PART 2

OXIDATIVE DEHYDROGENATION OF ETHANE OVER REDUCED HETEROPOLYANION CATALYSTS

CHAPTER 5

INTRODUCTION

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5.1 Introduction

Acetic acid is one of the world's most important chemical products. It is primarily used for the production of acetate esters that are further processed to films, textiles, paints, dyes, artificial fibers, and glues. In 1997, worldwide production of acetic acid was 5.4 million tons.[1] As evidenced from the recent major expansion of acetic acid production capacity in China, the demand for acetic acid continues to rise. The dominating manufacturing process for acetic acid uses an iodide-promoted rhodium catalyst to very efficiently carbonylate methanol and was pioneered by Monsanto in 1968.[2] However, the process has several disadvantages. Methanol is already partially oxygenated and the process requires very high purity carbon monoxide. The gas phase oxidation of ethylene to acetic acid over a palladium based catalyst has recently been announce by Showa Denko.[1] Ethylene, mostly produced from high temperature dehydrogenation, is relatively expensive. Ethane, on the other hand, is abundantly and economically available from natural gas, where it accounts for between 3 and 20% of the molar content.[3] Thus, the activation of ethane to partially oxygenated products such as ethylene and acetic acid is extremely desirable. Unfortunately, activation of alkane C-H bonds is very problematic[4,5] and often results in deep oxidation products instead of partially oxygenated products.

Thorsteinson and co-workers were able to selectively catalyze the production of ethylene from ethane over a mixed metal oxide of molybdenum, vanadium and niobium at atmospheric pressure and moderate temperatures.[6] It was later discovered that acetic acid could be synthesized in high yield directly from ethane over the same catalyst at 2.1 MPa.[7] Production of acetic acid from ethane at atmospheric pressure has also been demonstrated.[8] When doped with palladium, the production of acetic acid at elevated pressure was greatly increased at the expense of ethylene production; this was explained by the consecutive reaction of ethylene over a palladium-based Wacker-like active center.[9] Other mixed oxide systems such as VO_x,[10] VPO,[10] and Mo-V-Nb-Te-O_x[11,12] have also shown the ability to perform oxidative dehydrogenation of ethane to ethylene and acetic acid. A more complete summary of catalysts capable of ethane oxidation to ethylene and acetic acid can be found elsewhere.[13] No mixed metal oxide catalyst has been able to catalyze the production of acetic acid without the presence of vanadium.

Heteropolyanions provide tunable acid and redox properties and are thus well suited for use in the study of alkane activation.[14-22] Indeed, heteropolyanions have received significant interest for selective alkane activation reactions,[20,21,23-31] including the reaction of ethane to ethylene and acetic acid.[27,28,32-36] Ueda showed that a pyridine exchanged molybdovanadophosphate partially reduced during thermal treatment was active and selective for the oxidation of propane to acrylic and acetic acids.[35] Shortly afterwards, Li and Ueda demonstrated that pyridine exchanged phosphomolybdic acid could selectively oxidize isobutane to methacrylic acid and ethane to acetic acid.[36] Davis, Holles, and Dillon investigated the use of niobium and pyridine exchanged phosphovanadomolybdic and phoshpomolybdic acids for the selective oxidation of propane and butane.[23-25] It was also

demonstrated that the same catalysts were active for the selective oxidation of ethane to ethylene and acetic acid.[23] Here, the reaction of ethane to ethylene and acetic acid over phosphovanadomolybdic and phosphomolybdic acids is studied in detail to determine the identity and function of necessary components for active ethane oxidation.

5.2 References

(1) Sano, K.-I.; Uchida, H.; Wakabayashi, S. *Catalysis Surveys from Japan* 1999, *3*, 55-60.

(2) Centi, G. *Selective oxidation by heterogenous catalysis*; Kluwer Academic/Plenum Publishers: New York, 2001.

(3) Banares, M. A. *Catalysis Today* 1999, *51*, 319.

(4) Labinger, J.; Bercaw, J. *Nature* 2002, *417*, 507-517.

(5) Labinger, J. A. *Journal of Molecular Catalysis A: Chemical* 2004, *220*, 27-35.

(6) Thorsteinson, E. M.; Wilson, T. P.; Young, F. G.; Kasai, P. H. *Journal of Catalysis* 1978, *52*, 116-132.

(7) Ruth, K.; Burch, R.; Kieffer, R. *Journal of Catalysis* 1998, *175*, 27-39.

(8) Merzouki, M.; Taouk, B.; Monceaux, L.; Bordes, E.; Courtine, P. Studies in Surface Science and Catalysis, 1992; p 165-179.

(9) Linke, D.; Wolf, D.; Baerns, M.; Timpe, O.; Schlogl, R.; Zeyβ, S.; Dingerdissen, U. *Journal of Catalysis* 2002, *205*, 16-31.

(10) Tessier, L.; Bordes, E.; Gubelmann-Bonneau, M. *Catalysis Today* 1995, *24*, 335-340.

(11) Botella, P.; Garcia-Gonzalez, E.; Dejoz, A.; Nieto, J. M. L.; Vazquez, M. I.; Gonzalez-Calbet, J. *Journal of Catalysis* 2004, *225*, 428-438.

(12) Nieto, J. M. L.; Botella, P.; Concepcion, P.; Dejoz, A.; Vazquez, M. I. *Catalysis Today* 2004, *91-92*, 214-245.

(13) Ruth, K.; Kieffer, R.; Burch, R. *Journal of Catalysis* 1998, *175*, 16-26.

(14) Yang, S. Y.; Xiao, S. X.; Chen, T. L.; Wang, R. S. *ACTA CHIMICA SINICA* 2000, *58*, 43-49.

(15) Xiao, S. X.; Yang, S. Y.; Chen, T. L.; Wang, R. S. *Huaxue Xuebao* 2001, *59*, 1165-1170.

(16) Lapham, D.; Moffat, J. B. *Langmuir* 1991, *7*, 2273-2278.

(17) Song, I. K.; Barteau, M. A. *Journal of Molecular Catalysis A: Chemical* 2004, *212*, 229-236.

(18) Ghizdavu, L.; Fodor, A.; Szasz, G. S. *Journal of Thermal Analysis and Calorimetry* 2001, *63*, 907-9012.

(19) Kaba, M. S.; Song, I. K.; Barteau, M. A. *The Journal of Vacuum Science and Technology A, Vacuum, surfaces, and films* 1997, *15*, 1299-1304.

(20) Langpape, M.; Millet, J.-M. M. *Applied Catalysis A: General* 2000, *200*, 89-101.

(21) Dimitratos, N.; Vedrine, J. C. *Applied Catalysis A: General* 2003, *256*, 251-263.

(22) Marchal-Roch, C.; Millet, J.-M. M. *Comptes Rendus de l'Académie des Sciences - Series IIC - Chemistry* 2001, *4*, 321-329.

(23) Holles, J. H.; Dillon, C. J.; Labinger, J. A.; Davis, M. E. *Journal of Catalysis* 2003, *218*, 42-53.

(24) Dillon, C. J.; Holles, J. H.; Davis, R. J.; Labinger, J. A.; Davis, M. E. *Journal of Catalysis* 2003, *218*, 54-66.

(25) Davis, M. E.; Dillon, C. J.; Holles, J. H.; Labinger, J. *Angewandte Chemie International Edition* 2002, *41*, 858-860.

(26) Grate, J. H. *Journal of Molecular Catalysis A: Chemical* 1996, *114*, 93-101.

(27) Min, J.-S.; Mizuno, N. *Catalysis Today* 2001, *66*, 47-52.

(28) Min, J.-S.; Mizuno, N. *Catalysis Today* 2001, *71*, 89-96.

(29) Mizuno, N.; Yahiro, H. *Journal of Physical Chemistry, B* 1998, *102*, 437-443.

(30) Cavani, F.; Mezzogori, R.; Pigamo, A.; Trifiro, F. *Topics in Catalysis* 2003, *23*, 119-124.

(31) Casarini, D.; Centi, G.; Jiru, P.; Lena, V.; Tvaruzkova, Z. *Journal of Catalysis* 1993, *143*, 325-344.

(32) Schindler, G.-P.; Knapp, C.; Ui, T.; Nagai, K. *Topics in Catalysis* 2003, *22*, 117-121.

(33) Albonetti, S.; Cavani, F.; Trifiro, F. *Catalysis Letters* 1995, *30*, 253-262.

(34) Haddad, N.; Rabia, C.; Bettaha, M. M.; Barama, A.; p 1841-1846.

(35) Ueda, W.; Li, W.; Chen, N. F.; Kida, M.; Oshihara, K. *Res. Chem. Intermed.* 2000, *26*, 137-144.

(36) Li, W.; Ueda, W. Studies in Surface Science and Catalytsis, 1997; p 433-442.