

Modified Aluminas : Relationship Between Activity in 1-Butanol Dehydration and Acidity Measured by NH_3 TPD

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ABSTRACT

We have investigated the changes of the catalytic properties in 1-butanol dehydration of γ -alumina modified by introduction of small amounts (0.2-2.0 wt %) of ions : SO_4^{2-} , PO_4^{3-} , Cl^- , F^- , Mg^{2+} and Na^+ . The acidic properties of the catalysts were investigated by NH_3 TPD. Ionic additives principally affected the intermediate acidity strength (NH_3 desorption temperature range 473-673 K), which varied from 1.1 (Mg^{2+}) to 3.2 (SO_4^{2-}) $\mu\text{mol.m}^{-2}$. The relative number of acid sites was increased by anions (x 4.6 for SO_4^{2-}) and decreased by cations (x 2.2 for Na^+). We propose a classification of the modified catalysts, according to their acidic properties, in the order : $\text{SO}_4^{2-} \gg \text{Cl}^- \geq \text{PO}_4^{3-} > \text{F}^- > - > \text{Mg}^{2+} \gg \text{Na}^+$. The catalytic activity varied in the range 0-400 $\mu\text{mol.h}^{-1}.\text{m}^{-2}$ and appeared to be only dependent on intermediate acidity, which is assumed to play the central role in 1-butanol dehydration. There exists an acidity optimum (2-3 $\mu\text{mol.m}^{-2}$), observed for PO_4^{3-} and Cl^- . The product selectivities are dependent on intermediate acidity. Dibutylether is formed preferably to 1-butene when acidity is increased, due probably to a parallel increase of the number of acid sites.

INTRODUCTION

Recently, the search for petroleum independent energy sources has led to investigate the possibility to obtain several alcohols from fermentation of biomasses and wastes (ethanol process in Brazil, acetonobutylic fermentation). We have conducted a programme aimed at the use of 1-butanol issued from acetonobutylic fermentation, for producing valuable products, namely olefins. Alcohol dehydration, which gives olefins and ethers, is a typical acid-base catalyzed reaction. Since a few years, acid catalysis benefits from renewed interest, because of its industrial role for fine transformations of high value added molecules (specialty chemicals, pharmaceutical products, ...).

Previous studies in our laboratory dealt with 1-butanol dehydration on alumina and modified aluminas [1, 2], phosphates [3], mixed oxides [4] and

montmorillonites [4]. It is well-known that the acid-base properties of the catalysts play a central role in alcohol dehydration. As we have at hand a γ -alumina which presents particularly adequate acid-base centres for 1-butanol dehydration, we recently focused our attention on the acid properties of aluminas and modified aluminas. Our first publication was aimed at applying several techniques to investigate acidity and basicity [5]. We used essentially TPD (NH_3 , CO_2 , 1-butene) and IR spectroscopy (pyridine, pyrrole). A dependence between surface acidity and basicity of aluminas and their catalytic activities in 1-butanol dehydration was found. This work showed that it would be sufficient to make slight modifications of the acid-base characteristics of $\gamma\text{-Al}_2\text{O}_3$ to obtain an adequate catalyst which should exhibit ideal catalytic properties (activity, selectivity, stability). These modifications are realized by incorporation of ionic additives. A compound (= precursor), which contains the desired ion, is deposited on γ -alumina (drying under vacuum). A further calcination of the sample leads to the elimination of the volatile part of the compound and the impregnation of the ion. The modification of the acid-base properties of our γ -alumina by several common ions appeared to be interesting. The present study discusses the effects of the introduced ions, the measure of acidity by NH_3 TPD and the catalytic properties of the modified aluminas in 1-butanol dehydration. We tried to establish some relationship between activity and acidity.

The NH_3 TPD method is a rapid and simple technique, which offers good reproducibility [6]. Typical TPD profiles for aluminas are presented in our previous work [5]. TPD curves propose a realistic picture of the distribution of the acid sites on the catalyst surface, in strength (X-axis) and number (Y-axis). Currently, authors propose a scale of acidity strengths based on the temperature scale (X-axis). It is well known that a low/high NH_3 desorption temperature corresponds to weak/strong acid sites. Three classes of acid sites are currently defined : weak (298-473 K), intermediate (473-673 K) and strong (> 673 K) [7, 8]. This procedure is similar to the one of the titration methods in the fact that an arbitrary acid strength scale is related to a directly measurable parameter (pKa of an indicator or desorption temperature).

The main default of TPD technique is that it does not establish an acid strength profile in H_0 units, but relating to the amount of desorbed base with its desorption temperature. Nevertheless, this argument ran down since the recent publication of a work by Yori et al. [9]. These authors observed a linear correlation between acid strength (H_0) determined by indicators and the reciprocal of ammonia desorption temperature for

aluminas and silica-aluminas. This is a fundamental work and, as far as we know, the first one which clearly shows a direct relationship between these two techniques. By using these correlations, and measuring the ammonia desorbed at different temperatures, acid strength distribution profiles can be obtained.

EXPERIMENTAL

Catalysts

A Rhône-Poulenc G.F.S.C. γ - Al_2O_3 was used as starting material. The modified γ - Al_2O_3 samples were prepared by wet impregnation. A 500 ml aqueous solution of the ion, containing 40 g γ - Al_2O_3 , was mechanically stirred during 24 h at room temperature. Water was then evaporated under vacuum and the solid was dried overnight at 383 K and calcined in air during 4.5 h at 823 K.

The reference materials were samples prepared following the above method, but where no precursor was present. For this series of reference materials, we reproduced the real pH of the impregnating solution (pH range 1.6-12.1, for SO_4^{2-} and Na^+ , respectively). But, as these samples did not exhibit significantly different catalytic properties, we kept only one (pH = 5.8, as F^-), which is called the reference alumina and noted A.

Table 1 presents the characteristics of the various samples which were prepared.

TABLE 1
Characteristics of the prepared samples

Catalyst	Name	Introduced ion content (wt %)	Precursor	
γ - $\text{Al}_2\text{O}_3/\text{H}_2\text{O}$	A	0		
γ - $\text{Al}_2\text{O}_3/\text{SO}_4^{2-}$	SO_4	1.0	H_2SO_4	UCB p.a. > 99%
γ - $\text{Al}_2\text{O}_3/\text{PO}_4^{3-}$	PO_4	1.0	H_3PO_4	UCB p.a. > 89%
γ - $\text{Al}_2\text{O}_3/\text{Cl}^-$	Cl	1.0	HCl	Merck p.a. > 37%
γ - $\text{Al}_2\text{O}_3/\text{F}^-$ (1)	F1	1.0	NH_4F	Merck p.a. > 95%
γ - $\text{Al}_2\text{O}_3/\text{F}^-$ (2)	F2	2.0	NH_4F	Merck p.a. > 95%
γ - $\text{Al}_2\text{O}_3/\text{Mg}^{2+}$	Mg	1.0	$\text{C}_4\text{H}_6\text{MgO}_4 \cdot 4\text{H}_2\text{O}$	UCB tout pur
γ - $\text{Al}_2\text{O}_3/\text{Na}^+$	Na	0.2	NaOH	Merck p.a. > 99%

BET

Specific surface areas were determined by adsorption of nitrogen at 77.4 K with a conventional volumetric BET apparatus.

NH₃ TPD

NH₃ TPD profiles were obtained with a versatile apparatus working under atmospheric pressure. The following procedure was applied : (a) heating of a sample of ca. 150 mg under helium at 823 K during 1 h; (b) cooling in the helium stream until room temperature; (c) adsorption of pure ammonia at room temperature during 30 min; (d) flowing of helium at room temperature during 1 h in order to eliminate physisorbed ammonia; (e) TPD measurement, under helium, with a heating rate of 10 K.min⁻¹, from room temperature to 823 K. The ammonia desorbed during the temperature rise was analyzed by a thermal conductivity detector. For quantitative analysis, we calibrated the apparatus with the empty reactor. The amount of desorbed ammonia is expressed as mol NH₃ per g or specific surface area of catalyst.

In order to exploit the TPD results in a quantitative way, we distinguished, among the whole NH₃ desorption temperature range (298-823 K), 10 ranges of desorption temperature (width : 50 K, with an exception for the first range : 298-373 K). Each range is characterized by a value of partial acidity. The sum of the partial acidities equals total acidity. These restricted partial acidities will be useful in order to visualize the effects of the introduced ions into γ -alumina and allow to compare quantitatively well defined acidity strengths.

Figure 1 illustrates the methodology we applied in order to exploit the TPD curves and to quantify partial acidities.

For the investigation of the relationship between activity and acidity, we will apply partial acidities relating to larger ranges of NH₃ desorption temperature. We will distinct weak acidity (w, 298-473 K) and intermediate (i) and strong (s) ones, for 473-673 K and 673-823 K ranges, respectively. These distinctions are based on the reaction temperature range observed for 1-butanol dehydration. Weak acidity is situated below (no catalytic activity), intermediate acidity coincides with measurable activity (5-95% of conversion) and strong acidity is situated beyond 100% of conversion.

Catalytic test

1-Butanol dehydration was carried out in a continuous fixed bed glass reactor (4 mm, i.d.) working under atmospheric pressure. A sample of ca. 100 mg (100-200 μ m fraction) was placed in the reactor and heated under helium (100 ml.min⁻¹) at a temperature between 573 and 623 K (i.e. the maximum reaction temperature + 20 K) during 2 h. Helium was then saturated with 1-butanol vapour (saturator heated at 323 K; 1-butanol

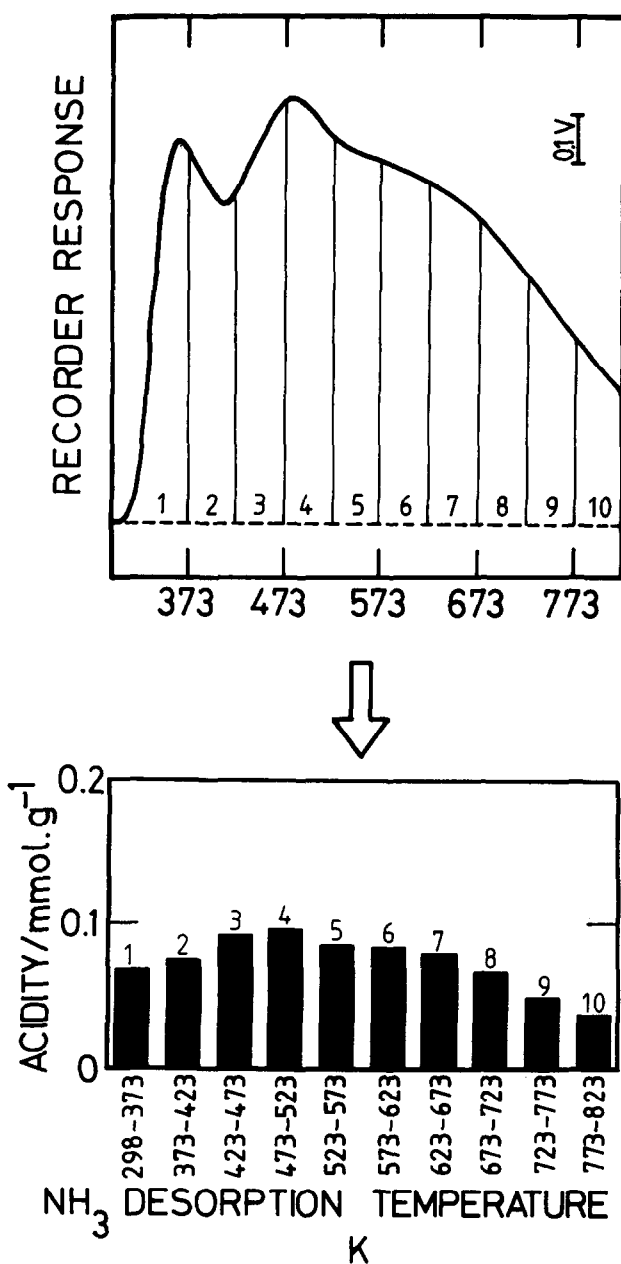


FIGURE 1 Methodology to quantifie partial acidities starting from a TPD curve : the example of reference alumina.

partial pressure : 4.4 kPa) and passed through the catalytic bed (LHSV : 4.7 h⁻¹) at temperatures between 473 and 603 K (5-95% of conversion). The unconverted 1-butanol and the dehydration products were analyzed by a Shimadzu GC-8A gas chromatograph working with helium as carrier gas, at 343 K, using a thermal conductivity detector. 1-Butanol (BuOH), dibutylether (DBE) and butyraldehyde (BAL) were analyzed on a 2 m 20% Reoplex 400/Embacel column and 1-butene (1B) and 2-butenes [cis (C2B) and trans (T2B)] on a 1.5 m n-octane/Porasil C column.

Catalyst activities remained stable during all the catalytic tests [10].

Conversion (C/%) is defined as the ratio between the amount of converted 1-butanol to the amount of 1-butanol supplied at the reactor inlet. Selectivity (S/%) for produced butenes or dibutylether is defined as the molar ratio of each product to 1-butanol converted.

RESULTS

BET

The specific surface areas of the studied aluminas are listed in Table 2. The reference alumina presents a specific surface area of 218 m².g⁻¹ and the ion-modified aluminas exhibit specific surface areas of 214 (-1.4%) to 226 m².g⁻¹ (+4.1%). The specific surface areas remained thus unchanged after the incorporation of ions in the range 0.2-2.0 wt %.

TABLE 2
Acidity of the catalysts

Catalyst	BET specific surface area (m ² .g ⁻¹)	Introduced ion content		Total acidity ^a		Partial acidities ^b			Specific effect on total acidity ^e
		(c)	(d)	(c)	(d)	w (%)	i (%)	s (%)	
A	218	0	0	0.73	3.3	32.0	46.9	21.1	0
SO ₄	226	0.104	0.46	1.23	5.4	21.8	58.1	20.1	4.57
Cl	225	0.282	1.25	1.14	5.1	20.7	60.3	19.0	1.44
PO ₄	214	0.105	0.49	0.84	3.9	19.1	49.2	31.7	1.22
F ₂	217	1.053	4.85	0.89	4.1	47.6	35.8	16.6	0.16
F ₁	218	0.526	2.41	0.83	3.8	42.2	39.4	18.4	0.21
Mg	224	0.424	1.89	0.55	2.5	24.1	45.0	30.9	-0.42
Na	225	0.083	0.37	0.57	2.5	18.1	50.9	31.0	-2.16

^a temperature range 298-823 K

^b w : weak (298-473 K)

i : intermediate (473-673 K)

s : strong (673-823 K)

^c mmol.g⁻¹

^d μmol.m⁻²

^e μmol_{NH₃}.m⁻²/μmol_{ion}.m⁻²

NH₃ TPD

Table 2 presents the NH₃ TPD results. The first information concerns total acidity, which relates to the whole range of NH₃ desorption temperature (298-823 K). The reference γ -Al₂O₃ (A) exhibits a total acidity of 3.3 $\mu\text{mol.m}^{-2}$ and the ion-modified aluminas present total acidities in the range of 2.5-5.4 $\mu\text{mol.m}^{-2}$. The modification by cations (Mg²⁺, Na⁺) decreases total acidity (- 24%) while the modification by anions increases total acidity (+64% for the highest acid SO₄ sample).

The second information concerns the relative importance of the three classes of acidities, weak, intermediate and strong. These results will be presented below in parallel with Figure 2.

Figure 2 presents the TPD histograms for the studied catalysts. The reference alumina exhibits a broad distribution of acid strengths with a maximum in the range of 473-523 K. Table 2 shows that 32.0% of the sites are weak acid sites, 46.9% intermediate acid and 21.1% strong ones. Among the anion-modified aluminas, SO₄ and Cl present the highest total acidities : 5.4 (+64%) and 5.1 (+55%) $\mu\text{mol.m}^{-2}$, respectively. These two samples exhibit similar distributions of acid strengths, with a maximum, marked for Cl, in the temperature range of 523-573 K. The principal effect of SO₄²⁻ and Cl⁻ is to increase significantly the intermediate acidity. Indeed, among the total number of sites, 60% are of the intermediate strength, while weak and strong ones are 20% each (see Table 2). The modification of γ -Al₂O₃ with PO₄³⁻ causes a decrease in weak acidity and an increase in intermediate-strong acidities of the range of 573-773 K (see Figure 2). Total acidity is thus increased to 3.9 $\mu\text{mol.m}^{-2}$ (+18%) as can be seen in Table 2. The fluorine-modified aluminas show acid strengths distributions close to the one of reference alumina (Figure 2), except for the range of 373-473 K (weak acidity) for which we observe a strong increase (factors 1.5 to 2.6). Total acidity is increased to 3.8 (like for PO₄) and 4.1 $\mu\text{mol.m}^{-2}$ for F1 and F2 respectively (Table 2). The cation-modified aluminas show a decrease of total acidity to 2.5 $\mu\text{mol.m}^{-2}$ (-24%). The modifications by Mg²⁺ and Na⁺ affect exclusively the sites of acidity strengths of the ranges < 573 K, the other sites being practically unchanged.

The specific effects on acidity (for the definition, see discussion) of our aluminas are listed in Table 2. We observe that the highest specific effect is presented by SO₄ (4.57), followed by Cl and PO₄ (close to 1.5) and F (0.2). Of course, Mg and Na develop a negative specific effect with -0.42 and -2.16, respectively. The classification of our catalysts, according to the specific effect is : SO₄ >> Cl ≥ PO₄ > F > reference alumina > Mg >> Na.

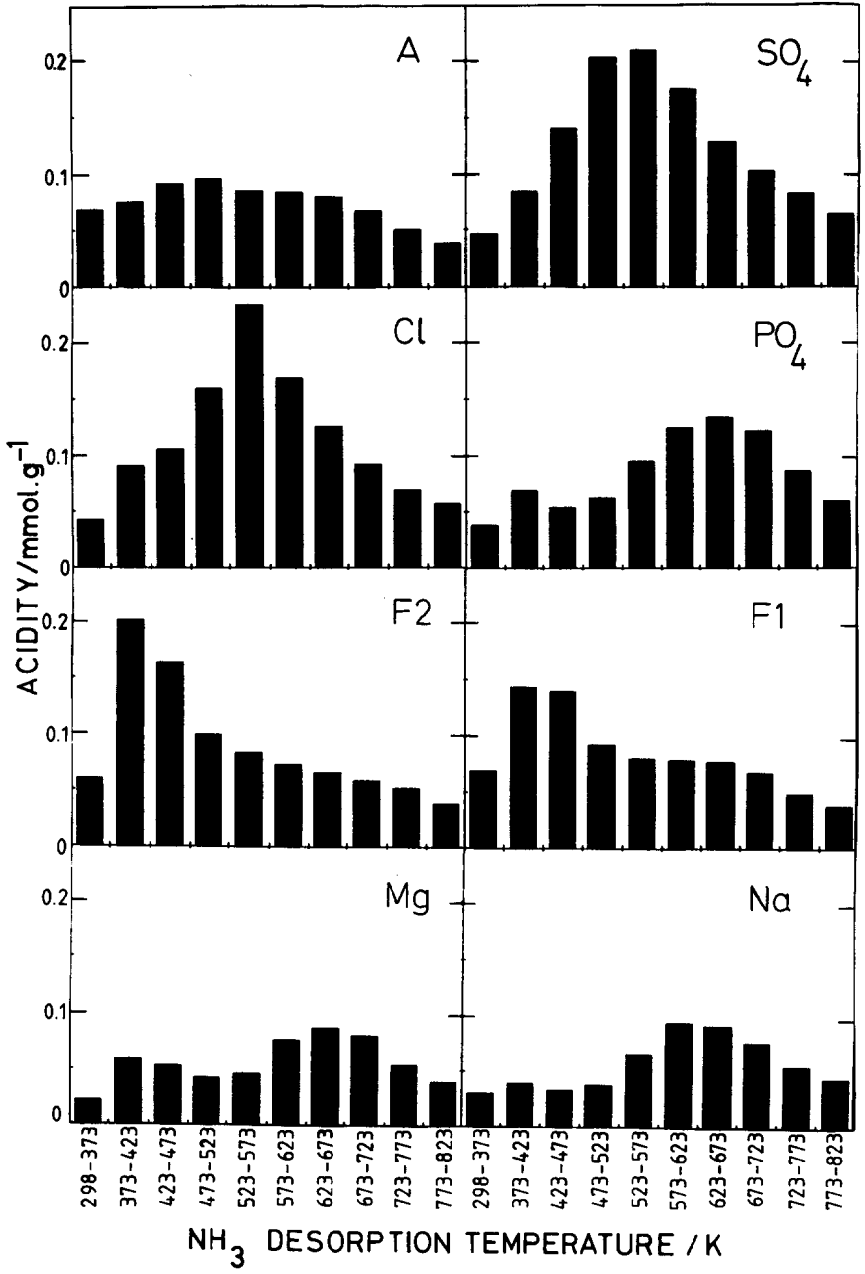


FIGURE 2 Partial acidities of aluminas as a function of ammonia desorption temperature.

Figure 3 presents the evolution of the three classes of partial acidities (weak, intermediate, strong) as a function of the specific effect of ions on total acidity. The weak acidity (298-473 K) increases progressively from 0.5 (Na) to 1.2 $\mu\text{mol.m}^{-2}$ (SO_4) for all catalysts, except for the two F-modified aluminas. These two samples exhibit a particularly great amount of weak acidity : 1.6 and 2.0 $\mu\text{mol.m}^{-2}$ for F1 and F2 respectively, i.e. approximately a factor 2 higher compared to the other samples. The intermediate acidity (473-673 K) is close to 1.2 $\mu\text{mol.m}^{-2}$ for Na and Mg and increases beyond specific effect value of zero (A sample). Cl and SO_4 present significantly higher intermediate acidities (3.2 $\mu\text{mol.m}^{-2}$). Like weak acidity, the strong one (673-823 K) increases progressively from 0.8 $\mu\text{mol.m}^{-2}$ (Na) to 1.1 $\mu\text{mol.m}^{-2}$ (SO_4).

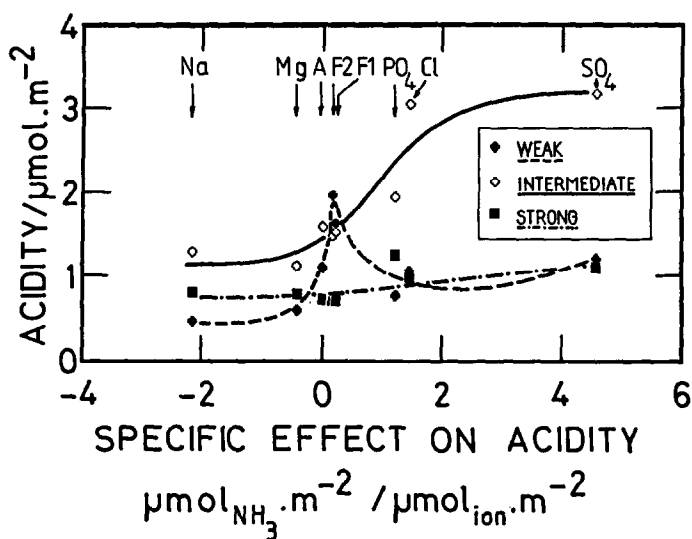


FIGURE 3 Evolution of partial acidities as a function of the specific effect on total acidity.

Catalytic test

1-Butanol dehydration on reference alumina

We observed the 1-butanol dehydration on reference alumina between 473 and 538 K (conversion range 5-95%) (see Figure 4).

In order to investigate the evolution of product distribution (DBE and 1B) in dependence of conversion, we varied the BuOH partial pressure (0.9-13.3 kPa), at 513 K. Figure 5 presents the results of this study. The

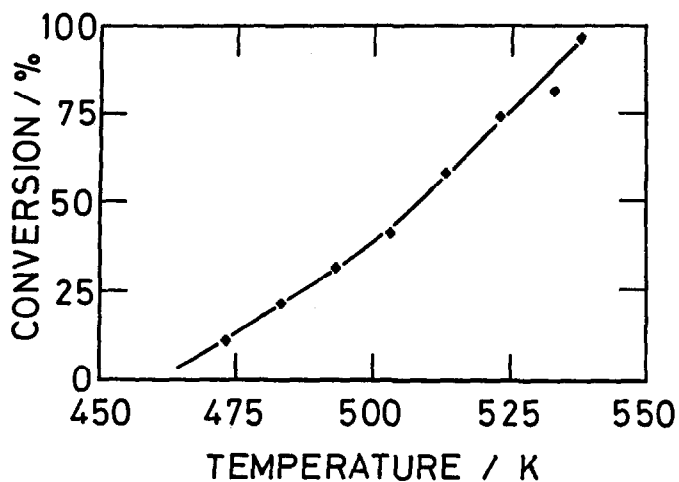


FIGURE 4 Evolution of 1-butanol conversion as a function of reaction temperature on reference alumina.

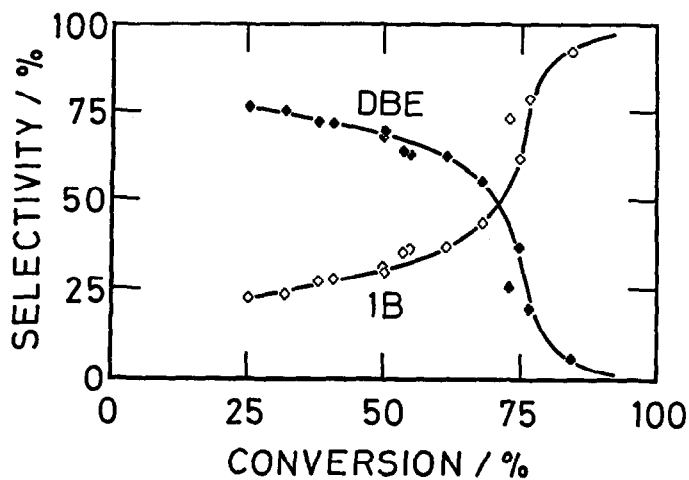


Figure 5 Selectivities to dibutylether (DBE) and 1-butene (1B) versus 1-butanol conversion at 513 K, on reference alumina.

evolution of DBE and 1B selectivities is complementary as a function of BuOH conversion. DBE is favoured at low conversion (< 60%), while 1B is favoured at high conversion (> 60%). Beyond 90% of conversion, 1-B is the sole product formed. Below 20% of conversion, both selectivities reach constant values of 80% for DBE and 20% for 1B.

1-Butanol dehydration on modified aluminas

Figure 6 shows the evolution of BuOH conversion as a function of reaction temperature for the various modified aluminas. These samples exhibit a behaviour similar to that of the reference alumina. The modification of $\gamma\text{-Al}_2\text{O}_3$ with various ions leads to important changes in activity. Table 3 summarizes the most characteristic catalytic properties, as measured in experiment at 50% conversion.

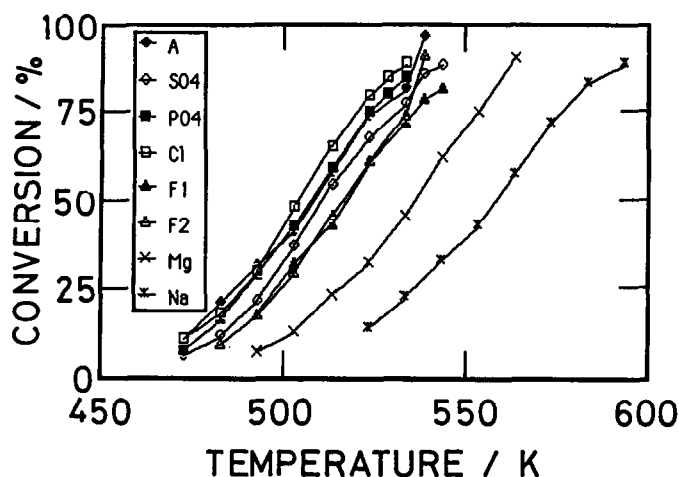


FIGURE 6 1-Butanol conversion as a function of reaction temperature for the various modified aluminas.

TABLE 3

Catalytic properties (conversion = 50%) of the modified aluminas

Catalyst	Reaction temperature (K)	Selectivity ^a (%)			
		DBE	1B	C2B	T2B
A	508	65.2	34.3	0	0
SO ₄	510	71.1	27.9	0	0
Cl	504	67.1	32.0	0	0
PO ₄	507	62.4	36.6	0.1	0
F2	516	58.7	28.1	8.7	3.5
F1	517	58.8	39.0	1.2	0
Mg	536	58.0	40.7	0.1	0
Na	558	64.9	33.9	0	0

^a BAL selectivity = balance

Cl, PO₄ and SO₄ exhibit activities close to the one of the reference alumina. Their characteristic temperatures vary between 504 and 510 K, close to the one of A (508 K). Cl presents a little bit higher activity, PO₄ a similar one, and SO₄ a lower activity. F-modified aluminas show lower activities : a substantial increase of temperature (+ 8 K) is necessary to maintain the same half conversion. Cation-modified aluminas show a dramatic inhibition of activity as the temperature (at C = 50%) reaches 536 K (+ 28 K) for Mg and 558 K (+ 50 K) for Na.

Table 3 presents also the selectivities (at C = 50%) for the products. DBE selectivity varies from 58.0% (Mg) to 71.1% (SO₄). The evolution of the butenes selectivities is complementary of the DBE one. Generally, the isomerization reaction is not important. C2B is only formed with negligible selectivities (0.2% maximum at high conversion). There is an exception for the F-modified aluminas which exhibit important isomerization activities, as F2 presents a C2B selectivity of 8.7% and T2B one of 3.5%.

DISCUSSION

NH₃ TPD

The NH₃ TPD results (Table 2 and Figure 2) show that ions incorporated into alumina induce very important changes in the amount of acidity and in the acid strengths distribution. Histograms (Figure 2) are particularly indicative of the evolution of the partial acidities as a function of the NH₃ desorption temperature. This representation clearly shows the various distributions of the acidity strengths in the aluminas. In terms of amounts

of acidities, the TPD results will be exploited later in activity-acidity relationships.

Another way of applying TPD results lies in the effects of ions in modifying the acidic properties of γ -alumina. In order to classify our catalysts according to an acidity scale, we applied the **specific effect of ions on acidity**. It is defined [11] as follows :

$$\frac{\text{acidity of ion-modified alumina} - \text{acidity of reference alumina}}{\text{unit concentration of ion into alumina}}$$

and expressed in $\mu\text{mol}_{\text{NH}_3} \cdot \text{m}^{-2} / \mu\text{mol}_{\text{ion}} \cdot \text{m}^{-2}$. This definition leads to a specific effect on acidity of zero for the reference alumina. Generally, the specific effect on acidity is related to total acidity, corresponding to the whole range of NH_3 desorption temperature (298-823 K). But the specific effect on acidity could also be related to partial acidities; the specific effect on weak acidity (298-473 K) being an example. The specific effect on acidity quantifies the number of acid sites which are created (positive effect) or destructed (negative effect) by the impregnation of one mol of ion per m^2 of active surface of catalyst. It must be noted that the destruction of acidic sites is finally directly compensated by the creation of basic sites [5].

In applying the above notion, we are able to propose a classification of the ion-modified aluminas related to an acidity scale. This sequence is established for 1 wt% ion, except for Na (0.2 wt%) because of the dramatic inhibiting effect of this ion on the dehydrating activity of alumina. It is also worth mentioning that this classification agrees with the one observed by Jiráková and Beránek, who applied a titration method with n-butylamine and indicators [11].

Catalytic test

Previous results

The knowledge of reaction pathways on aluminas (see [1]) is a preliminary condition to the comprehension of the individual action of the ionic additives.

In Figure 5, 1B is the only product formed at high BuOH conversions (> 90%). This situation corresponds to low BuOH partial pressure (< 1.2 kPa). Occupied active sites are distant and DBE production would be impossible. Indeed, the formation of one DBE molecule requires that two BuOH molecules be adsorbed on two neighbouring sites. On the contrary, 1B formation is always possible as it requires that only one BuOH molecule be adsorbed on one active site. Consequently, there would exist a minimal BuOH partial pressure under which DBE formation is impossible. In

conclusion, at high conversions, the only reaction which occurs on alumina is the dehydration of BuOH to 1B and water.

In the intermediate range of BuOH conversion (90-20%), related to BuOH partial pressure range 1.2-11.0 kPa, there is a competition between 1B and DBE formations. From high to low conversions, DBE selectivity increases and, consequently, the 1B one decreases (see Figure 5). This phenomenon could be understood if we assume that the probability of producing DBE increases as the amount of available BuOH molecules increases. DBE, formed from two adjacent adsorbed BuOH molecules, would be rapidly desorbed as a consequence of a strong adsorption competition between BuOH and DBE. Indeed, great amounts of adsorbed BuOH molecules imply that the access to the surface of large DBE molecules should be made difficult.

When conversion becomes lower than 20%, selectivities remain constant. This situation is related with a simultaneous constant BuOH consumption and corresponds to a complete saturation of the catalyst surface with chemisorbed BuOH molecules. In this region of low conversions, we could assume that DBE formation monopolizes all the sufficiently neighbouring sites ("twin sites") and that 1B formation occurs on the lone sites ("isolated sites").

1-Butanol dehydration on modified aluminas : activity-acidity relationship

The only credible, though complex, relationship between activity and acidity was found when we considered intermediate acidity, i.e. the one relating to NH_3 desorption temperature range 473-673 K.

Figure 7 shows the evolution of activity (converted BuOH) as a function of intermediate acidity. We observe an increasing activity with increasing intermediate acidity from Na to A. At 533 K, the Na-modified alumina presents a poor activity ($102 \mu\text{mol.h}^{-1}.\text{m}^{-2}$) and the reference alumina exhibits a 3.6 times greater activity ($369 \mu\text{mol.h}^{-1}.\text{m}^{-2}$). Beyond reference alumina, the activity increase diminishes and PO_4 and Cl present the highest activities, close to $400 \mu\text{mol.h}^{-1}.\text{m}^{-2}$. SO_4 , which presents the greater acidity, exhibits a lower activity ($346 \mu\text{mol.h}^{-1}.\text{m}^{-2}$). The same dependence is observed on all the range of reaction temperatures.

The fact that activity would be dependent on only intermediate acidity is not to be considered as so surprising because this dependence would have been assumed. We could propose a preliminary explanation to this relationship if we reconsider Figure 3.

Strong acidity would not explain the activity changes (Figure 7) because it was practically not affected by the incorporation of ions (Figure 3).

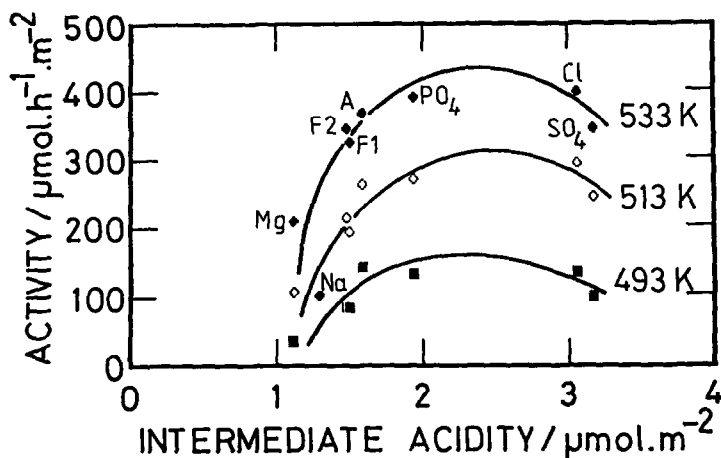


FIGURE 7 Relationship between activity and intermediate acidity.

Weak acidity could also be considered as unchanged, except for F samples which exhibit higher weak acidities (Figure 3). Nevertheless, these high values do not contribute to the activities observed for the F samples (Figure 7).

Consequently, we could assume that strong and weak acidities would not play a determining role in 1-butanol dehydration.

Finally, only intermediate acidity would play the central role because it was significantly affected by the incorporated ions (Figure 3). This influence is clearly seen in Figure 7. The activity increase from Na to PO₄ could be explained by the similar increase of intermediate acidity. Beyond PO₄, the intermediate acidity increase is unnecessary as activity reaches a maximum (Cl) and, finally, starts to decrease (SO₄). The optimum relationship between activity and acidity is overlooked.

The 1-butanol dehydration would require acid sites, in number and strength, at least as the reference alumina. Despite adequate acidic properties presented by this alumina, Figure 7 shows that there exists an acidity optimum where activity is improved. This optimum is situated between PO₄ and Cl samples. Cations, which present a negative specific effect on acidity, have to be eliminated for application in alcohol dehydration.

In conclusion, we propose that 1-butanol dehydration would require an acidity slightly enhanced by ionic additives which bring about a particular "quality" of acid sites (nature, density, distribution). This "quality" notion requires an IR spectroscopic approach (adsorption of probe molecules) to be quantitatively determined.

Selectivity-acidity relationship

Figure 8 shows the influence of intermediate acidity on dibutylether (DBE) and butenes (B) selectivities (see Table 3). The overall trend is a DBE selectivity increase when acidity increases. The B selectivity dependence on acidity is complementary of that of DBE. The same trends are observed on all the conversion range.

A simple qualitative view could explain the selectivities' dependence on intermediate acidity. An acidity increase corresponds to the creation of new acid sites. The specific effect on acidity illustrates and confirms this assumption. Consequently, if the number of acid sites is increased, the probability that two BuOH molecules are on two sufficiently neighbouring sites is greater. Then, DBE will be formed preferably on B. This assumption would explain the DBE selectivity increase observed in Figure 8.

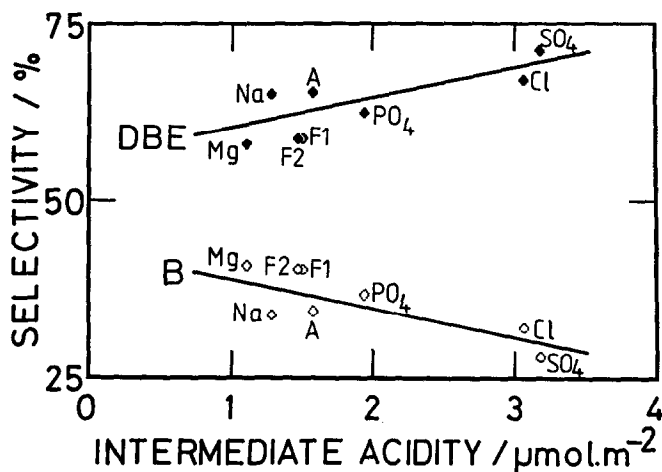


FIGURE 8 Selectivities to dibutylether (DBE) and butenes (B) as a function of intermediate acidity.

CONCLUSION

The NH_3 TPD technique, interpreted in terms of amounts of NH_3 desorbed in well-defined temperature intervals, gives extremely useful information for describing acidic properties of ion-modified aluminas. These results can be correlated to the catalytic activities. The intermediate acidity strength plays the central role in 1-butanol dehydration. An activity optimum is observed with PO_4^{3-} - and Cl^- -modified aluminas. The product selectivities are also dependent on intermediate acidity. Dibutylether is formed preferably to 1-butene when the number of intermediate strength acid sites is increased.

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