462f High Surface Area Nitrides: New Base Catalysts

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Introduction

Early transition metal nitrides have received considerable attention for use as replacements for Pt-group metal catalysts. The nitrides are interstitial compounds. Charge transfer between the transition metal and nitrogen atoms as a consequence of the significant difference in electronegativity has been reported [1]. This charge transfer is expected to facilitate the creation of acid and base sites. Acid sites for high surface area Mo_2N catalysts have been reported [2]. The purpose of work described in this paper was to continue our investigation of the base properties of high surface area Mo_2N using CO_2 and NH_3 temperature programmed desorption (TPD) and the thermal decomposition of vapor phase 2-methyl-3-butyn-2-ol (MBOH). MBOH decomposes over weak base sites to form acetone and acetylene. Dehydration and isomerization occur over acid sites to form 3-methyl-2-buten-1-al (prenal) and 3-methyl-3-butene-1-yne (MByne), respectively [2, 3]. Although the basic site pathway is of primary interest here, acid products will be considered in order to fully elucidate the effect of pretreatment on the acid-base characteristics of Mo_2N. Because of its pyrophoric nature, the Mo_2N catalyst was passivated following synthesis in a mixture containing 1% O_2 in He to prevent bulk oxidation upon exposure to air. This formed an oxide or oxynitride passivation layer. This layer must be removed prior to activity and desorption studies. This paper describes the influence of the pretreatment conditions on the surface character of Mo_2N. The effects of reduction in H_2, as well as renitridation of the passivated catalyst in 10% NH_3 in He on acetone and MByne formation as well as CO_2 and NH_3 desorption were investigated.

Results and Discussion

Renitriding the Mo_2N surface at the synthesis temperature (700 °C) maximized basic surface density while minimizing surface acidity. This was evidenced by a comparison of acetone and Mbyne formation rates following the various pretreatments. The unpassivated sample possessed rates comparable to the renitrided surface, while the H_2 reduced sample exhibited slightly lower acetone formation rates and higher MByne rates. The degassed sample did not form acetone and displayed Mbyne formation rates comparable to the reduced sample. The renitrided and unpassivated catalysts desorbed the most CO_2 and the least NH_3 during TPD. There was significant CO_2 uptake from the reduced sample while the degassed sample did not desorb any CO_2. The highest amount of NH_3 was desorbed from the reduced and degassed surfaces. The presence of surface oxygen appeared to contribute to the acid-base character of the Mo_2N catalyst and its removal via reduction of the passivation layer enhanced surface basicity. Renitridation at 700 °C resulted in a slightly higher CO_2 uptake and significantly lower NH_3 desorption than those for the unpassivated catalyst, suggesting that the basic character of Mo_2N was enhanced by the addition of nitrogen to the surface and lattice structure. The effect of pretreatment on nitrogen and oxygen content at the Mo_2N surface is currently being investigated using x-ray photoelectron spectroscopy (XPS) and will be discussed along with an investigation of the MBOH reaction mechanism and effect of pretreatment on surface basicity using Diffuse Infrared Reflectance Transmission spectroscopy (DRIFTs). Finally, corresponding data for W_2N and VN will be presented.

References

1. H.O. Pierson, *Handbook of Refractory Carbides and Nitrides*, Noyes Publications, New Jersey, (1996). 2. Keller V., Lauron-Pernot, H., Djega-Mariadassou, G., *J. Mol. Catal. A*, 188 (2002) 163. 3. Handa, H., Fu, Y., Baba, and Ono, Y. *Catal. Lett.*, 59, (1999) 195.