

High selectivity to isopropyl ether over sulfated titania in the isopropanol decomposition

E. Ortiz-Islas^{a,b}, T. López^a, J. Navarrete^b, X. Bokhimi^c, R. Gómez^{a,b,*}

^a Universidad Autónoma Metropolitana-Iztapalapa, Dpto. Química, POB 55-634, México 09340 D.F., Mexico

^b Instituto Mexicano del Petróleo, Programa de Ingeniería Molecular, Eje central 152, A.P. 14-805, 07730 México D.F., Mexico

^c Instituto de Física, Universidad Nacional Autónoma de México (UNAM), A.P. 20-364, 01000 Mexico D.F., Mexico

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Abstract

Sulfated titania was prepared by in situ gelling titanium alkoxide with sulfuric acid and by impregnation with ammonium sulfate of titania gels, after annealing gels at 600 °C, the BET specific surface areas were of 46 and 177 m²/g for sulfuric and ammonia sulfate preparations, respectively. XRD patterns showed for “in situ” preparation anatase (92%) and rutile phases (8%), while for ammonium sulfate sample only anatase phase was observed. FTIR-pyridine adsorption identified Brønsted (B) and Lewis (L) sites for titania impregnated with ammonium sulfate, however, only Lewis (L) sites were identified in titania prepared with sulfuric acid. In the isopropanol conversion, similar activities were obtained. However, in sulfuric preparation the selectivity was 22 and 78 mol% to propene and isopropyl ether, respectively, while in ammonium sulfated catalyst the selectivity was 70 mol% to propene and 30 mol% to isopropyl ether. The results are discussed with regards to the acidity requirements explaining the role of acid sites in the selectivity.

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1. Introduction

Since the legislation appeared around the world over clean air, fundamental changes in fuels composition were made. These changes restricted the use of heavy metal like tetraethyl lead, lowered permissible levels of light hydrocarbons and benzene in the fuel and raised the minimum fuel oxygenate content. This led to substantial interest in alcohols and ethers which can be used as oxygenated compounds which increase the octane number in gasoline. C₁ to C₃ alcohols, whilst having high octane number and being less expensive than ethers, their disadvantage is that they have a high blending Reid vapor pressure, and that they are very soluble in water. Since 1990, the oxygenate compounds most used have been the methyl *tert*-butyl ether (MTBE) and *tert*-amyl methyl ether (TAME) [1]. However, we can consider as a good option the use of the di-isopropyl ether (DIPE), although being scant

literature over their use. The information relates mostly to its blending behavior and the production economics [2–4]. DIPE has a poorer octane number, but a favorable blending Reid vapor pressure. Moreover, it can be produced from isopropanol.

Decomposition of 2-propanol is frequently used as a test reaction to determine acid–base properties of oxide catalysts in many laboratories [5,6]. It has been reported that the decomposition of 2-propanol occurs by two parallel reactions: (1) the dehydration carried out in acid sites giving the olefin and the ether, in particular propene and isopropyl ether (DIPE) and (2) the dehydrogenation to acetone occurring in basic sites or concerted acid–base pair sites [7–9]. However, the role of acid and basic sites in the formation of propene isopropyl ether and acetone is not well established. Recent reports propose that dehydrogenation and dehydration reactions are not only determined by the surface acidity or by the basic properties, they also depend on the reaction conditions employed, such as reaction temperature, isopropanol partial pressure, the nature of the carrier gas and so forth [5,10–12].

* Corresponding author. Tel.: +52 5 8045668; fax: +52 5 8044666.

E-mail address: gomr@xanum.uam.mx (R. Gómez).

Isopropanol decomposition has been carried out in several metal oxides with different acid–basic properties, among others MgO, CaO and SrO which are known as basic oxides [13], or ZrO₂, Al₂O₃ and TiO₂ with acid properties were studied [14–16]. The results show that the selectivity in this reaction depends on the strength and distribution of the acid and/or basic sites, in particular, the formation of propene and DIPE depends on the acidity present in the catalysts. As a consequence, great efforts have recently been made to design catalysts with controlled acidity.

Sulfated metal oxides are good candidates for this purpose, since they have been tested as catalysts for the isomerization of paraffins [17], acylation of aromatics [18] and dehydration of alcohols [19,20]. Some of them are highly stable in several environmental reactions [21,22]. The most studied sulfated oxides are ZrO₂ [23,24] and TiO₂ [25–27]. In particular, sulfated titania has been found to be efficient for isomerization [28], alkylation [29], Friedel–Crafts acylation [30], esterification [31], photocatalytic oxidation [32] and reduction of NO_x [33].

With the aim to prepare sulfated oxides with controlled acidity giving high selectivity to isopropyl ether, in the present work sulfated titania was prepared by the sol–gel method and was evaluated in the isopropanol decomposition. The solids were characterized by nitrogen adsorption isotherms, X-ray diffraction (XRD) and FTIR–pyridine adsorption.

2. Experimental

2.1. Sample preparation

2.1.1. TiO₂–H₂SO₄

Deionized water (200 ml) was mixed with 200 ml of *tert*-butanol (Baker, 99%) in a reflux glass system. The mixture was heated at 70 °C, at this temperature concentrated sulfuric acid (Baker 98%) was dropped under constant stirring until pH 3 (0.5 ml) was reached. Thereafter, 85 ml of titanium *n*-butoxide was added to the mixture, maintaining the solution under reflux for 24 h.

2.1.2. TiO₂–HNO₃

Titania was prepared at pH 3 using nitric acid as hydrolysis catalyst following the same procedure described above.

2.1.3. TiO₂–HNO₃–(NH₄)₂SO₄

The dried sample, prepared with nitric acid, was impregnated with an aqueous 1N ammonium sulfate solution (5 ml of solution per gram of sample).

All the TiO₂–H₂SO₄, TiO₂–HNO₃ and TiO₂–HNO₃–(NH₄)₂SO₄ samples were dried in air at room temperature, thereafter, they were annealed at 600 °C in flowing air for 4 h.

2.2. Characterization

2.2.1. X-ray diffraction

X-ray diffraction patterns of the samples packed in a glass holder were recorded at temperature with Cu K α radiation in a Bruker Advance D-8 diffractometer that had theta–theta configuration and a graphite secondary-beam monochromator. Diffraction intensity was measured in the 2 θ range between 18 and 110°, with a 2 θ step of 0.020° for 8 s per point. Crystalline structures were refined with the Rietveld technique by using DBWS-9411CODE [34]; peak profiles modeled with pseudo-Voigt function [35] contained average crystallite size as one of its characteristic parameters [36].

2.2.2. BET specific surface areas

Nitrogen adsorption isotherms were obtained on the samples annealed at 600 °C with an Autosorb-3B Quantachrome equipment. The surface areas were calculated using the BET equation and the mean pore size diameter was calculated using the BJH method.

2.2.3. FTIR–pyridine adsorption

The type and quantity of acid sites (Brønsted and/or Lewis) was determined with a Fourier transform infrared (FTIR) Nicolet 170 SX spectrometer by means of pyridine adsorption. The annealed material was pressed into thin self-supported wafers. Then, they were placed in a glass Pyrex cell with CaF₂ windows coupled to a vacuum line, in order to be evacuate (1×10^{-6} Torr) in situ at 400 °C for 30 min. The adsorption was carried out on the cell at 25 °C by breaking a capillary tube, which contains the pyridine. The pyridine excess was desorbed with vacuum from room temperature to 400 °C in 100 °C steps. The quantities of adsorbed pyridine were obtained from the integrated absorbance of the respective bands, following the procedure and coefficient extinction reported elsewhere [37].

2.2.4. Decomposition of 2-propanol

The reaction of 2-propanol was carried out in a tubular glass flow reactor (3 ml) under atmospheric pressure. Prior reaction test, the catalyst (50 mg) was pretreated at 300 °C for 1 h with N₂ flow (60 ml/min). To carry out the decomposition, 2-propanol vapor was supplied into the reactor by bubbling nitrogen gas through the alcohol container at 25 °C. The reaction temperature was 150 °C. The products were analyzed with an on-line VARIAN CP-3800 gas chromatograph with WCOT fused silica column.

3. Results and discussion

3.1. X-ray diffraction

XRD patterns of titania and sulfated titania samples annealed at 600 °C are shown in Fig. 1. In the spectrum for TiO₂–HNO₃ we can see two peaks at 2 θ = 25.38 and

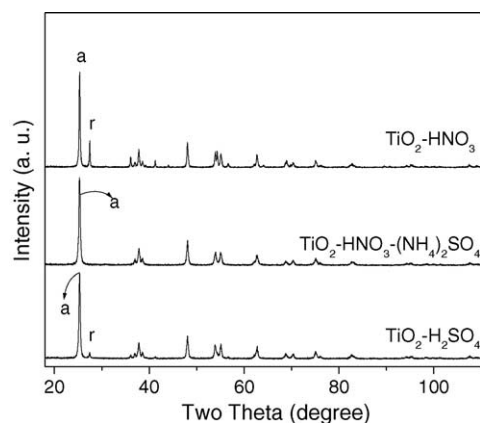


Fig. 1. X-ray diffraction patterns of the sulfated samples prepared with nitric acid, and annealed at 600 °C. 'r' corresponds to rutile phase and 'a' corresponds to anatase phase.

Table 1
Mean crystallite size (in nm) of the different samples annealed 600 °C

Catalyst	Anatase, <i>d</i> (nm)	Rutile, <i>d</i> (nm)
TiO ₂ -H ₂ SO ₄	37 (2)	40 (22)
TiO ₂ -HNO ₃	48 (3)	59 (15)
TiO ₂ -HNO ₃ -(NH ₄) ₂ SO ₄	34 (2)	

$2\theta = 27.42$ with crystallite size of 48 and 59 nm (Table 1) which corresponds to anatase and rutile crystalline phases, respectively. When the above sample was impregnated with ammonium sulfate, the titania was transformed totally into anatase with crystallite size of 34 nm. On the other hand, when titania was prepared with sulfuric acid, we can see the peaks corresponding to anatase and rutile phases with crystallite size of 37 and 40 nm, respectively (Table 1). The relative abundance of the phases was different in all samples and influenced by the presence of sulfate groups. For the sample prepared with nitric acid, this contains about 77 wt.% of anatase and 23 wt.% of rutile (Table 2), but the one prepared with sulfuric acid had 92 wt.% of anatase and 8 wt.% of rutile. For the sample prepared with nitric acid and sulfated with ammonium sulfate, pure anatase was obtained (Table 2). This means that the sulfate ions stabilized the anatase phase.

The refinement of titania crystalline phases was made in order to determine the average crystallite size of each phase. Anatase was modeled with a tetragonal unit cell having two titanium and four oxygen atoms, distribute according to space group *I4₁/amd*. The unit cell for rutile was also tetragonal, however, its atom distribution was given by space group *P4₂/mnm*.

Table 2
Crystalline phase concentration (in wt.%) for catalysts annealing at 600 °C

Catalyst	Anatase	Rutile
TiO ₂ -H ₂ SO ₄	92 (3)	8(1)
TiO ₂ -HNO ₃	77 (2)	23(2)
TiO ₂ -HNO ₃ -(NH ₄) ₂ SO ₄	100	

Table 3
Specific surface area and mean pore size diameter of the titania catalysts annealing at 600 °C

Catalyst	Surface area, BET (m ² /g)	Pore diameter (Å)
TiO ₂ -H ₂ SO ₄	46	133
TiO ₂ -HNO ₃	23	123
TiO ₂ -HNO ₃ -(NH ₄) ₂ SO ₄	117	120

3.2. Specific surface areas

The specific surface areas of the titania and sulfated titania are summarized in Table 3. For titania prepared with nitric acid, the specific surface area was 23 m²/g and the mean pore diameter was 123 Å. The specific surface area and mean pore diameter were 117 m²/g and 120 Å, respectively, for titania impregnated with ammonium sulfate. In titania prepared with sulfuric acid, the specific surface area was 46 m²/g and the mean pore diameter 146 Å. In Table 3, it can be seen that the samples with bigger surface area correspond to sulfated titania.

3.3. FTIR-pyridine adsorption

The FTIR spectra of pyridine thermodesorption on sulfated titania samples annealed at 600 °C are shown in Fig. 2. For the sample prepared with nitric acid and sulfated with

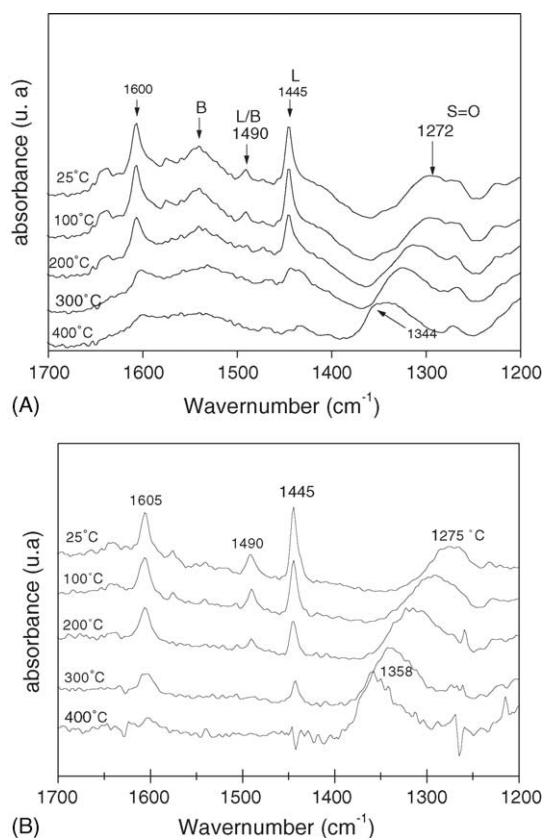
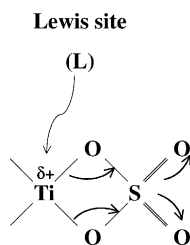
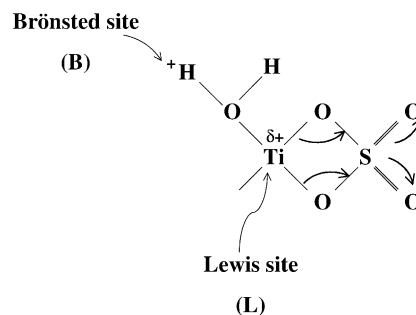


Fig. 2. FTIR-pyridine adsorption on (A) TiO₂-HNO₃-(NH₄)₂SO₄ and (B) TiO₂-H₂SO₄ annealed at 600 °C.



Scheme 1.



Scheme 2.

ammonium sulfate a fine peak is observed around 1445 cm^{-1} assigned to the adsorption of pyridine coordinated in Lewis sites. The band located at highest energy (1490 cm^{-1}) is associated to the presence of Lewis and Brönsted acids sites. The

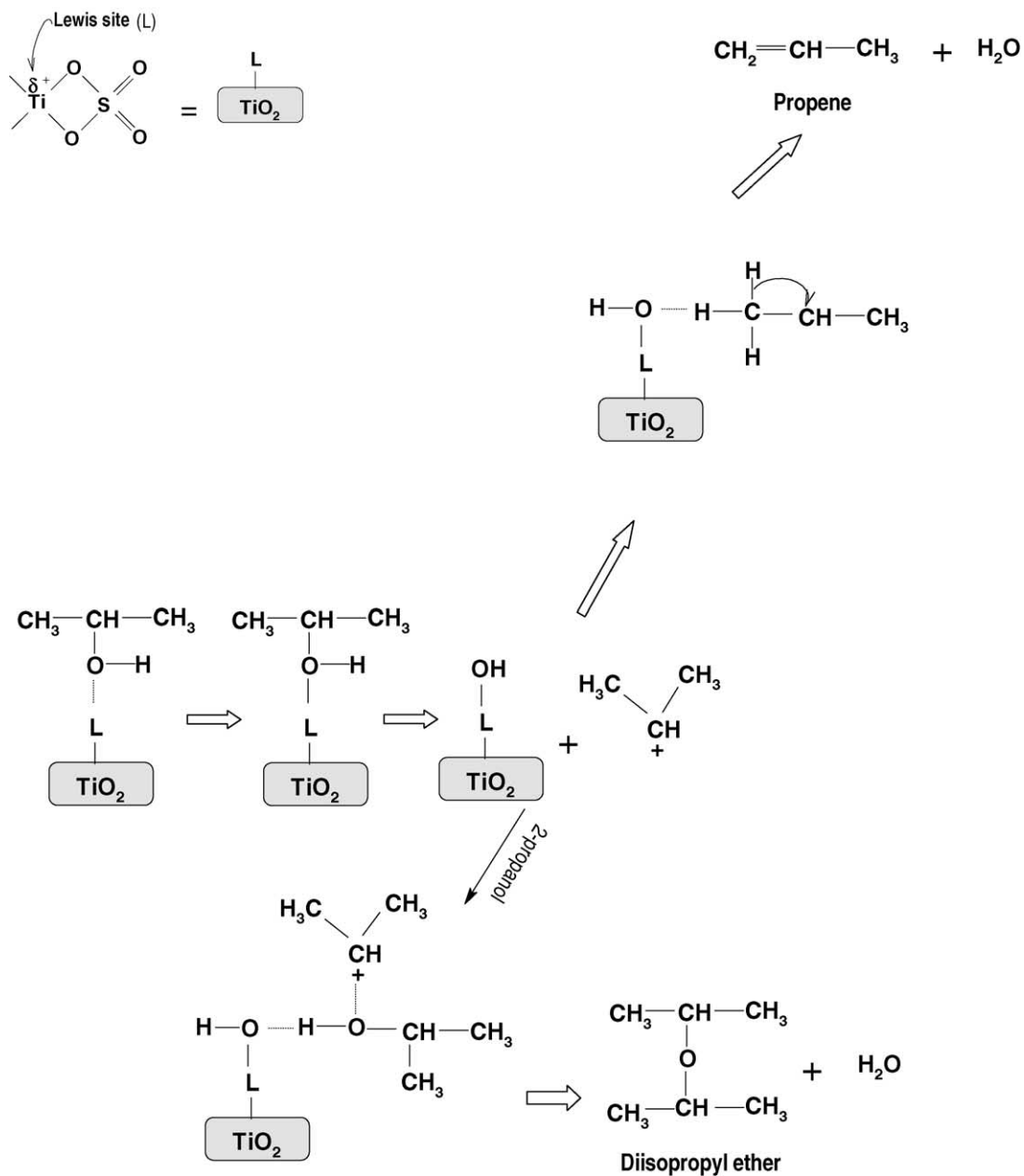
Fig. 3. Mechanism proposed for the 2-propanol decomposition over $\text{TiO}_2\text{-H}_2\text{SO}_4$.

Table 4
Pyridine adsorbed (mmol) in sulfated titania annealing at 600 °C

Catalyst	Adsorption temperature (°C)	Brönsted acidity	Lewis acidity	Total acidity
TiO ₂ -H ₂ SO ₄	25	0	160	160
	100	0	114	114
	200	0	62	62
	300	0	42	42
	400	0	4	4
TiO ₂ -HNO ₃ -(NH ₄) ₂ SO ₄	25	92	247	339
	100	79	128	207
	200	57	104	161
	300	26	69	95
	400	2	14	34

band at 1543 cm⁻¹ indicates the presence of Brönsted acids sites in the catalysts. The 1600 cm⁻¹ band follows a similar behavior to that of the 1445 cm⁻¹ band. This band identified strong Lewis sites. The band at 1575 cm⁻¹ identified weak Lewis acid sites, and it disappears at 200 °C under vacuum.

The wide band observed in the region of lower energies of the spectra presents a particular behavior during the thermal treatments. During this process, it is shifted towards high wavenumbers (1275–1358 cm⁻¹). This band is related to the vibrations of S=O bonds (sulfate anchored on the surface of the solid). Morterra et al. [38] observe the same behavior on sulfated zirconia, and they attributed the band shift to the presence of water which coordinates with S=O bonds.

For the sample prepared with sulfuric acid only the band corresponding to Lewis acid sites (1445 cm⁻¹) is clearly identified. Also, we can observe the displacement of the band at low energies corresponding to the S=O bonds by effect of water coordinated to adsorbed pyridine as occurring on the impregnated samples.

The density of Brönsted and Lewis acid sites at different desorption temperatures for all the samples are listed in Table 4. In general, the concentration of acid sites is bigger for titania impregnated with ammonium sulfate.

3.4. Catalytic activity

Activity and selectivity for the different samples are reported in Table 5. It can be seen that for TiO₂-H₂SO₄ catalyst, the selectivity to propene and DIPE were 22 and 78%, respectively, while for TiO₂-HNO₃-(NH₄)₂SO₄ the selectivity to propene and DIPE were 70 and 30%, respectively. The

Table 5
Catalytic activity and selectivity of sulfated titania annealed at 600 °C, in the 2-propanol decomposition

Catalyst	Conversion (mol%)	$r_a \times 10^{-6}$ (mol/s g)	Selectivity (mol%)	
			C ₃ =	DIPE
TiO ₂ -H ₂ SO ₄	5.76	3.7	22	78
TiO ₂ -HNO ₃ -(NH ₄) ₂ SO ₄	6.82	4.4	70	30

C₃= is propene and DIPE is di-isopropyl ether.

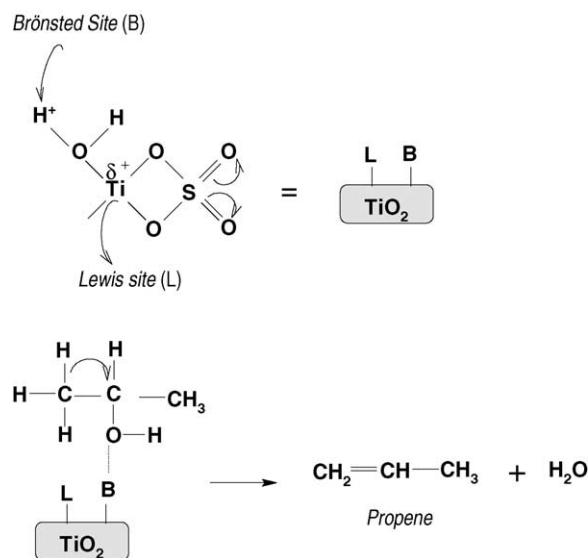


Fig. 4. Mechanism proposed for the 2-propanol decomposition over TiO₂-HNO₃-(NH₄)₂SO₄.

only difference between the two catalysts is the preparation method. This suggests that the sulfate ions were bonded in different forms in each catalyst. The literature indicates that the presence of sulfates species with covalent S=O bonds on the oxide surface is necessary to obtain superacidity [39], the exact nature of the catalytically active sites is not clear. Thus, it is suggested that the super acid centers are Lewis sites associated to the metal cation [40]. Acid strength is strongly enhanced by an electron induction effect of S=O in the sulfuric complex, as is shown in Scheme 1.

On the other hand, different authors suggest [40,41] that the Lewis and Brönsted (Scheme 2) sites generated from adsorbed water molecules are the responsible for the catalytic activity.

We can recapture the schemes shown above to propose a mechanism for the isopropanol decomposition reaction, taking into account that Scheme 1 corresponds to TiO₂-H₂SO₄ catalyst and Scheme 2 corresponds to TiO₂-HNO₃-(NH₄)₂SO₄.

In general it is conventionally accepted that acid sites are responsible for the dehydration activity giving propene and DIPE. An E1 mechanism is suggested for the dehydrogenated reaction where only acid sites are involved. In Fig. 3, it is explained the formation of propene and DIPE in Lewis acid sites.

In Fig. 4, the formation of propene and DIPE over the titania impregnated with ammonium sulfate is explained. In this catalyst is favored the formation of propene, because in this catalyst were identified both Lewis and Brönsted acid sites.

4. Conclusions

Sulfated titania can be obtained by the sol-gel method using sulfuric acid as titanium alkoxide hydrolysis catalyst

and by impregnating with ammonium sulfate of TiO₂ gel. The methods allow the formation of anatase and rutile in different amounts. In the sample prepared with sulfuric acid, Brönsted acid sites are not developed. In ammonium sulfate sample, both Brönsted and Lewis acid sites are formed. High selectivity to isopropyl ether was originated in Lewis acid sites, while propene formation is favored in the sample in which Lewis and Brönsted co-exist.

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