



## Decomposition of 2-propanol over Alumina supported Thoria and Potassium ion modified catalysts

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### ABSTRACT

A series of alumina and K ion modified supported thoria catalysts were prepared using thorium nitrate hexahydrate at different loading levels (3–20 wt% of thoria) by the impregnating method. The decomposition of 2-propanol on the surface of these catalysts was investigated. Pure  $\gamma$ -alumina catalyst shows low activity and higher selectivity towards dehydration reaction. In contrast, thoria catalyst shows low activity and higher selectivity towards dehydrogenation reaction. The activity and selectivity of alumina supported thoria catalyst towards dehydrogenation reaction was increased with increasing the amount of  $\text{ThO}_2$  on  $\gamma$ -alumina. However, the activity and selectivity of these catalysts towards dehydration reaction were observed to be decreased with increasing the amount of  $\text{ThO}_2$ . The surface of dehydrogenation reaction of 2-propanol was increased with increasing the addition of K ion on the surface of alumina supported thoria catalysts.

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### 1. Introduction

The catalytic decomposition of alcohols, via dehydration and dehydrogenation reaction is considered a straightforward means of producing materials of prime industrial importance (Wender *et al.*, 1984). Consequently, it has stimulated research curiosity, and a large number of papers have been published dealing with the subject from a range of important aspects (Cunningham *et al.*, 1981; Krylov *et al.*, 1970; Fahim *et al.*, 1982).

The two basic modes of alcohol decomposition are: (i) dehydrogenation to form aldehyde (in case of primary alcohols) or a ketone and hydrogen (in case of secondary alcohols), and (ii) dehydration to form an olefin and water. At high temperatures, several decompositions of an alcohol may occur leading to the cleavage of carbon-carbon bonds and result in the formation of paraffin's, CO, CO<sub>2</sub>, etc. The mechanism of alcohol decomposition was studied by Krylov *et al.*, (1970). A summary of conclusions, derived from some various theories of catalysis, for catalyst selection in alcohol decomposition is as follows:

(1) According to the widely known conclusions on the electronic theory of catalysis (Hauffe *et al.*, 1962), where the rate limiting step for dehydrogenation is the migration of vacancies, while for dehydration, it is the migration of free electrons in the catalyst; consequently, dehydrogenation is expected to be catalyzed by p-type semiconductors and dehydration should be catalyzed by n-type semiconductors.

(2) According to the classification of catalytic processes, dehydration is an acidic reaction and, therefore, should be catalyzed by solid and liquid protonic (Bronsted) and aprotic (Lewis) acids; dehydrogenation, being an electronic reaction, should be catalyzed by metals and semiconductors.

(3) Based on the premise that alcohol decomposition is a multi-step reaction (Gervasini *et al.*, 1991), dehydration requires acidic catalysts with n-type conductivity and dehydrogenation requires

basic catalysts with p-type conductivity. 2-Propanol decomposition has been employed to probe the acid and base character of metal oxides at elevated temperatures (Tanabe *et al.*, 1989). Selectivity in the decomposition reaction of 2-propanol has long been regarded as one of the typical reactions for the investigating the acid-base properties of the catalytic sites of metal oxides (Cunningham *et al.*, 1981; Tanabe *et al.*, 1989; Nollery *et al.*, 1984; Zaki *et al.*, 1990; Hussein *et al.*, 1989). The catalysts can be classified in regard to their propensity toward the dehydration or the dehydrogenation activity to propene or acetone, respectively. Ai *et al.*, 1974; Nollery *et al.*, 1984; Lercher *et al.*, 1985) assumed that the dehydration of 2-propanol is catalyzed by an acid sites, whereas the dehydrogenation is catalyzed by both acid and basic sites through a concerted mechanism.

The objective of the presented investigation is to focus mainly on the decomposition of 2-propanol on the surface of  $\gamma$ -alumina supported thoria catalysts. The effect of potassium ions on alumina supported thoria on the texture and phase structure of thoria was investigated. In order to accomplish these objectives, the following steps are carried out: 1- series of alumina supported thoria catalysts at loading varying in range 3–20 wt%  $\text{ThO}_2$ , were prepared by impregnation and calcined at 600°C for 2 h.

2- An analogous series catalysts of potassium ion modified alumina supported thoria samples in range 1–6 wt% K<sup>+</sup> were prepared by impregnation from an aqueous solution of potassium nitrate and then calcined in the same manner.

### 2. Catalysts preparation

#### 2.1. Materials

Thorium nitrate hexahydrate,  $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ , (Merck, Germany), with high purity of (99.0%), used as a precursor for supported and unsupported thoria catalysts. Potassium nitrate,  $\text{KNO}_3$ , (Merck, Germany), with high purity of (99.0%), used as the precursor for K ion modified alumina supported thoria catalysts. Thoria is usually produced by the thermal decomposition of

inorganic precursors. Powder of unsupported thoria, ThO<sub>2</sub>, was prepared by calcination of thorium nitrate hexahydrate at 600°C for 2 h in a static atmosphere of air. The calcination temperature was chosen on the basis of the thermal analysis results (Hussein et al., 1995). The material was white in colour, well crystallized (XRD-verified) and fine powdered.

Alumina gel, Al(OH)<sub>3</sub>, (Surechem Products Ltd, England, SCP), used as supplied. High surface area of  $\gamma$ -alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) was obtained by calcination of alumina gel (SCP) at 600°C for 3 h, in static atmosphere of air. The  $\gamma$ -alumina structure of the oxide was XRD-verified (JCPDS 29-1486).

Alumina supported thoria catalysts were prepared by impregnation (Mayers et al., 1985) of alumina gel with appropriate amounts of thorium nitrate hexahydrate solutions to obtain, 3, 5, 10 and 20 wt% of ThO<sub>2</sub> catalysts. A portion of alumina gel was added slowly into suitable volume (25 ml/gm) of an impregnated solution of the required concentration. Excess water was removed by evaporation at 100°C for 24 h. Impregnated support thus yielded were further dried at 100°C till constant weight. Supported thoria catalysts on alumina (xThAl) were obtained by calcination at 600°C for 2 h of the corresponding impregnated supports. The resulting catalysts were kept dry on CaCl<sub>2</sub>, until further use. For convenience, the various catalysts are denoted below by designations including the support and metal oxidations, and the loading levels. Thus 3ThAl indicates the 3 wt% ThO<sub>2</sub> loaded alumina supported thoria catalysts obtained by calcination at 600°C for 2 h.

K ion modified alumina supported thoria (xK5ThAl) catalysts were obtained by an impregnation method. A 2 gm portion of 5ThAl was added slowly into 50 ml of the impregnated solution of the required concentration. The impregnation solution was prepared by dissolving a calculated amount of the precursors KNO<sub>3</sub> of the required loads, 1, 2, 3 and 6 wt%. Excess water was removed by evaporation at 100°C for 1 h and the resulting materials were dried at 100°C for 24 h. The resulting catalysts were manually grounded in an agate mortar and then calcined at 600°C for 2 h. The samples were designated in the text as xK5ThAl, where x is the loading K ion (1, 2, 3 and 6 wt%). The resulting materials were obtained kept dry over CaCl<sub>2</sub>, prior to any further handling.

## 2.2. Apparatus and techniques

An all-Pyrex glass IR cell equipped with BaF<sub>2</sub> windows, specially designed for high-temperature measurements, was used to facilitate probing adsorptive and catalytic interactions of the 2-propanol (2-PrOH) gas phase on tested catalysts by in situ FTIR spectroscopy in the transmission mode. In situ Fourier-transform Infrared Spectra were recorded at 4000–400 cm<sup>-1</sup> by averaging 100 scans at the resolution of 4 cm<sup>-1</sup>. This was accomplished by using a Genesis II Thermo Mattson FT-IR Spectrophotometry (USA) powered with a Win First Lite software (Mattson Corp.) for data acquisition and handling.

A 10-Torr portion of the alcohol gas phase (air-free) was expanded into the cell, following an acquisition of background spectra of the cell at Room temperature (RT). The gas/solid interface was maintained at RT for 5 min before measuring a spectrum of the gas phase (plus cell background). Decomposition of 2-propanol occur on the surface of the tested catalyst at 250°C, but the spectra were measured following cooling to RT. Changes in the composition of the alcohol gas phase were monitored by subtracting the RT spectrum from the spectrum obtained at each reaction temperatures. The analysis implements the relationship.

$$\log(1/T) = \log(I^{\circ}/I) = A = abc$$

where :

$T$ = the transmittance	$I^{\circ}$ = incident radiation
$I$ = transmitted radiation	$A$ = absorbance
$a$ = absorption coefficient	$c$ = concentration
$b$ = sample thickness	

The band in the spectrum used for the quantitative (analytical

band) is not overlapped by other bands attributable to other components in the mixture. The single programme constructs a calibration curve (absorbance vs. concentration) based on as many as 12 different concentrations of a standard. Then, the concentration of the unknown is determined from the calibration curve. Six analytical band evaluation modes are available. One should choose the mode with the least relative error. Most probably it is either the peak-high or peak-area mode. In this work, we have used the peak-high mode.

After cleaning the sample wafer catalyst, the sample holder lowered into the IR transmitting section of the cell, then 10 Torr of 2-propanol introduced to the cell. The cell was transferred into the IR spectrophotometer, and then the temperature was adopted at the appropriate temperature, then the sample holder lifted up to the hot zone. When the sample temperature reached to the appropriate temperature the time was recorded. The spectral data must be recorded at the same resolution and the same path length.

## 3. Results and discussion

### 3.1. Decomposition of 2-PrOH on the surface of the catalysts

IR spectroscopy was used to investigate decomposition of 2-PrOH vapour over the catalysts at different temperatures. The gas-phase IR spectroscopy from 10 Torr dose of 2-PrOH in contact with catalyst at 250°C was obtained. These spectra of gaseous obtained over the catalysts after consecutive 5 min heating periods at the temperatures indicated between room temperature and 250°C. The spectra were measured after cooling the system once again to room temperature. The return to room temperature after each phase of the reaction is essential if accurate infrared evaluations are to be achieved by spectral subtraction techniques. These gas-phase spectra provided very effective qualitative and semiquantitative analysis of the gas mixtures from the infrared data. The results of 2-PrOH decomposition on examined catalysts are presented in Table 1 in terms of percentage conversion (Con.%), acetone selectivity percent (S<sub>A</sub> %) and propene selectivity percent (S<sub>P</sub> %).

#### 3.1.1. Support and unsupported catalysts

The dehydration and dehydrogenation of alcohols over metal oxide catalysts have been studied by many investigators. Some oxides particularly tend to promote dehydration, whereas others have mainly dehydrogenation effect. IR spectroscopy (250°C) has been used to investigate the decomposition of 2-PrOH over the catalysts listed in Table 1.

##### 3.1.1.1. Alumina

Table 1 shows the gas-phase decomposition of 2-PrOH over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst at 250°C. Propene was the spectroscopically dominant products at 250°C. The results listed in Table 1 indicated that the decomposition of 2-PrOH on the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> gave propene on dehydration at the reaction temperature (250°C) and acetone on dehydrogenation at the reaction temperature (250°C). These results indicate the surface of alumina have activity (32.8%) towards 2-PrOH decomposition and high selectivity (81.6%) towards dehydration reaction. These results are in a good agreement with the results obtained by Knozinger et al., (1972), they have studied the dehydration of alcohols on the surface of alumina.

##### 3.1.1.2. Thoria

The results of decomposition of 2-PrOH over ThO<sub>2</sub> catalyst are given in Table 1. The results clearly show that the supported catalysts display higher activity than other unsupported and support one. For thoria catalyst the major product of decomposition of 2-PrOH on ThO<sub>2</sub> is acetone (84.6%) and minor (15.4%) is propene at the reaction temperature (250°C). These results are in good agreement with the results obtained by Hussein et al., (1989), they studied IR spectroscopy of the decomposition of 2-PrOH over the surface of group (IV) B metal oxide catalysts.

**Table 1**

Percentage conversion of 2-PrOH and selectivities toward the formation of propene and acetone over alumina supported thoria catalysts.

Catalyst	Conversion % Conv. %	Selectivity %	
		S <sub>A</sub>	S <sub>P</sub>
Al600	32.8	18.4	81.6
ThO <sub>2</sub>	29.7	84.6	15.4
3ThAl	46.4	42.3	57.7
5ThAl	57.3	55.1	44.9
10ThAl	69.8	64.2	35.8
15ThAl	80.2	73.3	26.7
20ThAl	91.4	81.3	18.7

**Table 2**

Percentage conversion of 2-PrOH and selectivities toward the formation of propene and acetone over alumina supported thoria and K-ion modified catalysts.

Catalyst	Conversion % Conv. %	Selectivity %	
		S <sub>A</sub>	S <sub>P</sub>
Al600	32.8	18.4	81.6
ThO <sub>2</sub>	29.7	84.6	15.4
5ThAl	57.3	55.1	44.9
1K5ThAl	66.3	88.1	11.9
2K5ThAl	75.8	91.2	9.8
3K5ThAl	84.8	95.5	4.5
6K5ThAl	98.4	98.3	1.7

### 3.1.1.3. Supported catalysts.

#### 3.1.1.3.1. $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported ThO<sub>2</sub> catalysts.

The results of 2-PrOH decomposition activity for this series of catalysts are presented in Table 1. In general, the supported thoria catalysts exhibited relatively higher activity than the support and unsupported thoria. The activity increases with increasing the loading level of thoria from 46.4 % for 3ThAl to 91.4 % for 20ThAl.

Also, the selectivity towards the formation of acetone (main product, dehydrogenation process) increased with increasing the loading level of thoria, whereas the selectivity towards formation of propene (minor product, dehydration process) decrease with increasing the loading level of thoria. According to Ai et al., (1977), the dehydrogenation of 2-PrOH is catalyzed by both acid and basic sites through a concerning reaction mechanism involving both acid and basic sites. From the previous results of decomposition of 2-PrOH over xThAl we concluded that the dehydrogenation reaction increase with increasing the amount of ThO<sub>2</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> from 3 wt% to 20 wt% ThO<sub>2</sub>, and at the same time the dehydration reaction decreased by increasing the amount of ThO<sub>2</sub>. These results reveal that the acidity and basicity of the surface of these catalysts increase by increasing the amount of ThO<sub>2</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. These results are in good agreement with the results obtained by Lercher et al., (1985) have studied the acid-base properties of alumina-magnesia mixed oxides. Lercher et al., observed the similar trend for increasing the dehydrogenation reaction by increasing the added MgO as a basic oxide to Al<sub>2</sub>O<sub>3</sub> as an acid oxide. From these results we can conclude that the decomposition of 2-PrOH over these catalysts show the following order of the selectivity for acetone formation: ThO<sub>2</sub>> 20ThAl> 15ThAl> 10ThAl> 5ThAl> 3ThAl>  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, while order of the selectivity towards propene formation is:  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>> 3ThAl> 5ThAl> 10ThAl> 15ThAl> 20ThAl> ThO<sub>2</sub>.

#### 3.1.1.3.2. K ion modified alumina supported thoria catalysts

The quantitative analysis of gas-phase mixtures obtained from the decomposition of 2-PrOH over K<sup>+</sup>-modified alumina supported thoria catalysts at reaction temperature (250°C) are listed in Table 2. It can be deduced from Table 2 that the activity of K<sup>+</sup>- modified alumina supported thoria catalysts increased by increasing the addition of the amount of K ion to 5ThAl. Also, the dehydrogenation reaction of 2-PrOH was increased with increasing the addition of K ion to the surface 5ThAl catalysts from 1 wt% K<sup>+</sup> to 6 wt% K<sup>+</sup>. These results indicated that the basicity of the surface of these catalysts increases by increasing the amount of K<sup>+</sup>. Furthermore, the catalyst shows low selectivity for the formation of propene at 250°C.

The activity of these catalysts for the reaction of 2-propanol decreased as the following order: 6K5ThAl> 3K5ThAl> 2K5ThAl> 1K5ThAl>  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Whereas, the selectivity towards dehydrogenation reaction increased as the following order:  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>< 1K5ThAl< 2K5ThAl< 3K5ThAl< 6K5ThAl. These result are in good agreement with the results obtained from ex-situ FTIR spectroscopy for the appearance of carbonates on the surface of these catalysts, which increased with increasing the amount of K ion up to 6 w% (Bukhzam et al., 2017).

### 3.2. Catalyst activity

The activity and the selectivity of metal oxides in the conversion of alcohols were found to be dependent on chemical composition (Selim et al., 1980), chemistry of the surface and reaction temperatures (Youssef et al., 1990) in addition to acid-base properties of the surface (Ai et al., 1977; Gervasini et al., 1991). The distribution of acidic sites and basic sites are importance for determining the activity and selectivity of the catalysts. The catalytic activity of decomposition of 2-PrOH to acetone and propene was studied earlier by Ai et al., (1977). They have suggested that the catalytic activity for dehydration of 2-propanol to propene (*rp*) is proportional to the acidity of a catalyst, where *rp* is the rate of dehydration.

$$rp = k \cdot \text{acidity} \quad (1)$$

Gervasini et al., (1991) reveal that the dehydration of 2-PrOH to propene catalyzed by metal oxides, the number, the nature and the strength of the acid sites affect the catalytic activity. The nature and the concentration of acid sites influence mainly the entropic activation parameter, while the strength of acid sites on catalysts influences the activation energy. On the other hand, the activity for dehydrogenation of 2-PrOH to acetone (*ra*) is assumed to be proportional to the acidity and basicity of a catalyst, since the dehydrogenation is considered to proceed by a concerning mechanism (Mars, 1959)

$$ra = k' \cdot \text{acidity} \cdot \text{basicity} \quad (2)$$

where *ra* is the rate of dehydrogenation. From Eqs. (1) and (2), the following equation is derived

$$\text{basicity} = k'' \cdot ra/rp \quad (3)$$

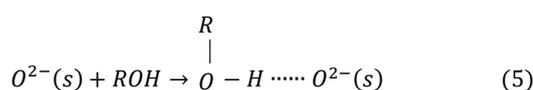
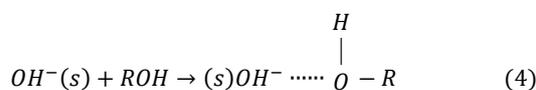
where *k*, *k'* and *k''* are constants. Thus, *ra/rp* can be used as a measure of the basicity of the catalyst. In the dehydrogenation of 2-propanol to acetone, the activity of the catalysts takes place through a concerted mechanism involving both acid and basic sites see above. Gervasini et al., (1991) stated that the concentration and the nature of the acid sites influence mainly the entropic term, but the activation energy is independent of the strength of both the acid and the basic sites.

The results obtained from the decomposition of 2-PrOH on the surface of pure Al<sub>2</sub>O<sub>3</sub> and supported catalysts show that the activity of these catalysts increases with increasing the amount of ThO<sub>2</sub> load. Gervasini et al., (1991) found that the decomposition of 2-PrOH on metal oxides depends on nature, number and the strength of acidic and basic sites on the surface. Thus, alumina supported thoria catalysts, the activity towards decomposition of 2-PrOH increases with increasing the amount of ThO<sub>2</sub>, this due to increasing of the acidic and basic sites on the surface of these catalysts which is in a good agreement with Gervasini et al., (1991). The increase in the selectivity of dehydrogenation reaction on the surface of xThAl catalysts is due to the increase of the surface basicity with increasing the thoria loading levels. Also, the higher selectivity decomposition of 2-PrOH on the surface of modified alumina supported thoria catalysts (xK5ThAl) are due to increases the surface basicity with increasing the modified K ion.

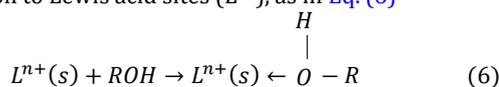
### 3.3. Catalyst Selectivity

The dehydration and dehydrogenation of alcohols over metal oxide catalysts have been studied by many investigators. Some oxides particularly tend to promote dehydration, where as other have mainly dehydrogenation effect.

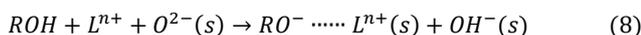
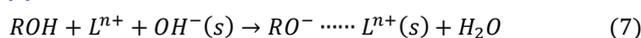
The results described above clearly show that 2-PrOH decomposition over the previous catalysts via dehydration to give propene (at 250°C) and via dehydrogenation to give acetone (at 250°C). The decomposition of 2-PrOH probably proceeding firstly by adsorption of 2-propanol on active sites. According to reported data (Nakajima, 1985; Graham, 1981; Graham, 1984), the IR studies of adsorbed alcohol over metal oxide surfaces show that mixture of adsorbed alcohol molecules and alkoxide species were formed. Adsorption of 2-PrOH was considered as the rate determining step (Colmenares, 1984). The adsorption of alcohol on the surface of oxide held by hydrogen-bonding to the surface in two ways, where



Or via coordination to Lewis acid sites ( $L^{n+}$ ), as in Eq. (6)



R denotes an alkyl group,  $OH^-$  and  $O^{2-}$  are groups on the surface of the oxide or via coordination to Lewis acid sites ( $L^{n+}$ ). 2-propoxide formation could occur in two straightforward ways, as in Eqs. (7) and (8):



#### 4. Conclusion

Pure  $\gamma$ - $Al_2O_3$  catalyst show low activity and high selectivity towards dehydration reaction. In contrast, thoria catalyst show low activity and high selectivity towards dehydrogenation reaction. The activity of alumina supported  $ThO_2$  catalyst towards decomposition of 2-PrOH increased with increasing the addition amount of  $ThO_2$  to  $\gamma$ - $Al_2O_3$ .

The selectivity of  $\gamma$ - $Al_2O_3$  supported  $ThO_2$  catalysts towards dehydrogenation reaction increase with increasing the amount of  $ThO_2$  on  $\gamma$ - $Al_2O_3$ . In contrast, the selectivity of these catalysts towards dehydration reaction decreased with increasing the amount of  $ThO_2$ . The activity of K ion modified alumina supported  $ThO_2$  catalysts increased with increasing the amount of K ion on supported thoria catalysts. Furthermore, the selectivity of these catalysts towards dehydrogenation reaction was increased. These catalysts show high selectivity towards dehydrogenation reaction. The decomposition of 2-PrOH to form acetone via dehydrogenation reaction on the surface of catalysts depend on nature, the number and the strength of acidic and basic sites on the surface. The present investigation has confirmed that IR spectroscopy is capable of unambiguous identification (and often quantitative evaluation) of virtually all small or medium sized reactants and products, including unexpected ones. The only exceptions are the symmetrical diatomic molecules such as  $H_2$ , which do not have infrared absorption bands.

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