



Kinetics and mechanism of hydrothermally prepared copper oxide nanorod catalyzed decomposition of ammonium nitrate



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ABSTRACT

One of the key aspects in the development of materials science is the synthesis of particles with specific size and morphology for catalytic applications. Nowadays, nanostructured materials with specific morphology are gaining great importance in the field of catalysis. Thin, one-dimensional, monodispersed CuO nanorods with a significantly higher aspect ratio of 5, were successfully prepared by the hydrothermal method with subsequent ultrasonication. The formation of pure monoclinic CuO nanorods was confirmed by powder XRD and SAED. The CuO nanorod growth mechanism is investigated by using TEM and further characterized by FTIR, UV–visible spectroscopy and thermogravimetry. The catalytic decomposition of ammonium nitrate, an environmental friendly rocket propellant oxidizer, over the synthesized CuO nanorods was investigated. The thermal kinetic constants for the catalytic and noncatalytic decomposition of ammonium nitrate samples were computed by using model free (differential and non-linear integral) and model fitting approaches. The catalytic influence was evident even with 1% catalyst concentration. The model fitting method suggested contracting cylinder mechanism as the effective mechanism for all the investigated samples. Apparently, the CuO nanorods provide Lewis acid and/or active metal sites, facilitating the removal of ammonium nitrate decomposition inhibition species such as NH₃ and thereby enhance the rate of decomposition.

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1. Introduction

Over the past couple of years, nanoscience and nanotechnology have been attracting worldwide attention and they constitute an active, frontier research area. Synthesis of nanostructured materials with specific size and morphology has recently gained much attention in the material science. Compared with the size control, morphology or shape control is more demanded by the chemical industry. Indeed the application of nanostructured materials is extended to almost all conceivable fields of science, ranging from products of everyday use to rocketry. This demand has stimulated the exploration of new phenomena leading to a technological revolution. A number of recent investigations have shown that, the catalytic activity of nanostructured materials depends on not only their sizes but also their shapes [1–4]. Hence, for catalytic applications the control of shape in addition to size of material is of significant importance [5–7]. An understanding of the mechanism involved in the formation of such nanostructures has been

recognized to be of great potential in the production of engineering materials. Thus, with greater understanding of the formation mechanism, catalyst particles of controlled size and morphology can be produced by such methods of synthesis.

CuO is a *p*-type narrow band gap ($E_g = 1.2$ eV) semiconductor and the band-gap is highly dependent on the morphology and the particle size of the material [8]. CuO, in micro as well as nanoscale, has been widely investigated as heterogeneous catalysts in many important chemical processes [9–13], especially in the selective catalytic reduction (SCR) of ammonia. CuO is also used as pigment, fungicide, metallurgy reagent, gas-sensors, magnetic storage media, electronics, lithium batteries, and solar cells owing to its photoconductive and photochemical properties [14]. Due to the extensive practical applications of this material, the synthesis of nanostructured CuO has attracted considerable attention from material scientists. Due to the outstanding properties of one dimensional (1D) nanostructured materials, nanorods are highly demanded by the chemical industry. Even though various synthesis methods are reported in literature to control the morphologies and microstructures, hydrothermal method is the simple and probably the most feasible method to prepare one-dimensional nanoscale materials [15–18]. As the crystal growth is anisotropic, it is prone to grow slowly toward one-dimensional direction under the hydrothermal conditions, such as high pressure and temperature [19]. In the present work, we report a bottom-up approach to prepare 1D

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