

Synthesis, Characterization and Phase Transition of Highly Porous γ - Alumina Nanoparticles

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ABSTRACT

Alumina is an important metal oxide used in a wide range of applications. It is a challenge to synthesize stable γ -alumina nanoparticles because; γ -phase of alumina is not as stable as α phase of alumina. But γ -alumina owns a higher surface area making it a good candidate for many industrial applications such as catalyst, catalytic support for petroleum refining, absorbent, alcohol dehydration, catalytic reduction of automotive pollutants like NO_x, CO and hydrocarbons. This research focuses on synthesis, characterization and study of phase identification of pure γ -alumina nanoparticles.

Modified “Pechini method” (Danks, Hall, and Schnepf (2016); Huizar-Félix, Hernández, de la Parra, Ibarra, & Kharisov, 2012; Naskar, 2010; Zaki, Kabel, & Hassan, 2012) was used for the synthesis. Transesterification of citrate and ethylene glycol makes a covalent polymer network with trapped Al atoms. Continuous stirring of the reaction mixture while maintaining an optimum temperature is an important factor affecting this reaction. Calcination was carried out at different temperatures to identify phase transitions of alumina nanoparticles. In order to further reduce the particle size and increase the surface area, reactant ratio of citric acid: aluminum acetate was modified to 1:1, volume of ethylene glycol was increased up to 90% of volume of the solution and Triton X was used as a surfactant.

PXRD confirmed the pure γ -alumina phase (JCPDS No. 00-010-0425) in samples calcined at 900 °C. At 1000 °C γ -alumina is converted to α -alumina (JCPDS No. 00-083-2080). After the modifications, γ -alumina was identified at 700 °C. FTIR-ATR analysis shows peaks around 1127 cm⁻¹ indicating the presence of Al-O-Al asymmetric bending modes and the peaks around 500 cm⁻¹-750 cm⁻¹ correspond to γ -AlO₆ octahedral sites and 800 cm⁻¹ correspond to AlO₄ tetrahedral sites in γ alumina spinel structure. Resulted product of low temperature, pure γ -alumina nanoparticles will facilitate the industrial development in various applications.

Keywords-- γ -Alumina, Alumina Nanoparticles, Phase Transitions of Alumina

I. INTRODUCTION

Alumina is one of the major ceramic oxides that are being used for applications in many fields. It is used as catalysts, catalytic supports, refractory materials, high strength materials, adsorbents, reinforcements of metal-

matrix composites and fire retardants (Naskar, 2010). It is also used as electronic insulators because of low electrical conductivity due to wide band gap. Alumina is a material with a high boiling point, and it can be used for bone and dental implants because of its biocompatibility and inertness. Historical background of Rome reveals that alumina was used as an anti-inflammatory substance and as a medicine to stop the blood flow.

There are different metastable crystalline phases in alumina. Among them α , β , γ , θ , and κ are common. The applications of alumina are mainly based on different properties of the corresponding crystalline phase. The most thermodynamically stable crystalline polymorph is α -Al₂O₃ which shows large surface area due to its porous nature at standard temperature and pressure. Maintaining the stability of γ alumina is a challenge, since γ phase is not as stable as α phase. Both α and κ phases are often used in wear resistant coatings because of their hardness and thermal stability. γ and θ phases are used as catalysts due to the high surface area and lower surface energy.

This research mainly focuses on the synthesis of pure γ alumina nanoparticles. There are many industrial applications of γ alumina nanoparticles as it has a very high surface area and a lower surface energy compared to other phases. During the synthesis of nanocrystalline polymorphs, γ alumina could maintain a surface area of ~150 m²g⁻¹ at 1073 K while nanocrystalline α alumina maintains ~50 m²g⁻¹ at such a temperature. (McHale, 1997), (Navrotsky, 2003). Because of its high porosity caused due to the cubic defect spinel structure, γ -alumina is used as a catalyst, catalytic support for petroleum refining, absorbent, alcohol dehydration, catalytic reduction of automotive pollutants like NO_x, CO and hydrocarbons etc. (Naskar, 2010), (Trueba & Trasatti, 2005).

Structure of γ alumina is not exactly defined. It is considered as a defect cubic spinel having space group Fd-3m. Proposed structure is assumed to be having a face centered cubic (FCC) oxygen lattice and a mixture of octahedral and tetrahedral coordinated aluminum ions. The FCC oxygen lattice is based on the ABCABC stacking. Aluminium ions are distributed between octahedral and tetrahedral sites (Naskar, 2010)

In order to maintain the stoichiometry, the unit cells consist of 32 oxygen and 64/3 aluminum ions. The defective nature of gamma alumina spinel structure is due

to the presence of trivalent aluminium cations. In order to satisfy the stoichiometry, some lattice positions remain vacant even though their precise location is a matter of dispute (Trueba & Trasatti, 2005) $MgAl_2O_4$ is an ideal spinel structure. In gamma alumina structure; Mg atoms are replaced by Al atoms to form the defected spinel structure (Trueba & Trasatti, 2005). Gamma alumina can also be derived from boehmite $[AlO(OH)]$ - or gibbsite $[Al(OH)_3]$ where there are both cubic lattice and tetragonal distortions. According to different studies, there can be vacancies in tetrahedral and octahedral sites. However, the exact positions of these vacancies are not yet revealed (Trueba & Trasatti, 2005). The most accepted model that describes the surface structure of γ alumina is developed by Knözinger and Ratnasamy (Trueba & Trasatti, 2005). According to that, there are different groups of OH on the surface having a distinct "net electric charge" (σ). This depends on the number of Al neighbors and the coordination of Al atoms. However, there are limitations of this model because it does not account for the surface hydroxylation/ dehydroxylation process that is induced by temperature effects (Trueba & Trasatti, 2005) At high temperatures, there is a possibility of removing surface OH groups which leads to the formation of a coordinative unsaturated surface. It has been found that there is pentahedral coordinated aluminum (AIV) concentrated on the surface of gamma alumina. According to reports, the content of AIV affects the crystallinity, pore-size distribution, and surface area. When the AIV content is high, the surface area is high and the crystallinity is low (Trueba & Trasatti, 2005). It is unlikely to occur the three coordinated Al on the surface of gamma alumina, but they can be expected in the bulk structure.

The AIV ions are mainly located in crystallographically defective configurations, which can act as strong acid sites. In addition, they show catalytic activity in dehydrated alumina as well. The partly uncoordinated metal cations and oxide anions that are on the surface can act as acids and bases. Nevertheless, the precise locations of these sites are still unknown.

II. MATERIALS AND METHODS

Aluminium acetate, Citric acid, and Ethylene glycol were used without further chemical purification and modifications. Water was used as the solvent and Triton-X was the surfactant for the synthesis of gamma alumina Nano particles.

Synthesis A

"Pechini method" which is a modified sol-gel technique was applied for the synthesis of alumina nanoparticles (NP). Transesterification between citrate and ethylene glycol was done to obtain a covalent polymer network with trapped Al atoms. Ethylene glycol was used as the surfactant which prevents the aggregation of NP. Maintaining the reaction temperature at 50 °C is a crucial point to obtain the particle size in nm range. This

reaction was carried out with continuous stirring after the addition of aluminum acetate, citric acid, deionized water and ethylene glycol. Then the temperature was increased until a gel is formed. Finally, calcination was done at different temperatures (500 °C, 600 °C, 700 °C, 800 °C, 850 °C, 900 °C, 950 °C, and 1000 °C) to observe phase transitions that occur at corresponding calcined temperatures.

Synthesis B

Further improvements were done to the synthesis A to get synthesis B. Reactant ratio of citric acid: aluminum acetate was changed to 1:1. Triton X was added as a surfactant and volume of ethylene glycol was increased up to 90% of volume of the solution, without changing the ratio of Aluminium acetate and citric acid. This method was not extended up to the formation of the gel. Thus, it was stopped at sol form and centrifugation was done to collect the precipitate followed by calcination at different temperatures.

III. CHARACTERIZATION

Samples calcined at different temperatures were analyzed by Powder X-ray diffractometer (Siemens D5000) of Cu K α radiation of wavelength $\lambda=1.54062$ nm. Characterization was done in 2θ values ranging from 5° to 75°. FTIR-ATR characterization was carried out to confirm the presence of octahedral and tetrahedral sites of the spinel structure of gamma alumina. Analysis was done within the wave number ranging from 0-4500 cm^{-1} .

Particle size was analyzed by the particle size analyzer and further confirmation was obtained using scanning electron microscopy (SEM) (Hitachi SU6600). Sputtering technique was used to prepare the samples by coating, gold/ palladium alloy.

IV. RESULTS AND DISCUSSION

Powder X-ray diffraction

Powder X-ray diffraction was carried out to confirm the phase transition and crystallinity of alumina Nano particles. Figure 1 and 2, clearly illustrate how changing of calcine temperature affects the phase transition of alumina Nano particles. According to JCPDS reference no. 00-010-0425 in the International Centre for Diffraction Data (ICDD) database; peaks corresponding to pure form of γ -alumina were clearly observed at 900 °C and 700 °C calcined temperatures in synthesis A and B respectively. When temperature is increased up to 1000 °C, γ -alumina is converted into the pure form of α -alumina (JCPDS No. 00-083-2080). This phase transition can be clearly identified in Figure 2; because of the mixture of peaks corresponding to both α and γ phases at 900 °C, where transition happens between 700 °C to 1000 °C. According to both figures it is observed that α -alumina is more crystalline compared to γ -alumina due to the presence of more precise and sharp peaks at 1000 °C

while an amorphous nature is observed in γ -alumina. Figure 3 is an illustration of pure form of γ -alumina from both synthesis A and B. Prominent peaks of γ -alumina corresponding to reflections of (311), (400), (440) planes were used to identify the γ phase properly. When the

reactant ratio of Citric acid: Aluminium acetate was changed to 1:1 in synthesis B, formation temperature of γ phase was lowered up to 700°C which is an industrially profitable aspect.

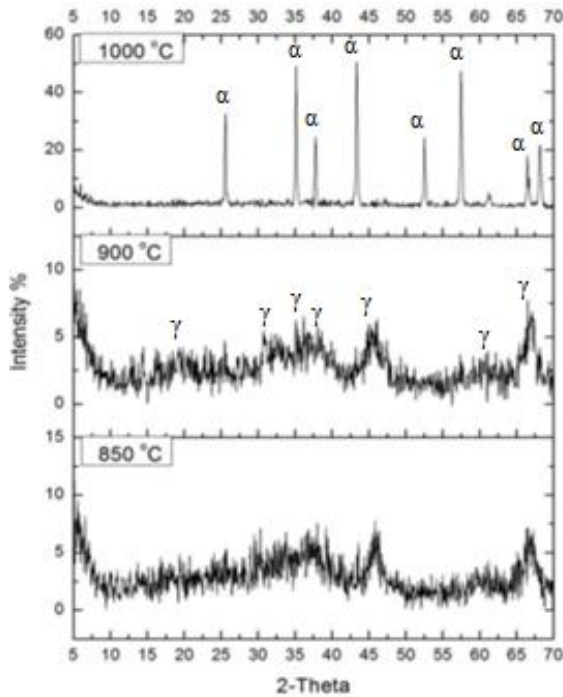


Figure 1: PXR D patterns for phase transitions of alumina obtained for the synthesis A

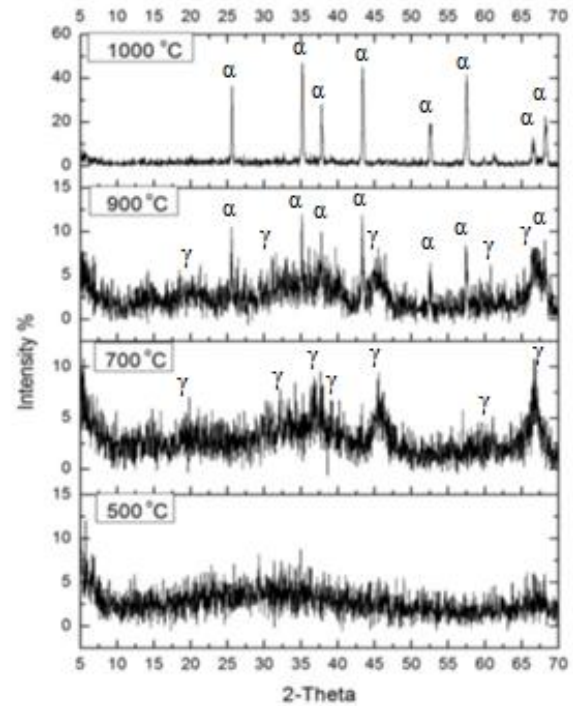


Figure 2: PXR D patterns for phase transitions of alumina obtained for the synthesis B

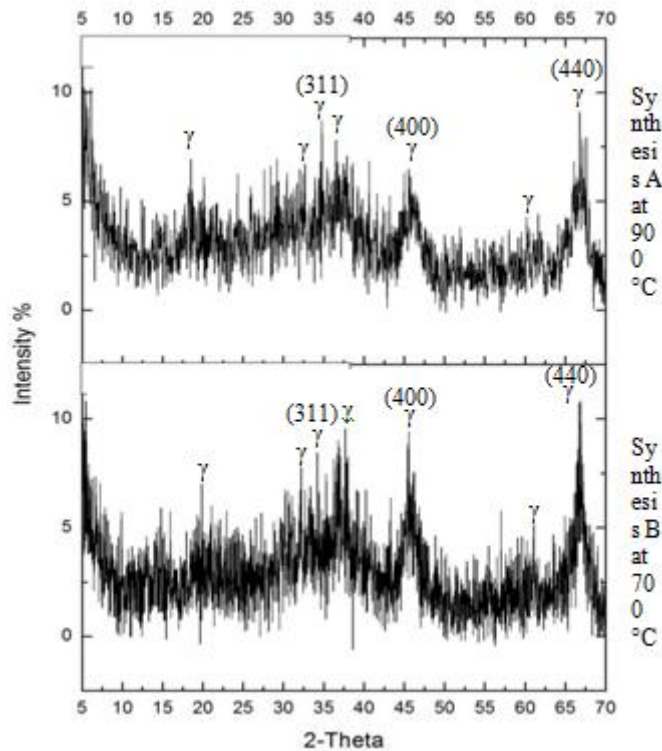


Figure 3: Comparison of the PXR D patterns of gamma alumina obtained from the Synthesis A and Synthesis B

FTIR-ATR

The spinel structure of γ -alumina could be confirmed by FTIR-ATR analysis method. Bonds in the 500 cm^{-1} - 700 cm^{-1} range show that there are octahedral sites and the bonds in the 800 cm^{-1} - 1000 cm^{-1} region shows that there are tetrahedral sites. Stretching and

bending modes of absorbed water are represented by the broadband around the wave number 3470 cm^{-1} . The spinel structure can be clearly identified in γ -alumina (Figure 4). Nevertheless, there are no bonds around 500 cm^{-1} to 1000 cm^{-1} region of the spectrum of α -alumina (Figure 5).

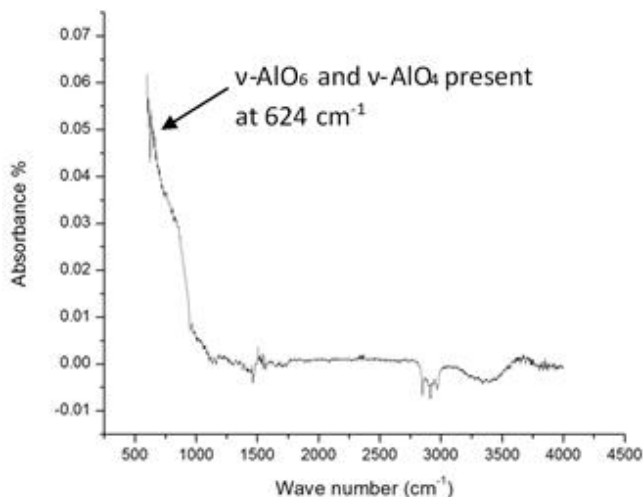


Figure 4: FTIR-ATR spectrum of γ -alumina

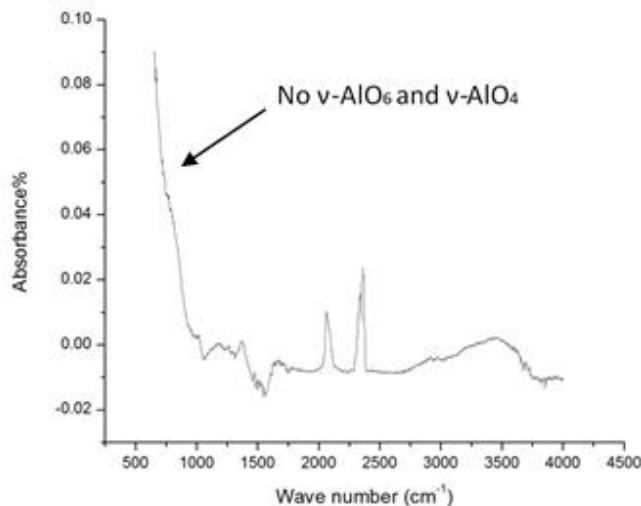


Figure 5: FTIR-ATR spectrum of α -alumina

Particle size analysis

Sizes of the gamma alumina particles were measured by the particle size analyzer using ethylene glycol as the solvent. The value was not in the nanometer range. It was more than 1000 nm. According to Suhaib Umer Ilyas et al., that was mainly due to aggregation of

the Nano particles. When the particle size decreases, the energy of them increases due to increase of entropy. To reduce the energy, particles get aggregated. Aggregation of alumina Nano particles is a very rapid process

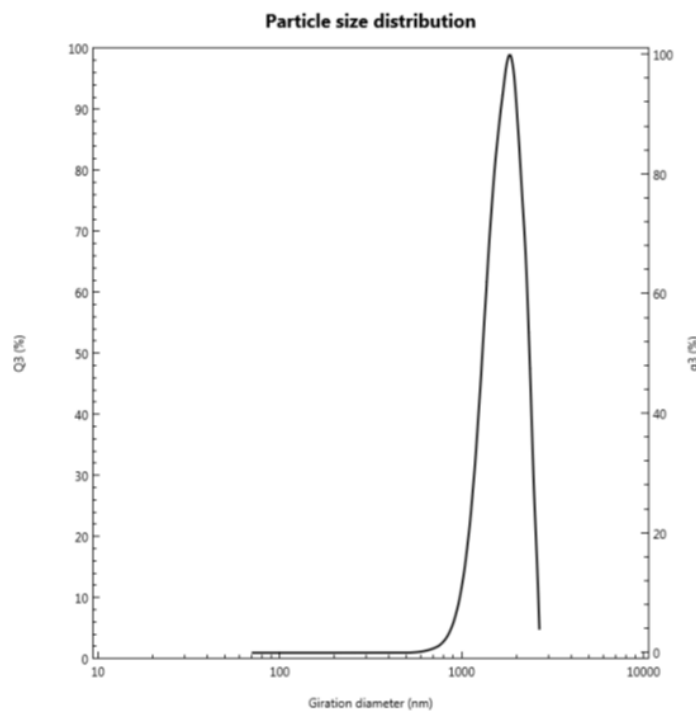


Figure 6: Particle size distribution of γ -alumina

SEM

Particles obtained from the synthesis B were within the nanometer range even though there are

aggregated particles. They were comparatively amorphous, and a porous nature could be observed from the SEM images of Figure 9 & 10.

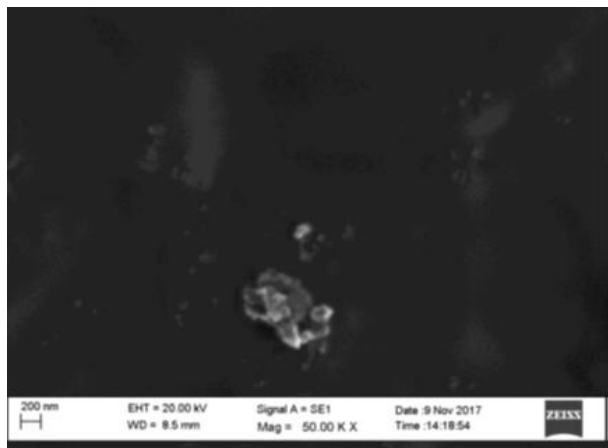


Figure 7: SEM of the γ -aluminan nanoparticles obtained from synthesis A after calcined at 900°C

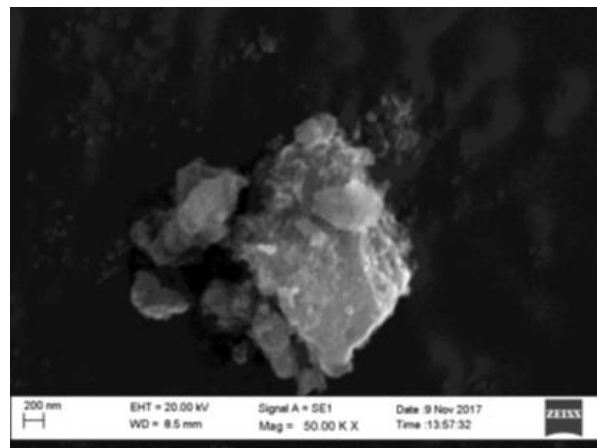


Figure 8: SEM of the γ -aluminan nanoparticles obtained from synthesis A after calcined at 700°C

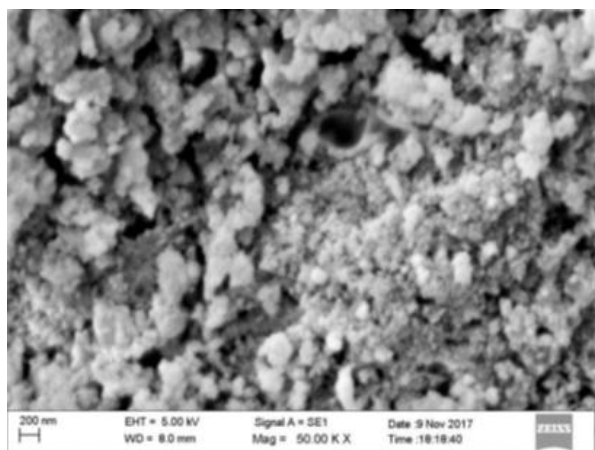


Figure 9: SEM of γ -aluminan nanoparticles obtained from synthesis B after calcined at 700 °C

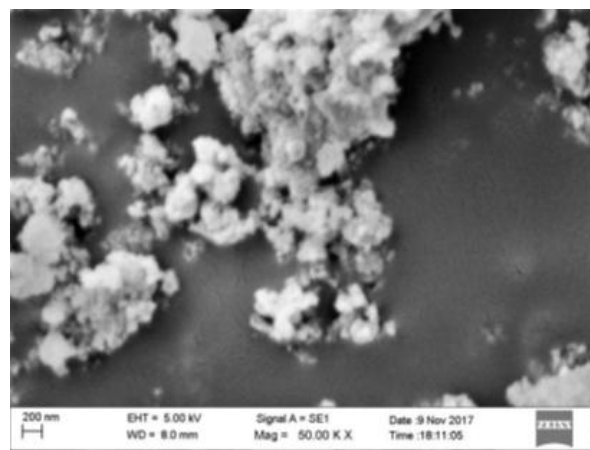


Figure 10: SEM image of γ -alumina nanoparticles obtained from synthesis B after calcined at 700 °C

V. CONCLUSIONS AND RECOMMENDATIONS

This research is successful in synthesis of γ -alumina nanoparticles at a comparatively lower temperature using sol-gel based “*Pechini method*”. Further reduction of particle size and introduction of a higher porosity were achieved by introducing modifications to the reactant ratio, volume of the solution and introducing a surfactant. Modifications were done by changing the reactant ratio of citric acid: aluminum acetate to 1:1, increasing the volume of ethylene glycol to 90% of volume of the solution and introducing Triton X as the surfactant.

γ and α phases were investigated using PXRD

and FTIR-ATR studies. According to PXRD analysis, in reference to JCPDS reference no. 00-010-0425, peaks corresponding to pure γ -alumina were identified in samples calcined at 900°C in synthesis A and at 700 °C in synthesis B. At 1000°C γ -alumina is completely converted to pure α -alumina.

According to FTIR-ATR analysis, peaks around 1127 cm^{-1} in the samples calcined at 900°C indicate the presence of Al-O-Al asymmetric bending modes. In addition, the peaks around 500 cm^{-1} -750 cm^{-1} correspond to γ - AlO_6 octahedral sites and 800 cm^{-1} correspond to AlO_4 tetrahedral sites in γ -alumina spinel structure.

Synthesis of γ alumina at a relatively lower temperature is an advantage achieved by this research. This can minimize the problem of high-energy consumption during industrial processes. Therefore, it is

industrially profitable aspect.

VI. REFERENCES

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