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Characterization of various zinc oxide catalysts and their activity in the dehydration–dehydrogenation of isobutanol

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Abstract: Mono and bifunctional zinc oxide catalysts were prepared to study their activity in the catalytic conversion of isobutanol. The prepared catalysts were characterized by X-ray diffraction analysis and nitrogen adsorption measurements. The conversion of isobutanol was taken as a model reaction to measure the catalytic activity of the prepared oxide catalysts. The overall conversion yield of competitive dehydration–dehydrogenation reactions of isobutanol was found to be higher over the binary oxide catalysts than over the single oxide one at all reaction temperature within the range 250–400 °C. The binary oxide catalysts were more selective for isobutene, as the predominant dehydrated product. The single oxide catalyst exhibited higher selectivity towards isobutyraldehyde as the dehydrogenated product, and the selectivity increased with increasing reaction temperature.

Keywords: metal oxides; acid–base catalysis; isobutanol conversion.

INTRODUCTION

Recently the United States Environmental Protection Agency announced a proposal to reduce the permissible lead level in U.S. leaded gasoline by 91 %. The importance of dehydration of higher alcohols, more than C₂, lies in the preparation of isobutene, which is one of the radiant for the production of gasoline octane enhancers. In addition, intermediate compounds for fine chemical industries, as 1,2-diphenylethanol, are produced.

Macho *et al.*¹ used alumina in the dehydration of C₄ alcohols whereby positional and skeletal isomerization of formed C₄ alkenes occurred in a fixed bed reactor operated under atmospheric pressure and at moderate reaction temperatures 300–470 °C.

Mixed oxides, such as ZrO₂/SiO₂^{2,3} or ZnO/Al₂O₃, modified with 23 ppm lithium, of different compositions were prepared by the sol–gel method.⁴ The catalysts exhibited high catalytic activity towards isopropanol dehydration, with a

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selectivity of 100 %. Vaidya *et al.*⁵ studied the dehydration of 1,4-butanediol to tetrahydrofuran using a strong acid cation exchange resin as the catalyst and found that the produced water adsorbed on the active resin inhibited the dehydration reaction.

Catalysts based on Keggin-type heteropoly acids supported on silica and tubular ceramic silica membrane^{6,7} were used for the dehydration of alcohol.

A series of metal phosphates (Al, Fe, Ni and Mn) were prepared by the ammonia gelation method and used in the competitive dehydration–dehydrogenation reaction of cyclohexanol. The results proved that the dehydration was realized not only on acid sites, but also on basic sites.⁸

The objective of this work was to study the structural phase changes accompanying the preparation of zinc oxide and binary zinc oxide catalysts. The catalytic behavior of the prepared zinc oxide catalyst and the role of adding TiO₂ and Cr₂O₃ on the performance of zinc oxide catalyst towards the isobutanol conversion reaction were studied.

EXPERIMENTAL

Preparation of the catalysts

Three different oxide catalysts: zinc oxide, zinc oxide–titanium oxide and zinc oxide–chromium oxide, all mixed with bentonite, were prepared.

The zinc oxide–bentonite catalyst (Z) was prepared by mixing an equal weight ratio of zinc oxide and acid activated bentonite (activated with 2 % HCl).

The zinc oxide–titanium oxide–bentonite catalyst (ZT) was prepared by mixing zinc oxide, titanium oxide and acid-activated bentonite at a weight ratio of 1.5:1:2.5, respectively, whereas the zinc oxide–chromium oxide–bentonite catalyst (ZC) was prepared *via* the mixing of hydrated chromium oxide (freshly precipitated from an aqueous solution of chromium chloride using an ammonia solution with subsequent washing and drying) with zinc oxide and acid activated bentonite at a weight ratio 1.5:1:2.5, respectively.

The prepared catalysts were dried at 120 °C for two hours with continuous agitation and then ground to mesh size 0.16 mm. Subsequently, the catalysts were calcined at a temperature of 750 °C for 12 h in presence of purified dry air to produce Z*, ZT* and ZC*.

Catalysts characterization

The structural changes of the prepared catalysts (zinc oxide, zinc oxide–titanium oxide and zinc oxide–chromium oxide–bentonite) were investigated by X-ray diffraction analysis (XRD) using a Shimadzu XD-D1-X-ray diffraction apparatus, equipped with a monochromator for CuK α radiation to determine their crystallization behavior. The apparatus was provided with a software program which allowed the changes in the crystallite size of the mono- and bi-metal oxide catalysts to be determined.

Nitrogen adsorption–desorption measurements were conducted at –196 °C using a Quantachrome Nova 2000 instrument. The samples were out-gassed (10^{–4} Pa) at 300 °C and the surface areas were calculated from the adsorption curves by the BET method.

Catalytic activity

The conversion reaction of isobutanol was taken as a model reaction for measuring the catalytic activity of the prepared catalysts. The isobutanol catalytic reaction was performed in

a pulse micro-catalytic reactor operated under atmospheric pressure at reaction temperatures ranging from 250–400 °C. The micro-reactor (diameter = 0.20 mm and length = 15 cm) was charged with 500 mg of dried catalyst. A 2.0 μl dose of isobutanol was injected into a nitrogen stream flowing continuously down the catalyst bed at a rate of 40 ml min^{-1} . The reaction outputs were immediately analyzed by flame ionization detector (FID) through a chromatographic column (silicon oil-550) directly attached to the reactor. The column was packed with chromosorb b of 80–100 mesh size.

RESULTS AND DISCUSSION

Catalysts characterization

X-ray diffraction analysis. The X-ray diffraction patterns for all the prepared catalysts are presented in Figs. 1–3. The diffraction pattern for acid-activated bentonite reveals the appearance of sharp and high intensity diffraction lines, characteristic for bentonite material (ASTM 03-0010).

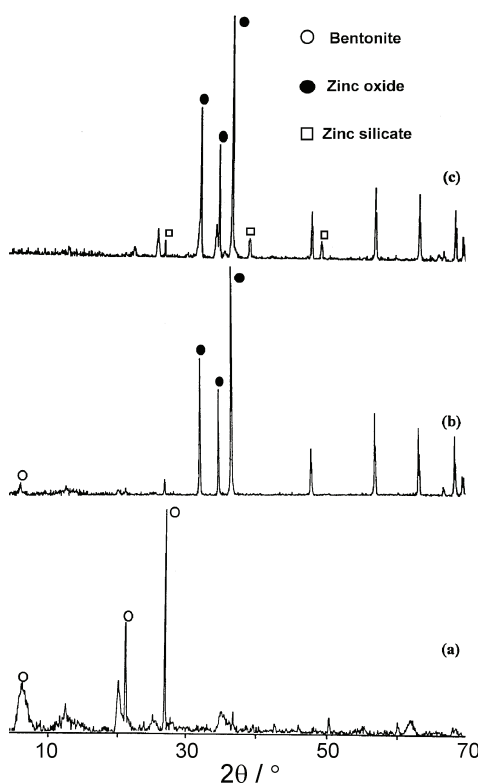


Fig. 1. X-Ray diffraction patterns for (a) bentonite, (b) Z- and (c) Z*-catalyst.

For the Z-catalyst (Fig. 1b), new diffraction lines with high intensity appeared which are characteristic for the ZnO phase (ASTM 05-0664). In addition, the lamella line of the bentonite was shifted to the left (to a higher d -spacing), which evidenced the penetration of ZnO to inside the bentonite lamella resulting in this expansion. The diffraction pattern for the calcined Z-catalyst, Z* (Fig. 1c), showed

the presence of a zinc silicate phase, according to ASTM (79-2005). The formation of zinc silicate actually arose from the interaction of zincite (a defected form of calcined ZnO which has the ability to trap electrons) with the bentonite structure during the calcination step at 750 °C.⁹

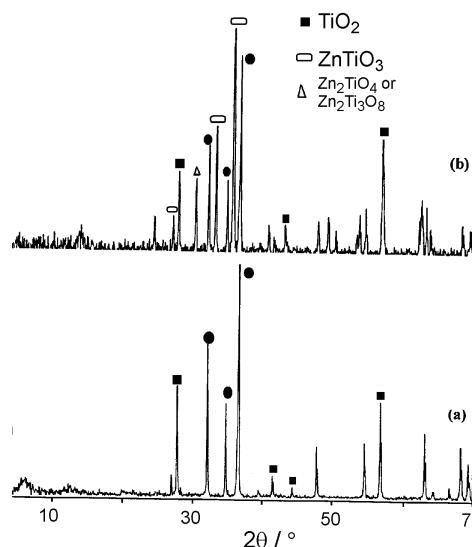


Fig. 2. X-Ray diffraction pattern for: (a) ZT- and (b) ZT*-catalysts.

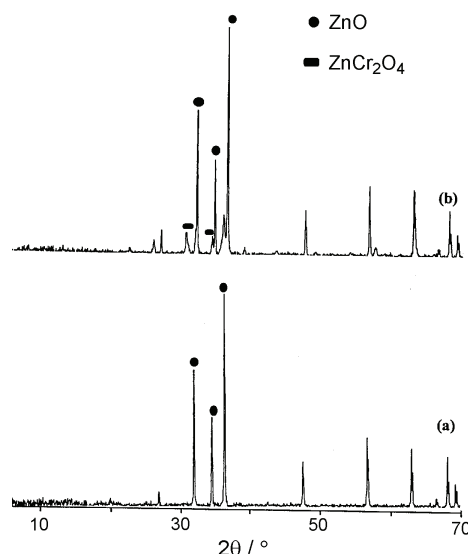


Fig. 3. X-ray diffraction pattern for: (a) ZC- and (b) ZC*-catalysts.

The diffractogram for the ZT catalyst (Fig. 2a) evidenced the presence of the anatase form of TiO_2 (ASTM 09-0240),¹⁰ in addition to the characteristic ZnO lines. The characteristic bentonite lines were still visible but with a low intensity, which indicates the insertion of both ZnO and TiO_2 into the bentonite lamella.

For the calcined ZT-catalyst, ZT* (Fig. 2b), new phases were detected, *i.e.*, the spinel crystalline structure Zn_2TiO_4 and/or the cubic $\text{Zn}_2\text{Ti}_3\text{O}_8$ (ASTM 13-0471), besides the hexagonal-coordinated ZnTiO_3 (ASTM 15-0591).

The X-ray diffraction pattern for the ZC-catalyst (Fig. 3a) revealed the disappearance of the main characteristic bentonite lines and a significant decrease in the intensity of the main ZnO lines. This indicates that the Cr_2O_3 particles may block the bentonite lamella and are probably trapped in the ZnO lattice.

For the calcined ZC-catalyst, ZC*, the intensity of the main ZnO lines sharply increased, in addition to the appearance of new lines at 2θ angles: 29.9 and 36.5° (Fig. 3b), which are related to the formation of the spinel crystalline structure ZnCr_2O_4 which favors catalyst dispersion.¹¹

Crystallite size. The crystallite sizes for bentonite, as well as for the prepared and calcined catalysts, are summarized in Table I.

The data for the Z-catalyst shows that the calculated crystallite size decreased from 27.5 to 17.1 nm on mixing ZnO with bentonite. This result suggests the

dispersion of ZnO particles into the bentonite lamella, in agreement with XRD data. Moreover, the interaction of the Z-catalyst with titanium oxide caused a decrease in the crystallite size, confirming that the TiO₂ species preserved the high dispersion of the ZnO particles and preventing them from growing. The reverse was the case after mixing the Z-catalyst with chromium oxide, *i.e.*, an increase in crystallite size was observed, indicating that the chromium oxide crystallites were larger than the titanium dioxide ones.

TABLE I. Crystallite size, nm, for the studied calcined catalysts

Position, Å	Bentonite	Z	Z*	ZT	ZT*	ZC	ZC*
14.46	27.5	17.1	—	9.1	—	—	—
3.33	179.5	141.3	—	157.3	—	193.1	—
2.60	—	199.1	180.5	151.1	227.5	203.9	261.8

The calcinations of the Z-catalyst (Z*) resulted in a decrease in the crystallite size, which is an indication for the formation of smaller "zinc silicate" crystallites, as verified by X-ray diffraction analysis.

The crystallite size increased, however, after calcination of the ZT and ZC catalysts (ZT* and ZC*). This increase is due to the formation of zinc, titanium and chromium binary oxides upon calcination, which may have larger crystallite sizes.

Nitrogen adsorption technique. The different surface characteristics, *i.e.*, specific surface area (S_{BET}), total pore volume (V_{p}) and average pore radius (r_{H}), for the studied calcined catalysts were determined from nitrogen adsorption isotherms conducted at -196°C and the results are given in Table II.

TABLE II. Surface properties of the studied calcined catalysts

Catalyst	$S_{\text{BET}} / \text{m}^2 \text{g}^{-1}$	$V_{\text{p}} / \text{ml g}^{-1}$	$r_{\text{H}} / \text{\AA}$
Z*	6.8	0.0056	16.5
ZT*	10.6	0.0090	17.0
ZC*	10.4	0.0086	16.5

The BET surface area for the Z*-catalyst increased from 6.8 to $\approx 10.5 \text{ m}^2 \text{g}^{-1}$ upon interaction of the zinc catalyst with chromium or titanium oxide, which resulted from the repulsive forces induced by the anionic sites "O" that aided in the dispersion of the particles and consequently the surface area increased.¹² Moreover, the increase in the surface area was accompanied with an increase in the pore volume without an increase in the pore radius (Table II), confirming the intrusion of chromium and titanium oxide phases inside the zinc oxide pores.

Catalytic activity

The catalytic activity and selectivity of the prepared catalysts in the competitive dehydration–dehydrogenation reaction of isobutanol were investigated at reaction temperatures in the range from 250–400 $^{\circ}\text{C}$. The data is illustrated graphically in Fig. 4.

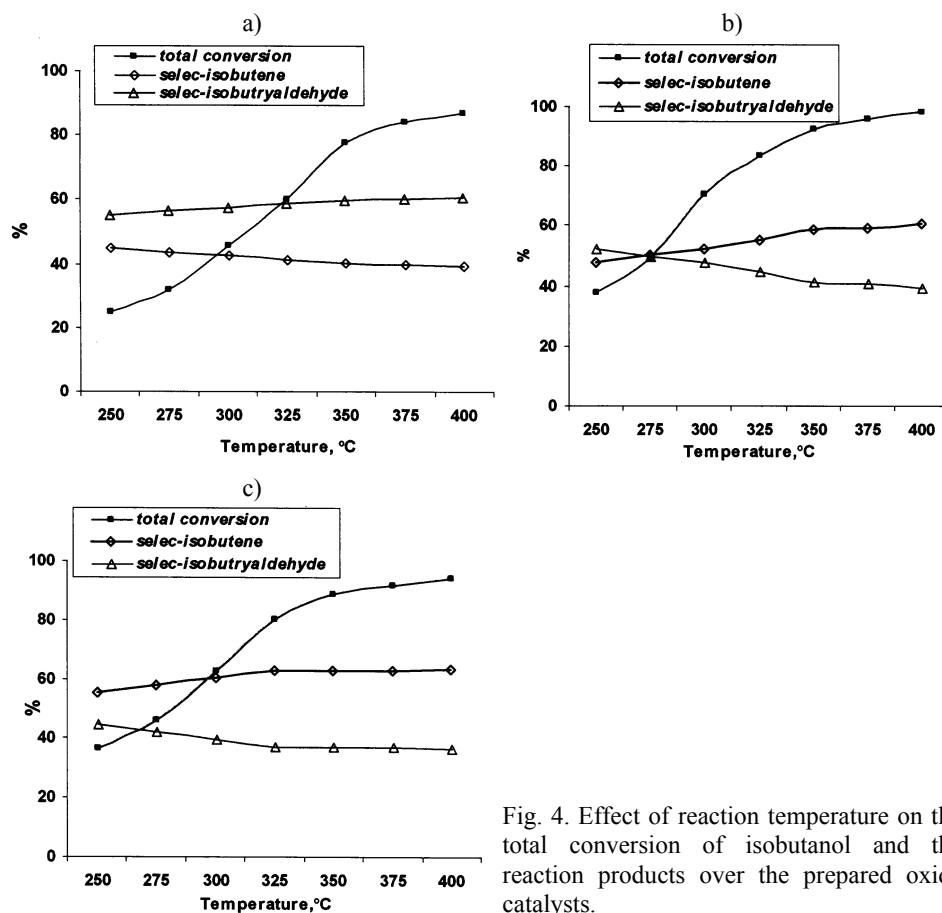


Fig. 4. Effect of reaction temperature on the total conversion of isobutanol and the reaction products over the prepared oxide catalysts.

For all the oxide catalysts, the total conversion increased continuously with increasing reaction temperature. Furthermore, the binary oxide catalysts (ZT* and ZC*) exhibited a higher conversion at all reaction temperatures, reaching near complete conversion at 400 °C compared with the zinc oxide catalyst (Z*).

The converted products mainly consisted of isobutene, as the dehydrated product, and isobutyraldehyde, as the dehydrogenated product. The yield of isobutene over all catalysts increased gradually with increasing reaction temperature, whereas considerable higher values were observed over the binary oxide (ZC* and ZT*) catalysts than over the zinc oxide catalyst (Fig. 4).

Meanwhile, the yield of isobutyraldehyde was similar at lower reaction temperatures, while drastic increase in the yield was obtained using the Z* catalyst. The difference in the activity of zinc oxide and binary oxide catalysts seems to depend on the surface electronegative character of each catalyst. The effect of surface electro-negativity on the activity was interpreted in term of the relative abundance of basic and acidic sites required for the chain growth pathway.¹³

Metal oxides are composed of a metal and oxygen and are consequently characterized by an almost ionic bond. The coordination of ions at an ideal surface is, by necessity, incomplete with respect to the bulk.¹⁴ Thus, the partially uncoordinated metal cations and oxide anions lying at the surface of metal oxide crystals can act as acids and bases, respectively. Hence, Lewis acid sites (coordinatively unsaturated cations) and basic sites are expected and found at ionic metal oxides. These coordinatively unsaturated cations exposed at the surface of ionic oxide can, consequently, interact with basic molecules forming a new coordination bond, thus completing or increasing the overall coordination at the surface cations.

Accordingly, the highest conversion of isobutanol was obtained with ZT* then ZC* and finally Z*, which could be attributed mainly to the difference in the acid–base feature of each oxide catalyst taking into account the incorporation of highly electronegative cations "Lewis acids", such as Ti^{4+} and Cr^{3+} . A highly Lewis acidic surface enhances the approach of basic reactants to the active site and consequently strong Lewis interaction with metal cations. Thus, the moderately reducible oxide catalyst (Z*) exhibits a lower conversion than the mixed oxide catalysts (Fig. 4).

Hence, the high activity of all the prepared oxide catalysts with increasing reaction temperature could be explained based on redox mechanisms.

On the other hand, the polarizing power (charge to ionic radii ratio) may also affect the overall conversion rate. The stronger are the polarizing power of an acidic Lewis cation and the basic strength of an adsorbate, the stronger is the Lewis interaction, *i.e.*, the greater is the Lewis strength of the surface sites. Thus, incorporation of Ti^{4+} and Cr^{3+} , which have a polarizing power of 6.6 and 4.9, respectively, should enhance the Lewis interaction with isobutanol molecules, compared with Zn^{2+} which has a polarizing power of 3.3.¹⁵

Consequently, the considerable increase in the yield of isobutene over the binary oxide catalysts comparing with the single oxide catalyst (Fig. 4) may be attributed to the additional Lewis acidity arising from the presence of Cr^{3+} or Ti^{4+} on the oxide surface, which is expected to enhance the dehydration reaction.

Meanwhile, the observed divergence in the yield of isobutyraldehyde at higher reaction temperatures (350–400 °C) in the ranking $\text{Z}^* > \text{ZT}^* > \text{ZC}^*$ (Fig. 4) could be explained on the basis of the reducing character on the surface of the catalysts. The lower density of exposed oxidizing centers (Lewis sites) on the surface of the ZnO catalyst compared with the binary oxides (ZT* and ZC*) and enrichment with oxygen anions seems to be responsible for the suppression of the dehydration reaction and the enhancement of the abstraction of the more acidic α -H from the alkoxy intermediates (see reaction mechanism), which gives rise to the abrupt increase in the yield of isobutyraldehyde.

On the other hand, the selectivity of the prepared oxide catalysts towards both dehydration (isobutene) and dehydrogenation (isobutyraldehyde) products

as represented by the histograms shown in Fig. 5, revealed that the selectivity to isobutene formation is greatly enhanced over the binary oxide catalysts (ZC* and ZT*), indicating a significant increase at higher reaction temperatures (350–400 °C). Moreover, the catalyst ZC* exhibited higher and relatively similar values of isobutene selectivity in comparison with the ZT* catalyst. Conversely, the Z* catalyst showed the highest selectivity to isobutyraldehyde formation, which was constant at all reaction temperatures. The selectivity of the binary oxide catalysts decreased gradually with increasing reaction temperature, revealing a higher selectivity to isobutyraldehyde formation over the ZT* catalyst.

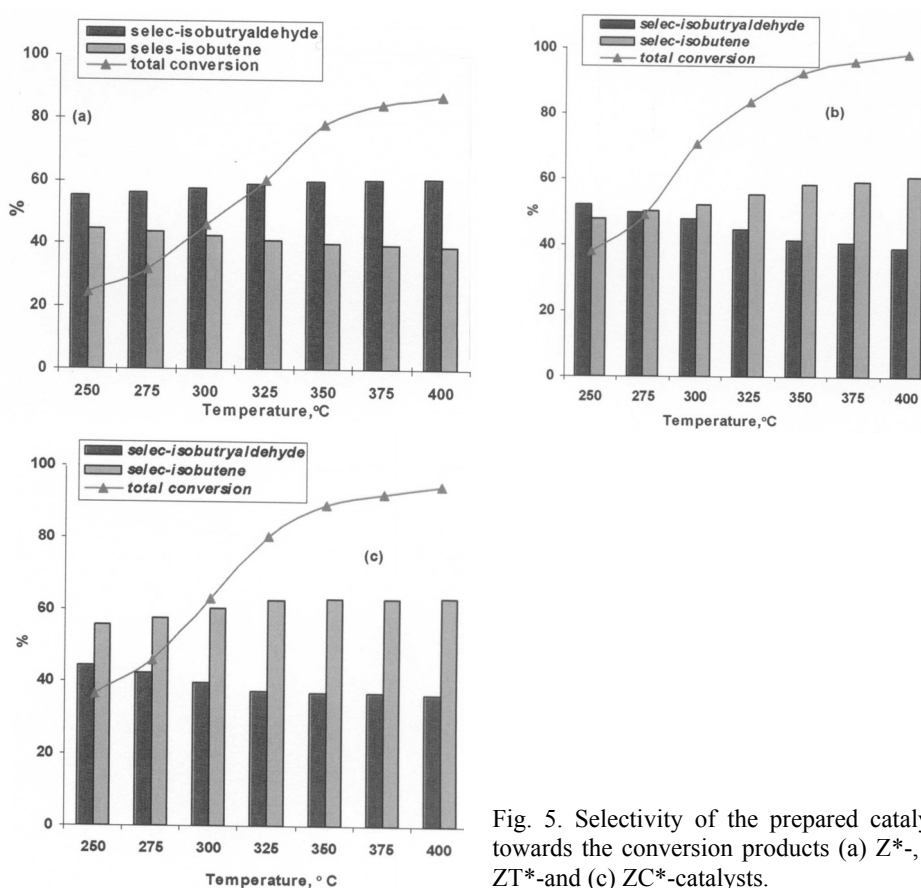
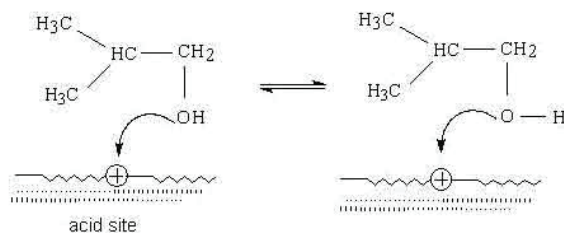


Fig. 5. Selectivity of the prepared catalysts towards the conversion products (a) Z*-, (b) ZT*-and (c) ZC*-catalysts.

The reversible selectivity trends for the prepared mono and binary oxide catalysts may be expressed due to a low oxygen supply resulting from the lower reduction potential of the Ti and Cr species (*i.e.*, a high attraction to oxygen), which limited the dehydrogenation reaction and enhanced the concerted attack by isobutanol molecules through Lewis acid–Brönsted base pair site ($T^{4+}O^{2-}$ and $Cr^{3+}O^{2-}$) of balanced strength.

However, dehydration is always developed in any solid in a concerted way but separately in every acid or base site (Figs. 6 and 7) through two steps of adsorption and desorption.^{16–18}

Adsorption Step



Concerted desorption step

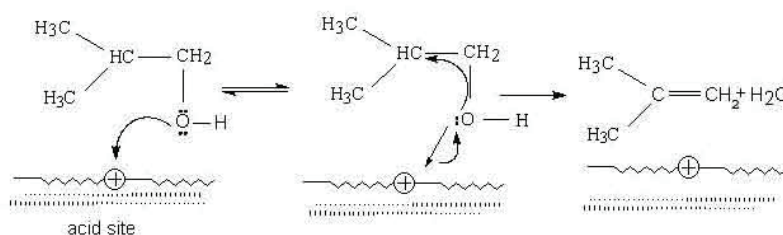
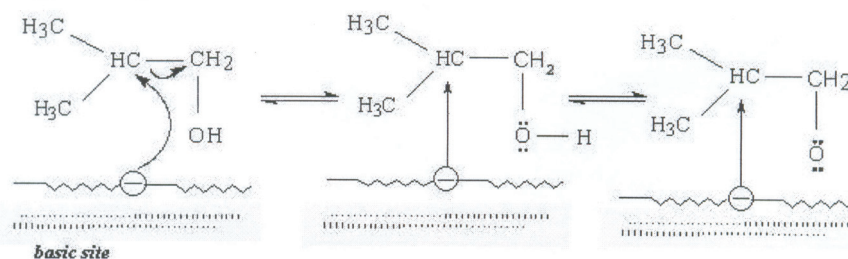


Fig. 6. Reaction mechanism of isobutanol dehydration to isobutene on surface acid sites *via* the concerted mechanism.

Adsorption step



Concerted desorption step

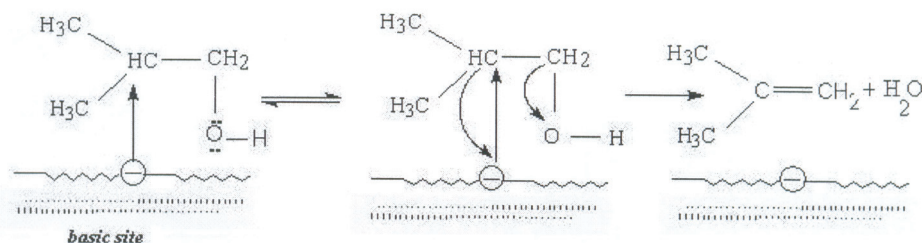
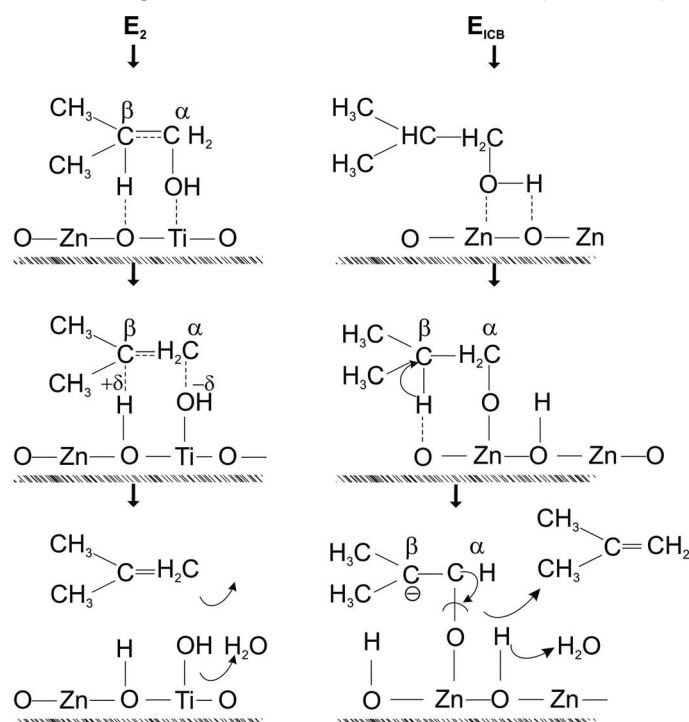


Fig. 7. Reaction mechanism of isobutanol dehydration on a basic site *via* the concerted mechanism.

Reaction mechanism of isobutanol conversion

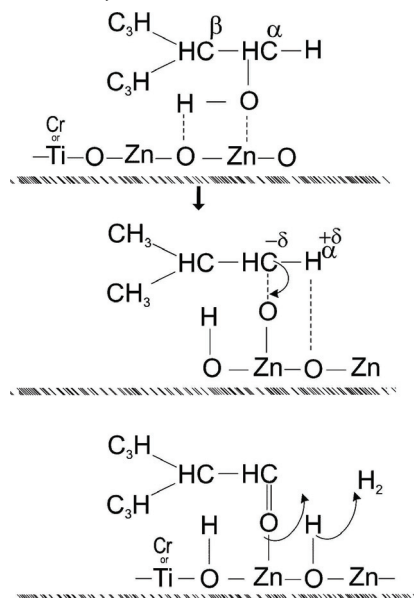
From a general point of view, dehydration of an alcohol to an olefin on single oxide and binary oxide catalysts can proceed through two different elimination mechanisms, E_{ICB} and E_2 .

Accordingly, the dehydration of isobutanol on the prepared metal oxide catalysts can proceed through the two-elimination mechanisms, E_{ICB} and E_2 , as shown in Scheme 1.¹⁹ The E_{ICB} pathway involves a surface alkoxy intermediate on both a strongly basic site and a weak Lewis acid site ($\text{Zn}^{2+}\text{O}^{2-}$ pairs). Formation of the olefin takes place by β -H elimination from the carbanion intermediate. Thus, ZnO contains strong basic sites consisting of O^{2-} anions, which catalyze alcohol dehydration to olefin *via* the E_{ICB} pathway. In contrast, the E_2 elimination is a single-step, concerted mechanism in which the OH group and β -H are simultaneously abstracted by a Lewis acid–Brønsted base pair site of balanced strength, such as $\text{Ti}^{4+}\text{O}^{2-}$ and $\text{Cr}^{3+}\text{O}^{2-}$ pairs. This mechanism leads to the formation of an olefin without the involvement of an ionic intermediate.¹⁹ The incorporation of more electronegative cations (Ti^{4+} and Cr^{3+}) increases the density and strength of the acid sites and thus decreases the activation energy of β -H abstraction.²⁰ Therefore, isobutanol dehydration on mixed oxide catalysts is more likely to proceed through the E_2 elimination mechanism (Scheme 1).



Scheme 1. Mechanism of isobutene formation.

Dehydrogenation of an alcohol to an aldehyde is a typical base catalyzed reaction, Scheme 2.^{21,22}



Scheme 2. Mechanism of isobutyraldehyde formation.

Weak Lewis acid–strong Brönsted base site pairs ($\text{Zn}^{2+}\text{O}^{2-}$) with strongly basic oxygen play an important role because they are required for hydrogen abstraction leading to an alkoxy intermediate. Dehydrogenation commences with alcohol chemisorption on $\text{Zn}^{2+}\text{O}^{2-}$ site pairs which cleavage the OH bond to form a surface alkoxy intermediate bound to a Zn^{2+} acid center. The α -hydrogen in the alkoxy group is abstracted by a neighboring basic site in order to form adsorbed aldehyde. Thus, the formation of isobutyraldehyde by isobutanol dehydrogenation prevails on a basic oxide.

However, samples which have Ti or Cr surface enrichment are suggested to provide additional Lewis centers which may stabilize the alkoxy intermediates; hence Ti–O–Zn and Cr–O–Zn species may be particularly effective and abundant sites for dehydrogenation. Moreover, benefit from the presence of these species is suggested to be enhancement of H₂ dissociation and O–H or C–H activation during the dehydrogenation of isobutanol.²³

CONCLUSIONS

From the previous discussion, it may be concluded that the catalytic dehydrogenation reaction of isobutanol to isobutene, in addition to its eminent practical interest, can be employed as a reaction model for the characterization of a solid acid base catalyst, but taking into account the dehydration reaction proceeds not only on acid sites but also on basic ones and that isobutyraldehyde, obtained through the dehydrogenation reaction, requires additional redox ability not necessary associated to basic sites.

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ИЗВОД

КАРАКТЕРИЗАЦИЈА РАЗНИХ ЦИНК-ОКСИДНИХ КАТАЛИЗАТОРА И ЊИХОВА АКТИВНОСТ ЗА ДЕХИДРАТАЦИЈУ–ДЕХИДРОГЕНАЦИЈУ ИЗОБУТАНОЛА

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Синтетисани су моно и бифункционални цинк-оксидни катализатори за потребе испитивања каталитичке конверзије изобутанола. Добијени катализатори окарактерисани су дифракцијом x -зрака и методом адсорпције азота. Реакција конверзије изобутанола узета је као модел реакција за испитивање каталитичке активности добијених оксидних катализатора. Утврђено је да је укупан принос конверзије у реакцији дехидратације/дехидрогенације изобутанола већи на катализатору од бинарног оксида него на катализатору од појединачног оксида при температурама у опсегу 250–400 °C. Катализатор од бинарног оксида је селективнији у случају изобутена као преовлађујућег производа дехидратације. Катализатор од појединачног оксида је селективнији у случају реакције дехидрогенације са изобутиралдехидом као производом реакције, а селективност се побољшава са порастом температуре реакције.

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