

Electrochemical characterization of obtained samples was performed by cyclic voltammetry (CV). All measurements were performed using Gamry electrochemical system (Gamry Instrumentation, potentiostat/galvanostat/ZRA 11076) in a three electrode configuration consisting of an Au rotating disk electrode (RDE) as the working electrode, a Pt mesh as the counter electrode, and Saturated Calomel Electrode (SCE) as the reference electrode. Catalyst inks were prepared by mixing 0.002 g of Sample 1 or Sample 2, 12.5 μ L Nafion solution and 990 μ L of isopropanol. The mixture is homogenized for 15 to 20 minutes in an ultrasonicator and 40 μ L of the mixture was then deposited onto the working electrode surface. CV data was obtained in 0.5M HClO₄ electrolyte before purging with nitrogen for 30 minutes to completely remove oxygen. The potential scan was carried out at rates of 20, 50 and 100 mVs⁻¹ in the range of -0.6 V to 1.0 V. After the scan was stabilization during the first 5-10 cycles, CV curves were recorded. All the CV curves are plotted against the SCE.

3. Results and Discussion

3.1. X-ray diffraction (XRD)

The XRD pattern of as prepared Sample 1 and Sample 2 are shown in Fig. 1. Inspection of Fig. 1 indicates difference that can be found between the two patterns of samples obtained using different starting procedures.

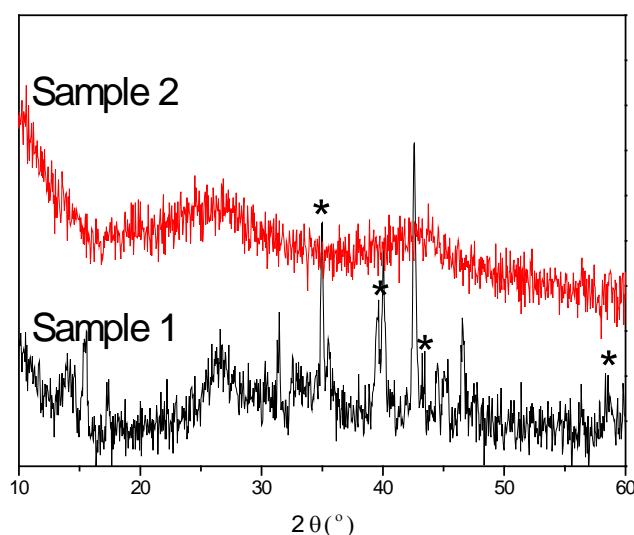


Fig. 1. XRD patterns of reaction products at 900°C.

*refers to peak of Mo₂C (ICSD: 36-863) and Co₃C (ICSD: 43-1144).

The most intense peaks of the Sample 1 pattern located at $2\theta = 32.8^\circ$, 35.84° , 43.08° and 47.1° match quite well with standard data of Co₆Mo₆C₂ (ICSD: 80-339) [1], except for a

some quantity of Mo_2C (ICSD: 36-863) and Co_3C (ICSD: 43-1144), marked as asterisks in the Fig. 1). The XRD pattern of Sample 2, exhibited a remarkable broadening in 2θ region from 20° - 30° and 35° - 50° 2θ which is associated with the reduced size of crystallites and low crystallinity (Fig. 1). The broadening of the diffraction lines in the region around 35 - 50° 2θ , indicates that nucleation and crystallization of $\text{Co}_6\text{Mo}_6\text{C}_2$ occurred at 900°C . However, quality of the XRD patterns did not allow indexing of the elementary cells of the obtained samples.

3.1. Scanning electron microscope and energy dispersive spectrometry (SEM/EDS)

The SEM micrograph of the SBA-15 template (Figs. 2a) and 2b)) and as-prepared Samples 1 and 2 are shown Figs. 2c) and 2d).

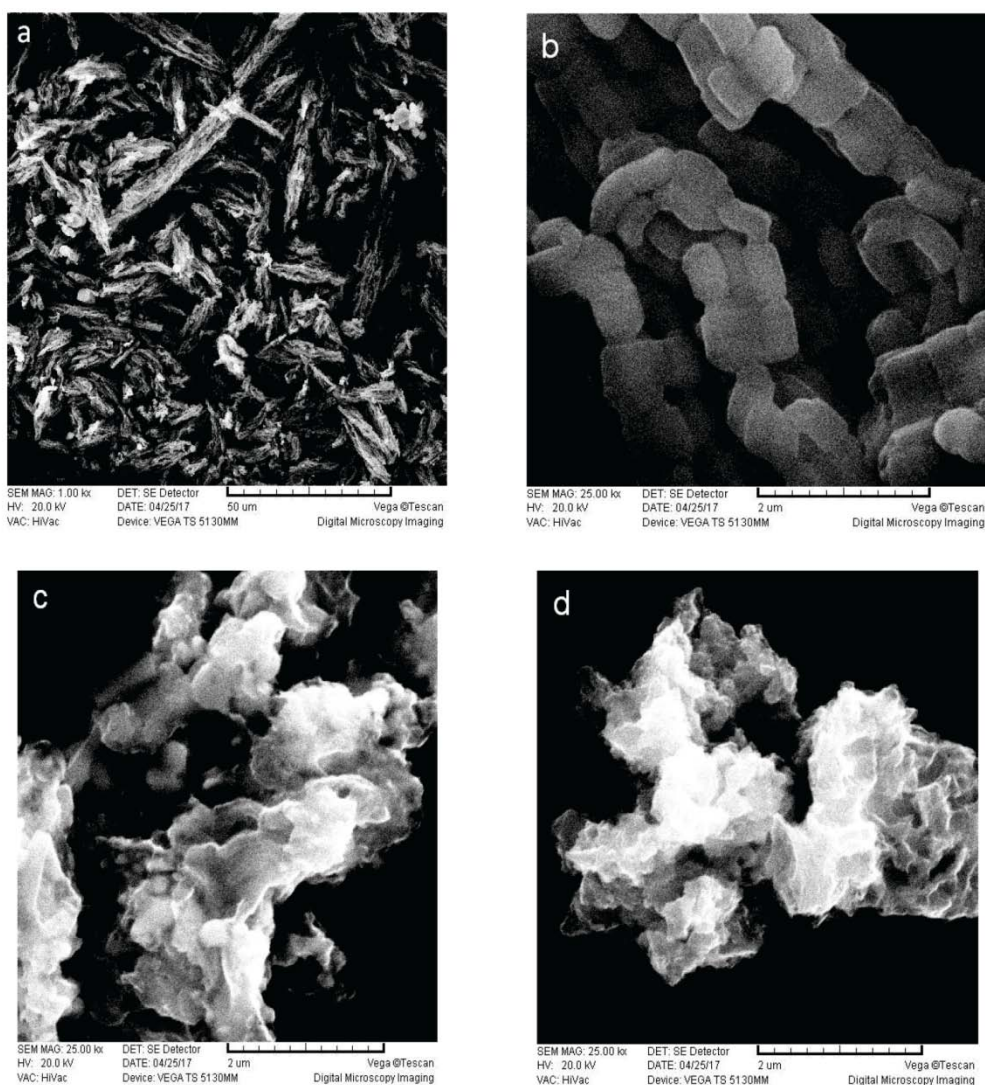


Fig. 2. SEM images of: (a) and (b) SBA-15 template, (c) Sample 1 and (d) Sample 2.

SBA-15 consists of many peanut-like domains with relatively uniform sizes (about $0.5\ \mu\text{m}$) which are aggregated into wheat-like structures. According to these images amorphous structure of the samples is evident. The SEM image of the as-prepared Sample 1

and Sample 2 shows that the obtained samples are porous materials with structure which is an inverse replica of the SBA-15 template. Both investigated samples exhibit irregular particles accumulating on large sandwich agglomerates with similar morphology, particle shape and size.

Detailed SEM/EDS analysis of the SBA-15 template and as-prepared powders, sintered at 900°C are given in Fig. 3.

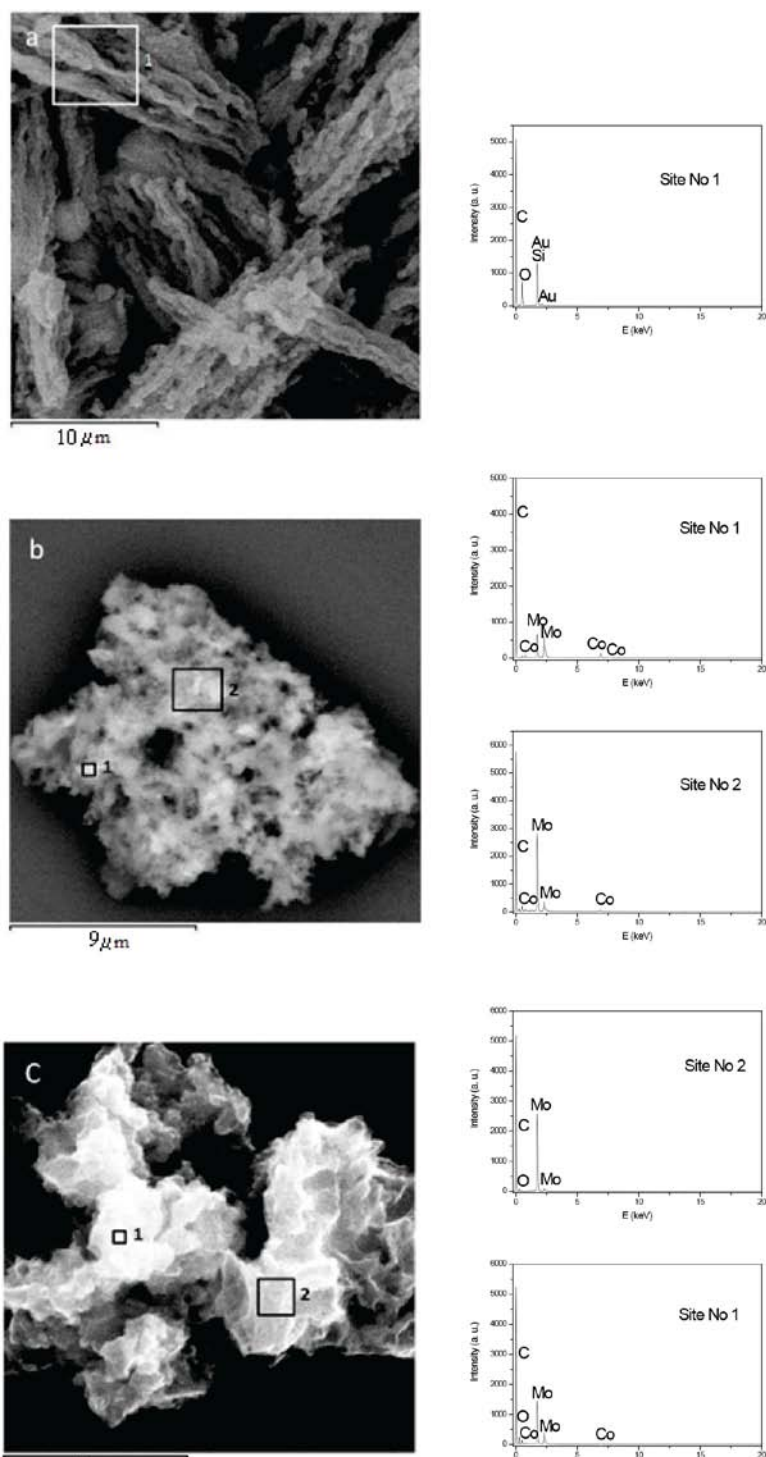


Fig. 3. SEM micrographs of: (a) SBA-15 template, (b) Sample 1 and (c) Sample 2.

Chemical composition of SBA-15 template obtained by EDS analysis of agglomerates, corresponds to the SiO_2 phase with a trace of Au peaks, due to Au coating of the samples (Site no. 1, Fig. 3a)). Chemical composition obtained by EDS analysis of agglomerates of Sample 1 and Sample 2 (Figs. 3b) and 3c)), corresponds to the result obtained by XRD analysis $\text{Co}_6\text{Mo}_6\text{C}$ phase.

3.3. Cyclic voltammetry

Cyclic voltammetry on Sample 1 and Sample 2 was performed in 0.5M HClO_4 in order to determine the stability in acidic conditions under the potential ranges suitable for operation in PEM fuel cells. Stability window is defined as the potential range in which the investigated catalyst support does not undertakes any irreversible change during anodic oxidation and cathodic reduction.

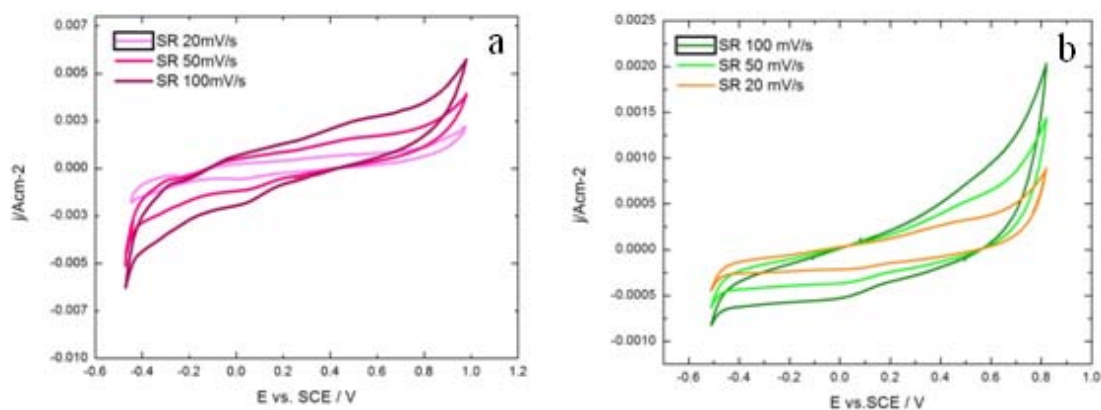


Fig. 4. Cyclic voltammograms for: (a) Sample 1 and (b) Sample 2 obtained in 0.5M HClO_4 electrolyte at different scan rates.

The results presented in Figs. 4a) and 4b) shows stability of 1.5 V and 1.3 V for the Samples referred to as 1 and 2, respectively. The cyclic voltammogram in Fig. 4a) for the Sample 1 exhibits pronounced hydrogen UPD (under potential deposition) region, compared to the Sample 2, Fig. 4b). Both cyclovoltammograms exhibit small peak at about 0 V vs SCE, which could originate from two effects. One is possible interaction of the carbides with the adsorbed hydrogen [20, 21] and the other is change in the oxidation state of the prepared Co-Mo carbides.

Taking into account the performed electrochemical measurements and the characteristics of the commercial carbon catalyst support, the prepared Co-Mo carbides could have few advantages. The pronounced H-upd region for the Sample 1 points catalytic effect of this type of catalyst support, which is favorable towards anodic hydrogen oxidation in PEM fuel cells. Also, the width of the electrochemical stability window is comparable to the commercial catalyst support, but due to the composition of these Co-Mo carbides, better stability towards electrochemical oxidation is expected. These results indicate that both of the investigated samples could serve as catalyst support to be applied in PEM fuel cells. The future investigations will consist of detailed electrochemical characterizations of Co-Mo carbides used as catalyst supports to Pt and Pt-Ru nanoparticles, and the application of these electrocatalysts in PEM fuel cell performance measurements.

4. Conclusion

The monometallic and bimetallic Co-Mo carbides were successfully prepared by impregnation into ordered mesoporous SBA-15 silica template with aqueous solution of metal salts and sucrose using carbothermal hydrogen reduction. In the case of sample which is not calcined at 500 °C, Co₆Mo₆C is formed. Also, Mo₂C and Co₃C are formed, too. For the sample calcined at 500 °C fine powder was obtained with low crystallinity. The SEM image of the as-prepared samples showed that the porous materials are obtained with structure which is an inverse replica of the SBA-15 as a template. Both samples are present as irregular particles accumulating on large sandwich agglomerates, with chemical composition obtained by EDS analysis of agglomerates matching well with the results obtained by XRD analysis. The results obtained with cyclic voltammetry indicate that both of the investigated samples could serve as catalyst support for PEM fuel cells application, which will be subject of our future work.

Acknowledgments

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5. References

1. N. Ćirović, P. Spasojević, L. Ribić-Zelenović, P. Mašković, A. Maričić, M. Spasojević, *Sci. Sinter.*, 48 (2016) 1.
2. J. Chen, W. Liu, X. Deng, S. Wu, *Sci. Sinter.*, 48 (2016) 41.
3. S. Izhar, M. Nagai, *J. Power Sources*, 182 (2008) 52.
4. R. B. Levy, M. Boudart, *Science*, 181 (1973) 547.
5. S. T. Oyama, *Catal. Today*, 15 (1992) 179.
6. J. G. Chen, *Chem. Rev.*, 96 (1996) 1497.
7. H. H. Hwu, J.G. Chen, *Chem. Rev.*, 105 (2005) 185.
8. J. K. Norskov, T. Bligaard, A. Logadottir, S. Bahn, L. B. Hansen, M. Bollinger, H. Bengaard, B. Hammer, Z. Sljivancanin, M. Mavrikakis, Y. Xuc, S. Dahl, C. J. H. Jacobsen, *J. Catal.*, 209 (2002) 275.
9. P. Liu, J. A. Rodriguez, *Catal. Lett.*, 91 (2003) 247.
10. P. N. Ross, Jr., J. MacDonald, P. Stonehart, *J. Electroanal. Chem.*, 63 (1975) 450.
11. X. H. Wang, M. H. Zhang, W. Li, K. Y. Tao, *Catalysis Today*, 131 (2008) 111.
12. J. M. Newsam, A.J. Jacobson, L.E. Mccandlish, R.S. Polizzotti, *J. Solid State Chem.*, 75(1988) 296-304.
13. X. Ma, H., M. Cai, P. K. Shen, *J. Am. Chem. Soc.*, 134 (2012) 1954.
14. S. Korlann, B. Diaz, M. E. Bussell, *Chem. Mater.*, 14 (2002) 4049.
15. T. C. Xiao, A. P. E. York, H. Al-Megren, C. V. Williams, H. T. Wang, M. L. H. Green, *J. Catal.*, 202 (2001) 100.
16. C. Liang, W. Ma, Z. Feng, C. Li, *Carbon*, 41 (2003) 1833.
17. C. Liang, P. Ying, C. Li, *Chem. Mater.*, 14 (2002) 3148.
18. C. Liang, F. Tian, Z. Li, Z. Feng, Z. Wei, C. Li, *Chem. Mater.*, 15 (2003) 4846.
19. M. Kokunešoski, J. Gulicovski, B. Matović, M. Logar, S. K. Milonjić, B. Babić, *Mat. Chem. Phys.*, 124 (2010) 1248.

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20. V. Nikolic, D. Zugic, I. Perovic, A. Saponjic, B. Babic, I. Pasti, M. Marceta Kaninski, Int. J. Hydrogen Energy, 38 (2013) 11340.
 21. D. V. Anićijević, V. Nikolić, M. Marčeta Kaninski, I. Pasti, Int. J. Hydrogen Energy, 38 (2013) 16071.

Садржај: Со-Мо карбиди су добијени карботермалном редукцијом уређене SBA-15 силике која је предходно импрегнирана воденим растворима соли метала и сахарозе. За добијање карбида Со и Мо карботермалном редукцијом у струји водоника, однос прекурсора Со и Мо био је 1. За карактеризацију добијених узорака примењене су следеће методе: рендгенска дифракциона анализа, скенирајућа електронска микроскопија и енергетска дисперзиона спектроскопија. Електрохемијска карактеризација добијених материјала изведена је цикличном волтаметријом у киселом раствору.

Кључне речи: Со-Мо карбиди, SBA-15, импрегнација, карботермална редукција водоником, циклична волтаметрија.

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