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Ceramic Carbide Synthesis: Process Optimization of Adsorption and Carburization

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Ceramic Carbide Synthesis: Process Optimization of Adsorption and Carburization

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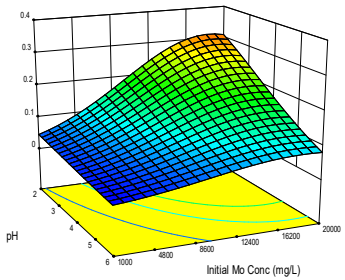
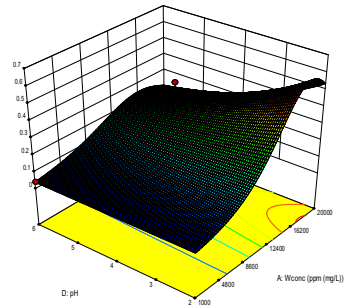
ANION ADSORPTION

Tungstate and molybdate loading were optimized using identical matrices of experimental conditions. To determine the optimal conditions for molybdate/tungstate adsorption, a statistical design of experiments was developed using DesignExpert 9 software (StatEase Inc.). A series of 30 individual experiments were carried out in order to mathematically model the effects of time, temperature, pH, and initial metal concentration on adsorption. Solution concentration were set at 1000 ppm, 10,500 ppm, and 20,000 ppm, temperature was held at 20ºC, 40ºC, and 60ºC, reaction time was set at 1 h, 12 h, and 24 h, and the pH of each solution was held at 2, 4, and 6 using hydrochloric acid (HCl). Solutions were prepared by adding sodium molybdate/tungstate to 100 mL of deionized water. Sodium chloride (NaCl) was also added to the solution so that a concentration of 0.2 M NaCl was achieved to promote adsorption [3]. A 2.5 g sample of activated carbon was added to each solution and the solutions were agitated to keep the activated carbon suspended in solution. Experiments carried out at 20ºC were agitated on an orbital shaker table at 480 rpm, and the experiments carried out at elevated temperatures were agitated on a hot/stir plate at 480 rpm. Following adsorption, the activated carbon was removed from solution via vacuum filtration and the solution was analyzed via ICP-OES using an ICP Thermo-Scientific iCAP 6000 instrument. The ICP-OES results were used to produce a response surface model of the adsorption data, and a mathematical model was generated using DesignExpert 9 to determine optimal adsorption parameters. The adsorption behavior of tungstate and molybdate anions was modelled using DesignExpert 9. Molybdate adsorption was mathematically modelled using a base 10 log transform and a modified quadratic relationship. Molybdate adsorption onto the activated carbon matrix was expressed as the mass (g) of adsorbed Mo per gram of activated carbon. A three-dimensional response surface model of tungsten adsorption was developed using the experimental design matrix prepared using DesignExpert9. Tungsten adsorption was modelled using an inverse square root transform and a modified quadratic relationship.

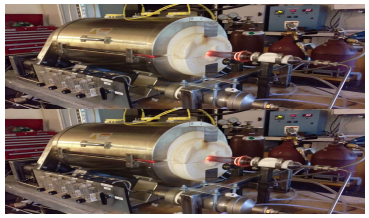
Optimal conditions for Mo and W adsorption were determined to occur at a pH of 2, a reaction time of 2 h, 20ºC, and an initial Mo/W concentration of 18,000 ppm.

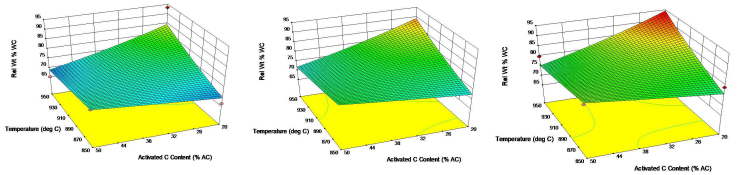




TUNGSTEN CARBURIZATION

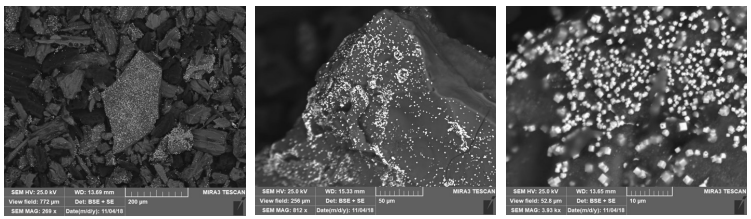
Carburization samples were prepared in 25g batches by blending W-loaded precursor with virgin activated carbon in a ceramic ball mill for five minutes so that each carburization sample was composed of 20-50% virgin activated carbon. This preparation step was added because previous research indicated that additions of virgin activated carbon increased the production of WC on the W-loaded precursor [10]. The blended samples were placed inside a quartz kiln and heated inside an ATS 3210 rotary furnace to a temperature of 850-950ºC under argon gas at a rate of 5.3ºC/min. Once the kiln interior reached the desired final temperature, a reducing gas mixture of methane, hydrogen, and carbon monoxide was introduced to the furnace with the flow of each gas regulated by Omega flowmeters. The ratio of methane to hydrogen gas was set at 2:1 or 8:1 for each carburization experiment and the total gas flow through the furnace was held at approximately 0.5 L/min. Samples were held at the desired temperature for 6 or 8 h. Following carburization under the reducing gas atmosphere, the samples were cooled back to room temperature under an argon purge gas and removed from the furnace for analysis. The compositions of the carburized samples were determined with X-ray diffraction using a Rigaku Ultima IV diffractometer with a Cu-kα X-ray source. Qualitative analyses of all samples were done using the Whole Pattern Powder Fitting Method (WPPF).





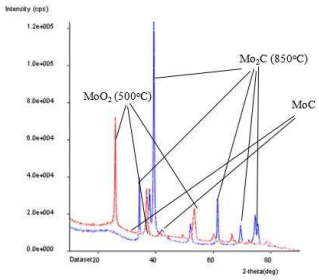
Tungsten carbide was synthesized at 950ºC under a reducing gas mixture of methane, hydrogen, and carbon monoxide from a precursor material consisting of tungstate anions adsorbed onto an activated carbon matrix. Conversion to the desired tungsten carbide species, WC, was achieved with values exceeding 90%.

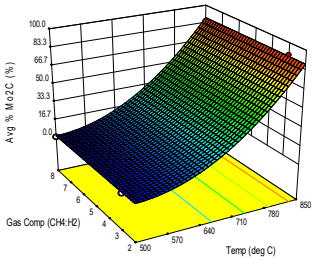
Experimental results were used to produce a preliminary model of carburization behavior for the W-loaded precursor. A 2-factorial analysis of the XRD data was used to produce this model and a power series transform was used in conjunction with a linear relationship to produce the mathematical model for predicting optimal carburization conditions. From this model, it was determined that maximum conversion to tungsten carbide can be achieved through the use of temperatures approaching 950ºC, a reaction time of 8 h, and an activated carbon content that does not exceed 20% of the total mass of the sample prior to carburization. Modelling carburization behavior indicated that activated carbon additions greater than 20% of the total sample mass reduced the conversion of the W-loaded precursor to tungsten carbide and may kinetically inhibit this process.

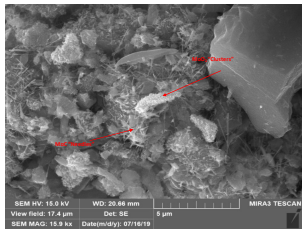


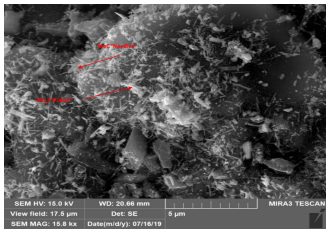
Images of the carburized material were produced using a Tescan MIRA 3 scanning electron microscope using electron back-scattering detection (EBSD). The images showed the presence of crystalline species on the surface of the activated carbon. All of these crystalline species were found to contain tungsten and carbon using energy-dispersive X-ray spectroscopy (EDAX). From the images of the crystalline species, it was observed that the W-containing crystals were of a relatively uniform size (approximately 2 µm cubes).

MOLYBDENUM CARBURIZATION









A preliminary model of carburization behavior was produced using DesignExpert9 software (StatEase Inc.). Modelling was carried out on the WPPF relative weight percentages of Mo_2C from the XRD data from each carburization experiment. Carburization data was modelled using a square root transform and a modified 2FI relationship. The statistical model generated from the XRD data was verified using multiple statistical diagnostic methods including analysis of variance (ANOVA), and Cook's Distance formula. Samples carburized at 850ºC were observed to contain two crystalline species: Mo_2C and MoC, with no other crystalline species present. Samples carburized at 500ºC were observed to contain MoC and a molybdenum oxide, MoO_2, with no Mo_2C present.

Because the needle-like crystals were observed in micrographs of both high-temperature and low-temperature samples, it is most likely that these crystals are composed of MoC as this molybdenum species was detected in both sample types. The crystal "flakes" present in samples carburized at 850ºC are proposed to be composed of Mo_2C and the crystal "clusters" observed in samples carburized at 500ºC are proposed to be composed of MoO_2.

CONCLUSIONS

Tungsten carbide was synthesized at 950ºC under a reducing gas mixture of methane, hydrogen, and carbon monoxide from a precursor material consisting of tungstate anions adsorbed onto an activated carbon matrix. Conversion to the desired tungsten carbide species, WC, was achieved with values exceeding 90%.
Experimental results were used to produce a preliminary model of carburization behavior for the W-loaded precursor. From this model, it was determined that maximum conversion to tungsten carbide can be achieved through the use of temperatures approaching 950ºC, a reaction time of 8 h, and an activated carbon content that does not exceed 20% of the total mass of the sample prior to carburization. Modelling carburization behavior indicated that activated carbon additions greater than 20% of the total sample mass reduced the conversion of the W-loaded precursor to tungsten carbide and may kinetically inhibit this process.

Molybdenum carbide, Mo_2C, has been synthesized from the carburization of a Mo-loaded precursor at conversion rates approaching 90%. A preliminary mathematical model of the carburization process has been produced that indicates that this process is primarily thermodynamically driven with high degrees of conversion to Mo_2C possible at 850ºC. The model may indicate that shorter reaction times and less aggressive gas atmospheres may be more effective than originally expected though further refinement of the model is necessary in order to confirm this possibility. Micrographs of the products carburized at 850ºC indicate that the carbide crystals produced by this process are submicron in size and may be suitable for both structural and catalytic applications.

ACKNOWLEDGEMENTS

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