Research Article

Size and Shape Dependent Catalytic Activation Energy of Different Nano Structures

Purvi A. Bhatt[1], Arun Pratap[2] and Prafulla K. Jha[3]

[1,2]Condensed Matter Physics Laboratory, Applied Physics Department, Faculty of Technology & Engineering, The M. S. University of Baroda, Vadodara, India.

[3]Department of Physics, Faculty of Science, The M. S. University of Baroda, Vadodara, India.

Correspondence should be addressed to: Purvi A. Bhatt; purvi.physics.712@gmail.com

Abstract

In the present work, we report the effect of size and dimension on catalytic activation energy (E_C) of some dioxide nano structured materials using a simple analytical model. We report the variation of catalytic activation energy with the size from 1 nm to 30 nm and 0-,1-,2- dimensions of TiO_2, CeO_2 and SnO_2 nanoparticles. The catalytic activation energy decreases as the size of these nanoparticles decreases and is minimum for zero dimensional structure of all considered materials. We show that the nano sized TiO_2 has the minimum value of catalytic activation energy indicates its being better catalyst than other nanostructures. The shape dependence of catalytic activation energy has also been discussed. The particles having tetrahedral shape exhibit minimum catalytic activation energy, thus they show better efficiency as catalysts.

Keywords: Catalysis, Activation energy, nanostructure, TiO_2, CeO_2, SnO_2

Introduction

The size and shape dependent properties of nanomaterials have been extensively studied during the past few years. Once the size of the matter approaches to atomic scale, it exhibits fascinating electrical, optical, magnetic, vibrational, thermo dynamical and catalytic properties than its bulk counterpart resulting from salient features like large surface-to-volume ratio and quantum effect (Alivisatos et al., 1998, Alivisatos, 1996, Gupta et al., 2009, Gupta et al., 2008, Gupta and Jha, 2009, Mankad et al., 2011, Talati and Jha, 2005, Gupta et al., 2010, Jha et al., 2006). Researchers have shown that the size and shape of a particle are key factors to influence the various phenomena including melting, interface energy, surface diffusion, catalysis, etc (Bhatt et al., 2012, Mishra et al., 2012, Gleiter, 2000, Zhang et al., 2000, Jiang and Lu, 2008, Jiang et al., 2004, Zhou et al., 2010, Gupta et al., 2008).

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In recent years, enormous efforts have been devoted to study the size and shape dependence of nanoparticles to understand the catalytic and electro catalytic performances (Narayanan and El-Sayed, 2004, Burda et al., 2005, Li et al., 2000). Nanoparticles of different materials act as efficient catalysts for oxidation of hydrocarbons, C-C coupling, hydrogenation-dehydrogenation, redox and other chemical transformations (Zhou et al., 2010, Burda et al., 2005, Somorjai et al., 2006, Ertl et al., 1997, Bell, 2003, Chen and Goodman, 2006, Crooks et al., 2001, Lewis, 1993, Astruc et al., 2005, Roucoux et al., 2002, Schmid, 2004, Wasylenko and Frei, 2007, Kung et al., 2007). Past studies show that the titanium dioxide (TiO$_2$) is a promising candidate for the decomposition of wide variety of organic and inorganic moieties in both liquid and gas phases (Mankad et al., 2011, Gupta et al., 2010, Jha, 2013, Desai et al., 2011). The nano scale cerium dioxide (CeO$_2$) has also advantages as a support for catalysis since it can enhance the reactivity for the oxidation reaction and CO oxidation when supported to gold nanoparticles (Guo et al., 2010, Carrettin, 2004). Although nanoparticles of tin dioxide (SnO$_2$) are of less interest particularly for catalytic applications, Sharghi et al., (2006) have found that the SnO$_2$ nanoparticles are highly reactive in the Knoevenagel condensation process.

Catalytic activation energy (E$_C$) is one of the important kinetic parameters, which measures the chemical activity of the catalyst to catalyze different reactions (Narayanan and El-Sayed, 2004). In the present paper, we have calculated and compared the catalytic activation energy (E$_C$) of three different nanostructures i.e., titanium dioxide (TiO$_2$), cerium dioxide (CeO$_2$) and tin dioxide (SnO$_2$). The size and shape dependent catalytic activation energy of TiO$_2$, CeO$_2$ and SnO$_2$ nanostructures has been calculated using a simple model based on analytical approach. Further, to analyze the dimension dependency on the catalytic activity of these nanostructures, we have also calculated the activation energy for- 0-,

1- and 2- dimensional TiO$_2$, CeO$_2$ and SnO$_2$ nanostructures that correspond to spherical nanoparticles, nanowires and thin films respectively. We observe that the different shapes have considerable effect on the catalytic activation energy. The paper is divided into four main sections. In section 2, brief description of theoretical model is presented. Section 3 describes the results and discussion followed by a summary of the present work in section 4.

Methodology and Computation

The catalytic activation energy in the present study is determined using a theoretical model based on an analytical approach which includes the shape factor (Lu and Meng, 2010). The size and temperature dependent rate constant of any chemical reaction as per Arrhenius equation is expressed as,

$$K(D,T) = K_0(D)\exp\left(\frac{-E_a}{RT}\right)$$

$$\ldots (1)$$

Where, K is a rate constant of the reaction, K_0 is the pre-exponential factor, E_a is activation energy (here considered as catalytic activation energy), R is a universal gas constant and T is the temperature.

At the melting temperature (T_m), if rate constant (K) is independent of melting temperature and size of the particle, the rate constant will be the same for all the nanoparticles of a given system. Therefore,

$$K[(D,T_m(D)] = K[\infty,T_m(\infty)]$$

$$\ldots (2)$$

Where, $T_m(D)$ and $T_m(\infty)$ are the melting temperatures for size dependent (i.e., nanostructure) and bulk system, respectively.

By rewriting Eqns. 1 and 2, the following expression can be obtained,

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$$K_0(D)\exp\left(\frac{-E_a(D)}{RT_m(D)}\right) = K_0(\infty)\exp\left(\frac{-E_a(\infty)}{RT_m(\infty)}\right)$$

$$\ldots (3)$$

The effect of pre-exponential factor $K_0(D)$ on $K(D,T)$ is negligible in comparison to the $\exp[-E_a(D)/(RT)]$ hence using first order approximation, we can assume $K_0(D)\approx[K_0(\infty)]$. This leads to the expression,

$$\frac{E_a(D)}{E_a(\infty)} = \frac{T_m(D)}{T_m(\infty)}$$

$$\ldots (4)$$

The liquid-drop model and (BOLS) mechanism suggest that both melting temperature T_m and cohesive energy E_C, are related to the bond energy of crystalline atoms hence $T_m(\infty)\alpha E_C(\infty)$ (Nanda et al., 2002, Sun, 2007). If the nature of the chemical bonds remains the same, this relationship can be written for nano scaled region i.e. $\frac{T_m(D)}{T_m(\infty)} \approx \frac{E_C(D)}{E_C(\infty)}$. Lu and Meng, (2010) modified the thermodynamic model proposed by Yang et al., (2008) and include the shape factor (λ) to calculate size and shape dependent catalytic activation energy. From that consideration, one can get E_C as a function of size and shape,

$$\frac{E_C(D,\lambda)}{E_C(\infty)} = \left(1 - \frac{1}{12D/D_0 - 1}\right)\exp\left(-\frac{2\lambda S_b}{3R}\frac{1}{12D/D_0 - 1}\right)$$

$$\ldots (5)$$

Here, $S_b = E_b/T_b$ is the bulk coherent entropy of crystals with T_b being the bulk solid-vapor transition temperature and R is the ideal gas constant. Due to the instability in semiconductor compounds, it is difficult to find the value of S_b value therefore we have used the value of S_b equal to the 13R in our calculations (Yang and Jiang, 2006). The shape factor, λ depends on the ratio of surface atoms to total atoms. For the different shapes, the value of the shape factor (λ) is used from reference (Lu and Meng,

2010). In addition to the shape effect, the dimension dependence of E_C for the different size of TiO_2, CeO_2 and SnO_2 nanoparticles is also reported. In eqn. 5, D denotes the diameter of nanoparticles while D_0 is the diameter at which all atoms are located on surface. D_0 can be expressed as,

$$D_0 = 2 (3-d) h$$

$$\ldots (6)$$

Where h and d denote the value of atomic diameter and different dimensions of nanoparticles, i.e. $d=0$ for spherical nanoparticles, $d=1$ for nanowires and $d=2$ for thin films (Li et al., 2004).

Results and Discussion

Figure 1[a] presents the variation of $E_C(D)/E_C(\infty)$ (ratio of size dependent activation energy to its bulk counterpart) of rutile TiO_2 nanoparticles of different dimensions which shows that the catalytic activation energy decreases as the size of the TiO_2 nanoparticle decreases. The value of activation energy rapidly decreases below 5 nm. It is clear from this figure that after 15 nm, the ratio of catalytic energies becomes almost constant. The figure also depicts that the catalytic activation energy is minimum for spherical nanoparticles while it is maximum for the two dimensional case. This indicates that the spherical nanoparticles can act as better catalysts compared to one and two dimensional nanostructures. The decrease in the catalytic activation energy with the decreasing size reveals efficiency of nanoparticles to catalyze any chemical reaction. Fig. 1[b] and Fig. 1[c] present size and dimension dependence of $E_C(D)/E_C(\infty)$ for another nanoparticles of this group CeO_2 and SnO_2 respectively. Both figures show similar behavior as observed in the case of TiO_2 nanoparticles. However, it saturates after 10 nm in the case of CeO_2 and SnO_2 nanostructures in contrast to TiO_2 nanostructure. Spherical nanoparticles indicate good catalytic performance rather than nanowires and thin films.
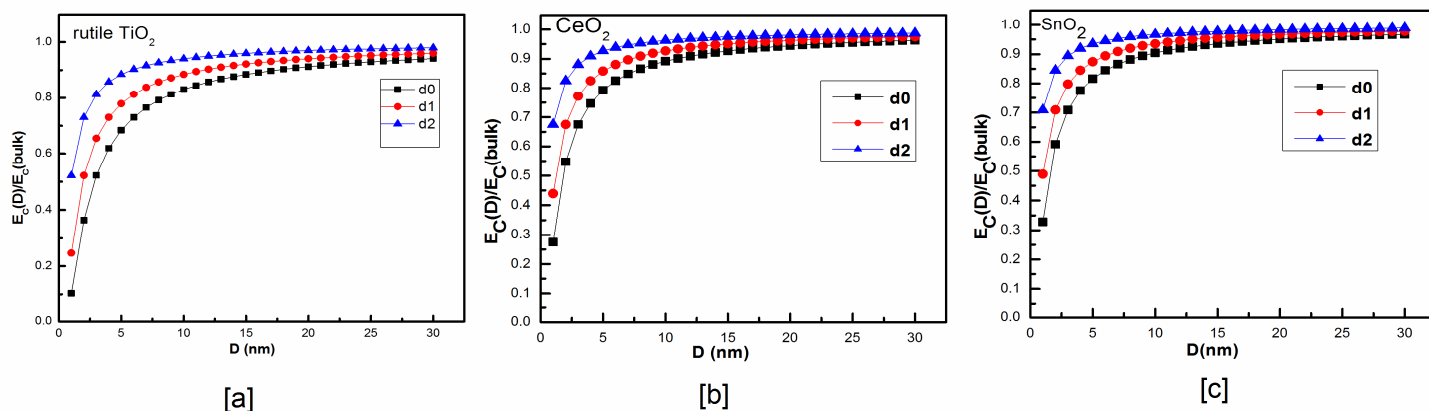
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Figure 1: [a] $E_C(D)/E_C(\infty)$ as a function of size and dimensions for rutile TiO$_2$ using Eq.5. The related parameters in Eq.5 are h = 0.3768 nm (Li et al., 2004), S_b=13R = 108.03 Jmol^{-1}K^{-1} (Yang and Jiang, 2006). **[b]** $E_C(D)/E_C(\infty)$ as a function of size and dimensions for CeO$_2$ using Eq.5. The related parameters in Eq.5 are h = 0.2342 nm (Yang and Li, 2008), S_b=13R = 108.03 Jmol^{-1}K^{-1} (Yang and Jiang, 2006). **[c]** $E_C(D)/E_C(\infty)$ as a function of size and dimensions for SnO$_2$ using Eq.5. The related parameters in Eq.5 are h = 0.2057 nm (Yang and Li, 2008) , S_b=13R = 108.03 Jmol^{-1}K^{-1} (Yang and Jiang, 2006).

Figure 2 shows the variation of $E_C(D)/E_C(\infty)$ with size and different shapes of TiO$_2$ nanoparticles. For a particular size, a tetrahedral shaped particle with (111) facet exhibits maximum value of E_C compared to octahedral and cubic shaped nanoparticles. It can be observed from the figure that the cubic nanoparticles are having the minimum value of E_C for a given size. This nature of catalytic activation energy indicates that the tetrahedral shaped nanoparticles are the most catalytically active. For CeO$_2$ and SnO$_2$ nanoparticles, we obtain similar behavior where tetrahedral shape of the particles show higher value of E_C (not shown here). It can be explained by a fact that the small tetrahedral particles have sharp edges and corners (Narayanan and El-Sayed, 2004). It is found that the atoms located on these sites are chemically very active. In cubic nanoparticles, most of the atoms are located on (100) facets and found to be least active, consequently these particles possess higher value of E_C (Narayanan and El-Sayed, 2004).
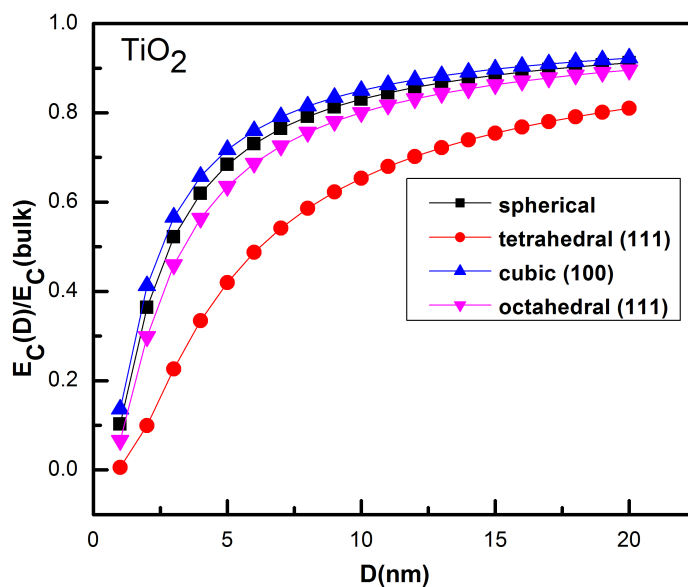
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Figure 2: $E_C(D)/E_C(\infty)$ as a function of size and shapes for rutile TiO_2 using Eq. The related parameters in Eq. are h = 0.3768 nm (Li et al., 2004) , S_b=13R = 108.03 Jmol^{-1}K^{-1} (Yang and Jiang, 2006).

Figure 3 shows comparison of all the three tetrahedral shaped nanostructures (i.e., TiO_2, CeO_2 and SnO_2) in terms of size dependent catalytic activation energy. It is clear from the figure that the TiO_2 nanoparticles have minimum catalytic activation energy which implies that the nano structured TiO_2 can be considered as an efficient candidate for catalytic activities. Although nano sized SnO_2 has advantage for a particular reaction when used as a catalyst, it shows the least chemical activity in present study while CeO_2 has the intermediate value of E_C between TiO_2 and SnO_2. The similar trend of size and shape dependent catalytic activation energy is reported in case of platinum nanoparticles (Lu and Meng, 2010).
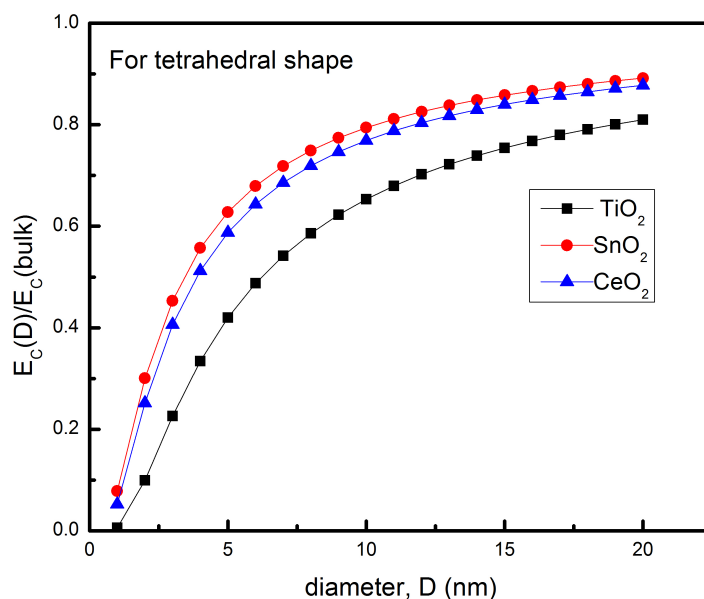
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Figure 3: $E_C(D)/E_C(\infty)$ as a function of size for tetrahedral shaped TiO_2, CeO_2 and SnO_2 nanoparticles.

Conclusion

In summary, we have calculated the shape and size dependent catalytic activation energy of TiO_2, SnO_2 and CeO_2 nanostructures. The catalytic activation energy decreases with the decrease in particles' size. It becomes almost size independent when size of the particle exceeds 10 to 15 nm. We observe that zero dimensional (i.e., spherical) nanoparticles have minimum catalytic activation energy than the two and one dimensional structures. The considerable difference is found for E_C in the case of different shapes of nanoparticles, and tetrahedral shaped particles showed maximum efficiency for catalysis. In the case of TiO_2, CeO_2 and SnO_2, TiO_2 has minimum value of catalytic activation energy hence considered as better catalyst. Our study will find its implications in catalytic activity based applications.

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