Dehydration of 2-octanol over zirconia catalysts: Influence of crystal structure, sulfate addition and pretreatment

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Abstract

Two phases of zirconia, monoclinic (m-ZrO_2) and tetragonal (t-ZrO_2), and their sulfated forms (m- or t-ZrO_2-S) were evaluated for 2-octanol conversion. Unsulfated zirconia resembles thoria for both dehydration and 1-alkene selectivities for 2-ol conversions. Its catalytic properties differ greatly from two other members of the group 4B family, titania and hafnia. Independent of crystal structure, sulfated and oxygen pretreated zirconia catalysts exhibit high activity for dehydration reaction. The sulfated and hydrogen pretreated and the unsulfated (both H_2 and O_2 pretreated) zirconia catalysts were less active for 2-octanol conversion. Hydrogen pretreated sulfated zirconia catalysts show high selectivity for 1-octene compared to oxygen pretreated and sulfated zirconia catalysts. The results show that the pretreatment influences the dehydration selectivity but the activity and selectivity are essentially independent of zirconia crystal phase.

1. Introduction

Zirconia is widely used as a catalyst since it exhibits acidic, basic, oxidizing and reducing properties [1]. In particular, zirconia is used as a catalyst in the synthesis of isobutene or methanol from carbon monoxide and hydrogen [2,3], hydrogenation of butadiene, H_2–D_2 exchange [3–7], isomerization of 1-butene [8], and dehydration of alcohols, especially for the production of α-olefins from 2-alcohols [9,10]. The activity, selectivity and stability of the catalyst overall are dependent on the method of preparation, the precursor, and on the pretreatment [11,12]. Pretreatment of the catalyst usually affects the activity and selectivity in heterogeneous catalysis.

According to Tanabe [1], most of the reactions on zirconia catalysts proceed by acid–base bifunctional catalysis and the orientation of these sites plays an important role in governing the reaction.

Sulfated zirconia catalysts are known for their superacidic behavior [13–16]. Recent reports [17,18] show that the addition of moisture causes an overall reduction of catalytic activity of sulfated zirconia catalysts for the isomerization/cracking of paraffins. According to Tanabe et al. [19] the solid superacids, when they are exposed to the air at ambient temperature, lose their superacidity by absorbing moisture. Nevertheless, Wen et al. [15] found that the presence of small amounts of moisture in the reaction system enhanced the catalytic activity of a platinum-doped solid superacid

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$(Pt/ZrO_2/SO_4)$ for the hydroisomerization and hydrocracking of n-heptane.

Zirconia resembles thoria [20,21] for both dehydration and 1-alkene selectivities in 2-ol conversions. Its catalytic properties differ greatly from two other members of the group 4B family, titania [22] and hafnia [23]. To answer questions about some of the issues discussed above, two types of zirconia catalysts, namely monoclinic and tetragonal zirconia, have been tested for 2-octanol conversion. These catalysts were subjected to either oxygen or hydrogen pretreatments prior to the reaction studies. The impact of sulfate addition to zirconia catalysts was also investigated. The activity and selectivity data of these catalysts for 2-octanol conversion are compared with the crystal type of zirconia, its precursor and the pretreatment procedures.

2. Experimental

2.1. Preparation

2.1.1. Zirconia

Zirconia was precipitated from an aqueous (0.3 M) solution prepared from anhydrous zirconium tetrachloride, by rapid addition of concentrated (~ 30 wt%) aqueous ammonium hydroxide to produce a final pH of 10.5. The resulting precipitate was collected by filtration, washed and dried at 383 K in air for 20 h. The dried sample was amorphous to X-rays. X-ray

diffraction studies of the calcined (at 773 K, 4 h) material show that the sample was mostly monoclinic zirconia $(m-ZrO_2)$ with a small amount (about 10%) of tetragonal zirconia $(t-ZrO_2)$. A portion of the dried but uncalcined sample was sulfated [12] by immersing the sample in 0.5 M H_2SO_4 (10 cc/g zirconia) for one hour followed by filtration and drying at 383 K. The dried material contained 9.7 wt% sulfate. The resulting unsulfated $(m-ZrO_2)$ and sulfated $(m-ZrO_2-S)$ zirconia samples were stored in closed bottles until utilized as a catalyst.

Another catalyst $(t-ZrO_2)$ was prepared by precipitation by slowly adding an aqueous ammonia solution to obtain a pH of 10.5 to a $ZrO(NO_3)_2$ solution followed by filtration, washing and drying at 383 K. The XRD pattern of the calcined (773 K, 4 h) sample showed that it was nearly pure tetragonal zirconia. A portion of this dried zirconia $(t-ZrO_2)$ was sulfated as described above for the $m-ZrO_2$ sample $(t-ZrO_2-S$, sulfate content of 10.5 wt%). A second batch of the sulfated catalyst $(t-ZrO_2-S(2))$ was prepared by the same procedure as described above. The sulfate content in the calcined sample was about 1 wt%. A summary of the properties of these precipitated catalysts are provided in Table 1.

Portions from a batch of hydrous zirconia $(t-ZrO_2)$, dried at 383 K, were impregnated with sufficient 0.5 M sulfuric acid to produce materials to contain 1.0, 2.0, 4.2, 6.1 and 8.9 wt% sulfate (determined by chemical analysis). These materials were calcined in air at 773 K for 4 h

Table 1
Sulfate content and surface area of zirconia catalysts

Catalyst ID	Sulfate content (wt%)		BET surface area of fresh catalyst (m^2/g catalyst)	
	fresh	after reaction	dried at 383 K	calcined at 673 K
$t-ZrO_2$	—	—	325	84
$t-ZrO_2-S/O_2$	10.5	1.2	290	90
$t-ZrO_2-S(2)/O_2$	11.0	—	262	90
$t-ZrO_2-S/H_2$	10.5	1.0	290	—
$m-ZrO_2$	—	—	300	90
$m-ZrO_2-S/O_2$	9.7	1.0	300	—
$m-ZrO_2-S/H_2$	9.7	1.4	300	—

prior to cooling to reaction temperature and used for the conversion of 2-pentanol.

Samples of zirconium sulfate hydrate (reported to be $ZrOSO_4$ and/or $Zr(SO_4)_2$ by different vendors) were decomposed by heating in air at 923, 973 or 998 K for 4 h. The calcined materials were again heated at 773 K for 4 h prior to cooling to reaction temperature in a flow of dry nitrogen.

2.2. Characterization

A Quantachrome Autosorb 6 instrument was used for nitrogen sorption isotherms measurements. The sample was outgassed at 373 K and < 5 mTorr for at least 8 h. The surface area was calculated using the BET equation [24] and the nitrogen sorption data. X-ray diffraction studies were carried out using a Philips X-ray diffractometer operating at 25 kV, 20 mA and CuK_α ($\lambda = 1.5418$ Å) radiation. Data were collected at a step width of 0.02°, counting 2 s at each step. The sulfate content of the catalysts was determined using a SC-432 sulfur analyzer.

2.3. Reaction studies

2-Octanol reaction was conducted at atmospheric pressure in a fixed bed tubular glass reactor. In each experiment (unless specified otherwise), about 1.0 g of the catalyst sample was accurately weighed and packed in the reactor between two glass wool plugs. The reactor was wrapped with a heating tape connected to a Varian and temperature controller with an indicator. A water cooled condenser was also attached to the bottom of the reactor. The catalyst was pretreated in oxygen or hydrogen at 773 K for 4 h prior to the reaction study. The reactor was then cooled to reaction temperature (493 to 603 K) in a flow of nitrogen. The 2-octanol liquid hour space velocity (LHSV) was varied between 0.32 to 9.7 cc/h. The products were collected at regular intervals of time and analyzed by gas chromatography using a flame ionization detector and a DB5 capillary column.

3. Results and discussions

The conversion of 2-ols, 2-octanol for the present study, provides a number of selectivities in addition to reaction rate to utilize to define the catalyst properties. Thus, the selectivity network illustrated in Scheme 1 provides a description of these selectivities (g = gas phase; a = adsorbed phase):
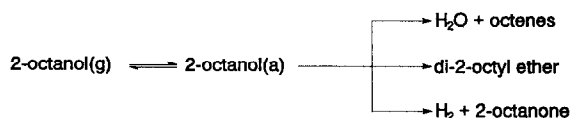
The above scheme is even more complex due to the possibilities of other conversions as outlined in Scheme 1.Thus, this scheme provides the following selectivities:

Dehydration selectivity

$$= S_d = [\text{alkene} + \text{ethers}]$$
$$/[\text{alkene} + \text{ethers} + \text{ketone}]$$

1-octene selectivity

$$= S_1 = 1\text{-octene/total octenes}$$

$$cis\text{-2-octene} = S_c = cis\text{-2-octene}/cis\text{-2-}$$
$$+ trans\text{-2-octene}.$$

Other selectivities, such as ether formation, depend upon total conversion and will not be considered in this paper. Also not included in this presentation is a measure of the extent of secondary conversions such as the isomerization of 1-octene to 2-octene(s) and the cis- to trans-2-octene conversions as well as the conversion of di-2-octyl ether to 2-octanol plus an octene isomer or to two octene isomers plus water.
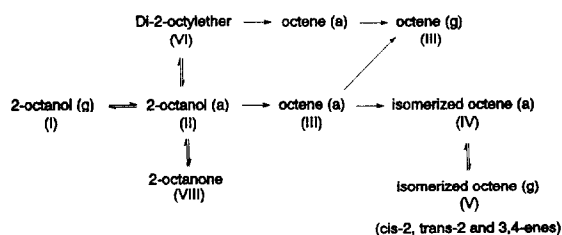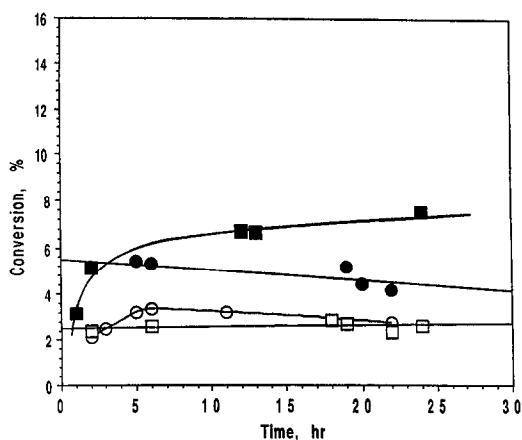

Scheme 1.

Fig. 1. Effect of crystal structure and pretreatment on conversion of 2-octanol on unsulfated zirconia catalyst (– · – = tetragonal oxygen pretreated; – ○ – = tetragonal hydrogen pretreated; – ■ – = monoclinic oxygen pretreated; – □ – = monoclinic hydrogen pretreated). Reaction temperature = 493 K and 2-octanol flow rate = 0.32 cc/h; 0.101 MPa.

Fig. 2. Arrhenius type plot for the dehydration of 2-octanol over zirconia catalysts (– · – and – ○ –, tetragonal sulfated and unsulfated zirconia, respectively; – ■ –, unsulfated monoclinic zirconia catalyst). All the three catalysts are pretreated in oxygen prior to the reaction.

The sulfate containing sample is much more active for the conversion of 2-octanol than the samples that do not contain sulfate. This rapid dehydration rate precludes a determination of whether the small amount of dehydrogenation observed with the unsulfated catalyst is formed with the sulfated sample. Thus, the total conversion of 2-octanol using the unsulfated catalysts (m- or t-ZrO$_2$) is less than about 8% at a
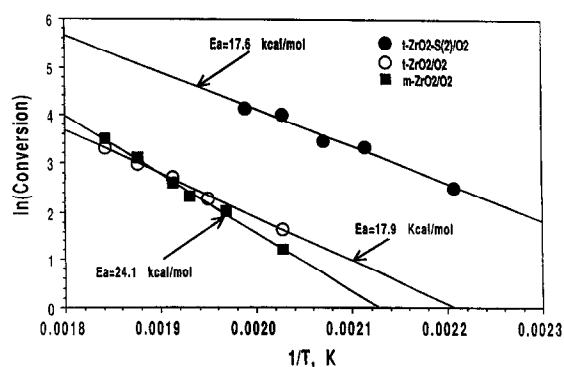
reaction temperature of 493 K and a low flow (LHSV = 0.32 mL/h) (Fig. 1). For the unsulfated samples, the oxygen pretreated catalysts exhibit slightly higher activities for 2-octanol conversion than the corresponding hydrogen pretreated catalyst (Table 2). The activity of the unsulfated catalysts increases, as expected, with increasing reaction temperature (Table 2). The activation energy for the conversion of 2-octanol with the m- and t-ZrO$_2$ catalysts are 24 and 18 kcal/mol, respectively for the reaction temperature range of 493 to 543 K (Fig. 2). The

Table 2
Conversion of 2-octanol over zirconia catalysts (reaction temperature = 493 to 543 K, P = atmospheric and fixed catalyst bed conditions)

Reaction temperature (K)	LHSV [a]	Conversion [b]	Distribution of octenes (mol%)				Octanone (mol%)	Dioctylethers (mol%)
			1-	c-2	t-2	3 and 4		
m-ZrO$_2$, unsulfated and oxygen pretreated								
493	0.32	5.2	80.6	11.7	7.3	0.4	1.7	0.4
513	0.32	9.8	81.4	10.5	7.4	0.7	2.6	0.1
523	0.32	14.7	84.2	8.8	6.5	0.5	4.0	0.2
533	0.32	19.7	76.8	13.8	8.8	0.6	5.0	1.3
543	0.32	27.8	63.1	22.8	12.9	1.2	5.4	2.0
t-ZrO$_2$, unsulfated and oxygen pretreated								
493	0.32	5.2	80.5	7.3	11.5	0.7	1.5	0.4
503	0.32	9.8	81.4	7.4	10.5	0.7	2.3	0.7
513	0.32	14.7	84.2	6.5	8.8	0.5	3.5	1.1
523	0.32	19.5	79.8	7.9	11.7	0.6	4.1	1.6
533	0.32	25.2	72.9	10.2	16.1	0.8	6.2	3.0

[a] Liquid hourly space velocity in cc/h.
[b] Conversion is given for olefins, octanone, dioctylethers and other products.

high activity of the sulfated zirconia required that a smaller amount of catalyst (0.1 g) and lower reaction temperatures be utilized to remain the lower conversions needed for the Arrhenius plot. The activation energy for a sulfated zirconia catalyst (t-ZrO$_2$-S(2)) is 17.6 kcal/mol for the reaction temperature range of 403 to 453 K (Fig. 2). These activation energies are reproducible for these samples; thus, it appears that there is a dependence of the activation energy upon the crystal phase. The value of 24 kcal/mol obtained in this study for m-ZrO$_2$ agrees very closely to the value obtained earlier with a different sample of m-ZrO$_2$ [25]. The activation energies for the sulfated and unsulfated tetragonal zirconia samples are the same, and this is surprising.

The presence of sulfate in the t-ZrO$_2$ sample increases the conversion. The variation of the conversion of 2-octanol with changes in the liquid hourly space velocity (Fig. 3) is typical of that obtained with other alcohol dehydration catalysts (e.g., [26]). The conversions at lower levels correspond to a zero order reaction but they appear to change so as to fit a first order rate at the higher conversion levels. Since alcohol dehydration is a zero order reaction in alcohol pressure at lower conversion levels, the rate constant is comparable to alcohol conversion. Thus, the lines in the Arrhenius plot (Fig. 2) can

Fig. 4. Conversion of 2-octanol with m-ZrO$_2$ (593 K, 0.101 MPa; LHSV = 0.7; 0.5 wt% pyridine added following 50 h, 5% after 74 h).

be extrapolated to a common reaction condition; this shows that the presence of sulfate increases the catalytic activity by a factor of about 100 over that of an unsulfated sample of the same zirconia. While the presence of the sulfate may result in a higher surface area following calcination compared to the similarly treated unsulfated sample ([12]), the difference is seldom greater than a factor of 2 whereas the activity difference is by a factor of about 1,000 (considering the relative conversions and the smaller amount of catalyst used with the sulfated sample). Thus, it is the presence of sulfate, and not a higher surface area, that is responsible for the higher catalytic activity.

An unsulfated zirconia sample (t-ZrO$_2$) is not poisoned when, at 50 h on stream, 0.5 wt% pyridine was added to the charge and then at 74 h on stream the pyridine concentration was increased to 5 wt% (Fig. 4). Thus, it is concluded that either 2-octanol is more strongly adsorbed than pyridine or that the catalytic site for the alcohol dehydration reaction does not strongly adsorb pyridine. Since the 1-octene that is formed as a product of 2-octanol dehydration undergoes isomerization when the 2-octanol conversion is at the 80% level, as it is for the data shown in Fig. 4, it is concluded that it is not the strong adsorption of 2-octanol but rather the very weak, if any, adsorption of pyridine
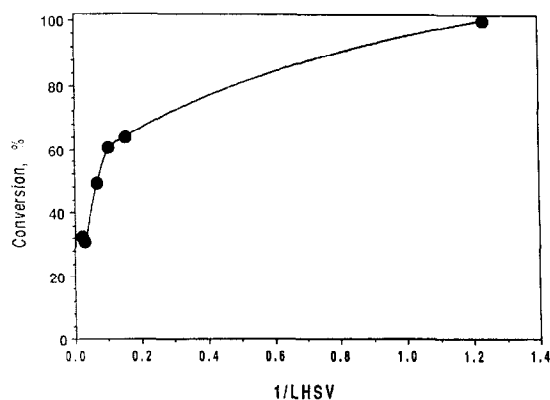

Fig. 3. Effect of liquid hour space velocity on the conversion of 2-octanol over sulfated and oxygen pretreated monoclinic zirconia catalysts. Reaction temperature = 493 K and 2-octanol flow rate = 0.82 to 25 cc/h; 0.101 MPa.
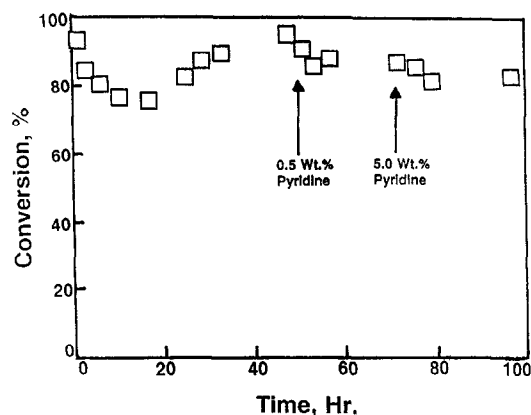
that is illustrated by the data in Fig. 4. It is therefore concluded that, for the sulfate free catalyst, the site responsible for 2-octanol dehydration does not have either strong Lewis or Brønsted acid sites.

The results for the conversion of 2-octanol over a sulfated zirconia are summarized in Fig. 5 and clearly show that the oxygen pretreated sulfated zirconia (monoclinic or tetragonal-zirconia precursors) exhibit such a high activity that the conversion was almost 100% at a reaction temperature of 493 K and a high flow rate (LHSV = 9.7 mL/h). Because of the boiling point of 2-octanol, condensation would likely occur if an attempt was made to operate at temperatures much lower than 493 K; likewise, the ability to maintain the temperature of the catalyst bed and an operable pressure drop across the bed provides an upper limit to the flow rate. With this limitation, it appears that the sulfated m- and t-ZrO_2 catalysts have similar activity for 2-octanol dehydration.

A comparison of the sulfated and unsulfated zirconia catalysts (Tables 2 and 3) shows that the activity of either sulfated zirconia phase catalyst decreases to less than 5% (Fig. 5) when either is treated at 773 K for 4 h in a flow of hydrogen prior to the conversion measurements.

The analyses for the total sulfur content of the used catalysts show that about 1 wt% S remains independent of the crystal phase and whether the pretreatment was in air or hydrogen. Thus, the activity difference following the two pretreatments cannot be due to the total sulfur content of the sample. XPS measurements show that the sulfur present in the surface region remains in the sulfate form when a similar catalyst is treated for up to 80 h in a flow of hydrogen at 423 K ([27]). While it would be hazardous to extrapolate the XPS data obtained at 423 to 773 K to conclude that the surface sulfur remains in the sulfate form, parallel thermal gravimetric and differential thermal analyses combined with mass spectroscopic analysis of the evolved gases suggest that reduction of the sulfate group with the evolution of sulfur occurs at temperatures higher than 773 when the heating rate is 20 K/min ([12]). Thus, it seems likely that the reason for the lower activity following pretreatment in hydrogen is the removal of the small fraction of sulfur on the surface as H_2S. The amount of water needed to poison a similar catalyst is consistent with only a small fraction of the sulfur being located on the surface and available for catalytic activity ([28]).
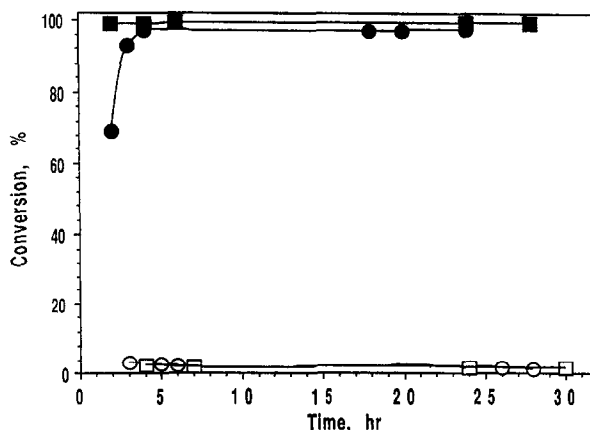

Fig. 5. Effect of crystal structure and pretreatment on the conversion of 2-octanol with sulfated zirconia catalysts (– • –, tetragonal oxygen pretreated; – ○ –, tetragonal hydrogen pretreated; – ■ –, monoclinic oxygen pretreated; – □ –, monoclinic hydrogen pretreated). Reaction temperature, 493 K; flow rate = 0.81 cc/h; 0.101 MPa.

Table 3
Conversion of 2-octanol over sulfated and unsulfated zirconia catalysts (reaction temperature = 493 K, P = atmospheric and fixed catalyst bed conditions)

Catalyst and pretreatment	LHSV [a]	Conversion (mol%) [b]	Distribution of octenes (mol%)				Octanone (mol%)	Dioctylethers, (mol%)	Oligomers (mol%)	Cracking products (mol%)
			1-	c-2	t-2	3 and 4				
t-ZrO$_2$/H$_2$	0.81	2.09	70.7	10.5	18.4	0.4	0.33	0.12	—	—
t-ZrO$_2$/O$_2$	0.32	5.16	80.5	7.3	11.7	0.4	1.70	0.38	—	—
t-ZrO$_2$-S/H$_2$	0.81	4.22	63.8	14.4	19.1	2.6	1.15	0.12	—	—
t-ZrO$_2$-S/O$_2$	9.70	99.8	8.2	32.3	29.1	30.4	0.65	—	—	—
m-ZrO$_2$										
m-ZrO$_2$-H$_2$	0.81	3.9	92.9	2.7	3.4	1.0	0.35	2.30	—	—
m-ZrO$_2$/O$_2$	0.32	6.7	80.6	11.7	7.3	0.4	1.60	0.90	—	—
m-ZrO$_2$-S/H$_2$	0.81	1.8	84.3	5.8	9.0	0.9	0.18	—	—	—
m-ZrO$_2$-S/O$_2$	0.81	99.9	4.2	26.2	13.7	55.9	0.51	—	4.0	traces
m-ZrO$_2$-S/O$_2$	9.70	60.8	46.0	19.1	27.9	7.0	0.82	—	0.8	traces

[a] Liquid hourly space velocity in cc/h.
[b] Conversion is given for olefins, octanone, dioctylethers and other products.

The activity of the materials that resulted from the thermal decomposition of ZrOSO$_4$ at 923, 973 or 998 K all exhibited high conversions (nearly complete conversion at 493 K and 9–10 mL/h 2-octanol). Furthermore, these catalysts appeared to produce essentially an equilibrium, or near equilibrium, mixture of the octene isomers. It therefore appears that the material prepared by the thermal decomposition of the sulfate salt retains a significant amount of the sulfate and resembles sulfated zirconia catalysts.

In order to operate at lower temperatures without condensation of the reactant, 2-pentanol was converted at 413 K using varying space velocities. At low levels of conversion, the reaction appeared to follow zero order kinetics. The catalysts used for this reactant were prepared by loading several portions from a common batch of hydrous zirconium oxide (t-ZrO$_2$) with varying levels of sulfate. The catalysts were activated for 2 h at 773 K in air prior to testing for catalytic activity. These materials, except for the unsulfated material and the catalyst containing 1 wt% sulfate, exhibited high activity at this low reaction temperature. The data illustrated in Fig. 6 show that the lines defining the dependence of conversion upon the sulfate concentration ex-

trapolates to essentially the same level for zero sulfate content, 16 ± 3%. However, both the unsulfated zirconia and the zirconia containing only 1 wt% sulfate produced very low conver-
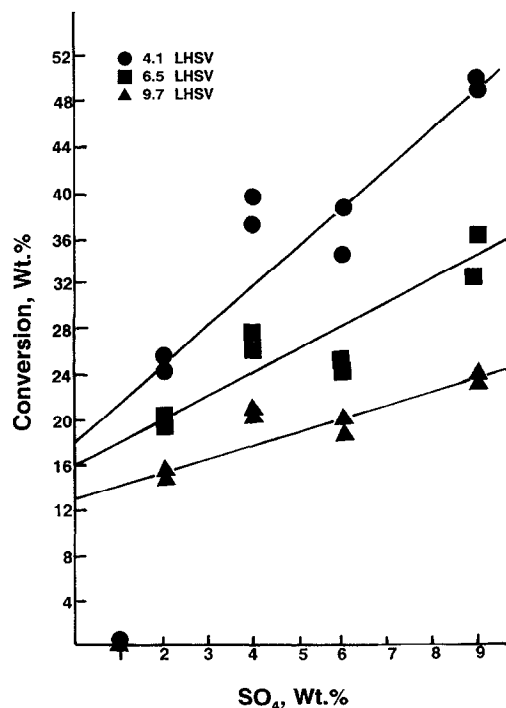

Fig. 6. Conversion of 2-pentanol with sulfated zirconia catalysts (calcined in air at 773 K) at LHSV = 4.1, 6.5 and 9.7 mL/h/g mL, 0.101 MPa, and 413 K.
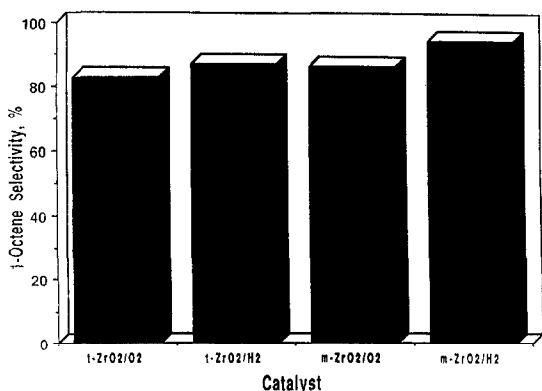
Fig. 7. Effect of crystal structure and pretreatment on the selectivity for 1-octene among octenes over unsulfated zirconia catalyst. Reaction temperature = 493 K; 2-octanol flow rate = 0.32 cc/h; 0.101 MPa.

sions (less than 1%) for the reaction conditions shown in Fig. 6. Thus, those samples containing 2 or higher wt% sulfate exhibit a high catalytic activity relative to the unsulfated material and, furthermore, the activity increases slowly with increasing sulfate concentration (about 2.6% conversion/1% additional sulfate). Thus, the higher concentrations of sulfate appear to exhibit a lower activity than those of the lower (2 wt%) concentration; one explanation for this is that the presence of water allows the hydrolysis of the zirconia-sulfate complex to produce H_2SO_4 that is mobil on the surface. Thus, if the

sulfate was present in sulfuric acid clusters, the surface area of the acid could provide catalytic sites that would increase more slowly than the wt% sulfate. In any event, the sulfate present in the material calcined in air at 773 K appears to differ from that of the material calcined at 923 K or higher.

The selectivity for 1-octene among the octene isomers for the unsulfated zirconia varies from about 80 to 93%. The 1-octene selectivity among the octene isomers of the unsulfated m- or t-ZrO_2 does not strongly depend upon the pretreatment gas (Fig. 7), although the H_2 treatment samples are slightly more selective for 1-octene production. The impact of pretreatment with air or hydrogen is common with other metal oxide catalysts (for example, references [29] and [30]). Thus, an unsulfated zirconia, whether the t- or m-phase, exhibits a selectivity for the formation of the 1-alkene from 2-ols (Fig. 7) that resembles that of thoria [20,21].

While the dehydration selectivity is nearly 100%, the octene selectivities of the sulfated zirconias varies between 75 to essentially 100%. The lower values for octene selectivity are obtained for the air pretreated samples and they are due primarily to the formation of di-2-octyl ether, and minor amounts of oligomers of octenes and cracked products. The hydrogen
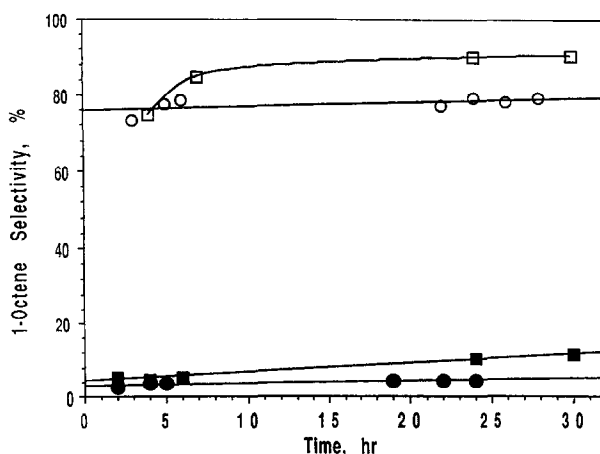

Fig. 8. Effect of crystal structure and pretreatment on % selectivity for 1-octene among octenes on sulfated zirconia catalyst (– • –, t-ZrO_2–S, oxygen pretreated; – ○ –, t-ZrO_2–S, hydrogen pretreated; – ■ –, m-ZrO_2–S oxygen pretreated; – □ –, m-ZrO_2–S, hydrogen pretreated).

pretreated materials are less selective for alkene formation than the air pretreated samples, and this is due primarily to the formation of 2-oc-tanone because of the dehydrogenation activity of this catalyst.

A comparison of the catalytic activity and octene isomer distributions for the oxygen pre-treated sulfated and unsulfated catalysts clearly show that incorporation of the sulfate greatly increases the catalytic activity and dramatically decreases the 1-octene selectivity. The former selectivity for the oxygen pretreated sulfated zirconia catalysts is less than 10%, a value close to that expected for equilibration among the octene isomers (Figs. 8 and 9). In contrast, the 1-octene selectivity is in the range of 80 to 90% for the hydrogen pretreated sulfated t- and m-ZrO_2–S catalysts (Figs. 8 and 9). Thus, the selectivity of the hydrogen pretreated sulfated zirconia catalysts approaches or equals the se-lective formation of 1-octene that was observed with the hydrogen pretreated unsulfated zirconia samples. This latter observation is in agreement with the hydrogen pretreatment at 773 K remov-ing sulfur from the surface.

The unsulfated zirconia catalysts produce about 80% or greater of 1-octene, 20% or less of cis- plus trans-2-octene, and less than 1% of the (3- + 4-)-octene isomers; about equal amounts of the cis- and trans-2-octene isomers
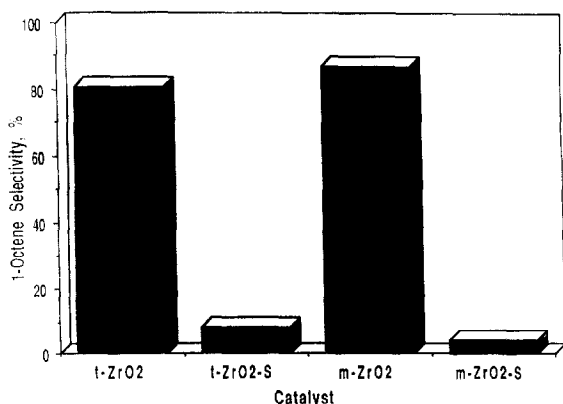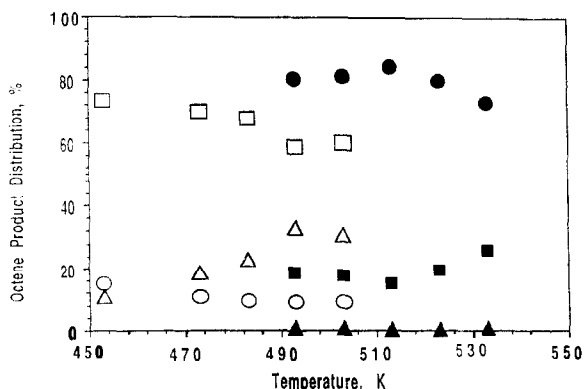

Fig. 10. Effect of reaction temperature and sulfate addition on the distribution of octenes during the conversion of 2-octanol over tetragonal zirconia catalysts (filled and open symbols represent the unsulfated and sulfated zirconia catalysts, respectively; – • – and – ○ –, 1-octene; – ■ – and – □ –, cis- and trans-2-octenes; – ▲ – and – △ –. 3 and 4-octenes).

are formed. Furthermore, for the unsulfated zir-conia catalysts the octene distribution is nearly independent of temperature within the range used in this study (Fig. 10). However, there may be a slight decrease in the 1-octene selectivity above a temperature of about 523 K, and a corresponding increase in the 2-octene isomers. The octene distributions obtained at higher con-versions are not considered because of sec-ondary reactions. The octene distributions ob-tained in Table 4 with the sulfated and oxygen pretreated samples are markedly different: 9 to 15% 1-octene, 60 to 73% (cis- + trans-)-2-octenes, and 11 to 33% (3- + 4-)-octenes over the temperature range of 453 to 503 K. The distribution of octene isomers, considering only the 1- and 2-isomers, is at, or nearly at, the one expected for an equilibrium distribution. On the other hand, the 3- and 4-octene isomers are present in concentrations considerably lower than the equilibrium value. Thus, it appears that the initial alkene products are limited to the 1- and 2-isomers, and that the 3- plus 4-octenes are formed solely, or predominantly, during sec-ondary isomerization reactions. This observa-tion is consistent with the view that with the oxygen pretreated sulfated zirconia catalysts, the primary octene isomeric products are formed

Fig. 9. Percent selectivity of 1-octene among octenes for the sulfated and unsulfated t- and m-ZrO_2 catalysts pretreated in oxygen flow.

Table 4

Effect of reaction temperature on the conversion of 2-octanol over sulfated and oxygen pretreated tetragonal zirconia catalyst (reaction temperature = 453 to 503 K, catalyst weight = 0.10 g, LHSV = 6.5 [a] and P = atmospheric)

Reaction temperature (K)	Conversion (mol%) [b]	Distribution of octenes (mol%)				Dehydration Sel (mol%) [c]	Dioctylethers (mol%)	Oligomers (mol%)	Cracking products (mol%)
		1-	c-2	t-2	3 and 4				
t-ZrO$_2$–S(2)/O$_2$									
453	16.3	15.2	43.5	30.1	11.0	98.8	0.12	0.6	0.1
473	27.9	10.8	38.1	32.2	18.7	99.4	0.54	0.5	traces
483	34.4	9.4	36.2	31.6	22.8	99.1	0.48	0.8	0.1
493	55.0	9.1	28.5	30.3	33.1	98.5	0.42	0.9	0.3
503	62.8	8.9	32.1	28.2	30.7	98.5	0.42	1.0	0.5

[a] Liquid hourly space velocity in cc/h.
[b] Conversion is given for olefins, octanone, dioctylethers and other products.
[c] Defined as % moles of octenes plus dioctyl ethers formed * 100/% 2-octanol converted.

from a common intermediate whose stability is determined by those factors that determine the stability of the isomeric octene products. This view is the same as is commonly held for the homogeneously catalyzed dehydration of 2-ols by sulfuric acid; here the view is commonly held that the intermediate is a carbenium ion.

4. Conclusions

Zirconia catalysts exhibit a range of catalytic activities and selectivities towards 2-octanol conversion that depends upon the zirconia, the sulfate content and the catalyst pretreatment. Unsulfated zirconia is both a selective dehydration catalyst and a selective catalyst for the production of the 1-alkene from 2-ols. Sulfated zirconia that has been activated by heating only to about 773 K exhibits a selectivity and activity towards the conversion of 2-pentanol that resembles that expected for sulfuric acid acting as a homogeneous Brønsted acid catalyst. When the sulfated zirconia catalyst is activated in air at a higher temperature (923 K or higher) or when a catalyst is prepared by heating ZrOSO$_4$ in air, the material exhibits high activity for alcohol dehydration and an octene distribution that is consistent with a reaction mechanism that involves a carbenium ion (or ion-like) reaction intermediate. Heating a sulfated zirconia at 773

K in hydrogen at 0.101 MPa for 4 h leads to a material that resembles an unsulfided zirconia that has undergone a similar treatment.

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