390a Fundamental Insights into Sintering of Ag/α-Al2o3 Catalysts

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Ethylene oxide production continues to be one of the most important processes in the basic chemicals industry [1]. This reaction is typically catalyzed by silver particles supported on a-Al2O3. One of the primary issues with respect to commercial practice is the short catalyst lifetimes as these catalysts readily deactivate with time due to a loss of active surface area via silver agglomeration on the support [2]. While various mechanisms have been proposed to describe Ag sintering in these materials, experimental studies suggest that metal particle growth follows Ostwald-Ripening kinetics and behavior rather than coalescence dominated sintering [3]. In this work, we have used first-principle density functional theoretical studies in order to explore the elementary surface diffusion processes necessary to describe Ostwald-Ripening over different alumina surfaces. In particular, we examine the adsorption and diffusion of various different potential mobile species including single Ag atoms, small Ag clusters, AgOH, AgCl, and Ag2O over various surface terminations of α-Al2O3(0001). In order to establish the influence of the working environment we specifically probe the adsorption and diffusion of the mobile Ag species on Al-terminated, O-terminated and various different hydroxylated a-Al2O3 surfaces. Experiments on hydroxylated surfaces indicate that the presence of water serves to lower barriers to diffusion for Ag atoms as compared to the oxygen terminated surface but decreases diffusion as compared to the more stable aluminum terminated surface. We have also examined the influence of adsorbed heteroatoms on the detachment of silver from large particles. It is seen that the presence of Cl lowers the barrier to Ag atom emission.

References 1. Weissermel, K., and Arpe, H.J., in “Industrial Organic Chemistry” 4th ed., p.146. Wiley-VCH Weinheim, Germany, 2003. 2. Macleod, N., Keel, J.M., and Lambert, R.M. Catal. Lett. 86, 51 (2003) 3. Lai, X., and Goodman, D.W. J. Mol. Catal. A. 162, 33 (2000)