Synthesis of methyl *tert*-butyl ether on sulfur-promoted ZrO$_2$

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Abstract

The synthesis of methyl *tert*-butyl ether (MTBE) from methanol and isobutylene in a gas–solid heterogeneous system over sulfur-promoted zirconias calcined at different temperatures between 400 and 700°C was studied. The reaction temperature was varied in the range 90–110 °C, and methanol to isobutylene molar ratios were changed from 1.0 to 1.3. The catalyst acidity was a direct function of the sulfur load, in turn a consequence of the calcination temperature. Temperature programmed reduction experiments allowed us to observe that the sulfur reduction process is different according to the calcination temperature. The highest activity was observed on the sample calcined at 600 °C, which was comparable with that of the reference catalyst Amberlyst 15 under the same conditions. A direct relationship between catalyst acidity and conversion was not observed. The injection of water completely poisoned the catalyst activity in a reversible manner. © 1997 Elsevier Science S.A.

Keywords: MTBE; Acidity; Zirconia

1. Introduction

The demand for methyl *tert*-butyl ether (MTBE) has been growing steadily since it became one of the main gasoline additives, playing the double role of octane booster (substituting lead compounds) and oxygenate component, as a consequence of more restrictive legislation about gasoline composition [1]. Its commercial production is based on well known technology which uses strongly acidic ion exchange resins as catalysts for the highly selective addition of methanol and 2-methyl-propene (isobutylene) [2]. The growing importance of ethers, and particularly MTBE, has increased the research effort for alternative processes from the standpoints of (a) raw materials, since isobutylene, which is mainly supplied by catalytic cracking of hydrocarbons in refineries, might suffer from shortages [3], (b) the catalysts, since productivity could be increased with more active catalysts [4], or (c) technology, since the reaction is limited by thermodynamics [4,5].

Concerning the catalysts, it is known that strong acidity is necessary to catalyze the addition reaction between methanol and isobutylene. As a consequence, alternative catalyst screening studies have focused on highly acidic materials like, for example, various zeolites [6–8] or heteropolyacids [9,10]. However, few studies were conducted in order to clarify the role played by the acid function of the catalysts. Kogelbauer et al. [7] controlled the acid strength of HY zeolites by exchanging various alkali metal cations to the same degree, observing no differences in the initial rates of MTBE formation; on the contrary, Y zeolites dealuminated by different techniques showed a strong influence of the ratio between framework and non-framework Al [8]. The promotion of zirconia with sulfur to produce strongly acidic catalysts has been investigated intensively lately [11,12]; besides some stability matters, the materials look promising when applied to reactions like isomerization [12], and hydrocracking [13]. A few studies were performed associated with ether synthesis [3], but not with the direct methanol–isobutylene addition [14].

It is the objective of this work to determine the influence of catalyst pretreatment and experimental conditions on the gas-phase synthesis of MTBE over sulfur-promoted zirconia and to establish the role played by different acid sites.

2. Experimental details

The catalyst used was zirconium oxide, synthesized starting from a ZrOCl$_2\cdot$8H$_2$O (Strem Chemicals, 99%) solution by addition of an NH$_4$OH solution (Merck, 25% ammonia) up to pH 10 [15]. It was utilized without additional treatments and promoted by dipping into a 1 N H$_2$SO$_4$ solution

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for 1 h at room temperature, filtration and drying at 120 °C. Samples were calcined in situ under air flow at 400, 500, 600 and 700 °C for 3 h to obtain samples designated ZR-*i* and ZRS-*i* (where *i* indicates the calcination temperature, and S the sulfur promotion treatment). The sulfur content of the catalyst was determined by conventional chemical analysis. Commercial Amberlyst-15 polystyrene–divinylbenzene ionic exchange resin (Rohm and Haas Company), sample A-15, was used as a reference catalyst; it was purged in situ under N_2 flow at 110 °C for 1 h.

Physical properties of the catalyst were determined by means of nitrogen adsorption isotherms measured with Micrometrics Accusorb 2100 equipment.

Acidity was measured by means of NH_3 temperature programmed desorption (TPD). Samples were calcined at the pretreatment temperatures in flowing air for 3 h. After that, NH_3 was adsorbed at 100 °C, purged at 200 °C for 2 h under flowing N_2, and then desorbed at a rate of 10 °C min^{-1} up to 600 °C. Desorbing NH_3 was detected by a thermal conductivity detector, the response of which was calibrated against chemical titration of ammonia absorbed in an acidic solution. Sample ZRS-400 was heated only up to 400 °C, owing to instabilities caused by SO_2 and SO_3 losses.

Temperature programmed reduction (TPR) experiments were performed using Ohkura TP2002S equipment with a thermal conductivity detector. Samples pretreated in situ were heated from 100 to 800 °C at 10 °C min^{-1} in a gas stream of 4.8% hydrogen in argon.

The conversion of methanol (Carlo Erba, 99.9%) and isobutylene (AGA, >99%) was conducted in a conventional gas phase flow fixed bed tubular reactor (0.26 m × 0.0125 m i.d.) in the 90–110 °C range. Pure reactants were mixed after methanol vaporization and fed at atmospheric pressure. Experiments, considered isothermal, were performed for approximately 4 h, with 1.4 g of catalyst particles sized in the 7×10^{-6}–4.47×10^{-4} m range. The same catalyst mass was used for the reference catalyst A-15. Liquid methanol was injected at a constant volume flow rate of 3.7×10^{-10} m^3 s^{-1} and gaseous isobutylene was fed at different flow rates. Molar methanol to isobutylene ratios and weight hourly space velocities (WHSV, defined as the ratio between total mass flow rate and catalyst mass) were varied between 1.0 and 1.3, and

2.05 and 1.75 respectively. In order to avoid secondary reactions like isobutylene oligomerization, methanol was injected first over the fresh catalyst. Water injection experiments at 100 °C were performed by stopping the reactant feed and injecting pure liquid water at a rate of 3.7×10^{-10} m^3 s^{-1} (at room temperature and 1 atm) for 20 min, with a neat excess over the amount of catalyst acid sites. After that, a nitrogen flow of 3.33×10^{-7} m^3 s^{-1} was passed over the sample for 10 min to purge the system; finally the reactants flow was restored. The methanol to isobutylene molar ratio for the mentioned experiments was unity. Effluents were analyzed by on-line gas chromatography using a thermal conductivity detector.

3. Results and discussion

Sulfur-promoted zirconias have received widespread attention owing to their properties as superacid solid catalysts [16]. Concerning applicability to ether synthesis, they have been tested in the compound conversion (dehydration and addition) of isobutanol and methanol [3].

Since the properties of SO_4^{2-}/ZrO_2 catalysts are highly dependent on pretreatment conditions [15], various calcination temperatures were chosen to produce different samples. Resulting catalyst properties are shown in Table 1. Concerning specific surface area, it can be seen that the unpromoted sample calcined at 600 °C showed a value of 3.4×10^4 m^2 kg^{-1}, which can be considered typical for the precursor used; sulfur addition produced a significant increase in specific surface area (ZRS-600, 1.1×10^5 m^2 kg^{-1}), a fact that had been observed [12,17] and attributed to an increase in the Zr–Zr atomic separation due to the replacement of hydroxo bridges (3.3–3.7 (10^{-9} m)), by sulfate bridges (3.5–4.3 (10^{-9} m)) [18]. For the series of promoted catalysts, the higher the calcination temperature, the lower the specific surface area. Considering that all the samples had the same initial sulfur loading (8.38 wt.%) after impregnation, it can be seen that there is a direct relationship between the calcination temperature and the loss of specific surface area, which also holds true for the sulfur content and total catalyst acidity.

Table 1
Catalyst properties as a function of pretreatment conditions

Catalyst	T calcination (°C)	Sulfur load (wt.%)	Acidity (eq NH$_3$ kg^{-1})	Surface area $\times 10^{-5}$ (m^2 kg^{-1})	$\bar{r} \times 10^{8}$ [c] (m)
ZR-600	600	0.0	0.0637	0.34	35
ZRS-400	400	5.3	0.289 [a]	2.15	n.a.
ZRS-500	500	4.0	0.317	1.37	26
ZRS-600	600	1.8	0.152	1.10	27
ZRS-700	700	1.3	0.106	0.78	n.a.
A-15			4.8 eq H$^+$ kg^{-1} [b]	0.43	125

[a] Final desorption temperature 400 °C.
[b] Determined by proton exchange and chemical titration.
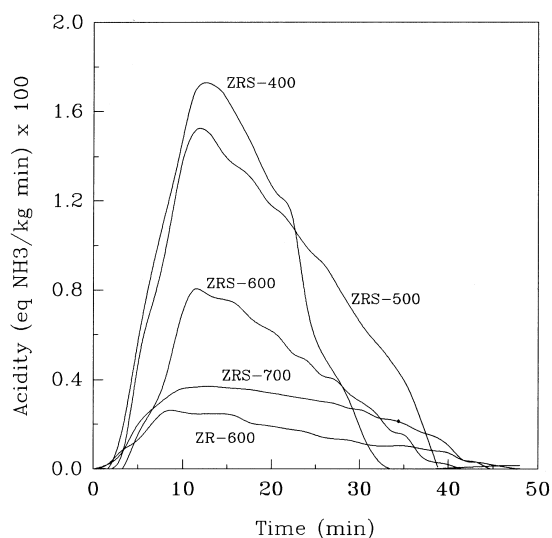[c] Wheeler mean pore radius.

Fig. 1. Ammonia temperature programmed desorption profiles for unpromoted and sulfur-promoted zirconia calcined at various temperatures.

Resulting NH_3 TPD profiles are presented in Fig. 1. Sulfur-promoted zirconia profiles are characterized by a single, wide desorption peak, its maximum being located at about 310–335 °C for all the samples, while non-promoted zirconia calcined at 600 °C has a very low acidity and a flat desorption profile. It has to be pointed out that Xiao and Le Van Mao [19] observed a second peak at higher desorption temperature on sulfur-promoted zirconia produced from zirconyl nitrate and calcined at 600 °C. The mechanism by which sulfur promotes acidity on the surface is accepted to be of inductive type [11], although there is not complete agreement about the actual sulfur species on the surface [16]. Then, the promoting action of varying loads of sulfur is built on the amount of acidity, though the strength of acid sites as expressed by the desorption temperature in NH_3 TPD profiles, is not modified significantly. The resulting amount of acidity on these modified zirconia catalysts can be directly correlated with the sulfur loading that remains on the surface (refer to Table 1 and Fig. 1): the higher the loading, the more acidic the catalyst. It is to be noticed that a quasi-linear relationship prevails among the samples calcined at 500, 600 and 700 °C, a trend that could also apply to the sample ZRS-400, whose final desorption temperature is lower.

Fig. 2 shows TPR profiles obtained for samples ZRS-400, ZRS-600 and ZRS-700. When experiments were carried out in argon atmosphere, without hydrogen, no peaks were detected; moreover, unpromoted ZR-600 did not show reduction peaks, thus indicating that the peaks observed on the other samples correspond to the reduction of sulfur species. The diminution of the total area defined by the profiles as calcination temperature increases would indicate the loss of sulfur caused by pretreatment, although a direct relationship between area and sulfur content cannot be established, since the amount of sulfur being reduced changes with calcination temperature. The profiles are characterized by the presence of a single, wide reduction peak with the location of the

maximum changing between 620 and 650 °C, in the order ZRS-700 < ZRS-600 < ZRS-400; since this is not the ordering followed by the activities of the samples, this phenomenon might show that different sulfur species are present as a function of calcination temperature which would have different catalytic influence. Dicko et al. [20] observed a very similar profile for a sample calcined at 600 °C, but those calcined at lower temperatures exhibited two reduction peaks, both of them generating SO_2. TPR profiles in Fig. 2 might reflect the different degree of hydration on the various samples, since FTIR analysis on sulfated zirconia calcined at different temperatures showed that highly hydrated sulfates are mainly in an ionic configuration resembling that of inorganic (bidentate) sulfate complexes, whereas on dehydrated surfaces the sulfates tend to acquire a highly covalent configuration, resembling that of organic sulfonic derivatives [21]. The catalyst calcined at 400 °C also showed a very sharp peak at lower temperatures that might correspond to easily reduced sulfur species which were not completely eliminated or transformed in the calcination treatment.

The activities observed at 100 °C for the various samples for different molar methanol to isobutylene ratios r and WHSV are shown in Table 2. In all the cases the selectivity to the formation of MTBE was 100%, and catalyst stability was observed constant for the length of the experiment. While the oxide without promotion calcined at 600 °C (ZR-600) and sulfur-promoted catalyst calcined at 700 °C (ZRS-700) showed no activity, all the other catalysts were active, maximum activities corresponding to the promoted sample calcined at 600 °C (ZRS-600). Conversions over ZRS-600 were comparable to that of the Amberlyst-15 sulfonic resin. It can be seen that as the molar ratio of the reactants increases, isobutylene conversion decreases for all the catalysts. This observation is consistent with results published about liquid phase MTBE synthesis on sulfonic resin catalysts (e.g. see Ref. [4]), on which the reaction rate decreases with methanol
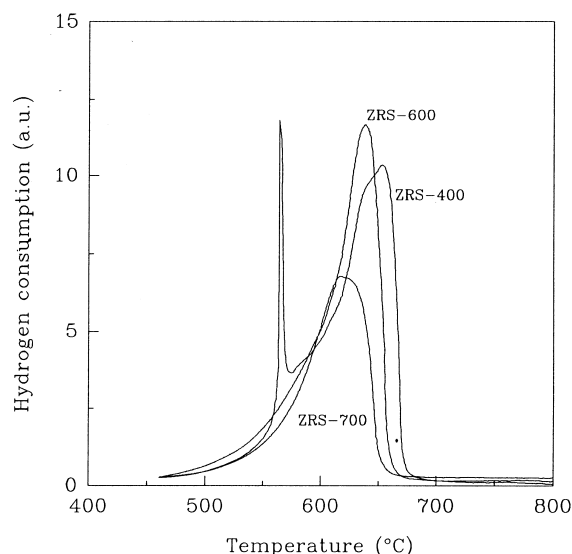

Fig. 2. Hydrogen consumption profiles (TPR) for sulfur-promoted zirconia calcined at various temperatures.

Table 2
Catalyst activity at 100 °C and various molar methanol to isobutylene ratios *r* and weight hourly space velocity WHSV

Catalyst	Isobutylene conversion (%)			
	$r = 1.0$ WHSV = 2.05	$r = 1.1$ WHSV = 1.93	$r = 1.2$ WHSV = 1.83	$r = 1.3$ WHSV = 1.75
A-15	35.1	33.7	32.2	30.7
ZR-600	0.0	0.0	0.0	0.0
ZRS-400	9.0	8.6	8.3	7.9
ZRS-500	22.3	21.0	19.6	18.3
ZRS-600	32.1	31.7	31.3	n.a.
ZRS-700	0.0	0.0	0.0	0.0

n.a. not available.

concentration under a certain range; also the isobutylene concentration decreases, thus impacting negatively on the observed conversions.

It is apparent that there is not a direct relationship between activity for MTBE synthesis and total acidity in sulfur-promoted catalysts, as had already been observed over other types of catalyst including partially dealuminated zeolites [8] and various zeolites and fluorine promoted silica–alumina samples [22]. Yet the catalyst activation (calcination) process seems to be critical, as shown by the maximum activity on the sample calcined at 600 °C, also observed over other reaction systems, such as *n*-butane isomerization, with the same catalyst [12]. However, this peak activity cannot be associated with the crystalline structures present since, depending on the zirconium source and the calcination temperature, sulfur-promoted zirconia may show either a single phase or mixtures of the tetragonal, the thermodynamically favored monoclinic, or amorphous phases. Crystalline structures would start to form at about 400 °C and, for the temperature range we studied (400–700 °C), sulfur addition would favor and stabilize the formation of the metastable tetragonal phase, which is essentially the only one present [12].
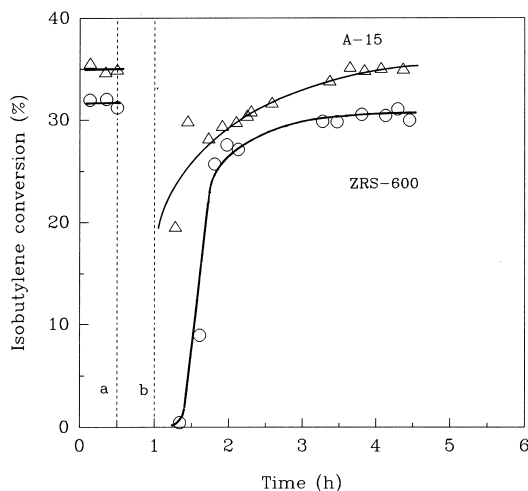

Fig. 3. Water injection experiments. Conversion as a function of time on stream on samples ZRS-600 and A-15, temperature 100 °C: (a) interruption of reactant flow and start of water feed; (b) restitution of reactant flow.

The acidic sites on the surface of sulfur-promoted zirconia are of both Lewis and Brönsted type [16,19,23], their relative amounts depending on the treatment conditions [24,25]. The presence of Brönsted sites at the surface of sulfur-promoted zirconia systems calcined at rather high temperatures has been demonstrated as long as thermal treatments did not exceed 600 °C [25,26]. The partial interconversion of Lewis into Brönsted type acid sites follows a rather complex pattern in which the form of the acidic-OH groups depends on the degree of hydration [25]. In order to confirm the role played by Lewis acid sites in the synthesis of MTBE, we decided to adsorb an important amount of water on samples calcined at 600 °C, just stopping the reactant feed and shifting to water. Results are shown in Fig. 3, in which it can be seen that after water injection, ZRS-600 completely lost its activity. However, this effect was reversible, since after restoring the original reactant flow rate, the activity was gradually recovered without increasing temperature, suggesting that water was loosely bound to those sites accepting it and was removed by reactants. Again selectivity to MTBE was 100% all through the experiment. It can be concluded that Lewis acid sites are responsible for catalyst activity in methanol–isobutylene addition reaction over sulfur-promoted zirconias, as shown by their reversible poisoning (though never eliminated, Brönsted sites are expected to be present in very small amounts, consistent with the degree of hydration reached when the sample was calcined at 600 °C). Acidic protons involved in multiple H-bondings, expected at the high degree of hydration due to the adsorption of water at 100 °C [25], would not be able to promote the addition reaction.

However, performing the same experiment on resin sample A-15, on which Lewis type sites are not expected, produced a different pattern: the loss of activity was only partial and again reversible (refer to Fig. 3), which shows that the inhibition of active sites is limited under those conditions. More significantly, a transient change was observed in reaction selectivity, since *tert*-butyl alcohol coming from the addition of water to isobutylene was detected, declining among products as long as the catalyst was recovering its initial activity and selectivity and there was water remaining adsorbed on the catalyst surface. When water is adsorbed on a resin of this
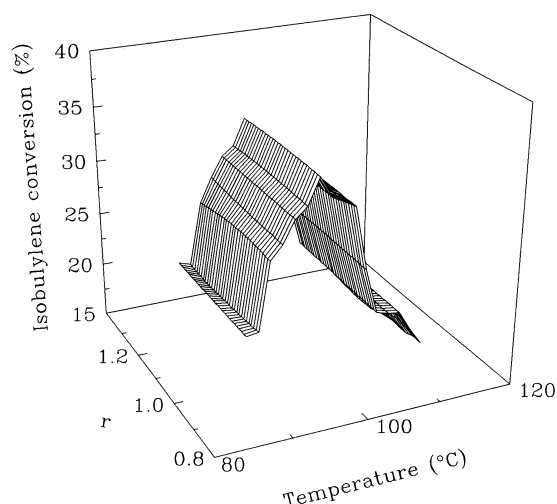
Fig. 4. Conversion as a function of temperature for various methanol to isobutylene ratios, sample ZRS-600.

type at a temperature close to 100 °C, a network of hydrogen-bonded water and –SO_3H groups is expected, while no free –OH groups are observed [27]. Results would show that water cannot fully displace reactants from the resin surface under our experimental conditions.

Isobutylene conversions obtained over the sample ZRS-600 in the 90–110 °C reaction temperature range, with different molar reactant ratios r, are shown in Fig. 4. It can be seen that the maximum conversion was obtained at 100 °C and unity molar ratio. The evolution of the surface defined by the experimental values in the conversion–temperature–molar ratio space, points to intrinsic reaction thermodynamics limitations, which, in the range of interest, under small temperature changes would produce notorious methanol equilibrium conversion variations. In fact, after defining the maximum conversion at 100 °C, experimental values tend to equilibrium conversion (not included in the graph for the sake of clarity). Though the effect has been described elsewhere [8], comparisons should be carefully performed, since there is a certain dispersion in published thermodynamic parameters [28].

4. Conclusions

Sulfur promotes the amount of acidity in zirconia according to the load remaining on the surface, which is a function of pretreatment temperature, making it an effective catalyst for the synthesis of MTBE. Activity was the highest for the sample calcined at 600 °C, with values close to those of the reference catalyst Amberlyst-15, but a clear relation between acidity and activity was not observed.

TPR showed that sulfur is reduced differently according to the calcination temperature, thus suggesting the existence of distinct species or environments. Water injection produced reversible poisoning of active sites and showed that Lewis type acid sites are responsible for catalyst activity in this reaction over sulfur-promoted zirconia.

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