Synthesis and characterization of nanostructured molybdenum & tungsten carbide materials, and study of diffusion model

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Powders of two molybdenum carbides (Mo_2C and MoC_{1-x}) and tungsten carbide (WC) were prepared by means of temperature programmed reaction (TPR) method. Mo_2C and MoC_{1-x} were synthesized by reacting MoO_3 with a preselected molar ratio of methane/hydrogen and carbon monoxide/hydrogen gas mixtures respectively. WC was prepared using tungsten oxide (WO_3) and a methane/hydrogen gas mixture. These carbides were ultrasonically dispersed in de-ionized water. Samples were characterized using room temperature x-ray diffraction and scanning microscopy. A kinetic diffusion model is also studied to determine diffusivities in solids where the diffusing species desorbs or reacts at the external surfaces, and where the diffusivity does not vary appreciably with concentrations. The method involves measuring the flux of the diffusive species into the solid under the influence of a temperature program.

Keywords: molybdenum carbide, tungsten carbide, temperature programmed reaction, sonochemistry, nanostructure.

INTRODUCTION

The carbides of molybdenum and tungsten constitute a diverse class of materials with many technological applications. Because of their great strength and durability, they have been traditionally used at extreme conditions of temperature and pressure, for example, in rocket nozzles and drill bits. Their hardness has given them applications in cutting tools, golf shoe spikes, and snow tires¹⁻³. These compounds have shown great potential for use as a commercial hydrodenitrogenation^{4,5} catalyst. Nanostructured carbide materials can help the microelectronics industry by providing the manufacturers with nanocrystalline starting materials, ultra-high purity materials, materials with better thermal conductivity, and longer–lasting, durable interconnections (connections between various components in the microprocessors).

Nanocrystalline Mo₂C can be synthesized using sodium metal in the co-reduction reaction of molybdenum pentachloride (MoCl₅) and carbon tetrabromide (CBr_4) in a benzene reaction medium at 350°C for 12 h (hours)⁶. Hyeon et al.,⁷ synthesized nanostructured molybdenum carbide from the ultrasonic irradiation of molybdenum hexacarbonyl in hexadecane. One of synthesis methods of Tungsten Carbide is by reaction between tungsten powder and soot⁸. Weimer⁹ reported a number of processes for the production of WC. A simple, inexpensive, and versatile route for the synthesis of metal carbides (Mo₂C and WC) nanoparticles were set up by Giordano and her co-authors¹⁰. Patel and Subrahmanyam¹¹ synthesized Mo₂C of less than 10 nm by solution route. Keller et al. 12, obtained a new medium specific surface area one-dimensional WC nanostructure by the shape memory synthesis method, in which they maintained the macrostructural features of a carbonaceous 1-D (dimensional) preformed template during the carburization of tungsten-oxide and determined the resulting carbide morphology. Singh¹³ developed thermochemical route for the synthesis of WC nanoparticles. Yamada¹⁴ presented a fast formation mechanism of WC from a tungsten-acetylene black powder mixture by an oblique shock wave technique. Kurishita et al.,¹⁵

presented a contemporary status of the development of nanostructured refractory transition metals of W and Mo emphasizing the effects of nano-structures upon the mitigation embrittlement by high ductile-to-brittle transition temperature (low temperature embrittlement) and by irradiation (radiation embrittlement). There are also many other recent investigations that have been carried out on WC synthesis¹⁶⁻¹⁸.

In this research temperature programmed reaction (TPR)¹⁹ method was applied for the synthesis of Molybdenum and Tungsten carbides. TPR is one of the thermoanalytical techniques for the characterization of chemical interactions between gaseous reactants and solid substances. This is a transient response technique in which some characteristic property of a solid sample is related to its temperature in a process of programmed heating. Exchange of matter and/or energy between the sample and its surroundings provide means as a function of temperature, the thermogram, reflects the nature of the system under study and the experimental conditions. Thermal analysis is used as a tool for quantitative analysis for the evaluation of the influence of different factors on the reactivity. The comprehensive review on this technique is illustrated by several investigators²⁰⁻²⁵. This method of preparation consists in treating the temperature in a uniform manner. The precursor can be an oxide, sulfide, nitride, or other compound while the reactive gas can be a mixture of a hydrocarbon and hydrogen for carbides¹. Sonochemistry principles were used to propose a mechanism to disperse the as-prepared particles followed by TPR. Finally XRD, elemental analysis, and SEM were employed to characterize the particles.

EXPERIMENTAL METHODS AND MATERIALS

Powders of two molybdenum carbides (Mo₂C and MoC) were synthesized by reacting MoO₃ with pre–selected molar ratios of CH₄ (Air Products and Chemicals Inc., CP grade) / H₂ and CO (National Welders, CP Grade)/ H₂ gas mixtures respectively. WC was produced by



Figure 1. Porous Interstitial Compound Synthesis Apparatus

reacting WO₃ in a CH₄/H₂ environment. The reaction gases were mixed and monitored through a mixing board that contained needle valves and rotameters (Omega Engineering, Inc). Approximately 100 mg of the parent oxides were loaded into (4x8x457.2 mm³) stainless steel swagelock tube reactors (Charlotte Valve and Fittings, Inc.) and secured either by a 10 mm quartz glass frit (Technical Glass Products, Inc.) or by glass wool (Johns Manville, E-glass). The reactors were then placed inside a 30 cm tube furnace equipped with a multi-programmable controller (Barnstead/Thermolyne, Model F79345) and connected to a gas mixture supply. Subsequent back pressure tests were conducted to ensure that the reactant gas volumetric flow rate ($\sim 1 \text{ m}^3/\text{hr}$) was not being inhibited. The process temperature was \sim 950–1050°C, whereas the startup temperature was ~650-1050°C. Each synthesis reaction began with a 5 to 10 minutes period for gas flow stabilization, which was followed by the initiation of the temperature ramping sequence. After completion of the temperature ramping program, the furnace was opened to allow rapid reactor cooling to room temperature under the reactant gas flow. Once room temperature was reached, the samples were passivated by slowly allowing air to diffuse through the reactor to the sample over a period of 24 hours. The passivation procedure was very important because transition-metal nitrides and carbides are extremely sensitive to air. Ultrasonic dispersion of interstitial transition-metal carbide materials is a convenient route for the large-scale synthesis of metallic nanoparticles. Porous Interstitial Compound Synthesis apparatus is shown in Fig 1. All materials were sonicated using the same procedure. Approximately 50 mg of the carbide material was placed in 50 ml of 11.2 M Ω -cm deionized water to form solid–liquid slurry. The deionized water was prepared by a Corning Mega Pure

System using Barnstead Ultra-High Purity Disposable Deionizer Cartridges. As a preliminary step, the slurries were subjected to agitation for approximately 30 seconds using a variable speed touch mixer (Fisher Scientific, Model 232). The solid-liquid mixtures were then placed in a solid-state ultrasonic bath (L&R Manufacturing, Model T-28B) and sonicated for 15-30 minutes. A portion of the ultrasonically dispersed solution was extracted (using a 30 ml syringe) immediately following sonication and allowed to settle over a period of 96 to168 hours. After settling, the resulting liquid was extracted once more and the remaining solids were dried under vacuum at 398°K for 4 to 5 hours. In order to establish the structural characteristics of dispersed and undispersed carbide materials XRD, elemental analysis, and SEM were used to inspect the compound identity, composition, and particle surface morphology respectively.

RESULTS AND DISCUSSIONS

The temperature programmed reduction is a convenient technique for the characterization of supported metal oxide catalysts. Generally, TPR is used to provide the information on the influence of support materials, preparation and pretreatment procedures, and metal additives on catalyst reducibility. The directly observable quantities include the total consumption of the reducing agent and the temperatures of the reduction rate maxima26. A series of molybdenum carbides were prepared by the temperature programmed reduction/carburization of MoO₃ with equimolar mixtures of CH₄/H₂ and CO/H₂. The materials resulting from CH₄/H₂ synthesis were identified through XRD as a hexagonal form of Mo₂C that is in good agreement with α -Mo₂C. Carbide materials produced with CO/H₂ agreed spar-

ingly with few XRD PDF's and most closely resembles a form of MoC_{1-x}. The carbide materials (MoC₅, MoC₆, and MoC₈) prepared with a 1:1 ratio of CH_4/H_2 were similar upon the visual inspection of the products extracted after the reaction completion. These powders were composed of grayish-metallic crystallites. Contrary to these observations, the carbide powders synthesized using the CO/H_2 reaction gas mixture (MoC₁₂ and MoC_{16}) displayed a copperish-brown metallic appearance and were composed of relatively larger coarse particles. The product was accessed by cutting the reactor open with a mechanical cutting lathe. During the sonication individualized waves were observed to move throughout the mixture. These actions were most visible by looking down into the solution as the jet waves could be seen impeding the opaque viscous layer. Immediately after sonication, the solution was noticed to continue a "swirling" action and was opaque and grayish-black in color. Over a period of several days of settling, the aqueous solution became clear and dark-blue as the nanoparticles settled out. The identity of the molybdenum carbide materials was confirmed using the RTXRD measurements. Average crystallite sizes were determined for the ultrasonically dispersed and non-dispersed molybdenum carbide materials. Using the SEM, elemental analysis was performed to identify the composition of the molybdenum carbide products. Lastly the surface morphology was studied using SEM.

The results of MoC₅, MoC₆, and MoC₈ used CH₄ as the carburization agent and produced essentially the same diffraction pattern when analyzed using RTXRD (Fig 2a, 2b). The only crystalline phase observed in this carbide group was Mo₂C. This observation was anticipated since according to the Mo–C phase diagram only hexagonal Mo₂C is thermodynamically stable under the conditions employed in Rudy *et al.*²⁷ These results are consistent with the XRD analysis conducted by Choi *et al.*,⁴ and Oyama et al.²⁸ X–ray reflections found at 39.4°, 37.4°, and 34.4° correspond to (101), (002), and (100) planes respectively. An average crystallite size is approximately 10.5 nm in the (101) direction, larger than 10 nm in the (002) direction and slightly smaller than 14 nm in the



Figure 2. XRD analyses: (a) comparison of Mo₂C X-ray diffraction patterns of the Methane Synthesis Group (b) relevant orientation planes of Hexagonal Mo₂C (101), (002), and (100) directions shown (c) crystalline α -Mo₂C and Mo₂C nanoparticles produced by ultrasonic irradiation of crystalline α -Mo₂C (d) pattern of MoC1₃. (pattern mostly resembles a form of MoC_{1-x}) [θ is in unit ""(degree)]

(100) direction. Line broadening of the sonicated Mo_2C reveals that the average crystallite size extends in the (101) direction to slightly more than 11 nm and less than 15 nm in the (100) direction. Comparison of the sonicated Mo₂C with the undispersed Mo₂C shows that the bulk phase remains that of Mo₂C (Fig 2c). The results of MoC₁₃ and MoC₁₆ used CO as the carburization agent and produced essentially the same diffraction pattern when analyzed using the RTXRD. The diffraction pattern of MoC_{13} was analyzed with a scan speed equal to 1. In this case, increasing the scan speed gave the pattern greater distinction during peak identification. The XRD pattern of MoC₁₃ is given in Fig 2d. The most intense peaks occur at 25.5° and 38.1°. Matching this pattern to a specific material was relatively difficult because there was not any one distinguishable PDF that corresponded in great detail with MoC_{13} . Although the most intense do not match any of the files, a few of the secondary peaks match up with a form of MoC_{1-x} . Possible reasons for this occurrence are given in the discussion section. Using the most intense peak, the average crystallite size was determined to be approximately 43 nm. The results of scanning electron microscopy on the molybdenum carbon compounds reveal several different characteristics. SEM analysis of the Mo₂C was taken at a range interval from 10 microns to 100 nm at magnifications varying from 1000 to 40000. As shown in Fig 3a, the undispersed at 10 μ m and 5000 magnifications, displays a collection of platlets or flake structures, which may be analogous to small "playing cards" on the right hand side. Small resemblances of macro crystals at the top middle and needle-like crystals along the bottom left side. Fig 3b shows dispersed Mo₂C where there is an absence of macrocrystals. Flake and needle-like particles appear to be more dispersed; in addition, layered thin crystals are present in the upper left corner. There exists some speculation that preparing Mo₂C using the TPR method may yield intermediate compounds, such as molybdenum oxycarbide (MoO_xC_{1-x}). The XRD analyses performed in this study confirmed that Mo2C were produced and that there was no evidence of the oxy-carbide compounds.

A series of tungsten carbides (WC) was prepared by the temperature programmed reduction/carburization of WO₃ with equimolar mixtures of CH₄/H₂. XRD analyses reveal that hexagonal WC was produced. Other trials of tungsten carbide synthesis produced a form most notably corresponding to WC_x. Carbide materials (WC₉, WC₁₀, WC₁₇) prepared with a 1:1 ratio of CH₄/H₂ yielded different results upon visual inspection of the products. WC_9 powders were comprised of grayish-metallic grains similar to those of Mo₂C and Mo₂N. WC10 powders were brown, while WC₁₁ and WC₁₇ yielded dark-purple powders. The only noticeable difference in the preparation of these materials was the change in temperature ramping rates Δ_1 and Δ_2 . These values are shown in Table 1. All WC products were obtained by cutting the reactors open in a similar fashion as that of MoC₈. Preparation of tungsten carbide nanoparticles was completed using WC₉. Upon the addition of deionized water to the tungsten carbide,





Figure 3. SEM micrograph: (a) undispersed α -Mo₂C (b) dispersed α -Mo₂C

Table 1. Change in temperature ramping rate (Δ – temperature ramping rate, K – Kelvin, h – hour, MSHV – mass hourly space velocity)

Product Code	Δ ¹ -0.5 (K/h)	Δ 2 (K/h)	MHSV (1/h)	Final Temperature (K)
MoC ₅	27	60	30	1093
MoC ₆	27	60	30	1093
MoC ₈	27	120	30	1093
MoC ₁₂	27	120	45	1093
MoC ₁₆	27	120	45	1093
WC ₉	10.75	120	30	1148
WC ₁₀	21.5	120	30	1148
WC ₁₇	21.5	180	30	1148

the solution turned dark gray and an opaque charcoal layer formed above the aqueous solution, a result similar to that of Mo₂C. As with the Mo₂C solid–liquid mixture, only rigorous agitation using a touch mixer dispelled the charcoal-like layer into the solution. Additionally the "jet waves" described during Mo₂C sonication were also observed during the WC dispersion. During the settling period, the solution became clear and light gray in color. RTXRD was used in order to confirm the identity of WC_9 as hexagonal carbide. The identity of WC_{10} , WC_{11} , and WC_{17} most closely corresponds to a form of WC_{1-x} . Fig. 4a displays the collected XRD pattern for WC₉. As shown, the most intense peaks occur at diffraction angles $2\theta = 35.6^{\circ}, 48.2^{\circ}, \text{ and } 31.5^{\circ}$. These peaks correspond with the (100), (101), and (001) orientation planes respectively. Computed average grain size yields approximately 9.6 and 9.7 nm in the (100) and (101) directions respectively. Although the crystallite sizes reported in this work are approximately half of those measured by Oyama et al.⁵ the XRD pattern of WC₉ strongly agrees with Oyama's¹ study. X-ray diffraction was used to analyze the ultrasonically dispersed WC product. Comparison of the WC nanoparticles and the hexagonal-WC material show that



Figure 4. XRD analyses: (a) patterns of WC produced by TPR of WO₃ and CH_4/H_2 reactant gas mixture (b) hexagonal WC and WC nanoparticles created by ultrasonic dispersion [θ is in unit "o"(degree)]





Figure 5. SEM analyses: (a) undispersed WC (b) ultrasonically dispersed WC

only peaks due to WC was observed (Fig. 4b). Scherrer analysis of the peak widths indicates little change in the size of the crystalline domains: the nanoparticles extend slightly to 10.2 nm in the (100) direction and 10 nm in the (101) direction.

The SEM analyses of the tungsten carbide products show a variety of different morphologies. Fig 5a shows non-sonicated WC_x at 10 μ m and 5000 magnifications. The micrograph shows a variety of fine needle like crystals, randomly directed but uniformly dispersed. Some crystals display a layered thin–flake appearance representative of high crystality. The ultrasonic irradiation effects are observed in great detail using SEM analysis of WC. Fig 5b shows undispersed WC as large macrocrystals surrounded by various spherical shaped particles.

KINETIC SYNTHESIS MODELS FOR MO2C AND WC

The kinetic diffusion model for the diffusion of oxygen and carbon was studied using the diffusion model proposed by Kapoor and Oyama²⁹. The mathematical calculations were also performed to transpire what is happening in the reduction of molybdenum and tungsten oxide with CO_2/CH_4 to produce molybdenum and tungsten carbide respectively. Oyama *et al.*,²⁸ have previously studied the diffusivities of oxygen and nitrogen in the V_2O_5 . Kapoor and Oyama²⁹ studied the diffusion coefficients of oxygen and nitrogen through the temperature programmed reactions. The same model was extended in determining the diffusivities of oxygen and carbon in oxide to carbide.

Diffusivity is determined by matching an observable experimental quantity, namely the peak temperature of the species diffusing out of the solid to a Fickian diffusion model for the process. Kapoor and Oyama²² assumed that one-dimensional diffusion was occurring in a semi-infinite slab, which meant the activated diffusion process could be applied by Fick's second law of diffusion equation. This expression is as follows:



Figure 6. Surface plot of concentration profiles within the slab: (a) Mo_2C (b) WC

 Table 2. List of parameters used in Kinetic model

$$\frac{\partial C}{\partial t} = \frac{D_o}{h^2} \exp\left(-\frac{E}{RT}\right) \frac{\partial^2 C}{\partial X^2}$$
(1)

Where *C* is the ratio of concentration at any time to the initial concentration, $C = c/c_0$, and *X* is the ratio of the distance from the center of the slab to its halfthickness, X = x/h. Then by inserting the temperature dependence $(T = T_0 + \beta_t)$ into Eq. 2, and applying boundary conditions final concentration profile (Eq. 2) and diffusion rate (Eq. 3) is determined.

$$C(X,t) = \sum_{n=1}^{\infty} \frac{2(-1)^{n-1}}{\lambda_n} \exp\left(\frac{\lambda_n^2 \tau}{h^2}\right) \cos(\lambda_n X)$$

$$2D^{\infty} \qquad (2)$$

$$r_{t} = \frac{2D}{h^{2}} \sum_{n=1}^{\infty} \exp\left(-\frac{\lambda_{n}^{*} \tau}{h^{2}}\right)$$
(3)

Here λ_n are eigenvalues $(2n-1)\pi/2$. These are calculated using Sturn-Liouville equation, for $n = 1, 2, 3, \dots, \infty$, and $\tau = \int Ddt = \int D_o \exp^{[-ERT]}$. E was calculated from the Redhead equation³⁰.

The parameters which were used in this study are listed in Table 2. In-situ HTXRD experimental data and solid state kinetic models indicate that the thermal activation of oxygen diffusion takes place at lower temperatures approximately 500 K than nitrogen infusion at 1250 K into the molybdenum lattice structure. For the case of tungsten lattice structure oxygen diffuses at 1400 K and nitrogen infuses at 2600 K. Concentrations profile is shown in Fig 6. Both activation temperatures strongly correspond to experimental observations and theoretical predictions. Dissociated hydrogen appears to act not only as a chemical trap for escaping oxygen atoms but also as a reactive species for the formation of possible molybdenum bronze materials between 400 to 1300 K and for tungsten materials between 1300 to 2600 K. Precision of the established model in this study was in our experimental data uncertainty ($\sim 2\%$ deviation). However, the results could not be validated further by any other literature values because no investigation was found so far in this maneuver.

CONCLUSION

Temperature Programmed Reaction (TPR) and ultrasonic irradiation provided an effective pathway to synthesize transition-metal carbide nanoparticles. Polycrystalline α -Mo₂C was synthesized from MoO₃ macrocrystals by TPR in CH₄/H₂ gases. The α -Mo₂C crystallites were relatively small and dark metallic-gray in color. Slight changes in temperature ramping rate did not change the structure of the resulting α -Mo₂C. A form of molybdenum carbide that closely resembled MoC_{1-x} was produced by TPR in CO/H₂. The MoC_{1-x} material appeared to have relatively larger and coarser grains than α -Mo₂C. Hexagonal WC was prepared by TPR in a CH₄/H₂ reactant gas mixture. Unlike α -Mo₂C synthesis

parameters	Мо	W	unit
D _o (diffusivity coefficient)	0.000013	0.0000085	m²/s
<i>h</i> (particle size)	14	10	nm
E (activation energy)	101000	260000	J/mol
β (temperature coefficient)	0.083	0.083	K/s
T_o (reference temperature)	298.15	298.15	K
R (gas constant)	8.314	8.314	J/mol/K

the WC products were affected by slight changes in the temperature ramping program. WC was obtained using Δ_1 = 11 K/h^{-0.5} and Δ_2 = 120 K/h, and was metallic-gray in color. In addition to hexagonal WC, a form of tungsten carbide that strongly agreed with XRD patterns of WC_x was also produced. Ultrasonic irradiation provided a convenient route to produce nanoparticles from refractory carbide powders. XRD analyses displayed that α -Mo₂C crystallite size was 10-14 nm, while the ultrasonically dispersed a-Mo₂C nanoparticles extended to 10.5-15 nm. WC had an average crystallite size of 9-14 nm and extended slightly to 10-14 in the nanoparticles. This work has determined that TPR synthesis of topotactic molybdenum and tungsten carbide powders followed by ultrasonic irradiation can produce transition-metal carbide nanoparticles.

LITERATURE CITED

1. Oyama, T., (1996). "The chemistry of transition metal carbides and nitrides," London, Chapman and Hall.

2. Storms, E.K., (1967). The Refractory Carbides, Academic Press, New York.

3. Toth, L.E., (1971). Transition Metal Carbides and Nitrides, Academic Press, New York.

4. Choi, J., Brenner, J. & Thompson, L. (1995). Pyridine Hydroenitrogenation Over Molybdenum Carbide Catalysts, *Journal of Catalysis*, 154, 33–40. DOI:10.1006/jcat.1995.1143.

5. Oyama, S.T., Schlatter, J.C., Metclafe, J.E. & Lambert, J.M., (1988). Preparation and Characterization of Early Transition-Metal Carbides and Nitrides, *Ind. Eng. Chem. Res.*, 27, 1639–1648. DOI: 10.1021/ie00081a013.

6. Gu, Y., Li, L., Chen, Z., Yang, Y. & Qian, Y., (2003). Synthesis of nanocrystalline Mo_2C via sodium co-reduction of MoCl5 and CBr4 in Benzene, *Mater. Res. Bull.*, 38, 1119–1122. DOI:10.1016/S0025-5408(03)00132-6.

7. Hyeon, T., Fang, M. & Suslick, K., (1996). Nanostructured Molybdenum Carbide: Sonochemical Synthesis and Catalytic Properties, *J. Am. Chem. Soc.*, 118, 5492–5493. DOI: 10.1021/ ja9538187.

8. Mcgee, R., Bej, S. & Thompson, L., (2005). Basic properties of molybdenum and tungsten nitride catalysts, *Appl. Catal. A.*, 284, 139–146. DOI:10.1016/j.apcata.2005.01.029.

9. Weimer, A. (1997). Carbide, Nitride and Boride Materials Synthesis and Processing, New York, Chapman and Hall.

10. Giordano, C., Erpen, C., Yao, W. & Antoniettin, M., (2008). Synthesis of Mo and W Carbide and Nitride Nanoparticles via a Simple "Urea Glass" Route, *Nano Lett.*, 8, 4659–4663. DOI: 10.1021/nl8018593.

11. Patel, M. & Subrahmanyam, J., (2008). Synthesis of nanocrystalline molybdenum carbide (Mo_2C) by solution route, Mater. Res. Bull., 43, 2036-2041. DOI:10.1016/j.mater-resbull.2007.09.025.

12. Keller, N., Pietruszka, B. & Keller, V. (2006). A new one-dimensional tungsten carbide nanostructured material, *Mater. Lett.*, 60, 1774–1777. DOI:10.1016/j.matlet.2005.12.017.

13. Singh, R.P., (2008). Synthesis and characterization of tungsten carbide nanoparticles. School of Physics & Materials Science, MS Thesis., Thapar University, Patiala.

14. Yamada, K., (2000). Synthesis of tungsten carbide by dynamic shock compression of a tungsten-acetylene black powder mixture, *J. Alloy Compd.*, 305, 253–258. DOI:10.1016/S0925-8388(00)00700-3.

15. Kurishita, H., Matsuso, S., Arakawa, H., Hirai, T., Linke, J., Kawai, M. & Yoshida, N. (2009). Development of nanostructured W and Mo materials, *Adv. Mater. Res.*, 59, 18–30. DOI: 10.4028/www.scientific.net/AMR.59.18.

16. de Medeiros, F.F.P., da Silva, A.G.P., de Souza, C.P. &

Gomes, U.U., (2009). Carburization of Ammonium Paratungstate by Methane: The influence of Reaction Parameters, *Int. J. Refract. Metals and Hard Materials.*, 27, 43–47. DOI:10.1016/j. ijrmhm.2008.03.001.

17. Reddy, K.M., Rao, T.N., Radha, K. & Joardan, J. (2010). Nanostructured Tungsten Carbides by Thermochemical Processing, *J. Alloys and Compounds.*, 494, 404–409. DOI:10.1016/j. jallcom.2010.01.059.

18. Cetinkaya, S. & Eroglu, S. (2011). Comparative Kinetic & Structural Analysis of Nanocrystalline WC Powder Synthesis from Pre-reduced W under Pure and Diluted CH_4 Atmospheres, *Int. J. Refract. Metals and Hard Materials.*, 29, 214–220. DOI:10.1016/j.ijrmhm.2010.10.009.

19. Oyama, S.T. (1981). "Ammonia synthesis and decomposition on molybdenum and its interstitial alloys." PhD Dissertation, Stanford University, Stanford, CA.

20. Kanervo, J. (2003). "Kinetic analysis of temperature programmed reactions." PhD Dissertation, Helsinki University of Technology.

21. Knotzinger, H. (1997). "Temperature-programmed reduction, In Handbook of Heterogeneous Catalysis," Eds. Etrl, G., Knozinger, H., Weitkamp, J., Vol 2, VCH, Weinheim, pp 676.

22. Bhatia, S., Beltramini, I. & Do, D.D. (1990). "Temperature-programmed analysis and its applications in catalytic systems." *Catal. Today*, 7, 309–438.

23. Jones, A. & McNicol, B. (1986). "Temperature-programmed reduction for solid materials characterization." Marcel Dekker Inc., New York.

24. Lemaitre, J.L. (1984). "Temperature-programmed methods, in characterization of heterogeneous catalysts." Ed. Delannay, F., Marcel Dekker, Inc., New York, pp 29–70.

25. Hurst, N.M., Gentry, S.J. & Jones, A. (1982). "Temperature – programmed desorption and reduction." Catal. Rev. -Sci. Eng., 24, 233–309.

26. Kanervo, J.M. & Krause, A.O.I. (2001) "Kinetic Analysis of temperature programmed reduction: behavior of a CrO_x/Al_2O_3 Catalyst." *J. Phys. Chem. B*, 105, 9778–9784.

27. Rudy, E., Windish, S., Stosick, A. & Hoffman, J. (1967). Revision of the Titanium-Tungsten System, *Trans TMS-AIME*., 239, 1247–1267.

28. Oyama, S.T., Schlatter, J., Metcalfe, J. & Lambert, J. (1988). Preparation and characterization of early transition metal carbides and nitrides, *Ind. Eng. Chem. Res.*, 27, 1639–1648. DOI: 10.1021/ie00081a013.

29. Kapoor, R. & Oyama, S.T. (1997). Measurement of solid state diffusion coefficients by a temperature-programmed method, *J. Mater. Res.*, 12, 467–473. DOI: 10.1557/JMR.1997.0068.

30. Redhead, P.A., (1962). Thermal Desorption of Gases, Vacuum., 12, 203–211. DOI:10.1016/0042-207X(62)90978-8.