Surface properties and catalytic activity of TiO_2–ZrO_2 mixed oxides in dehydration of methanol to dimethyl ether

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A series of TiO_2–ZrO_2 mixed oxides with varying molar ratio of TiO_2 to ZrO_2 were prepared by the co-precipitation method. The crystalline phases of the oxides were characterized by XRD and their acid–base properties by TPD of NH_3 and CO_2 and IR of adsorbed pyridine. The catalytic activities were investigated for the vapor phase dehydration of methanol to dimethyl ether (DME) in a fixed-bed reactor under atmospheric pressure. The mixed oxides are highly amorphous in nature. The acid–base properties and CH_3OH conversion activity are increasing with TiO_2 content and an optimum value is achieved for a molar ratio of Ti/Zr in the vicinity of 1/1. At lower reaction temperature (< 300 °C), the selectivity for DME is nearly 100%. A good correlation is observed between dehydration activity and the acid–base properties of the TiO_2–ZrO_2 catalysts. It is significant to note that TiO_2–ZrO_2 catalysts show high stability against water during dehydration reaction. Based on our results, a surface mechanism involving both acid–base sites has been proposed for DME formation.

KEY WORDS: acid–base properties; dehydration; dimethyl ether; TiO_2–ZrO_2.

1. Introduction

Vapor phase dehydration of methanol is industrially important for the production of dimethyl ether (DME). With stringent environmental regulations, a clean alternate fuel has become a necessity. DME has received a world-wide attention as a clean alternative fuel for diesel engines since it has a thermal efficiency equivalent to the traditional diesel fuel, lower NO_x emission, lesser carbon particulates, near-zero smoke and lesser engine noise [1,2]. In addition, DME is also used as an intermediate for the preparation of many important value-added chemicals [3,4].

Several solid acid catalysts like Al_2O_3, modified-Al_2O_3 and zeolites, have been studied for the title reaction [5–8]. Commercially, γ-Al_2O_3 is used to a large extent. Though Al_2O_3 is very active, it tends to adsorb water on its surface and thereby loses its activity in the presence of water because of its hydrophilic nature. Also, water, one of the products during methanol dehydration reaction, competes strongly with methanol for the same active sites, as shown in equation (1) [6,9–12].

$$2CH_3OH \,\Delta\, CH_3\text{–}O\text{–}CH_3 + H_2O \qquad (1)$$

Apart from Al_2O_3, zeolites were also tested under similar reaction conditions [5]. It is well known that the strong acidic sites on zeolites promote the formation of secondary products like hydrocarbons. Modified H-ZSM-5 with suitable metal cations improved the dehydration activity as well as the selectivity for DME by preventing the formation of hydrocarbons [13].

There is still a constant search for the development of novel catalysts for DME synthesis showing better performance in terms of activity, higher selectivity and most importantly stability towards water. In this regard, less attention has been paid towards the commercial application of TiO_2 and ZrO_2 oxides. One of the disadvantages in using these materials is their poor thermal stability and low surface area. In addition, under reaction conditions, phase transformations of ZrO_2 and TiO_2 have also been observed [14,15]. Moreover, at high temperature and high pressure conditions, the surface area of these oxides reduces drastically. To overcome some of these problems, the use of TiO_2–ZrO_2 mixed oxides has attracted attention of researchers in recent years [2,16–22]. Pure ZrO_2 and TiO_2 are weakly acidic as compared to Al_2O_3. Since Zr and Ti belong to the same group (IV-B, d^2s^2) of periodic elements, they are expected to have similar physical and chemical properties. However, when their oxides are co-precipitated together, the mutual chemical interaction in forming a bond between them (–Ti–O–Zr–) is expected to have a profound effect on the catalytic properties [17]. Modified ZrO_2 based catalysts on exposure to air at ambient temperature lose their acidity by absorbing moisture but the presence of moisture enhances their catalytic activity [23]. The interesting feature of TiO_2–ZrO_2 mixed oxides is the presence of both acidic and basic sites. The co-ordinated unsaturated sites (CUS),

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the main active centers of the catalyst, are easier to form in the mixed oxides than on Al_2O_3 and their concentration is also larger [18]. Though TiO_2–ZrO_2 mixed oxides have been used as supports for various catalytic reactions, but as a catalyst, it is rarely being used. To the best of our knowledge, this is the first communication which deals with TiO_2–ZrO_2 as a catalyst for the dehydration of methanol to DME synthesis.

In our present study, a surface mechanism for DME is also attempted. Several approaches for DME formation from CH_3OH have been reported. A Lewis acid–base on the surface of Al_2O_3 is suggested for the ether formation [24–28]. However, study on CO_2 on the surface of γ-Al_2O_3 has indicated the absence of any strong basic sites [2]. Participation of Brønsted sites alone *via* an oxonium ion $[CH_3OH_2{}^+]$ as an intermediate is suggested for DME formation [29,30]. So far, no experimental study has been made to understand surface acid–base sites on the mixed oxides of TiO_2–ZrO_2.

The present work has been conducted to study the surface acid–base properties of TiO_2–ZrO_2 mixed oxides and their influence on methanol dehydration reaction to DME. For this purpose, different TiO_2–ZrO_2 mixed oxides were prepared by varying their TiO_2 content. The crystalline phases of the oxides were characterized by X-ray diffraction (XRD) and their acid–base properties by temperature programmed desorption (TPD) of NH_3 and CO_2 and infrared (IR) spectroscopy of adsorbed pyridine. Based on our results, a surface mechanism has been proposed for DME formation.

2. Experimental

2.1. Synthesis of mixed oxides

A series of TiO_2–ZrO_2 mixed oxides with varying molar ratio of TiO_2 to ZrO_2 designated as (Ti/Zr), were prepared by the co-precipitation method. To an appropriate amount of $TiCl_4$ and $ZrCl_4$ dissolved in distilled water, a sufficient quantity of ammonium hydroxide was added drop wise until the pH of the solution reached 9 with constant stirring. The precipitate was aged for 24 h, washed with de-ionized water until free from chloride ions, dried overnight at 110 °C and finally calcined at 550 °C for 6 h in air. For comparison, pure ZrO_2 and TiO_2 were also prepared using the same procedure.

2.2. Characterization

The crystalline phases of TiO_2–ZrO_2 were studied using XRD. The acid properties were measured by TPD of NH_3 and IR of pyridine adsorbed on the surfaces and the base properties by TPD of CO_2. XRD patterns of TiO_2–ZrO_2 samples were recorded using a Rigaku 2155 D6 diffractometer (Ni filtered CuK_α radiation, 40 kV, 50 mA). The BET specific surface areas of all samples were determined by a Micrometric ASAP 2400 adsorption analyzer.

The TPD of NH_3 was performed using 0.2 g of catalyst after pretreatment at 600 °C in a flow of He. NH_3 was introduced at 100 °C for 15 min on the catalyst, then it was purged with He flow at 100 °C for 0.5 h. The temperature of the sample was raised at a rate of 5 °C/min to 600 °C. The amount of NH_3 desorbed from the sample was obtained by comparing the areas under the curve with the sample of known amounts of NH_3 using thermal conductivity detector. For measuring basicity, CO_2 was used as a probe molecule in the place of NH_3, while the rest of procedure remained the same.

The nature of the surface acid sites (Brønsted or Lewis) was determined in a FT-IR spectrometer by means of pyridine adsorption. The mixed oxide samples were pressed into very thin wafers of about 20 mg and placed in an IR cell made of quartz with CaF_2 windows, connected to a high vacuum system. Following evacuation at 400 °C for 1 h, the sample was subjected to pyridine at 200 °C for 5 min and then evacuated at 200 °C for 30 min. All the IR spectra were measured at room temperature.

2.3. Catalytic activity

The mixed oxides TiO_2–ZrO_2 were tested for the dehydration of methanol reaction in a fixed-bed reactor (s.s.tubing, i.d. = 8 mm and length = 30 cm). Prior to the experiment, each catalyst (ca. 1.5 g; 20–40 mesh) was activated in a stream of pure N_2 at 300 °C for 1 h under atmospheric pressure. Methanol was fed into the reactor using a calibrated pump. The reaction products were analyzed by a gas chromatograph (GC) equipped with thermal conductivity and flame ionization detectors.

3. Results and discussion

The XRD spectra of pure ZrO_2, TiO_2 and TiO_2–ZrO_2 mixed-oxides, calcined at 550 °C for 6 h, are shown in

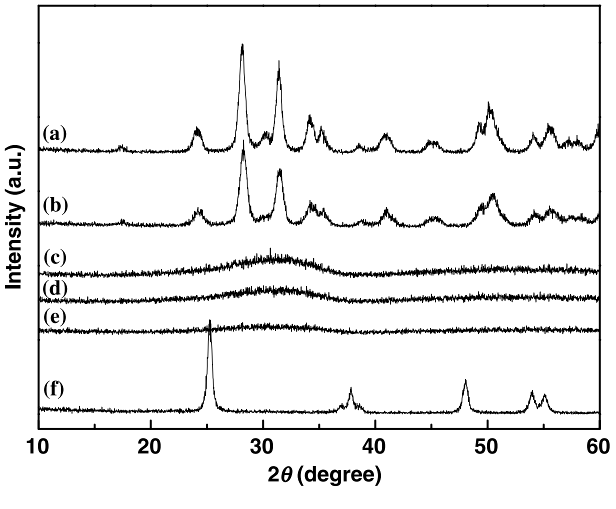

Figure 1. XRD patterns of oxides: (a) ZrO_2; (b) Ti/Zr = 1/9; (c) Ti/Zr = 3/7; (d) Ti/Zr = 1/1; (e) Ti/Zr = 7/3 and (f) TiO_2.

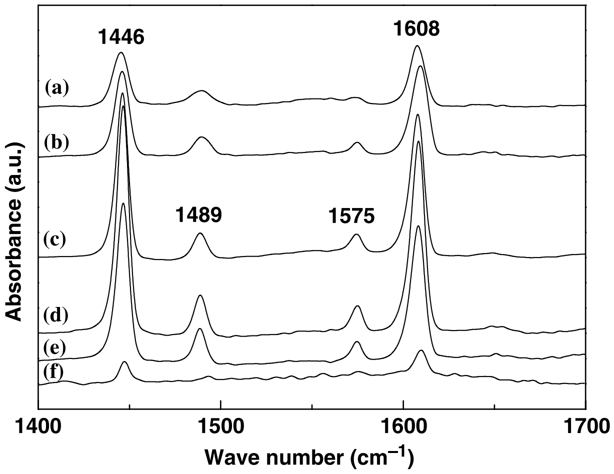

Figure 2. IR spectra of pyridine adsorbed on oxides: (a) ZrO_2; (b) Ti/Zr = 1/9; (c) Ti/Zr = 3/7; (d) Ti/Zr = 1/1; (e) Ti/Zr = 7/3 and (f) TiO_2.

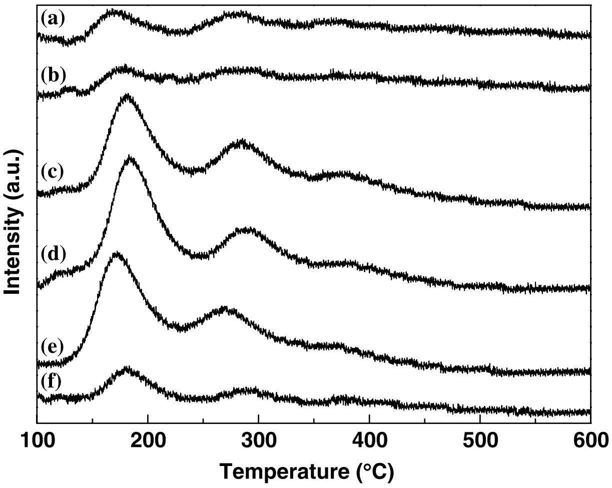

Figure 3. NH_3-TPD on oxides: (a) ZrO_2; (b) Ti/Zr = 1/9; (c) Ti/Zr = 3/7; (d) Ti/Zr = 1/1; (e) Ti/Zr = 7/3 and (f) TiO_2.

figure 1. Both pure ZrO_2 and TiO_2 have crystalline structures. Pure ZrO_2 exists in monoclinic ($2\theta = 28.1$ and 31.4) and tetragonal ($2\theta = 30.2$) forms (pattern a), while TiO_2 exists in an anatase form ($2\theta = 25.3$) (pattern f). In the case of mixed oxides, the sample Ti/Zr = 1/9 (pattern b), does not show any change in the XRD pattern from pure ZrO_2 except the disappearance of the tetragonal form ($2\theta = 30.2$). However, at higher concentration of TiO_2 (Ti/Zr = 3/7, 1/1 and 7/3), the mixed oxides are highly amorphous in nature (patterns c–e). The lack of crystallinity is attributed to a strong chemical interaction between the two individual oxides, TiO_2 and ZrO_2 during the co-precipitation stage. The amorphous nature of TiO_2–ZrO_2 in the vicinity of Ti/Zr = 1/1 is in agreement with other researchers [17,22].

The infrared spectra of pyridine adsorbed on pure ZrO_2, TiO_2 and TiO_2–ZrO_2 mixed oxides are shown in figure 2. The assignment of IR spectrum of pyridine either in co-ordinately bonded (Lewis) or in the form of pyridinium ion (Brønsted) is well known [31–33]. In figure 2, none of the mixed oxides show Brønsted acidity since no trace of characteristic band at 1540 cm^{-1} for PyH^+ was noticed. This is true with literature that no Brønsted site was reported over TiO_2–ZrO_2 catalysts under similar experimental conditions [34]. Pure ZrO_2 shows two intense bands at 1446 and 1608 cm^{-1}, a moderate band at 1489 cm^{-1} and a very weak band at 1575 cm^{-1} (spectrum a). All these bands confirm the presence of electron-acceptor (Lewis) centers on which pyridine forms a co-ordination bond. The two intense bands at 1446 and 1608 cm^{-1} are ascribed to strong Lewis bands while the band at 1575 cm^{-1} is ascribed to the weak Lewis sites [35,36]. The moderate band at 1489 cm^{-1} has been ascribed to both Lewis and Brønsted acid sites [35]. It is interesting to observe that the intensity of all these bands increases with TiO_2 content in the mixed oxides of TiO_2–ZrO_2. This increase in acidity is due to the distribution of an excess negative/positive charge with in the crystal structure of TiO_2–ZrO_2. This is in conformity with Tanabe's hypothesis [23].

TPD of ammonia was used to estimate the amount and strength of acid sites formed on the surface of TiO_2–ZrO_2 catalysts. It is known that ZrO_2 and TiO_2 are less acidic as compared to Al_2O_3. The NH_3-TPD patterns of TiO_2–ZrO_2 with TiO_2 varying from 0 to 100 mol% are shown in figure 3. Pure ZrO_2 and TiO_2 show similar desorption patterns, with two distinct regions I and II, from 150 to 250 °C and 250 to 350 °C (curves a and f), respectively. It is interesting to note that with an increase in TiO_2 content from 10 to 70 mol%, a large increase in surface acidity is observed (curves b–e). This increase in acidity is attributed to the creation of more Lewis acid sites on the surface of TiO_2–ZrO_2. This is in agreement with the increase in band intensity observed at 1446 and 1668 cm^{-1} from the IR spectra of adsorbed pyridine (figure 2). The fact that the increase in acidity with TiO_2 content is mainly contributed from the moderate strength of acid sites (region I, figure 3). Thus, one can anticipate a higher selectivity for DME formation over TiO_2–ZrO_2 as compared to the simple oxides, TiO_2 or ZrO_2, since relatively weak/moderate acid sites are active for ether formation [30].

The influence of surface acidity on methanol dehydration activity was studied by varying TiO_2 content in TiO_2–ZrO_2 mixed oxides as shown in figure 4. The acidity (as measured from NH_3-TPD) increases with increase in TiO_2 content and passes through a maximum at Ti/Zr = 1/1. Similarly, methanol conversion also increases with TiO_2 content and goes through a maximum at Ti/Zr = 7/3. It is an interesting observation that even though the sample Ti/Zr = 1/1 has more surface acidity than Ti/Zr = 7/3, the CH_3OH conversion is higher in the latter case. This suggests that Ti/Zr = 7/3

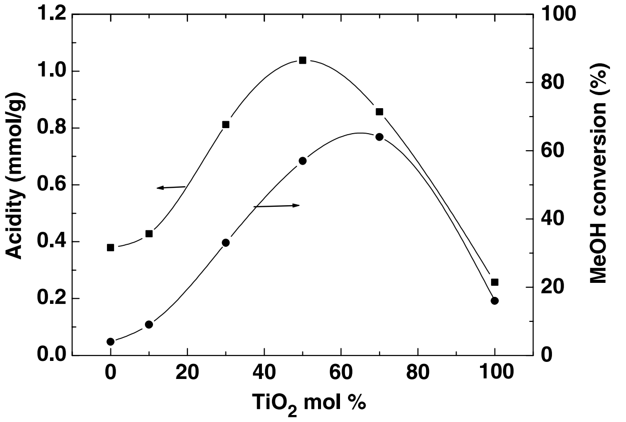

Figure 4. Influence of TiO_2 content in TiO_2–ZrO_2 on surface acidity and CH_3OH conversion (reaction conditions: $T = 280$ °C, catalyst = 1.5 g, WHSV = 0.316 h^{-1} and $P = 1$ bar).

Table 1
CH_3OH dehydration results over TiO_2–ZrO_2 mixed oxides

TiO_2/ZrO_2 (mol/mol)	Methanol conversion (%)	Product selectivity (%)	
		DME	Others
0/100	25.0	100.0	0.0
10/90	53.0	100.0	0.0
30/70	83.0	100.0	0.0
50/50	86.0	94.0	6.0
70/30	88.0	84.0	16.0
100/0	70.0	80.0	20.0

Reaction conditions: $T = 340$ °C, catalyst = 1.5 g, WHSV = 0.316 h^{-1} and $P = 1$ bar.

sample has more stronger acid sites than sample Ti/Zr = 1/1. This is supported in table 1 where Ti/Zr = 7/3 forms more hydrocarbons than Ti/Zr = 1/1. This is true since strong acid sites are required for the dehydration of alcohols to form hydrocarbons [30]. Also, table 1 shows that in addition to reaction temperature, even the TiO_2 content in TiO_2–ZrO_2 plays a role in determining DME selectivity. From table 1, it is clear that an optimum performance is achieved for a molar ratio of Ti/Zr in the vicinity of 1. It is also interesting to observe that the dehydration activity of TiO_2–ZrO_2 was comparable with two other commonly used solid acid catalysts, *viz.*, γ-Al_2O_3 and HZSM-5. Even though, γ-Al_2O_3 and HZSM-5, show the conversion of CH_3OH to DME as 79% and 72%, respectively, at 340 °C under normal atmospheric pressure as compared to TiO_2–ZrO_2 (table 1), their activity at lower temperatures (< 300 °C) was better. Also, with regards to DME selectivity, a 100% selectivity for DME was observed with TiO_2–ZrO_2 and with γ-Al_2O_3 as well. However, HZSM-5 shows a decrease in DME in selectivity with increase in temperature (> 300 °C). This is mainly attributed to the severe formation of hydrocarbons on the surface of the catalyst. It is well known that strong acid sites on the surface promote deactivation. The fact that TiO_2–ZrO_2 gives 100% selectivity for DME suggests the presence of more number of weak/medium acid-sites as compared to the strong sites are available on the surface.

Table 2
BET surface areas (S_{BET}) and ammonia uptakes of TiO_2–ZrO_2 catalysts

TiO_2/ZrO_2 (mol/mol)	S_{BET} (m^2/g)	NH_3 uptake	
		(μmol/g)	(μmol/m^2)
0/100	62	379	6.11
10/90	73	428	5.86
30/70	198	812	4.10
50/50	225	1038	4.61
70/30	206	857	4.16
100/0	45	257	5.71

The surface area as well as the surface acidity of the catalyst is also important for the enhancement of catalytic activity. Table 2 shows the BET surface area measured for TiO_2, ZrO_2 and their mixed oxides along with the uptake of ammonia measured from the TPD of NH_3. The surface areas of ZrO_2 and TiO_2 were found to be 62 and 45 m^2/g, respectively. On addition of TiO_2 to ZrO_2, the surface area of the mixed oxides increases sharply and reaches a maximum value for the mixed oxide having Ti and Zr molar ratio of 50/50. Further addition of TiO_2 then slowly decreases the surface area. This is in agreement with the literature where it was found that mixed oxides exhibit much higher surface area than their single oxide components [16]. The interesting observation is the correlation between the surface area and the acidity of the mixed oxides. The addition of TiO_2 to ZrO_2 increases the surface area of the mixed oxides sharply but the corresponding increase in surface acidity is not as proportionate to the increase in surface area (table 2). This is confirmed further from the decrease in surface density of ammonia as calculated from surface acidity by surface area. The surface density of ZrO_2 is found to be 6.11 μmol/m^2. On subsequent addition of TiO_2 to ZrO_2, the density value decreases to 4.16 μmol/m^2. More or less, a consistency in the surface density value around 4 μmol/m^2 was noticed for the mixed oxides having a molar ratio of Ti/Zr around 1/1. Though the surface acidity increases with increase in addition of TiO_2 to ZrO_2, the corresponding surface density of the acid-sites of the mixed oxides decreases. Further, when tables 1 and 2 are compared, it is observed that with decrease in surface density of acid-sites the conversion of methanol increases with the mixed oxides. This suggests that the presence of less number of acid-sites on a larger surface area of the catalyst, promote adsorption of methanol molecules to DME more effectively. It appears that in the mixed oxide, TiO_2 may be present either as fine microcrystals (as shown by

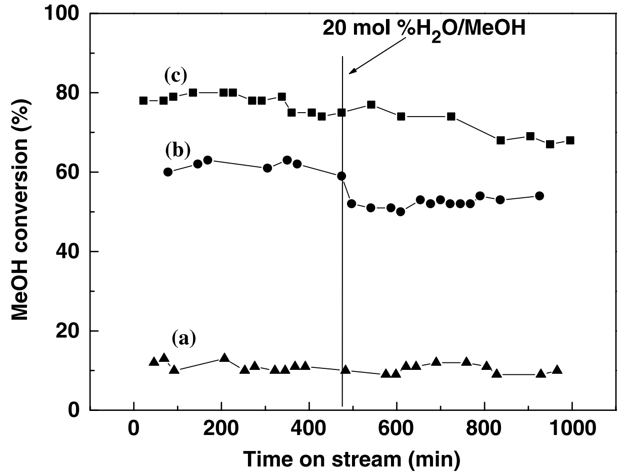

Figure 5. Effect of water on CH_3OH dehydration over TiO_2–ZrO_2 mixed oxides: (a) Ti/Zr = 1/9, (b) Ti/Zr = 3/7 and (c) Ti/Zr = 1/1 (reaction conditions: $T = 300$ °C, catalyst = 1.5 g, WHSV = 0.316 h^{-1} and $P = 1$ bar).

the XRD amorphous patterns of c–e in figure 1) or in a dense micro-porous form along with ZrO_2 [17]. These may be the primary Lewis acid centres which are kinetically efficient in adsorbing ammonia on the surface of the catalyst. The presence of more number of Lewis acid sites as compared to Brønsted on the mixed oxides is evident from figure 2. As the number of these Lewis acid sites increases with increase in TiO_2 in ZrO_2, the uptake of ammonia also increases, as shown in table 2.

It is known that Al_2O_3 has hydrophilic nature and has a tendency to adsorb water on its surface. As shown in equation (1), water is one of the side products in the dehydration reaction and competes with methanol for the same sites on the surface of Al_2O_3. To study the influence of water on TiO_2–ZrO_2 , 20 mol% H_2O was premixed with CH_3OH and was introduced as a feed under similar experimental conditions. Figure 5 shows the influence of water on CH_3OH dehydration reaction with reaction time. The mixed oxides show a significant resistance towards water and with lesser TiO_2 content, the effect is more profound.

Different mechanisms have been suggested for ether formation from alcohols [25–30]. DME formation from CH_3OH takes place *via* a surface reaction between two adsorbed molecules of CH_3OH of different strengths over TiO_2–ZrO_2. The participation of basic sites was studied using tetracyanoethylene which specifically poisons the basic sites on the surface of Al_2O_3 [32]. However, no study on the basic sites over TiO_2–ZrO_2 has been reported so far. The TPD of CO_2 was used to determine the surface basicity on TiO_2–ZrO_2 (figure 6). As compared to pure ZrO_2 and TiO_2, the mixed oxides show more basic sites. It is evident from the TPD results that TiO_2–ZrO_2 surface has the presence of both acidic and basic sites. Based on this, a surface bifunctional mechanism has been proposed (figure 7).

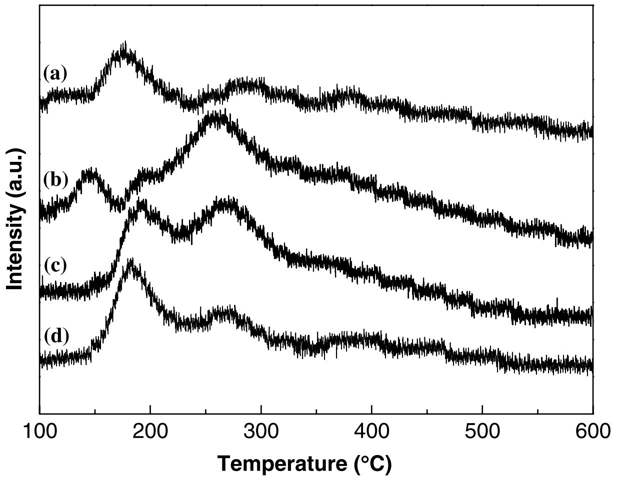

Figure 6. CO_2-TPD on oxides: (a) ZrO_2; (b) Ti/Zr = 3/7, (c) Ti/Zr = 1/1 and (d) TiO_2.

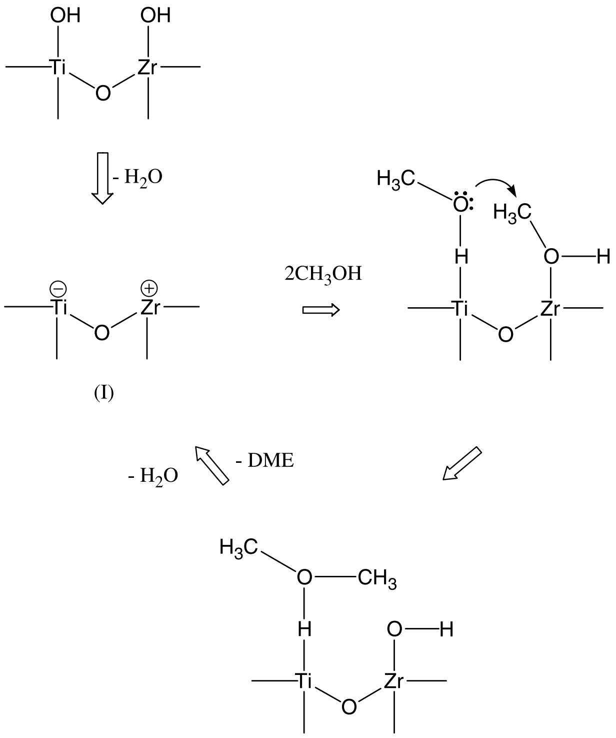

Figure 7. Acid–base bifunctional mechanism proposed for the DME formation from CH_3OH dehydration on TiO_2–ZrO_2 mixed oxides.

In a TiO_2–ZrO_2 crystal structure, the Ti, being more electronegative than Zr, acts as a basic site (nucleophilic center) while Zr acts as an acidic center (electrophilic center) [17], shown as structure I in figure 7. The bimolecular reaction possibly involves a weakly adsorbed CH_3OH on a basic site [Ti^-] through hydrogen bonding and a strongly adsorbed CH_3OH on an acidic site [Zr^+] through co-ordination bond. It is the strongly adsorbed CH_3OH molecule on the acidic site [Zr^+] polarizes the C–O bond and makes the hydroxyl a better leaving group. On the other hand, the weakly adsorbed CH_3OH on the basic site [Ti^-] enhances the nucleophilicity of the oxygen of that CH_3OH molecule. Such an alcohol molecule, considered to be an incipient alkoxide ion [25,26], can effect a nucleophilic displacement on a positively polarized carbon atom of the alcohol adsorbed on the acidic site to form ether. This mechanistic approach agrees well with others [27] in the formation of ethers from higher alcohols on the surface of Al_2O_3. A similar bifunctional mechanism on TiO_2–ZrO_2 has been considered for the non-oxidative dehydrogenation of ethylbenzene to styrene [16,17].

4. Conclusions

The following observations could be drawn from the present investigation:

1. The mixed oxides TiO_2–ZrO_2 catalysts prepared from the co-precipitation method are highly amorphous in nature.
2. The characterization results suggest the existence of moderate strength of acidic sites as well as basic sites on the surface of the catalyst.
3. Direct correlation is observed between dehydration activity and the surface acid–base properties of the TiO_2–ZrO_2 catalyst.
4. At lower reaction temperature, the selectivity for DME is nearly 100%.
5. A significant stability against water is observed with time on stream on TiO_2–ZrO_2 catalysts.
6. DME formation is a bimolecular reaction involving both acidic and basic sites on the surface of TiO_2–ZrO_2.

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