

TRANSITION METAL CARBIDE (TMC) NOVEL MATERIALS FOR
NOVEL CATALYTIC APPLICATIONS

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2015

PREVIEW

Dedication

This thesis is dedicated to my father- Valentine Pavlychev, an outstanding Russian engineer and chemist.

PREVIEW

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NOVEL CATALYTIC APPLICATIONS

by

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THESIS

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Abstract

Transition metal carbides (TMC) constitute a diverse class of materials and traditionally have many technological applications. TMC became a subject of extensive research since 1973, when their platinum-like properties were discovered. They demonstrated high catalytical activity and selectivity in a variety of chemical reaction and have potential for some novel catalytic application.

This research is an effort to design new high effective, selective and stable bimetal or alkali promoted TMC catalyst. After extensive theoretical research a wide range of TMC, including bimetal and alkali promoted carbides, were synthesized by different methods. All solids were characterized by XRD and microscopy. The way was found to obtain and control desirable structure of final product by applying method of synthesis, changing conditions and a choice of precursors.

The catalytic activity of new TMCs was tested in model reaction of hydrogenation and in Fisher-Tropsch synthesis for their production of alcohols. A lab scale gas to liquid system has been developed for that evaluation. Cobalt and nickel molybdenum carbides with different types of phases demonstrated high activity and selectivity. The spent catalysts were also characterized in order to establish its stability and changes in structure morphology.

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Introduction

Transition metal carbides (TMC) have attracted considerable attention for catalytic applications since 1973, when Levy and Boudart (1) first reported the Pt-like behavior of WC in the neopentane isomerization reaction. The first synthesis of TMC was derived from metallurgical processes at high temperatures and resulted generally in powders with low specific surface areas. Of prime importance for catalytic applications was the development of a temperature programmed method of synthesis at more moderate conditions. The use of this method allowed an optimal balance between sintering and synthesis rates and resulted in products with high surface area. This class of compounds has shown particularly excellent potential for use in hydroprocessing reactions, widely use in refining. Recently a great number of studies dealing with the application of TMCs in hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) reactions have been reported. Most of the work has concentrated on molybdenum carbide catalysts, which proved to be not only superior to commercial hydrotreating catalysts in terms of activity and selectivity but they were also sulfur resistant. Molybdenum sulfide-based hydrodesulfurization (HDS) catalysts have been the most popular commercial catalysts since their inception into the industrial hydrotreating process nearly 60 years ago. Over the last 30 years, nearly a 2-fold increase in HDS activity has been achieved. (2) Such improvements have allowed petroleum refineries to lower the sulfur content of transportation fuels in response to environmental regulations implemented in a number of countries. Given the likelihood of further reductions in the allowable sulfur content in fuels and the need to process lower quality petroleum feedstocks in future years, incremental improvements of molybdenum-sulfide-based catalysts may not be sufficient to meet environmental standards.

To complement research efforts aimed at optimizing sulfide-based catalysts, many laboratories have adopted the approach of investigating how main group elements other than sulfur modify the catalytic properties of molybdenum. In this vein, molybdenum carbide ($\text{-Mo}_2\text{C}$) has attracted attention as potential catalysts for use in the HDS process.

Transition metal carbides constitute a diverse class of materials and traditionally have many technological applications. Their great strength and durability allow them to be used at extreme conditions of temperature and pressure, for example, in rocket nozzles and drill bits. Their hardness has given them use in cutting tools and snow tires. They have applications in ferrous alloys as components responsible for the toughness of steels. Besides that, optical, electronic and magnetic properties of carbides have been used for optical coating, electrical contacts, diffusion barriers etc. In fact, the physical and mechanical properties of carbides resemble those of ceramics not those of metals. The materials are hard, strong, and somewhat brittle. In contrast, the electronic and magnetic properties of the carbides are similar to those with the metals. (3)

Although their activity is similar to those of the noble metals, kinetics and product selectivities are often different in the catalytic reactions involving oxygen- containing molecules and indicate that the carbides provide unique catalytic pathways.

Other important properties are vaporization behavior and solid state diffusivity. New applications of these materials are continuously being developed.

In addition to the technological uses of transition metal carbides which exploit their high hardness and stability at high temperatures, certain carbides have been examined for their catalytic properties in a number of reactions. This is in addition to their being potential supports for more traditional catalytic materials (Ni, Pt, Rh, etc.) due to their high heat stability. (3)

Historically the interest in the catalytic properties of TMC has been inspired by their “Platinum-like” properties in the transformation reactions of hydrocarbon molecules.

The observation has been made that tungsten was active as a catalyst and showed good selectivity toward xylene formation during the isomerization and hydrogenolysis of 1,1,3-trimethylcyclopentane, but only after an induction period, as is also characteristic of platinum and palladium. Base transition metals do not behave this way. The behavior was explained by invoking the formation of tungsten carbide on the surface of the metal. WC is similar to platinum in selectivity for neopentane isomerization as well. Molybdenum carbide has been found to behave similarly to Ru in CO-H₂ reactions. (1) These are merely two examples: in fact, carbides of the Group IV-VI metals have been studied for their activity in oxidation, hydrogenation/dehydrogenation, isomerization, hydrogenolysis, and CO-H₂ reactions, and in many cases have been found to rival the performance of the less economic Group VIII metals. While the refractory carbides do not show high activity for oxidation reactions (for example, the rate of H₂ oxidation follows the order metal >> carbide > oxide for Group V and VI metals, and the rate of NH₃ oxidation over refractory carbides is lower than that over Group VIII metals), they are as active as the transition metals themselves for hydrogenation and dehydrogenation reactions. In isomerization reactions, WC, Pt, and Ir are unique in their high activity and selectivity. However, it is not necessary for the refractory carbides to be more or even equally active in catalyzing given reactions compared with the noble metals, because the lower cost of the carbides will in many cases offset the losses in catalytic activity. (2) We discuss reaction of TMC in more details later. The surface science results on model carbide overlayers clearly indicate that the reactivities of transition metals can be modified by the formation of carbide overlayers, with the modified surface

reactivities being frequently similar to those of Pt-group metals. (4) Therefore, in many types of reactions TMCs display activity approaching or surpassing those of the best Group VIII metals.

The unique properties of TMCs have made them promising catalysts in a number of catalytic and electrocatalytic processes that involve the transformation of oxygen-containing molecules. For example, the catalytic and electronic properties of Group VI carbides have shown potential application as alternative electrocatalysts for direct alcohol fuel cells (DAFC) and for the conversion of biomass such as cellulose to lower order polyols. Carbides also have shown promise as water gas shift (WGS) catalysts. Leclercq et al reported the high selectivity of transition metal carbides for direct synthesis of alcohol in Fischer-Tropsch reactions. (2)

Fig.1 presents Arrhenius plots for Group V and VI metal carbides. The materials were reduced in flowing H_2 at 753-773K prior to determination of the reaction rate. The niobium carbide was not active.

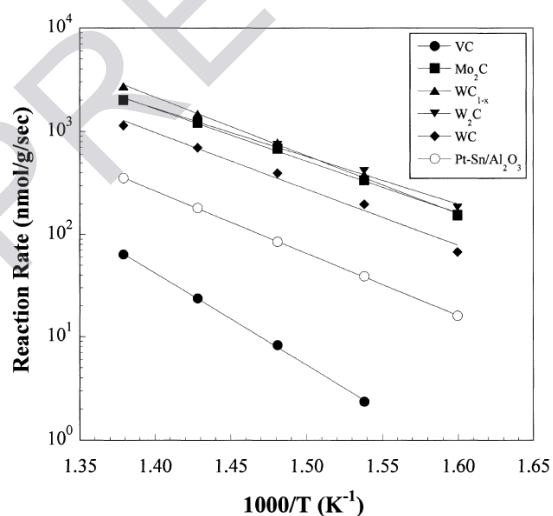


Figure 2: Arrhenius plot for Group V and VI metal carbides

Catalytic activity of butane conversion over mesoporous transition metal carbides W_2C , WC , Mo_2C , V_8C_7 and NbC has been reported by Neylon et al (4) and compared to that of Pt-based catalyst. The butane conversion rates for TMCs were generally higher than those for a Pt-Sn/ Al_2O_3

catalyst. However, the product selectivities were different. The abbreviations C₁, C₂, C₃, C₄, C₄⁼ and C₄⁼ represent CH₄, the total of C₂H₄ and C₂H₆, the total of C₃H₆ and C₃H₈, C₄H₁₀, C₄H₈ and C₄H₆ respectively. The niobium carbide was not active. (Fig.2)

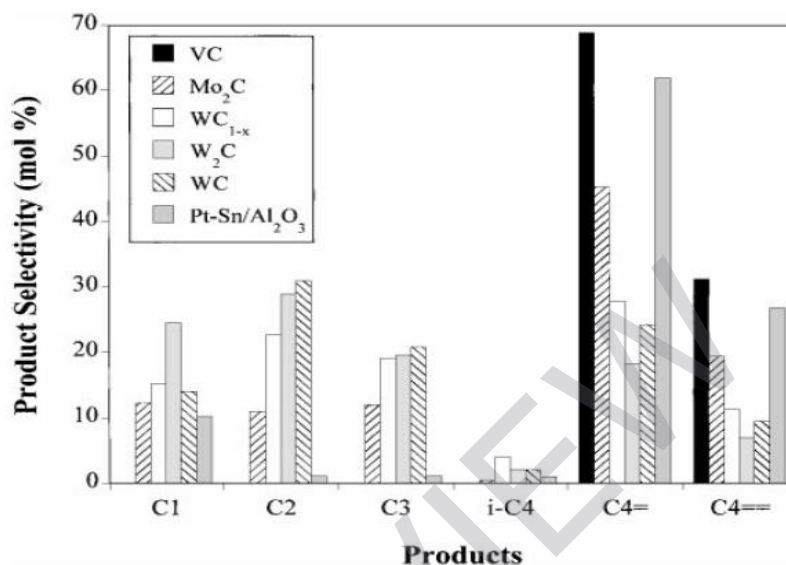


Figure 3: Butane activation selectivities for the Group V and VI metal carbides

Computational and experimental ammonia decomposition on various transition and noble metal catalysts have been investigated as a model reaction by Hansgen et al.. Volcano curve of predicted conversion of ammonia versus the nitrogen heat of chemisorption ($Q_{N(0)}$) at a reactor temperature of 850 K is presented (figure 3). (5) Among the single-metal catalysts studied, Ru was found to have the highest activity, consistent with their experimental data. Using the predicted volcano curve, the bimetallic transition-metal catalysts with the same activity of Ru have been designed. These bimetallic surfaces are then tested experimentally for their activity to validate the model predictions. On the plot red triangles show N-H bond scission and black circles show C-H bond scission.

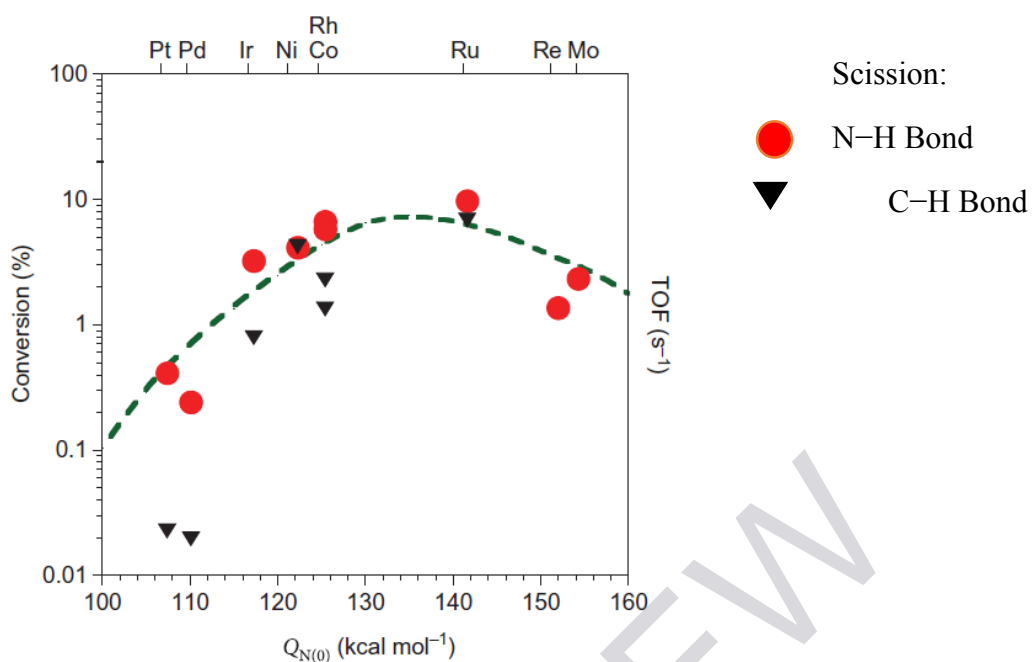


Figure 4: Ammonia decomposition on various transition and noble metal catalysts

Also many monometallic types of carbide have been studied for their catalytic activities; there are still a few reports on bimetallic carbides.

A micro-kinetic model for various transition metal and noble metal single and bimetallic catalysts was calculated by Dr. M. Ramos (6) (fig.4).

The volcano curve presented shows that bimetallic Ni-Mo and Co-Mo carbides possess a higher catalytic activity than that of platinum. Based on that fact and high commercial potential of Ni- and Co- containing precursors, this research was focused on studying bimetallic molybdenum carbides where the second metal is cobalt or nickel.

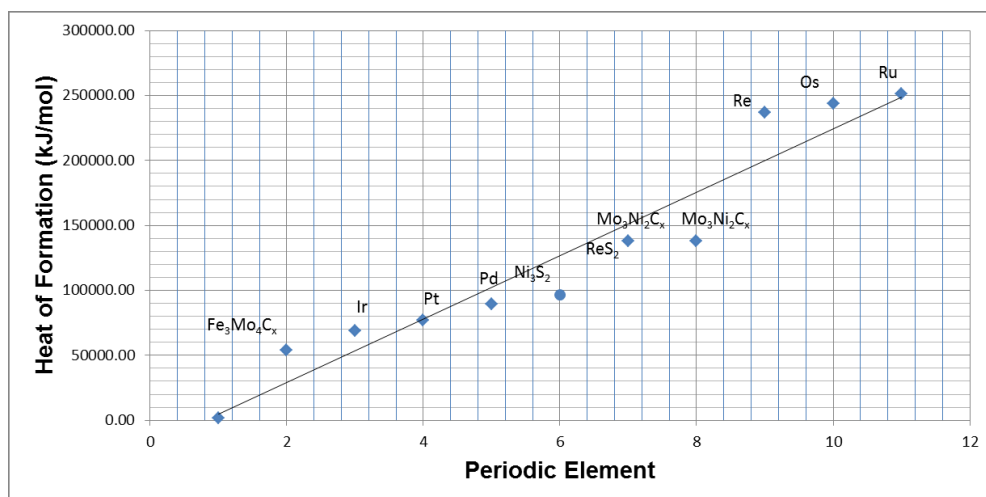


Figure 4. Micro-kinetic model for various TMC and noble metal single and bimetal catalysts.

The objective of this research project was to develop scientific data for variety of transition metal carbide catalysts, explore dependence of their structure on methods of synthesis applied, resulted in performance in different types of catalytic reactions, the effect of alkali promotion. The research involves the preparation, catalytic testing, and characterization of transition metal carbide catalysts, containing molybdenum, cobalt or nickel in different stoichiometric proportions. A series of Co-Mo and Ni-Mo carbides were prepared by different preparation methods. All solids have been characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), cryo-microscopy, high resolution. Characterization of these solids shows that the difference in the preparation methods results in different crystal phases.

The principal goals addressed are:

1. To synthesize TMC catalysts by different methods and find a way to control desirable structure of final product by applying method of synthesis, reaction conditions and a choice of precursors. To synthesize alkali promoted TMC catalysts.
2. To characterize obtained solids and explain their structure.

3. To test TMC catalysts in several type of catalytic reactions and determine the most effective and selective one.
4. To find connection between catalytic performance and structure of TMC.
5. To carryout characterization of fresh versus spent catalyst.

The chapters that follow will discuss the class of TMC, its typical reactions and structure, different methods of synthesis and characterization. They will provide the motive for utilizing the nickel and cobalt promoter and then alkali promoter to our catalytic series. Furthermore, they will describe a detailed schematic of the gas to liquid technology used for testing these catalysts. The final chapters will include experimental methods, characterization, results and discussion of the catalytic material and the conclusion.

Chapter 1: Transition Metal Carbides and Their Properties

The primary purpose of this study is to investigate the use of transition metal carbides as catalysts.

The incorporation of main group element, such as carbon, into the lattices of early transition metals produces compounds with unique physical, chemical, electronic, and catalytic properties. These resulting alloys are referred to as transition metal carbides (TMC). The carbides are well known for their hardness, strength, and high melting points, characteristics of ceramic materials. Interestingly, they also possess electronic and magnetic properties similar to those of metals. They often adopt simple crystal structures, such as face-centered cubic (fcc), body-centered cubic (bcc), or simple hexagonal (hex) structure, with the nonmetal elements occupying the interstitial spaces between metal atoms. For this reason, TMCs are often termed interstitial alloys. Theoretical band calculations indicate that the bonding in carbides involves simultaneous contributions from metallic, covalent, and ionic bonding. Metallic bonding is related to the metal-metal bonds; covalent bonding arises from the interaction of carbon $2s$ and $2p$ orbitals with metal d orbitals; and the ionic contribution is related to the charge transfer between metal and nonmetal atoms. (3)

Molybdenum carbide can occur in many crystalline forms, the most common of which is α -MoC and β -MoC. It is the latter phase which is stable at low temperatures and occurs in steels. β -MoC has a close-packed hexagonal crystal structure with the carbon atoms located in one half of the available octahedral interstices. The lattice parameters are $a=0.3007$ nm and $c=0.4729$ nm. In the MoC system at least six different phases have been identified, see Table 1, this even once called in the literature for "The Molybdenum Carbide Problem".

Table 1: Phases and structure of molybdenum carbides

phase	structure	stacking sequence
-MoC	orthorhombic	ABAB
-MoC	hexagonal	ABAB
-MoC	hexagonal	ABCACB
-MoC	cubic	ABCABC
-MoC	hexagonal	AAAA
-MoC	hexagonal	AABB

The two (possibly three) different MoC phases exhibit an ABAB stacking sequence of the metal planes with carbon in the octahedral sites. The difference between the MoC phases is due to order/disorder transformations of the carbon atoms. The cubic -MoC phase is isostructural with TiC, i.e, a NaCl-type structure, with the well-known ABCABC stacking sequence, while the phase denoted MoC is isostructural with WC and exhibits a simple hexagonal structure with an AAAA packing of the metal atoms. In addition, two more complex phases with hexagonal structures have been identified: the MoC phase with an ABCACB packing sequence and the -MoC phase with an AABB stacking of the metal planes. (7)

The most abundant carbide- Mo_2C presented in fig.5.



Figure 5: Molybdenum Carbide powder