An XRD and Fourier-transformed infrared spectroscopy investigation of single and mixed γ-alumina and thorium oxide

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Abstract

Mixed γ-alumina and thorium oxide samples were prepared with various compositions (100, 95, 90, 80, 50, 25, 15, 5 and 0 wt%, respectively) by addition of a solution of thorium nitrate to a slurry solution of aluminum isopropoxide [Al(OC$_3$H$_7$)$_3$] in deionized water. Mixed oxides (slurry solution) were heated at 120 °C (oil bath) for 24 h with mixing (for uniform distribution of oxides and to remove excess water) followed by calcinations at 600 °C for 6 h. New Fourier-transformed infrared spectroscopy (FTIR) absorption bands and the absence of crystallinity demonstrated by XRD analysis clearly show that γ-alumina and thorium oxide are mixed chemically and on atomic scale during the calcination period. The mechanically mixed oxide retained crystallinity and do not show mixing on the atomic scale. The evaluation for the catalytic activity of single or the chemically mixed catalysts for the dehydration of 2-hexanol and 1,2-diphenyl-2-propanol was investigated. The infrared spectrum of γ-alumina calculated by AM1 method show absorption pattern similar to FTIR.
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Keywords: γ-Al$_2$O$_3$/ThO$_2$; XRD; FTIR; Computational analysis; Dehydration of alcohol; Mixed oxide catalysts

1. Introduction

Metal oxides are excellent and widely used catalysts in a variety of industrially important applications. In recent years, there has been extensive investigation of the surface, active sites and pore structure of γ-alumina and morphology of thorium oxide [1–16].

The surface and interior structure of metal oxides are complex and remains to be defined. Understanding the structure of aluminum and thorim oxides and the way atoms arrange in space in these oxides is the cornerstone of investigations for the past century. The nature of active sites has gained most of the attention due to their important roles in chemical reactions. Several interpretations of the nature of active sites on the surface of γ-alumina are available [17]. The widely accepted model, proposed by Peri, assumes a random configuration of hydroxyl groups after dehydration leaving adjoining residual oxide ions, oxide vacancies and exposed aluminum ions [18]. The variation in the number of oxide ions surrounding the hydroxyl groups differentiate them into several types and imparts varying Brønsted-type acidity to each of the three groups (hydroxyl bands at 3680, 3720 and 3785 cm^{-1}). Cornelius et al. proposed the high energy sites on alumina are strained Al–O–Al linkages formed at high temperature by condensation of residual hydroxyl groups which are increasingly separated as the result of progressive dehydration [19]. The general older view of the structure of γ-alumina suggests that the unit cell of γ-alumina, a tetragonally formed spinel, consist of 32 oxides ions with 21 one-third aluminum ions arranged at random in the 16 octahedral and 8 tetrahedrol positions of the spinel structure [20]. The infrared investigation of γ-alumina indicates at least four bands are present in the ν(OH) region, due to different types of free surface hydroxyl groups. These are centered at 3790, 3773, 3727 and 3682 cm^{-1} [18,21]. In addition to these major isolated hydroxyl bands, two additional bands are often observed at 3733 and 3780 cm^{-1}. Various

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chemically distinct types of hydroxyl groups also persist on the surface of alumina even after heating at elevated temperatures (800–1000 °C) [18]. Removal of hydroxyl groups from alumina leaves a strained surface on which strained oxide linkages have been postulated as active sites [19]. Although "strain" sites are undoubtedly created by dehydration, characterization of such sites as strained Al–O–Al linkages seems inadequate [17]. If this was the case, γ-alumina should be the most strained and active catalyst. Rehydration of the surface between 400 and 800 °C was studied by direct spectroscopic observation of the alumina. Results show that hydroxyl groups, although apparently mobile, persist as such on the surface at high temperature on distinct type of sites rather than in completely random state [18].

Chokkaram et al. [22] characterized the structure of Co-Al and Ni-Al co-precipitated catalysts using XRD, DTA, TG-MS, BET surface area and pore volume. They concluded that introduction of cobalt or nickel into alumina may lead to a different type of spinal compound, segregation of an oxide phase or a mixture depending on the experimental conditions. The crystallinity of the spinel depends on the calcinations temperature [22].

Morterra et al. [23] investigated pure and PO4-doped alumina (≅3% P2O5) pretreated at three different temperature (773, 1273 and 1473 K). They concluded that addition of phosphate does not modify the phase transition of low temperature spinel aluminas (γ-alumina), to high temperature aluminas (δ-alumina), but delays somewhat the phase transition from spinel aluminas to a co-random phase (α-alumina).

Monlagne et al. studied the adsorption sites of thoria using scanning transmission electron microscopy (STEM) and Fourier-transformed infrared spectroscopy (FTIR) [24]. They concluded (based on STEM and FTIR results) that the local arrangement of ions on some faces induces the formation of different type of species.

Bosman et al. [25] used a combination of techniques (XRD, XPS and infrared spectroscopy) to help them gain insight into the nature of metal oxide active sites and the relation between catalyst properties and performance. They demonstrated that SiO_2 and ZrO_2 are mixed on the atomic scale in the amorphous co-precipitate. A good relationship was obtained between the strong acid site concentration of the mixed oxides and their activity in the acid catalyzed dehydration of cyclohexanol to cyclohexene.

Zhuang and Miller synthesized the mixed oxides, SiO_2/ZrO_2, by the sol–gel method [26]. They concluded the composition of mixed oxides had a strong influence on the surface area and pore volume. They believe metallic alkoxides, in general, undergo hydrolysis, and subsequent condensation to form highly mesoporous macro-polymeric oxide network.

Hubert et al. [27] reported the physical characterizations of powdered thoria samples and concluded that the precursor, the calcinations temperature, and especially the surface properties (surface area, surface state, size of aggregate) are important parameters influencing the activity.
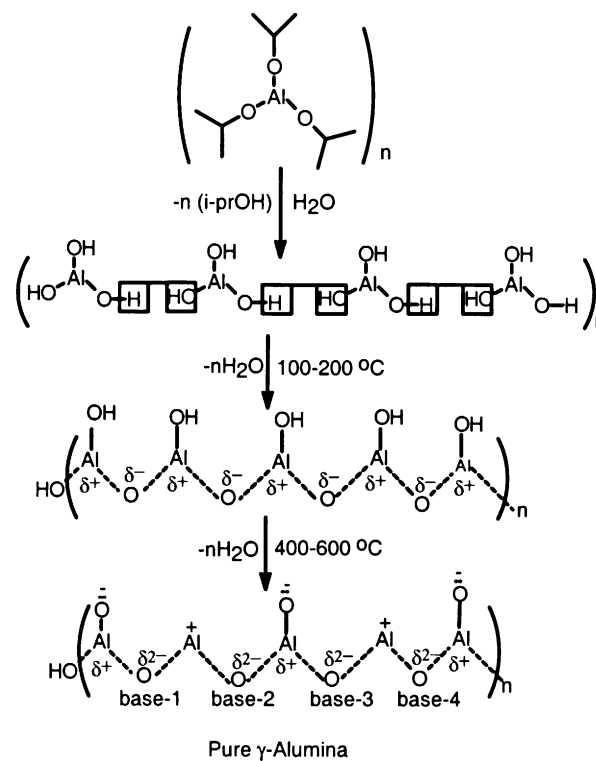
Scheme 1.

Dabbagh and Mohammad Salehi constructed new transition state models for the elimination reactions of alcohols over aluminum oxide [28]. They depicted the formation of pure γ-alumina from aluminum hydroxide as a polymerization process. The monomer (aluminum hydroxide) undergoes polymerization in three dimensions with random cross-linkage between the polymer chains (Scheme 1).

Chuah et al. investigated the effect of digestion of aluminum hydroxide precursor on the surface area and porosity of alumina [29]. They explained improved thermal stability on the basis of a reduction of the number of defect sites responsible for surface diffusion.

In this work, we initiated an investigation of the effect of mixing (by changing the mole composition) of γ-alumina and thorium oxide on the textural structure of mixed oxide γ-Al_2O_3/ThO_2. It is the purpose of the present paper to provide the evidence (using XRD and FTIR), which serves to establish the fact that γ-alumina and thorium oxide are mixed chemically at the atomic scale, but the smaller size aluminum oxide will circumvent the larger thorium oxide and the surface of mixed oxides is covered mostly by aluminum oxide.

2. Experimental

2.1. Catalyst preparation

γ-Alumina was prepared by hydrolysis of aluminum isopropoxide [Al(OC3H7)3] at room temperature; it was heated at 120 °C for 24 h to remove excess water followed by

calcinations at 600 °C for 6 h. Thorium oxide was prepared through calcination of thorium nitrate [$Th(NO_5)_4 \cdot 4H_2O$] at 600 °C for 6 h [28]. Mixed γ-alumina and thorium oxide were prepared with various compositions (100, 95, 90, 80, 50, 25, 15, 5 and 0 wt% Th, respectively) by addition of a solution of thorium nitrate to a slurry of aluminum hydroxide [$Al(OH)_3$] in deionized water at ambient temperature. Mixed oxides (slurry) were heated at 120 °C for 24 h with mixing (for uniform distribution of oxides and to remove excess water) followed by calcination at 600 °C for 6 h.

2.2. XRD measurements

The X-ray diffraction patterns for the dried single and mixed oxides are recorded by employing a Philips Xpert MPD diffractometer equipped with a Cu Kα anode (λ = 1.51418 Å).

2.3. Infrared measurements

The infrared spectra are recorded using a BOMEM, MB-100 FTIR and on Shimadzu ZU-435 spectrophotometer. Catalysts were diluted in KBr with the ratio of 1:100 catalyst:KBr.

2.4. Dehydration reaction

The catalytic reactions were performed in a vertical plug flow reactor made of Pyrex glass and fitted with a thermal well that extended to the center of the catalyst bed. About 20–30 cm^3 of the reactor volume above the catalyst bed contained Pyrex glass beads to serve as a preheater. Liquid products were collected at room temperature with increasing time intervals. Conversion of 2-hexanol or a mixture of 2-hexanol (94 wt%) and 1,2-diphenyl-2-propanol (4 wt%) at 280 °C (unless otherwise stated) was monitored by Shimadzu GC-14A gas chromatography using SE-30 column. All runs were performed over 2 g of fresh catalysts (to maintain low conversion and minimize side reactions, 0.50 g of catalyst was mixed mechanically with 1.5 g of powder glass beads) [24] and pretreated in situ in air for 2 h at 400 °C, and then with dry nitrogen for 30 min. The feed consist of 18 cm^3 of pure alcohol(s)/h giving LHSV = 0.036 l/(g catalyst h).

2.5. Computational analysis

Computational analysis of a portion of γ-alumina structure showing pores or crevices and the calculated IR spectrum of γ-alumina was performed by HyprChem-V.5.02 using Polak–Ribiere Algorithm.

3. Results and discussion

The formation of pure γ-alumina from aluminum hydroxide was recently depicted as a polymerization process in which the monomer (aluminum hydroxide) undergoes polymerization (losing water molecule) in three dimensions with random cross-linkage between the polymer chains [28a]. During this process a large number of vacancies (pores and crevices) are created to give high surface area γ-alumina. A high surface γ-alumina can be produced with proper selection of reaction conditions (starting material and temperature). At higher temperatures (700–1200 °C), the number of cross-linkage increases (losing more water) and the number of vacancies decreases leading to a very low surface area α-alumina (complete cross-linked polymer). Other oxides (SiO_2, ZrO_2 or ThO_2) are believed to polymerize in a similar process forming a specific network at the molecular scale. On subsequent drying and calcinations, a series of chemical and physical changes leads to highly mesoporous material [26].

3.1. Catalyst preparation

Mixed (various compositions with 100, 95, 90, 80, 50, 25, 15, 5 and 0 wt% alumina, respectively) γ-alumina and thorium oxide samples were prepared by hydrolysis of aluminum isopropoxide [$Al(OC_3H_7)_3$] or thorium nitrate [$Th(NO_5)_4 \cdot 4H_2O$] at room temperature with continuous stirring. This method allows a uniform distribution of aluminum and thorium within the solid. The mixtures were heated slowly to 120 °C (oil bath) with mixing for 24 h to remove solvent (excess water) and allow maximum interaction of the oxides. The dried mixture was heated slowly to 600 °C and allowed to remain at this temperature for 6 h.

3.2. XRD measurements

Fig. 1 shows the X-ray diffraction patterns of chemically mixed oxides, γ-alumina and thorium oxide. The X-ray pattern of γ-alumina ($Al_{100}Th_0$) shows good crystallinity, although the reflections are broad. The broadness has been attributed to preparation conditions and to a random distribution of the aluminum ions over the tetrahedron sites of the spinel lattice [29]. In contrast, thorium oxide (Al_0Th_{100}) is
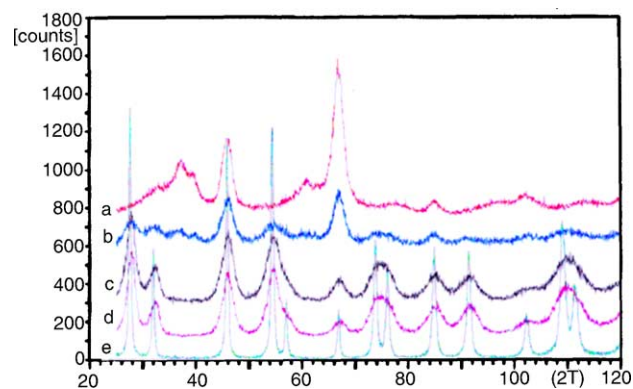

Fig. 1. X-ray diffraction patterns of chemically mixed γ-alumina and thorium oxide (wt%). (a) $Al_{100}Th_0$; (b) $Al_{80}Th_{20}$; (c) $Al_{50}Th_{50}$; (d) $Al_{25}Th_{75}$; (e) Al_0Th_{100}.
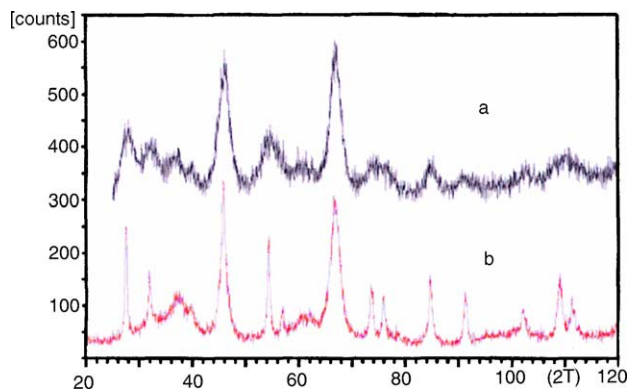
Fig. 2. X-ray diffraction patterns of mixed γ-alumina and thorium oxide ($Al_{80}Th_{20}$). (a) Chemically mixed; (b) mechanically mixed.

crystalline. The maximum reflections due to γ-Al_2O_3 at $36°$ and $68°$ disappear to a small broad reflection at higher wt% ThO_2. The maximum reflections due to ThO_2 at $2\theta = 28°$ and $55°$ disappear to a small broad reflection at higher wt% γ-Al_2O_3. The reflections due to γ-Al_2O_3 and ThO_2 at $2\theta = 46°$ are condensed to a larger reflection with small loss of crystallinity. The absence of crystallinity demonstrated by XRD analysis clearly show mixing of γ-alumina and thorium oxide is chemical and on an atomic scale after the calcination period. The XRD of mechanically mixed oxides ($Al_{80}Th_{20}$) show a superposition of crystalline ThO_2 and Al_2O_3, which indicates mixing is not on the atomic scale (Fig. 2).

3.3. Infrared measurements

Fig. 3 shows the Fourier-transformed infrared spectrum of γ-alumina ($Al_{100}Th_0$) and chemically mixed (Al_5Th_{95}, $Al_{25}Th_{75}$, $Al_{50}Th_{50}$; wt%) γ-alumina and thorium oxide. Fig. 4 shows FTIR of thorium oxide (Al_0Th_{100}). The spectrum of pure γ-alumina shows absorption at $580\,cm^{-1}$ (strong), $800\,cm^{-1}$ (strong), $1640\,cm^{-1}$ (weak) and a broad band at $3470\,cm^{-1}$ (medium) that are due to free surface hydroxy groups (n_{OH}). The spectrum of mixed γ-alumina thoria ($Al_{80}Th_{20}$) is similar to spectrum of pure γ-alumina with the appearance of several new very weak bands at 1400, 2900 and slight weakening of the strong absorption at $800\,cm^{-1}$. The spectrum of mixed γ-alumina thoria ($Al_{50}Th_{50}$) show major changes in the region of 300–$1000\,cm^{-1}$. The intensity of the absorption at $580\,cm^{-1}$ is reduced to a medium broad band. The intensity of the absorption at $1640\,cm^{-1}$ (weak) increased and a new sharp strong band appears at $380\,cm^{-1}$ (which we cannot assign). There was an increase in the intensity of the medium broad band at $3470\,cm^{-1}$. The intensity of absorption at $3450\,cm^{-1}$ of the mixed γ-alumina ($Al_{75}Th_{25}$) increased drastically with the reduction of intensity bands in the region of 300–$1000\,cm^{-1}$. The intensity of absorption at $3450\,cm^{-1}$ of the mixed γ-alumina (Al_5Th_{95}) is the dominant and more resolved absorption band. The peaks at 800 and $520\,cm^{-1}$ were reduced to sharp weak bands.

These observations clearly indicate that the mixed oxides change with variation in the wt% of single oxides. The most
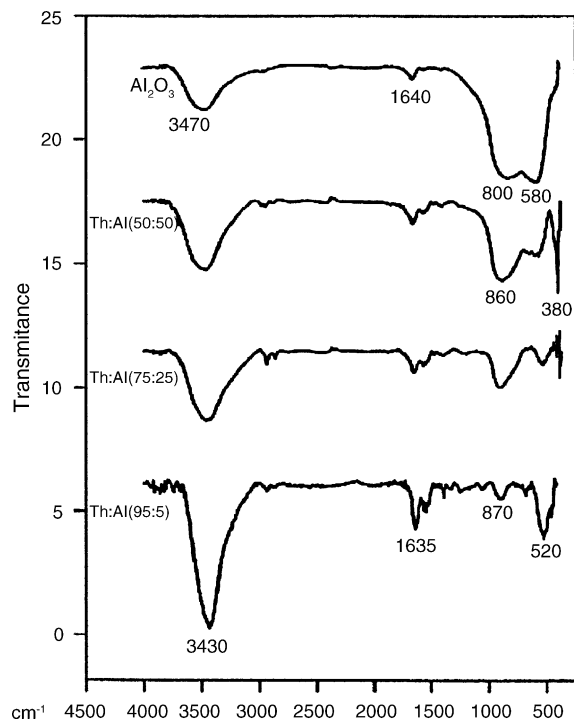

Fig. 3. Fourier-transformed infrared spectroscopy of single γ-alumina and chemically mixed γ-alumina and thorium oxide (wt%).

noticeable change is due to the disappearance of the bands at 300–$1000\,cm^{-1}$ and the appearance of a very strong broad absorption at $3450\,cm^{-1}$, which is the characteristic of an OH species bound by weak hydrogen bonds. This indicates that the number of hydroxy groups on the surface increases with increases in the weight percent of thorium oxide. In other words, the smaller size aluminum oxide will circumvent the larger thorium oxide and the surface of mixed oxides is covered mostly by aluminum oxide.

3.4. Evaluation of catalyst by dehydration reaction

The evaluation for the catalytic activity of single or the chemically mixed catalysts for the dehydration of 2-hexanol
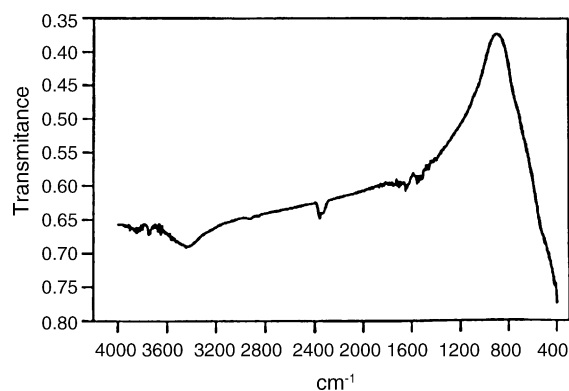

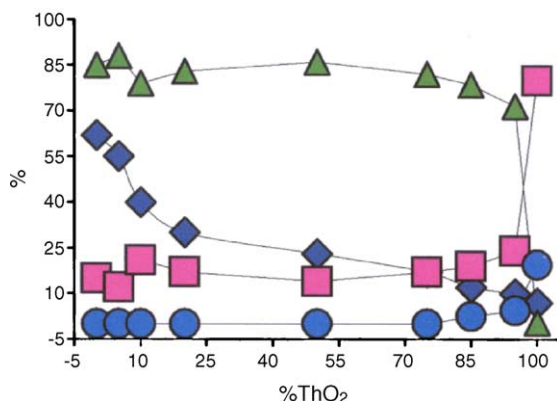Fig. 4. Fourier-transformed infrared spectroscopy of single thorium oxide (wt%).

Fig. 5. Conversion of 2-hexanol over single and mixed γ-alumina and thorium oxide (calcined at 600 °C for 6 h) at 280 °C: LHSV = 36 cm³/(g catalyst h); (▲) % 2-alkenes; (♦) % conversion; (■) % 1-alkene; (●) % ketone.

Fig. 6. Conversion of 1,2-diphenyl-2-propanol in 2-hexanol (solvent) over single and mixed γ-alumina and thorium oxide (calcined at 600 °C for 6 h) at 280 °C: LHSV = 36 cm³/(g catalyst h); (♦) % conversion; (■) % 1-alkene; (▲) % E-2-alkenes; (●) % Z-2-alkene.

and mixture of 2-hexanol and 1,2-diphenyl-2-propanol was performed in a continuous flow, fixed bed, micro reactor [28a–c]. The pure γ-Al₂O₃ at 280 °C converts 62% of 2-hexanol to 15% 1-alkene and 85% 2-alkene with no dehydrogenation adducts. Mixed (50:50) γ-alumina and thorium oxide converts 23% of 2-hexanol to 14% 1-alkene, 86% 2-alkene and 0% 2-hexanone. In other words, addition of thorium oxide (up to 85%) did not effect the selectivity of catalyst but reduced the rate of conversion. The higher compositions (above 85%) of thorium oxide increase the rate of dehydrogenation. The single thorium oxide at 280 °C converts 7% of 2-hexanol to 80% 1-alkene, 0.5% 2-alkene and 19.5% 2-hexanone (Fig. 5).

1,2-Diphenyl-2-propanol dissolved in 2-hexanol was converted over pure γ-Al₂O₃ to a mixture of E-alkene (28.5%), Z-alkene (21.5%) and 1-alkene (50%) (Fig. 6). Mixed (50:50) γ-alumina and thorium oxide converted 89% of 1,2-diphenyl-2-propanol to a mixture of 26% E-alkene, 18% Z-alkene and 56% 1-alkene. Thorium oxide at 280 °C converts 25% of 1,2-diphenyl-2-propanol to a mixture of 36.5% E-alkene, 20.5% Z-alkene and 43% 1-alkene.

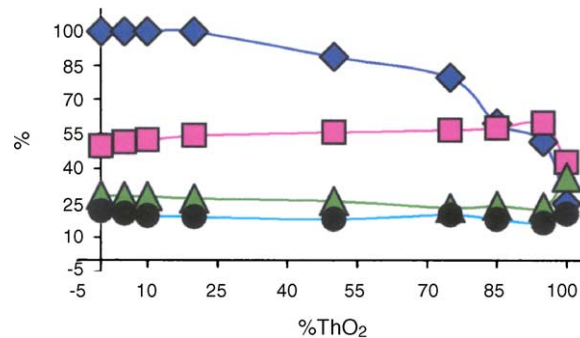The γ-alumina prepared by the method described in Section 3.1 possesses the potential to form a highly porous structure, giving large surface area and pore volume. The thorium oxide shows a low surface area. When mixed, the textural properties of γ-alumina and thorium oxide change due to the interactions of acid and base sites of both oxides. At higher ThO₂ content, the activity of γ-alumina decreases, revealing shrinkage of the structure and deactivation of certain active sites of aluminum oxide (limited alcohol adsorbed over the surface). But the selectivity of dehydration reactions over the mixed oxides is not influenced by increasing wt% ThO₂. This indicates there are enough free appropriate active sites to carry on the anti-E2 elimination reactions [28a].

3.5. Computational analysis

Computational analysis of a portion of γ-alumina structure with alcohol adsorbed on the surface proved to be a valuable tool for understanding the mechanism of the dehydration of alcohol over γ-alumina [28a]. In this work, we optimized the larger portion of aluminum oxide structure showing pores or crevices (Fig. 7). The infrared spectrum of γ-alumina calculated by AM1 method show absorption pattern similar to FTIR (Fig. 8). The calculated spectrum of γ-alumina shows absorptions in the range of 300–800 (medium) for –Al–OH, absorptions in the range of 900–1266 (strong) for –O–Al–O–Al– and absorptions in the range of 3545–3576 (strong) for –Al–OH.
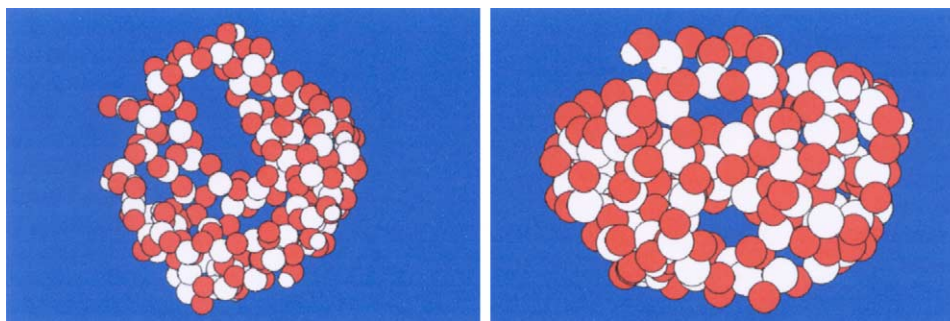

Fig. 7. Portion of hypothetical structure of Al₂O₃ in three dimensions, left (side view), right (front view) showing pores or crevices calculated by semi-empirical (AM1) method.
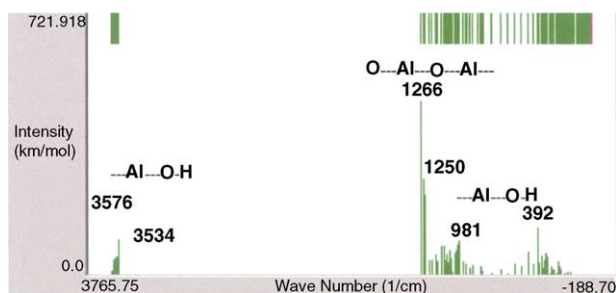
Fig. 8. Infrared spectroscopy of hypothetical portion of single Al_2O_3 calculated by semi-empirical (AM1) method.

4. Conclusions

Mixed γ-alumina and thorium oxide were prepared with various compositions among 100, 95, 90, 80, 50, 25, 15, 5 and 0 wt%. New FTIR absorption bands and absence of crystallinity demonstrated by XRD analysis clearly show that the mixing of γ-alumina and thorium oxide is chemical and on an atomic scale after the calcination period. In contrast, the mechanically mixed oxides retained crystallinity and do not show mixing on an atomic scale. At higher ThO_2 content, the activity of γ-alumina for the dehydration of alcohol(s) decreases, revealing shrinkage of the structure, but the selectivity is not influenced by an increase in the wt% ThO_2. The infrared spectrum of γ-alumina calculated by semi-empirical (AM1) method shows an absorption pattern similar to the FTIR.

Acknowledgment

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