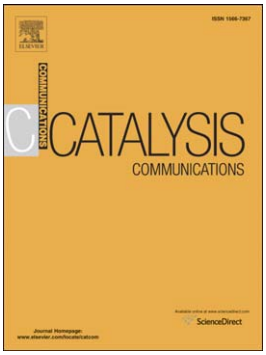

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ETHANOL DEHYDRATION ON SILICA-ALUMINAS: ACTIVE SITES AND ETHYLENE / DIETHYL ETHER SELECTIVITIES

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Abstract

Commercial silica-alumina catalysts prepared by different procedures have been characterized. Both present strong Lewis acidity together with Brønsted sites able to protonate pyridine. No evidence of “zeolitic” bridging OH’s but significant heterogeneity of terminal silanol groups, part of which are likely “pseudobridging”, was found. Similar high activity in ethanol conversion but markedly different selectivities to ethylene and diethyl ether were found. They are less active than both zeolites and γ-Al_2O_3. Lewis sites with alumina-like acidobasic neighbour are more selective for ethylene production while Lewis sites with silica-like covalent neighbour are more selective for diethyl ether.

Keywords: silica-alumina; ethanol; ethylene; diethyl ether; surface acidity; selectivity.

1 Introduction

Silica-aluminas are widely used as solid acid catalysts, catalyst supports and binders in various refining and petrochemical industrial processes, including hydrotreating, mild

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cracking, isomerization, oligomerization and alkylation [1-4]. Silica-aluminas are actually different materials depending on the preparation method, Si/Al ratio and pretreatments. Amorphous silica-aluminas (ASA) are silica-rich materials prepared by co-precipitation or co-gelling from mixed Si and Al precursors. Their most typical composition is with a SiO_2/Al_2O_3 molar ratio 10-12 corresponding to an alumina content of 12-15 wt.% [5,6]. In recent years, a number of materials belonging to this system with relevant mesoporosity have been prepared and developed at the industrial level [7]. Similar amorphous materials can be prepared by grafting moderate amounts of Al compounds on high surface area amorphous silica followed by calcination [8,9].

Another family of materials are prepared by grafting silica precursors on alumina or boehmite. This is the case in particular of the Siralox family of Sasol (previously Condea), whose preparation and characterization has been reported in some detail [10].

Silica-aluminas are usually reported possessing Brønsted acid sites together with Lewis acid sites, and have been characterized since early times by different methods [11-15]. However, still the nature of Brønsted acid sites in silica-alumina is not fully established. Several authors propose that Brønsted acidity of silica-alumina is due to small amounts of “zeolitic” bridging Si-OH-Al groups [16-18]. Other authors instead do not find in these samples the spectroscopic features typical of zeolitic OH’s (IR bands at 3650-3500 cm^{-1}, ^1H NMR bands at 3.8-5.2 ppm) but only those typical of terminal silanols ≡Si-OH (IR band at ca. 3745 cm^{-1} and ^1H peak at 1.7-1.8 ppm) [8,19-21], whose acidity may be enhanced by nearest aluminum ions. In agreement, theoretical studies suggest the presence of “pseudobridging” OH’s (i.e. terminal silanols prone to bridge over Al ions when they interact with a basic molecule) as the active sites [22,23]. A very recent study by Caillot et al. suggests that the nature of the active site may depend on the preparation procedure [24].

We recently investigated the activity of several acid catalysts in converting ethanol to ethylene [25-27]. Although zeolites are more active than silica-alumina, the key question is stability on time on stream, with reduced coking. Silica-aluminas have been used in the past and found suffuiciently stable for this reaction [28]. Over all catalysts, at low temperature and conversion, diethyl ether (DEE) is found as the main product, while, at higher temperature and conversion, ethylene becomes the main product. The mechanisms

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of these reactions are also the object of studies and some disagreement [29-31]. In this communication we report on our study of ethanol conversion on silica-alumina materials. The obtained data will allow us to propose some conclusions on both ethanol dehydration mechanism and on the surface acidity of silica-aluminas.

2 Experimental

The properties of the catalysts investigated and their notations are summarized in Table 1. Catalytic experiments were performed at atmospheric pressure in a tubular flow reactor feeding 7.9% v/v ethanol in nitrogen at 298 K (total flow rate of 80 cc/min) as described in our previous studies [25-27].

IR spectra were recorded using Nicolet 380 FT-IR spectrometers, with KBr disks for skeletal studies and pure powders pressed disks for adsorption studies, performed as described elsewhere [25,27]. Results

XRD analysis of the samples under study show complete amorphicity of the SiO_2 (S) and the SA87 samples. XRD of A and SA5 show the patterns of a spinel-type alumina phases, slightly different (γ-Al_2O_3 for A and γ,δ-Al_2O_3 for SA5), while that of SA30 shows the same features, weak and broad. The skeletal IR spectra of the catalysts are presented in Fig. 1. Two very broad and poorly resolved bands in the medium IR region in the spectrum of A at ca. 550 and 830 cm^{-1} are typical for γ-Al_2O_3 [32]. The spectrum of the sample SA5 is similar, but shows the evolution towards the spectrum of δ-Al_2O_3 (sharp components on the main absorption) and a pronounced broad feature in the region1150-980 cm^{-1}, due to Si-O stretchings of silicate species. The spectrum of SA87 and SiO_2 are typical of amorphous silica based materials (Si-O stretchings at ca. 1230 and 1090 cm^{-1}, Si-O-Si in plane deformation at 808 cm^{-1} and Si-O-Si rocking at 459 cm^{-1} [33]). In the case of silica gel the additional absorption at ca. 1000 cm^{-1} is due to the Si-O stretching of silanol groups, very abundant. The spectrum of SA30 combines those of amorphous silica alumina and spinel type Al_2O_3, in agreement with the XRD pattern.

The IR spectra of investigated samples in the region of the OH stretching of the surface hydroxyl groups, recorded after outgassing at 773 K, are presented in Fig. 2. The spectrum of A shows the main bands at 3770, 3725 and 3680 cm^{-1}, typical of the surface OHs of γ-Al_2O_3, as discussed previously [32,34]. SA5 shows weaker nearly the same bands with an additional sharp band at 3741 cm^{-1}, assigned to OH stretching of a silanol

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group. The spectra of SA30 and SA87, and that of Si as well, give rise to a single band at 3744 ± 2 cm^{-1} with a tail at lower frequencies, attributed to terminal silanol groups [34]. On SA30 and SA87 part of these groups may be "pseudobridging", i.e. located near Al cations and able to bridge after deprotonation [19,23]. As for comparison, in Fig. 2 the spectrum of a typical zeolite, H-ferrierite in this case, is also reported. In this case, together with a band due to silanol groups assumed to be located in the outer surface, the band of zeolitic bridging OH's at 3595 cm^{-1} is well evident [34]. It is clear that this band is absent in the spectra of silica-alumina samples.

Fig. 3 shows the IR subtraction spectra of residual adsorbed pyridine on investigated catalysts after outgassing at 373 K. Pyridine adsorbed on A gives rise to three 8a components observed at 1578, 1616 and 1624 cm^{-1}, corresponding to a complex 19b band center at 1452 cm^{-1}, revealing the existence of at least three different families of Lewis acid sites, and no significant Brønsted acidity, as typical of γ-Al_2O_3. It seems likely [32] that the most acidic sites are predominantly located on corners and edges in the nanocrystals of aluminas. The spectrum of SA5 is closely similar to γ-Al_2O_3, with possibly a smaller relative intensity of the 8a component at 1624 cm^{-1}. This indicates that this material does not show Brønsted acidity sufficiently strong to cause pyridine protonation. It possesses strong Lewis acidity, and that part of the strongest Lewis sites might be neutralized by interaction with silicate species.

In the case of both SA30 and SA87, the features of pyridine adsorbed on strong Lewis sites are also evident (8a mode at 1621 cm^{-1}, 19b mode at 1455 cm^{-1}) together with the bands associated to pyridinium ions at 1639 cm^{-1}, 8a, and 1547 cm^{-1}, 19a. This indicates, in agreement with literature data, that such silica-alumina samples have, together with strong Lewis acidity, also Brønsted acidity sufficiently strong to cause pyridine protonation. Pyridine adsorbs only weakly on S via H-bond and is fully desorbed at 373 K, thus confirming that amorphous silica neither possess Brønsted acidity sufficiently strong to cause pyridine protonation, nor Lewis acidity.

In Fig. 4 a full experiment of adsorption and desorption of pyridine on SA30, showing the formation of hydrogen bonded and weakly adsorbed pyridine (H), Lewis bonded pyridine (L) and pyridinium ion (Brønsted bonded, B,Fig. 4C). In Fig. 4A and 4B, the analysis of the region of the surface OH groups provides evidence of some complexity of the main band centered at ca. 3744 cm^{-1}, where three

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different components behaving differently can be distinguished at 3747, 3741 and 3726 cm^{-1}, likely due to different kinds of terminal and/or "pseudobridging" hydroxyl groups. The overall band shifts upon pyridine adsorption down to near 3000 cm^{-1}, in parallel to the formation of the H species,and is recovered by outgassing at increasing temperature when the species disappear. Components in the region 3650-3550 cm^{-1} are found neither in the normal spectra nor in the un-subtracted ones, thus excluding the presence of zeolite-like OH's. This agrees with the conclusion of Caillot et al. for the same sample [24]. The same is found for SA87, as already reported years ago [35].

In the table 2 and table 3, as well as in Fig. 5, the data concerning the catalytic activity of investigated catalysts in ethanol dehydration are summarized. The mass balance is essentially always fulfilled in these conditions. The trend of ethanol conversion in the experiments performed using the same catalyst weight (Fig. 5a) is A > SA87 > SA30 > SA5 >> S. γ-Al_2O_3, sample A, whose behavior has been discussed previously [25] and that is considered here as a reference catalyst, gives rise to the highest conversion at T ≥ 473 K. Pure SiO_2, sample S, has weak activity only at T ≥ 573 K. In the case of silica-aluminas, the activity trend is closely related to their surface area, the higher the surface area, the higher the catalytic activity. Looking at the product selectivities, all catalysts produce mainly DEE at low temperature and low conversion and ethylene at high temperature and high conversion (Table 2). Only SiO_2 produces also significant selectivities to acetaldehyde (~ 10%) at ≥ 623 K.

In the case of the experiments performed with the same catalyst surface area (Fig. 5b), the conversion on γ-Al_2O_3 is again definitely more than on all silica-aluminas, where similar conversions are found, the small differences being near the experimental error. However, the conversion trend is systematically SA5 > SA30 > SA87 at 573 K. Thus the catalytic activity of silica-aluminas seem to slightly decrease in parallel with increasing SiO_2/Al_2O_3 ratio in agreement with the data of Caillot el al. [24].

More important differences are found for product yield and selectivity. As evident in the lower sections of Fig. 5, the yields (and selectivities too) to ethylene markedly increase at similar conversion and temperature by increasing SiO_2/Al_2O_3 ratio, the reverse occurring to DEE yields and selectivities. Selectivities to other products are very small (≤ 0.3 %) except for SA5 where, at high temperature and conversion, they are ≤ 4.5 %.

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It must, in any case, be confirmed that the catalytic activity of silica-aluminas is lower than that of zeolites with comparable SiO_2-Al_2O_3 compositions [27]. In particular, experiments performed in the same conditions show that several zeolites give rise to detectable conversion of ethanol (mainly to DEE) already at 393 K where all silica-aluminas are still fully inactive.

3 Discussion

The data reported here confirm that silica-aluminas are active catalysts in converting ethanol to DEE and ethylene. However, they are less active than both zeolites and γ-alumina. Surface characterization confirms that silica-aluminas present strong Lewis acidity and also sufficient Brønsted acidity to protonate in part pyridine. IR spectra confirm that terminal silanol groups are the largely predominant surface hydroxyl groups on silica-aluminas. A detailed analysis of the spectra reveal some heterogeneity of these OH groups and do not produce any evidence of zeolitic hydroxyl groups [34]. It is consequently confirmed that the Brønsted acidity of silica-aluminas is due to very acidic terminal silanols.

The behavior, both from the point of view of the surface chemistry and from the point of view of the catalytic activity, suggest that silica-rich fully amorphous materials like typical co-precipitated or co-gelled cracking catalysts, and γ-Al_2O_3 containing sample such as Siralox 30/260 have close similarities, in agreement with Caillot et al. [24].

Concerning the ethanol dehydration reaction, the lower activity of silica-alumina with respect to protonic zeolites, the similar behavior with respect to aluminas and the conversion trend (more catalytic activity in absence of Brønsted acidity as for SA5) suggest that Lewis acidity is predominant in the catalysis of silica-aluminas in the reaction.

The significant difference found in the DEE *vs* ethylene selectivities at closely similar conversion and temperature conditions allows some mechanistic insight. In our previous papers we emphasized the parallel behavior of all different catalysts: in all cases DEE is found very predominant at low temperature and conversion, while ethylene is predominant at high temperature and conversion. Surface ethoxy groups were found to be the active surface intermediates for both reactions [31]

$C_2H_5OH \rightarrow C_2H_4 + H_2O$ (1)

$2\ C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O$ (2)

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Properly designed experiments [31] showed that the behavior is due to at least two factors: i) the two reactions are parallel and reaction (2) is characterized by lower activation energy and higher reaction order than reaction (1); ii) however, there is also a third reaction, the cracking of DEE to ethylene, showing that DEE can also act as intermediate in ethylene production.

$C_2H_5OC_2H_5 \rightarrow 2\ C_2H_4 + H_2O$ (3)

The experiments performed with different zeolites [27] suggested also that shape selectivity effects may also play a role, e.g. favouring ethylene formation also at low conversion when occurring in small pores: e.g. in the side pockets of mordenite and in ferrierite, where the addition of two molecules can be sterically hindered.

Here we show that the nature of different surface sites may also play a role. The increasing ethylene selectivity and decreasing DEE selectivity at the same temperature and conversion by increasing the silica content may be interpreted suggesting that the more active sites for DEE production may be different from the more active sites for ethanol ethylene production.

Our data [31] suggest that the main way to ethylene is essentially the elimination of an ethoxy group. Instead, the synthesis of DEE implies the reaction of ethoxy group with some form of undissociated ethanol. It can be supposed that activation of the second ethanol molecule on nearest acido-basic sites can be beneficial for DEE formation. This can more easily occur on silica-aluminas with lower SiO_2/Al_2O_3 ratio where the Lewis active sites should be more frequently surrounded by extended alumina-like surface. This is depicted in scheme 1. The activation of the second ethanol molecule could occur less efficiently in the predominantly covalent surface of silica-rich catalysts. This would explain why DEE selectivity at low conversion follows the trend (at similar low conversion): γ-Al_2O_3 (A)> SA5 > SA30 > SA87 > SiO_2 (S).

4 Conclusions

The conclusions of this paper are the following:

1. Amorphous silica-alumina and silica-alumina prepared by deposition of silicic acid on boehmite precursor (Siralox) have similar surface structures and behavior.
2. In all cases the materials present strong Lewis acidity together with Brønsted sites able to protonate pyridine.

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3. Both these materials do not show any evidence of “zeolitic” bridging OH’s, while they do show significant heterogeneity of terminal silanol groups, likely “pseudobridging”.
4. These materials show high activity in ethanol conversion to ethylene and diethyl ether.
5. The diethyl ether/ethylene selectivity depends on the nature of the active site, diethyl ether formation being more favoured for lower SiO_2/Al_2O_3 ratios where Lewis sites are more frequently surrounded by alumina-like surface.
6. The diethyl ether synthesis from ethanol occurs by reaction of ethoxy groups with an activated undissociated ethanol molecule.

Acknowledgements

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Table 1. The properties of investigated catalysts

Notation	XRD data	Commercial name	Manufacturer	SiO_2 wt%	Al_2O_3 wt%	Preparation	S_{BET} (m^2/g)
A	γ-Al_2O_3	Puralox SBa200	Sasol	0	100	From boehmite produced via Al alkoxides	~190
SA5	γ,δ-Al_2O_3	Siralox 5/170	Sasol	5	95	From silicic-acid impregnated boehmite produced via Al alkoxides	~170
SA30	γ-Al_2O_3, amorphous	Siralox 30/260	Sasol	30	70		~260
SA87	amorphous	Cracking catalyst	Strem Chemicals	87	13	Co-gel	~ 330
S	amorphous	Silica Gel SG127	Grace Davison	100	0	Gel	~ 300

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Table 2. Ethanol conversion and product selectivities (S) upon ethanol dehydration (experiments were performed with the same catalyst weight of 0.5 g, WHSV = 1.43 h^{-1})

Catalyst	Temp. (K)	Conversion (%)	$S_{Ethylene}$ (%)	S_{DEE} (%)	S_{Others} (%)
A	423	0.2	0.0	100.0	0.0
	473	20.8	0.9	99.1	0.0
	523	78.6	20.2	79.7	0.1
	573	97.7	99.7	0.3	0.0
	623	99.7	100.0	0.0	0.0
	673	99.9	99.8	0.0	0.1
	723	100.0	98.9	0.1	1.0
SA5	423	0.0	0.0	0.0	0.0
	473	2.6	0.0	100.0	0.0
	523	35.6	2.7	97.3	0.0
	573	74.1	24.3	74.3	1.4
	623	99.7	95.4	0.1	4.5
	673	100.0	96.1	0.0	3.9
	723	100.0	96.3	0.0	3.7
SA30	423	1.0	0.0	100.0	0.0
	473	8.3	6.6	93.4	0.0
	523	60.2	15.8	84.1	0.1
	573	84.5	23.8	76.0	0.2
	623	100.0	99.8	0.0	0.2
	673	100.0	99.7	0.0	0.3
	723	100.0	99.6	0.1	0.3
SA87	423	0.8	0.0	100.0	0.0
	473	15.7	13.7	86.3	0.0
	523	67.5	35.1	64.9	0.0
	573	96.0	99.6	0.3	0.1
	623	99.8	100.0	0.0	0.0
	673	100.0	100.0	0.0	0.0
	723	100.0	99.9	0.0	0.1
S	423	0.0	0.0	0.0	0.0
	473	0.0	0.0	0.0	0.0
	523	0.2	0.0	100.0	0.0
	573	0.6	24.6	75.4	0.0
	623	2.5	35.5	55.5	9.0
	673	8.6	48.8	31.8	19.4
	723	15.0	72.5	8.5	19.0

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Table 3. Ethanol conversion and product selectivities (S) upon ethanol dehydration (experiments were performed with the same catalyst surface area)

Catalyst	Temp. (K)	Conversion (%)	$S_{Ethylene}$ (%)	S_{DEE} (%)	S_{Others} (%)
A 2.97 h^{-1} WHSV	423	0.0	0.0	0.0	0.0
	473	9.5	0.9	99.1	0.0
	523	61.5	8.8	91.4	0.0
	573	91.5	94.1	5.5	0.4
	623	99.2	98.9	0.1	1.1
	673	100.0	99.4	0.0	0.6
	723	99.7	99.2	0.0	0.8
SA5 2.7 h^{-1} WHSV	423	0.0	0.0	0.0	0.0
	473	1.3	0.0	100.0	0.0
	523	31.0	2.2	97.8	0.0
	573	80.2	18.6	81.1	0.3
	623	98.3	98.4	0.6	1.0
	673	100.0	96.5	0.0	3.5
	723	100.0	96.8	0.1	3.1
SA30 4.0 h^{-1} WHSV	423	0.2	0.0	100.0	0.0
	473	2.8	8.0	92.0	0.0
	523	32.6	14.2	85.7	0.2
	573	74.8	41.8	58.0	0.1
	623	100.0	99.6	0.1	0.3
	673	100.0	99.6	0.0	0.4
	723	100.0	99.3	0.0	0.6
SA87 4.95 h^{-1} WHSV	423	0.3	0.0	100.0	0.0
	473	3.7	12.4	87.6	0.0
	523	26.0	30.5	69.5	0.0
	573	73.8	67.5	32.5	0.0
	623	99.0	99.6	0.4	0.0
	673	100.0	100.0	0.0	0.0
	723	100.0	100.0	0.0	0.0

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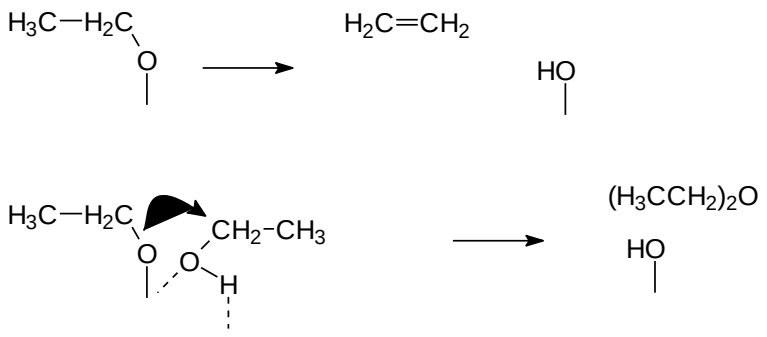

Scheme 1.

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Figure Captions

Fig. 1. FT-IR skeletal spectra (KBr pressed disks) of investigated catalysts.

Fig. 2. FT-IR spectra of investigated catalysts after activated at 773 K (νOH region).

Fig. 3. FT-IR subtraction spectra of surface species arising from pyridine adsorbed on investigated catalysts at 373 K.

Fig. 4. FT-IR spectra of the OH stretching region (A) and of adsorbed pyridine (C) on SA30. (B) spectra in the OH stretching region after subtraction of the spectrum of the activated sample. (a) sample activated at 500 °C in vacuum, (b) in contact with pyridine, later under outgassing at 300 K, 5 min (c), 300 K, 30 min, 5 min (d), 323 K, 5 min (e), 373 K, 5 min (f), 423 K, 5 min (g), 473 K, 5 min (h), 523 K, 5 min (i), 573 K, 5 min (l), 623 K, 5 min (m), 673 K, 5 min (n), 723 K, 5 min (o), 773 K, 5 min (p).

Fig. 5. Conversion of ethanol over investigated catalysts as a function of temperature: (a) performed using the same catalyst weight of 0.5 g, WHSV = 1.43 h^{-1} and (b) same catalyst surface area; (c) ethylene yield and (d) diethyl ether yield as a function of ethanol conversion in the case of experiments performed using same catalyst surface area.

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Fig. 1

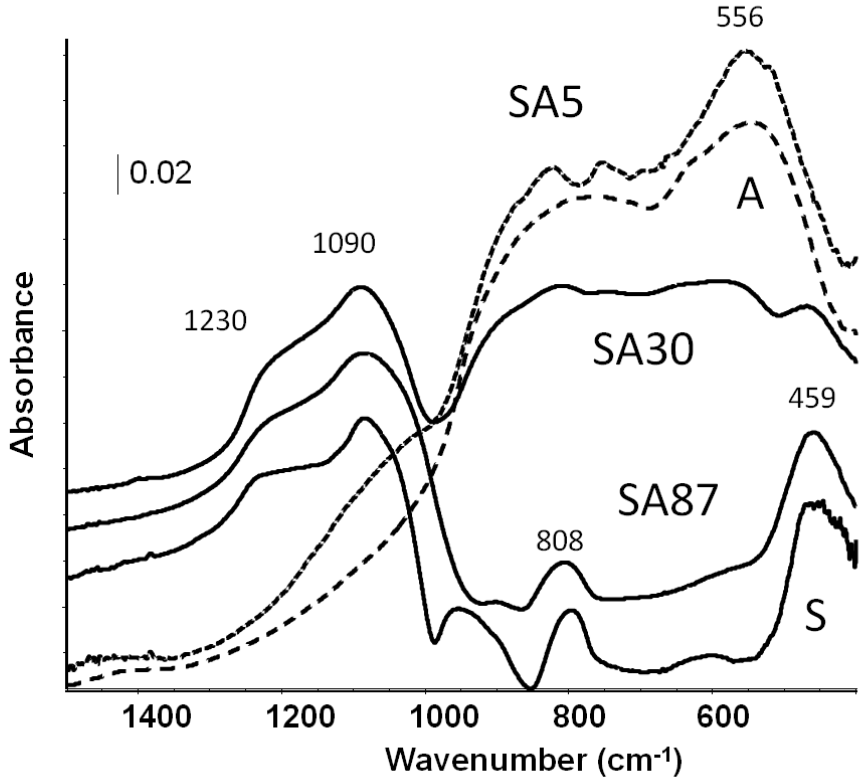

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Fig. 2

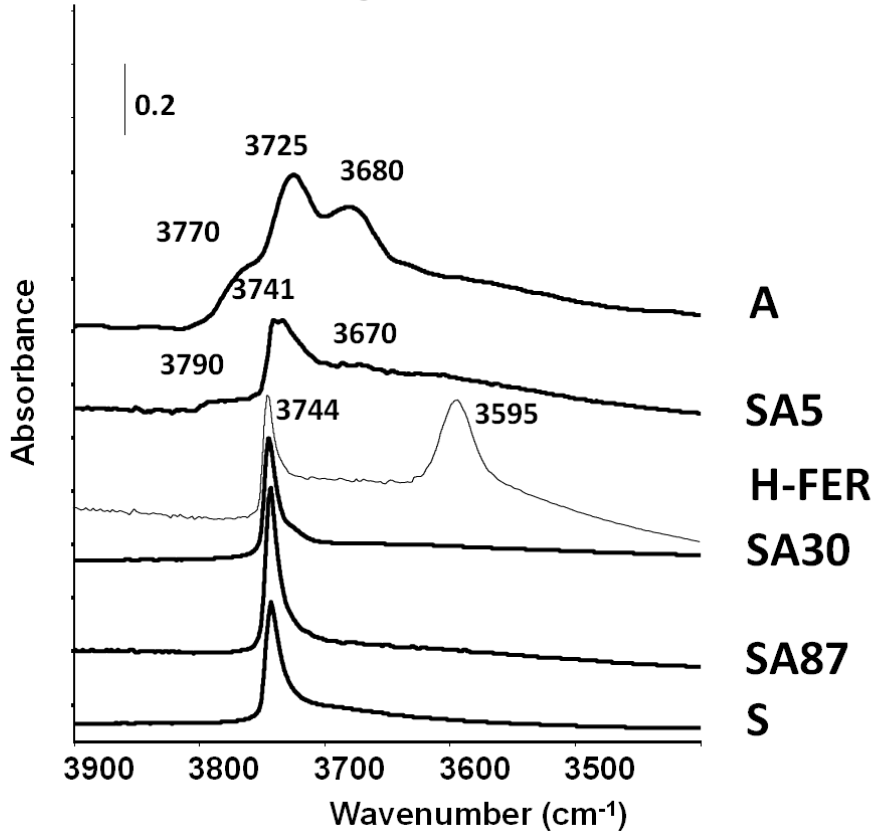

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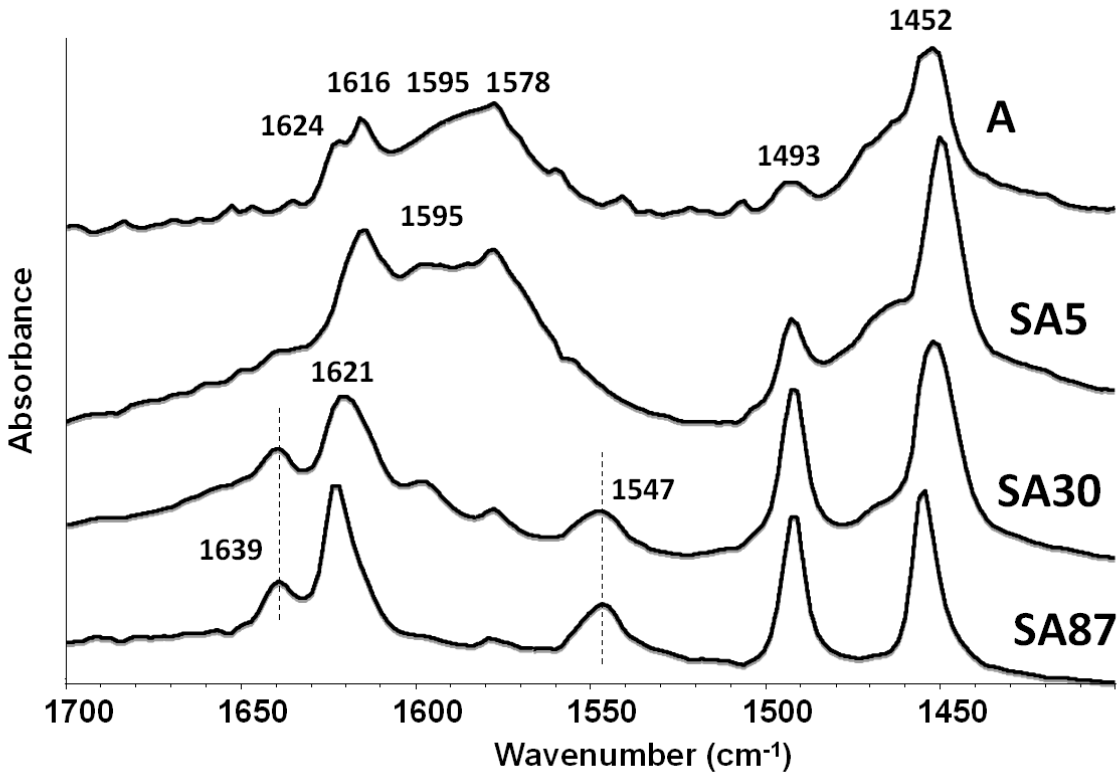
Fig. 3



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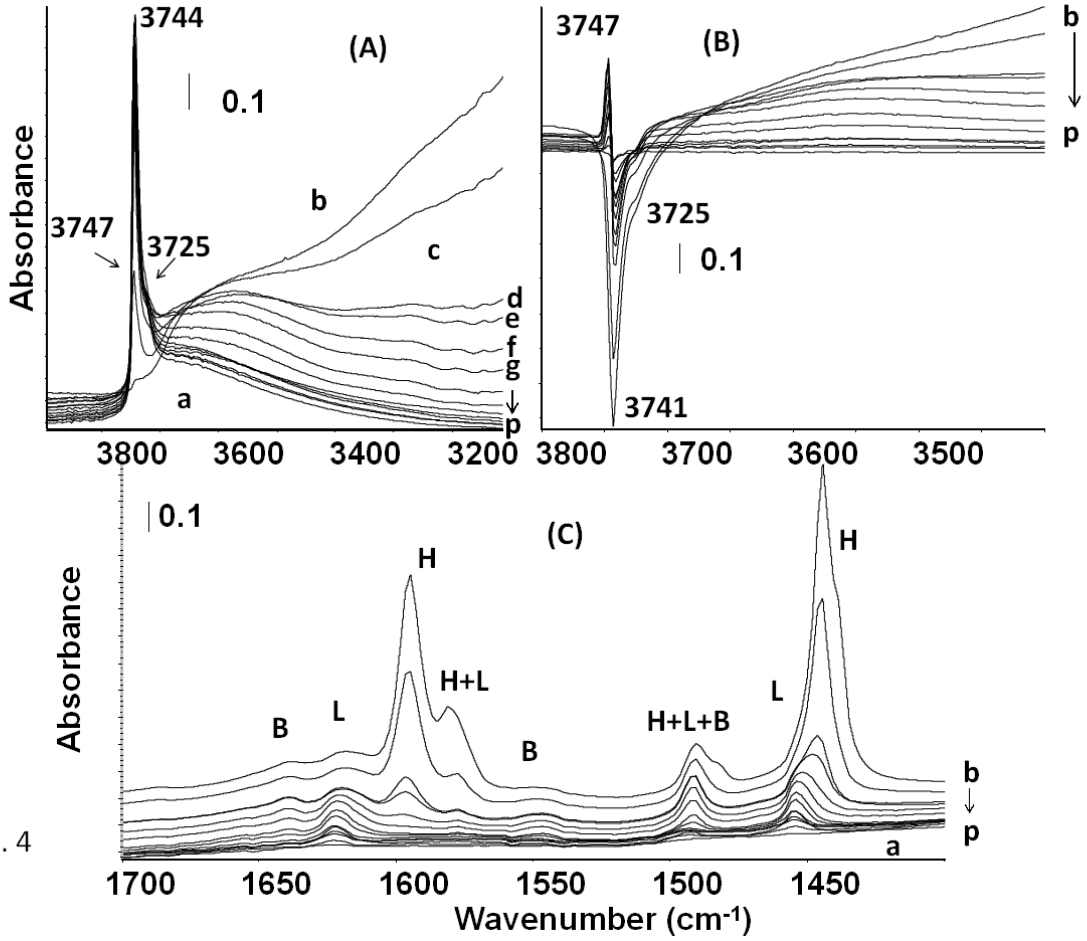

Fig. 4

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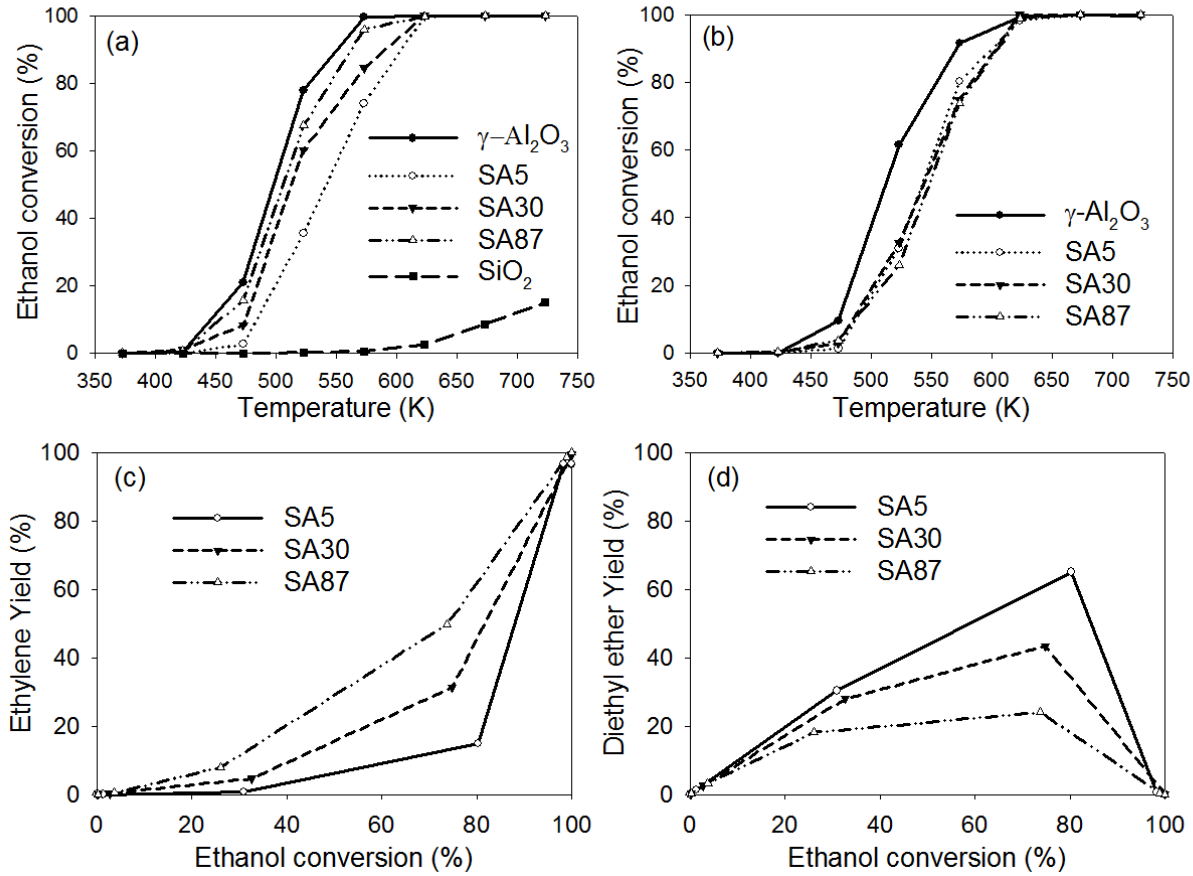
Fig. 5



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Highlights

- Differently prepared commercial silica-aluminas have similar surface sites
- Brønsted sites are pseudobridging terminal silanols.
- Ethanol conversion on slica-aluminas occurs on Lewis acid sites
- Lewis sites with alumina-like acidobasic neighbor are more selective for ethylene
- Lewis sites with silica-like covalent neighbor are more selective for diethyl ether

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