Vietnam School of Earth Observation (VSEO) Quy Nhơn

A STUDY OF ZrO_2 - TIO_2 CLUSTERS

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ABSTRACT Pure ZrO_2, TiO_2 and ZrO_2-TiO_2 mixed oxide nanoparticles were synthesized by hydrothermal method. The influence of preparation condition on the morphology, crystal phases and particle size in the sample was investigated in order to obtain high photocatalytic activity of ZrO_2-TiO_2 composite. Both Raman and XRD results indicated that a light structure disorder in the ZrO_2-TiO_2 mixed oxide samples related to an incorporation effect of ZrO_2 and TiO_2 nanocrystals. FTIR analysis confirms existence of the surface OH-groups on the sample, indicating the capability of the ZrO_2-TiO_2 catalyst. The photocatalytic activity of samples was evaluated by the degradation of methylene blue under UV-Vis irradiation. The results show that the mixed oxide ZrO_2-TiO_2 nanoparticles exhibited photocatalytic activity better than that of the pure oxides. In order to explain the properties of the mixed system, the structures of $(ZrO_2)_n$ (n=1-11) clusters and the ZrO_2-TiO_2 mixed oxide are built and analyzed using the framework of the Density Functional Theory (DFT). We calculate the formation energy, electronic structures and stabilities for varying configuration of $(ZrO_2)_n$ (n=1-11) clusters, and also $(ZrO_2)_n/TiO_2$ anatase (001) surface. The calculation results show that the surface characteristics of the mixed oxides may change due to the formation of new sites in the interface between the components. Compared with experimental results, a theoretical analysis by computer simulation is expected to clarify the enhanced photocatalytic activity of ZrO_2-TiO_2 mixed oxide in detail.

INTRODUCTION

ZrO_2 doped TiO_2 showed enhanced photocatalytic activity, many properties of this nanostructured mixed metal oxides were reported to be better than that of TiO_2.
In this work, ZrO_2; TiO_2 and ZrO_2-TiO_2 nanopowders were synthesized by hydrothermal method. We investigated the influence of the preparation condition on the morphology, crystal phases and particle size in the sample in order to obtain high visible photoactivity of nanocrystals.
We calculated the formation energy, electronic structures and stabilities for varying configuration of $(ZrO_2)_n$ (n=1-11) clusters, and also $(ZrO_2)_n/TiO_2$ anatase (001) surface.

SIMULATION METHOD

The structures and stabilities of $(ZrO_2)_n$ (n=1-:- 12) clusters are calculated using DFT. Geometry optimizations with full relaxation of all coordinates are done for these clusters in attempt to find the global minimum on the cluster potential hypersurface of each cluster size. Calculations of total energy and electronic structure were carried out using the CASTEP package within the framework of DFT. The Perdew-Burke-Ernzerhof (PBE) parameterization of the generalized gradient approximation (GGA) [1,2] was adopted for the exchange-correlation potential. Optimization, total density of state (DOS) and projected DOS (PDOS), adsorption energy, charge transfer, Raman modes calculations was performed.

RESULTS AND DISCUSSION

1. Experimental

ZrO_2, TiO_2 and ZrO_2-TiO_2 nanopowders were synthesized by hydrothermal method. Firstly $ZrOCl_2$ was added drop by drop to CA and NH_4NO_3 solvent, which was continuously stirred for 20 minutes Then the mixture was transferred into an autoclave and kept at 190^{o}C for 24h. After centrifugation, and washing, the samples were dried in the air at 50^{o}C.

1.1. Structural Characterization

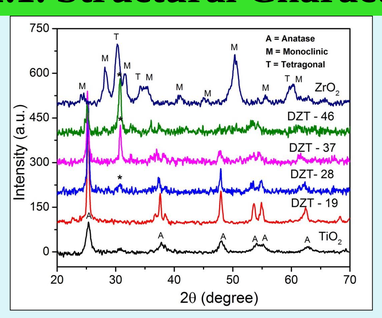


Fig1. XRD patterns of ZrO_2 – TiO_2 samples, pure TiO_2 and pure ZrO_2

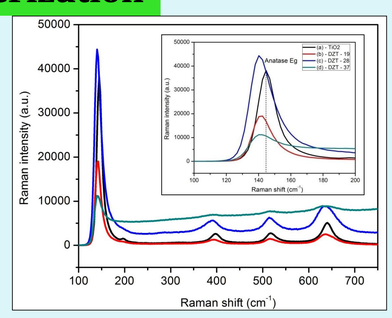
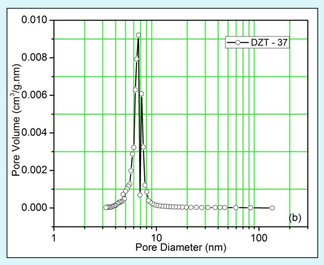


Fig2. Raman spectra of ZrO_2 – TiO_2 samples and pure TiO_2

TiO2 is anatase , for ZrO2 monoclinic being predominant phase.
For the mixed TiO2/ZrO2: new XRD peak (*) at 30,760^0 is peak (131) of orthorhombic $Zr_5Ti_7O_{24}$ (PDF card No.34 - 0209).
The anatase phase of TiO2 shows 6 active Raman modes.
Anatase TiO2 Eg (144cm-1) shifts towards lower wavenumbers with the ZrO2 content, that indicates the incorporation ZrO2-TiO2.



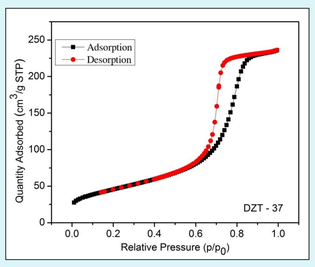


Fig3. Pore-size distribution and N2 adsorption–desorption isotherms of ZrO_2 – TiO_2

BET Surface Area: 163.40 (m^2/g); pore size 8.9 nm

1.2. Photocatalytic activity

The photocatalytic activity was evaluated by measuring the decomposition of MB under visible-light irradiation. Photocatalytic efficiency was evaluated by intensity peak at 665 nm in absor. spectra of MB solution

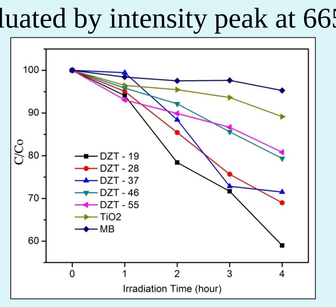


Fig4. Photodegradation of MB under visible light (λ = 665 nm)

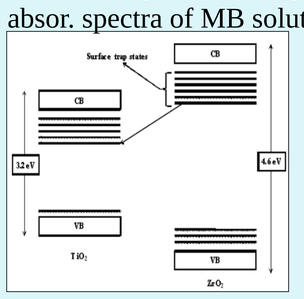


Fig5. Schematic Energy level diagram

2. Simulation method

2.1. ZrO_2 clusters

We built the $(ZrO_2)_n$ clusters (n=1-11). Among the different configurations of $(TiO_2)_n$ clusters we find that the most stable configurations (have a least total energy)

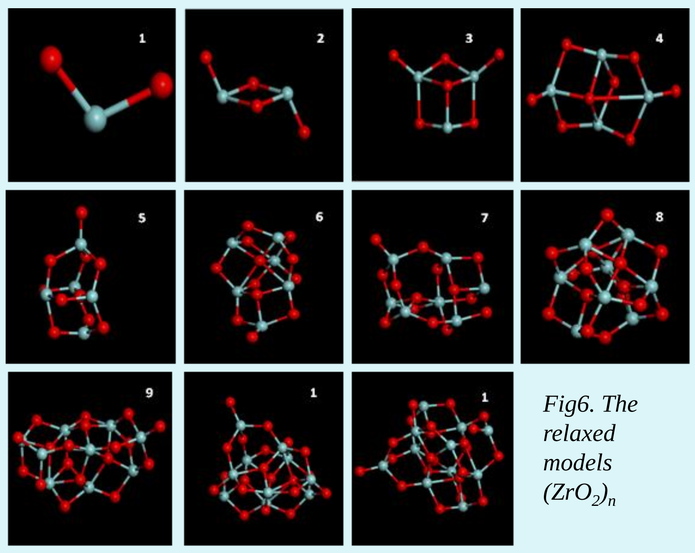


Fig6. The relaxed models $(ZrO_2)_n$

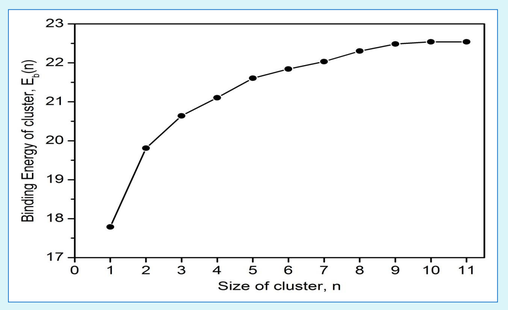
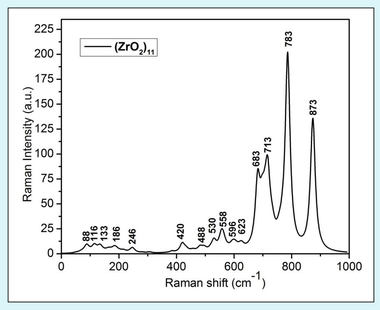


Fig7. The binding energy per ZrO2 unit of the models $(ZrO_2)_n$

Energies of stabilization of the particles per ZrO2 unit show that the stability does not decrease monotonically with increasing size, from n=5 the energies change very slow.
Raman calculations show 4 strong and sharp peaks in the range of 600-900 cm-1 (related O-O bonds)



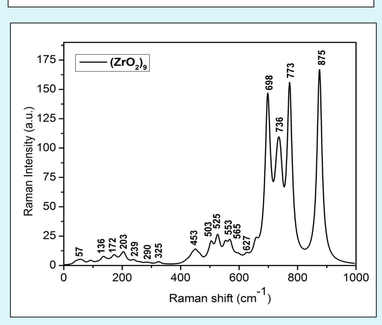
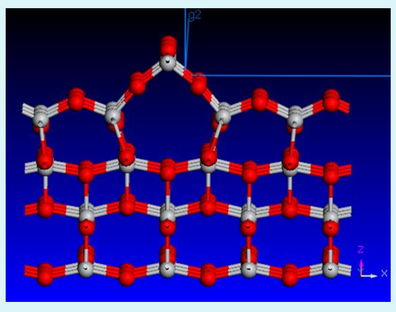


Fig 8. Raman activity modes of $(TiO_2)_n$ clusters n=9 and 11

2.2. TiO_2 anatase (001) –(1x4) surface

The anatase (001) - the chemically more reactive surface. We build the (1x4) reconstruction of the anatase (001) surface (ADM) : periodically adding rows of TiO2 molecules to the flat unreconstructed surface.[3] STM/AFM measurement is consistent with ADM models [4].



Based on results of the possible adsorption positions we have constructed the $(ZrO_2)_5$ /TiO_2 -001 models.
As for surface models, a vacuum region of 15A˚ is embedded along surface normal to minimize interactions between surfaces of adjacent slabs.
Based on result of the finding the local minimum (LM) of the total energy, we found the most possible adsorption position.

2.2. $(ZrO_2)_n/TiO_2$ anatase (001) ADM

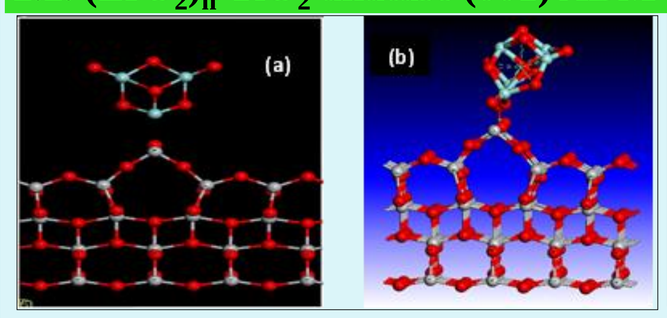
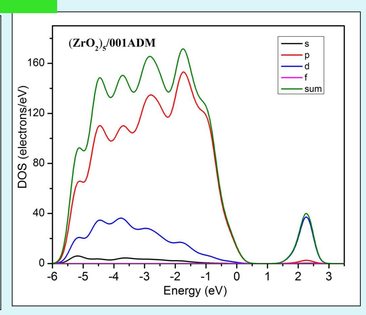


Fig. The relaxed models $(ZrO_2)_3$ and $(ZrO_2)_5$ adsorption anatase TiO2 (001) ADM surfaces



DOS and PDOS of $(ZrO_2)_n/TiO_2$

The $(ZrO_2)_5$ clusters /TiO2 001 ADM surface have chemical adsorption characters. The system has small band gap (~1eV).

An adsorption energy (ΔE_{ads}): $\Delta E_{ads} = E_{ads.sys} - (E_{001} + E_{cluster})$

Models	E_{surf} (eV)	E_b (eV)
$(ZrO_2)_3$/001ADM	-5.008	5.008
$(ZrO_2)_5$/001ADM	-8.451	8.451

A negative Δ_{Eads} indicates that the molecule adsorption is exothermic and thus the adsorption system is energetically stable [5].
The values of ΔE_{ads} show that the $(ZrO_2)_n$ clusters /TiO2 001 ADM surface have chemical adsorption characters, there are some strong bonds between them.
This result is consistent with the Raman measurements.

CONCLUSIONS

ZrO_2 ,TiO_2 and mixed oxides photocatalysts were prepared using a chemical method. The composite material can absorb at higher wavelength and the absorption even covers the whole range of visible region. The photocatalytic degradation of MB was observed over TiO2/ZrO2 composite catalysts, which exhibit higher photocatalytic activity in comparison with neat TiO2.
DFT calculations were successful performed to investigate the (ZrO2)n (n=1..11) clusters , $(ZrO_2)_n/TiO_2$ hybrid system. Adsorption energy calculation suggest that the (ZrO2)n clusters are flexible and coalescence into lager clusters on the anatase (001) surface .

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