Effect of Particle Size and Shape on NH_3 Decomposition on Ru

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Introduction

NH_3 synthesis and decomposition on Ru have been reported to be structure sensitive reactions [1-3]. The active sites for ammonia synthesis have been reported by Jacobsen et al. to be B_5-type step sites [1]. Several groups have hypothesized the optimal Ru particle size for the highest concentration of B_5 sites to be in the range of 1.8-2.5 nm [1-3]. If all types of step sites are considered, Gavnholt and Schiøtz reported the optimal Ru particle size to be around 3 nm [4]. However, to our knowledge, there has not been a study where the Ru particle size has been varied over a large range. In addition, different Ru particle shapes have not been investigated.

In this work, we synthesized Ru/γ-Al_2O_3 catalysts with different average Ru particle size, ranging from 0.8 nm to 7.1 nm. We show that catalyst pretreatment has a strong effect on Ru average particle size as well as particle shape. The average Ru particle size was measured using electron microscopy and the Ru dispersion was measured using CO chemisorption. In order to estimate the Ru particle shape, images of the spent catalysts obtained by high resolution transmission electron microscopy (HRTEM) were combined with the first four shell coordination numbers obtained from Extended X-ray Absorption Fine Structure (EXAFS). We show that for small particles, a unique solution for a single shape can be obtained by combining the results from electron microscopy, CO chemisorption and EXAFS. We show that the TOF of NH_3 decomposition increases by almost 2 orders of magnitude on Ru particle sizes ranging from 0.8-7.1 nm.

Materials and Methods

Ru/γ-Al_2O_3 catalysts were prepared using an incipient wetness technique from a Ru nitrosyl nitrate precursor. The kinetics of NH_3 decomposition on Ru/Al_2O_3 catalyst was measured in a ¼ inch stainless steel reactor. The product gas composition was analyzed by an online HP 6890 gas chromatograph using a TCD detector. The spent catalyst was characterized by electron microscopy (HAADF and HRTEM), XRD, EXAFS and CO chemisorption.

Results and Discussion

Table 1 shows a summary of the TEM, CO chemisorption and the first four shells coordination numbers for three of the studied catalysts. The first catalyst showed very small particle size by TEM (average = 0.8 nm), which was confirmed by the 95% dispersion measured by CO chemisorption and the first shell coordination number of 3.2 from EXAFS. Combining these results, the particle shape is found to be a 1 layer cluster of about 11-13 atoms, see Figure 1. The smallest Ru particles showed a low TOF for NH_3 decomposition, 0.02 s^{-1} at 350 °C. The Ru particle size was varied by increasing the calcination and/or reduction temperature. The effect of particle size on TOF for NH_3 decomposition is shown in Figure 1. The maximum TOF is found for Ru particles of ~7 nm, a size which is much higher than that estimated in the literature [1-4]. The particle shape effect on the optimal Ru particle size for ammonia decomposition will also be discussed and compared to results from microkinetic models.

Table 1. Summary of EXAFS analysis. Dispersion was measured using CO chemisorption

	Ru bulk	Foil	dispersion = 95% TEM average diameter = 0.8 nm	dispersion = 65% TEM average diameter = 2.6 nm	dispersion = 9% TEM average diameter = 7.1 nm
1NN	12	12.4 (0.7)	3.2 (0.7)	5 (0.5)	10 (0.7)
2NN	6	6.1 (2.1)	-	2.5 (1.8)	6.7 (2.5)
3NN	18	11.5 (3.3)	-	5.3 (4.1)	9.2 (3.1)
4NN	12	10.7 (5.5)	-	0.4 (0.9)	8.1 (4.5)

Significance

Structure sensitivity is traditionally defined as the change in TOF of a reaction over metal particles in the range 1-3 nm. This is due to a higher number of defect, corner, step and edge sites as a fraction of the total surface sites. In this work, we show that structure sensitivity extends to a much bigger particle sizes and is predominantly dependent on the type of active site and particle shape.

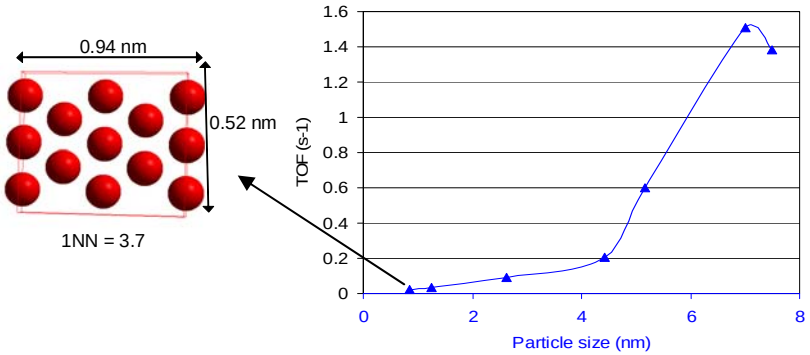

Figure 1. TOF of NH_3 decomposition on Ru/Al_2O_3 as a function of Ru particle size (average from TEM). T = 350 °C, total flow rate = 200 sccm, 10% NH_3 in He, 100 mg 4wt% Ru/Al_2O_3 diluted with 150 mg Al_2O_3.

References

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