

Chapter 1

Introduction

The primary purpose of this study is to investigate the use of transition metal carbides and nitrides as catalysts. The incorporation of main group elements, such as carbon or nitrogen, 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 and nitrides. The carbides and nitrides 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 [1]. They often adopt simple crystal structures, such as face-centered cubic (fcc), body-centered cubic (bcc), or simple hexagonal (hex) structure, with the non-metal elements occupying the interstitial spaces between metal atoms. For this reason, transition metal carbides and nitrides are often termed interstitial alloys. Theoretical band calculations indicate that the bonding in carbides and nitrides involves simultaneous contributions from metallic, covalent, and ionic bonding [2]. Metallic bonding is related to the metal-metal bonds; covalent bonding arises from the interaction of carbon or nitrogen 2s and 2p orbitals with metal d orbitals; and the ionic contribution is related to the charge transfer between metal and nonmetal atoms [2].

Transition metal carbides and nitrides have attracted considerable attention for catalytic applications since 1973, when Levy and Boudart [3] first reported the Pt-like behavior of WC in the neopentane isomerization reaction. The first synthesis of

transition metal carbides and nitrides was derived from metallurgical processes at high temperatures and resulted generally in powders with low specific surface areas (S_g). Of prime importance for catalytic applications was the development of a temperature-programmed method of synthesis at more moderate conditions [4,5]. The use of this method allowed an optimal balance between sintering and synthesis rates and resulted in products with high S_g .

This class of compounds has shown particularly excellent potential for use in hydroprocessing reactions. Hydroprocessing refers to a variety of catalytic processes that are used to substantially reduce the sulfur, nitrogen, oxygen, and aromatics content of petroleum feedstocks [6,7]. These processes represent one of the most important steps in refining. Recently a great number of studies dealing with the application of transition metal carbides and nitrides in hydrodenitrogenation (HDN) [8-13] and hydrodesulfurization (HDS) [8-10,12,14-16] reactions have been reported. However, most of the work has concentrated on molybdenum nitride [5,9,11,12,14-18] and carbide [5,9,10,12,19] catalysts. In those studies, molybdenum carbide and nitride proved to be superior to commercial hydrotreating catalysts in terms of activity and selectivity. Ramanathan and Oyama [10] completed a comprehensive study over a series of medium surface area carbides and nitrides encompassing groups 4-6. They found that not only were these materials highly active for HDN but they were also sulfur resistant.

Because Brazil has large deposits of niobium (greater than 70% of the world's economically extractable known reserves), and because scarce information is available about niobium-containing carbides and nitrides, we decided to carry out a careful investigation of such compounds containing niobium.

The dissertation is focused on the synthesis and characterization of a series of niobium-containing nitride and carbides, as well as on their applicability in hydroprocessing reactions. Additionally, this work encompasses a study of the HDN mechanism over transition metal carbides, with comparison made to a sulfide catalyst.

The remainder of the dissertation has been organized as follows:

Chapter 2 presents a detailed analysis of the synthesis process of niobium oxynitride. A description of its characterization and its activity for HDN and HDS reactions is also included.

Chapter 3 presents an investigation of a new bimetallic Nb-Mo oxycarbide supported system. The influence of the Mo/Nb ratio on the activity for HDN/HDS reactions is analyzed and the supported catalysts were carefully characterized with the use of the near-edge X-ray absorption fine structure (NEXAFS).

Chapter 4 presents the study of the HDN reaction mechanism over bulk unsupported Mo_2C , NbC, NbMo_2C , and a sulfide catalyst, $\text{MoS}_2/\text{SiO}_2$. The acid properties of the catalytic surfaces were characterized by temperature programmed desorption of ethylamine and infrared spectroscopy was used to investigate the nature of the acid sites.

Chapter 5 presents the study of the pyridine HDN network over the same catalysts of Chapter 4. A relation between the rate constants of the first two slow steps of the

reaction network was obtained for each catalyst. Comparison of the catalytic action of the carbides and a sulfide reference was examined.

Chapter 6 presents the general conclusions.

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