JOURNAL OF CATALYSIS **151**, 307–314 (1995)

Conversion of Alcohols (α-Methylated Series) on $AlPO_4$ Catalysts

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Received March 22, 1994; revised September 14, 1994

The conversion (dehydration/dehydrogenation) of alcohols in α-methylated series (methanol, ethanol, 2-propanol, and *tert*-butanol) on $AlPO_4$ catalysts differently prepared has been studied by microcatalytic pulse reactor technique at different temperatures and flow rates. The kinetic parameters have been obtained by analysis of the data through the Bassett–Habgood equation. Dehydration to ether and/or olefin is the major reaction process. Dehydrogenation product was only scarcely found in 2-propanol conversion. The influence of the reaction temperature upon the conversion of alcohols and the selectivities of the products was investigated. Activity increases as a function of surface acidity of the $AlPO_4$ catalyst as well as with the α-substitution in the alcohol. Moreover, selectivity studies indicated that ethanol and 2-propanol dehydration follows a combination pathway of parallel and consecutive reactions. A good correlation between the results of dehydration conversion and acid properties, gas-chromatographically measured through the irreversible adsorption of pyridine (473 and 573 K) and 2,6-dimethylpyridine (573 K), is observed. Also, activity poisoning results indicated that Brønsted acid sites of $AlPO_4$ catalyst participated in dehydration processes, thus strengthening the carbenium ion reaction pathway in $AlPO_4$ catalysts. © 1995 Academic Press, Inc.

INTRODUCTION

The conversion of aliphatic primary and secondary alcohols to olefins and/or carbonyl compounds on catalysts possessing either acidic or basic centres or only basic centres has been extensively studied (1–15). The dehydrogenation products (aldehydes or ketones) are preferentially formed on basic catalysts, while the dehydration products, olefins, and ethers are favoured when acid sites are present. The rate of dehydration of alcohols on a particular catalyst decreases in the sequence tertiary, secondary, and primary, parallel to the decrease in stability of the carbocation formed on cleavage of the hydroxyl group. The ratio of dehydrogenation to dehydration product is dependent not only on the nature of the catalyst but also on the reaction temperature. Thus, the dehydrogenation takes place, as a consequence of the higher activation energy which must be overcome, at higher temperature than in the case of dehydration (11).

On the other hand, Kanazirev *et al.* (12) found that the selective conversion of methanol to dimethyl ether is similar to the α-test (10) and is also suitable in the assessment of the catalytic activity as a measure of the overall acidic properties. Also, the dehydration activity of *tert*-butanol correlates with the total acidity. Furthermore, the conversion of 2-propanol is related to the number of both acid and basic sites, so that this reaction is used as a probe reaction to characterize acid–base catalysts (1, 3, 6–9, 11). 2-Propanol usually dehydrates to propene over acidic catalysts and dehydrogenates to 2-propanone over basic catalysts. These reaction products are considered to be stable, undergoing no further secondary reaction and so they can be used for a precise investigation of catalytic performance.

It is well known that Brønsted acid sites are able to catalyze the dehydration of alcohols to olefins but, however, the problem is the possible misinterpretation that olefin activity is only a result of Brønsted acidity. Thus, it has also been shown that alcohols can dissociatively adsorb over various metal oxides to form alkoxide intermediates (16–22) from which dehydration and/or dehydrogenation may occur. The pathway of the reacting alkoxide has been shown to depend on factors such as the structure (17) and electronic nature (16) of the oxide surface, as well as the structure (18, 20, 21) and partial pressure (16) of the reacting alcohol. Besides, Lahousse *et al.* (23) indicated that 2-propanol dehydrogenation requires an additional redox ability, since 2-propanol conversion on well-known basic oxides, such as MgO and magnesium aluminates, does not afford any dehydrogenation product.

The purpose of the present work was to study the effect of α-methyl substitution upon dehydration/dehydrogenation of alcohols [methanol (MeOH), ethanol (EtOH), 2-propanol (2-PrOH), and *tert*-butanol (*t*-BuOH)] on $AlPO_4$ catalysts, obtained by precipitation with several agents, with respect to reaction rate and selectivity. In addition, we investigate the correlation of the activity/

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0021-9517/95 $6.00

selectivity results with surface acid–base properties of these catalysts.

EXPERIMENTAL

Catalysts

Three $AlPO_4$ catalysts were used; they are obtained by precipitation with aqueous ammonia ($AlPO_4$–CA), propylene oxide ($AlPO_4$–CP), or ethylene oxide ($AlPO_4$–CE) from aqueous solutions of $AlCl_3 \cdot 6H_2O$ and H_3PO_4 (85 wt%), washed with 2-propanol, dried at 390 K for 24 h, and then calcined at 923 K for 3 h. Details on preparation as well as on the characterization of all the catalysts have been previously described (24, 25). The surface area (S_{BET}), pore volume (V_p), mean pore radius (r_p), and surface acidity estimated by the vapour-phase adsorption of pyridine (PY) and 2,6-dimethylpyridine (DMPY) are collected in Table 1.

DRIFT Measurements

Diffuse reflectance FTIR (DRIFT) spectra were recorded on a FTIR instrument (Bomem MB-100) equipped with an "environmental chamber" (Spectra Tech, P/N 0030/100) placed into a diffuse reflectance attachment (Spectra Tech, Collector). Pyridine and 2,6-dimethylpyridine were introduced by bubbling a stream of nitrogen through the liquid and into the sample chamber containing the neat $AlPO_4$ catalyst sample at 373 K. The detailed experimental procedure is described elsewhere (26).

Catalytic Measurements

The catalytic properties of $AlPO_4$ catalysts in the dehydration/dehydrogenation reaction processes of different alcohols were studied by using a pulsed microcatalytic fixed bed reactor inserted between the sample inlet and the analytical column of an HP-5890 II GC. Initially a series of pulses of varying sizes were injected onto the catalyst in order to optimize the pulse size within the linear range of adsorption isotherm. Thus, catalytic measurements were performed introducing a constant pulse of 1 μl of pure alcohol into the stream of dehydrated and deoxygenated nitrogen carrier gas (20–40 ml min^{-1}). A fresh catalyst was used on each run, and before each run the catalyst was pretreated *in situ* heating under nitrogen (30 ml min^{-1}) for 1 h at 473 K. A blank test showed that there was insignificant thermal reactivity in the absence of the catalyst.

Reaction kinetics were followed at different temperatures in the range 423–673 K, depending on the alcohol reactivity, and with different catalyst weight (5–20 mg in powder form). Only the data for 3–20% total conversion were used for the calculation. The gas mixtures were analyzed by GC with FID and column (1/8″, stainless steel) packed with 5% celanesse ester on Chromosorb W80/100 at a temperature of 323 K.

The reaction products, characterized by GC–MS (HP-5970 MSD-detector; 25 m HP-101 capillary column at 523 K) were dimethyl ether for methanol, diethyl ether and ethene for ethanol, propene and diisopropyl ether for 2-propanol, and isobutene for *tert*-butanol. Carbonyl compound is only scarcely found in 2-propanol conversion.

RESULTS AND DISCUSSION

Catalysts

The three $AlPO_4$ catalysts displayed nitrogen adsorption isotherms of type IV in the BDDT classification (27) exhibiting H1 hysteresis loops which corresponded to well-developed mesoporous solids. However, XRD mea-

TABLE 1

Textural and Surface Acid Properties of $AlPO_4$ Catalysts

		$AlPO_4$-CE	$AlPO_4$-CP	$AlPO_4$-CA
S_{BET} (m^2/g)		242	228	109
V_p (ml/g)		0.52	0.75	0.48
r_p (nm)		4.3	6.6	8.8
Pore size distribution (vol%)				
> 20 nm		7.4	7.1	4.6
10–20 nm		13.1	6.1	8.1
5–10 nm		36.0	18.1	32.6
2–5 nm		36.1	54.7	50.2
< 2 nm		7.3	13.9	4.6
Surface acidity (μmol/g) vs:				
Pyridine (PY)	473 K	240	166	81
	573 K	33	23	15
2,6-Dimethylpyridine (DMPY)	573 K	29	16	4

surements indicated that AlPO$_4$–CE and AlPO$_4$–CP were amorphous, while in the AlPO$_4$–CA catalyst an appreciable degree of crystallization was found. This is detrimental to both the textural stability and the acidic properties of AlPO$_4$ catalysts as shown in Table 1.

Moreover, the DRIFT spectra of AlPO$_4$ catalysts, in the region of OH stretching vibrations, show the characteristic bands of surface Al–OH (3793 cm^{-1}) and unbonded surface P–OH (3674 cm^{-1}) groups. A difference spectrum of the hydroxyl region taken after adsorption of pyridine (26, 28) demonstrates that both types of OH interact with pyridine molecules. Pyridine adsorption leads to the formation of protonated (bands at 1648, 1551, and 1493 cm^{-1}) and coordinated (bands at 1621, 1493, and 1454 cm^{-1}) species. Besides, the desorption of PY at increasing temperatures results in the removal of both Brønsted and Lewis bound PY but, however, the latter decreases significantly faster than the former.

Furthermore, the adsorption of DMPY, which is selectively adsorbed on Brønsted acid sites but not on Lewis acid sites because of a steric hindrance of two methyl groups (29–32), shows the characteristic absorption bands of DMPY interacting with Brønsted acid sites at 1628 and 1648 cm^{-1} (Fig. 1B). Simultaneously with the appearance of these bands, the Al–OH and P–OH bands disappeared, thus yielding downward bands in the DRIFT spectra. This is due to the fact that the reference spectra (fresh catalyst) has more OH population than the catalyst treated with DMPY (Fig. 1A). The latter indicates that DMPY interacts with both hydroxyls in AlPO$_4$ catalysts. When the desorption temperature increases (Fig. 1B) the Brønsted-associated DRIFT bands decreased. Thus, at 573 K almost all DMPY on AlPO$_4$–CA is lost and, thus, only a massif of two bands was observed.

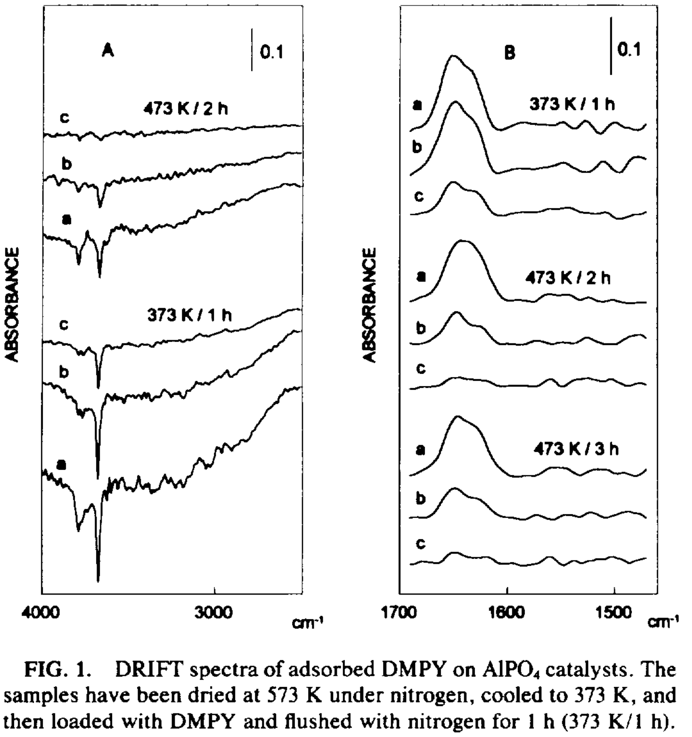


FIG. 1. DRIFT spectra of adsorbed DMPY on AlPO$_4$ catalysts. The samples have been dried at 573 K under nitrogen, cooled to 373 K, and then loaded with DMPY and flushed with nitrogen for 1 h (373 K/1 h). The temperature was then increased to 473 K and the catalyst remained, in the nitrogen stream, at 473 K for an additional 2 h (473 K/2 h) and 3 h (473 K/3 h). (a) AlPO$_4$–CE; (b) AlPO$_4$–CP; (c) AlPO$_4$–CA. All spectra were displaced for presentation.

On the other hand, and parallel to this, the Al–OH and P–OH bands increased (less negative) with desorption temperatures up to 573 K. So, DMPY desorption at various temperatures yields a good correlation between the decrease of the bands ascribed to Brønsted sites and the recovery of the OH bands confirming the hydroxyls to be Brønsted acid sites. A ranking of AlPO$_4$ samples according to the intensity of these bands yields the same acidity sequence (AlPO$_4$–CE > AlPO$_4$–CP > AlPO$_4$–CA) as found by pulse chemisorption.

In this way, molecular orbital calculations on acidic active sites on AlPO$_4$ catalyst (33, 34) showed that such P–OH groups represent the most stable Brønsted acid sites on AlPO$_4$ surfaces and are quite stable. In addition Al–OH groups can enhance the P–OH acidity by hydrogen bonding (34). On top of this, the presence of bridged P–OH–Al hydroxyl groups, which are more acidic than P–OH groups, cannot be ruled out. However, their relative surface concentration with respect to P–OH is very low and, therefore, the Brønsted acidity of AlPO$_4$ is determined by P–OH sites. In addition, the proton abstraction energies for Al–OH groups indicates that these centres cannot be considered as strong Brønsted sites but, however, might enhance the Brønsted acidity in P–OH groups through H-bonding (34).

Furthermore, the analysis of ^{1}H NMR spectra of AlPO$_4$ catalysts (35) has permitted us to show that AlPO$_4$–CE and AlPO$_4$–CP samples present a considerable amount of OH, while for AlPO$_4$–CA sample the amount of OH is lower. As concerns ^{1}H NMR spectra, this has permitted the identification of two components which are assigned to OH groups associated with Al and P atoms, in agreement with infrared data. Besides, the latter exhibited a higher thermal stability. On the other hand, CP-MAS ^{31}P NMR spectra supports the presence of P atoms bonded to OH groups. This higher Brønsted acidity is also responsible for the greater catalytic activity of AlPO$_4$–CE in relation to AlPO$_4$–CP and AlPO$_4$–CA, in reaction processes typically carbocationic, such as the cyclohexene skeletal isomerization (36) and the alkylation of toluene with methanol (37).

Catalytic Activity

Under the experimental conditions used, methanol was converted into dimethyl ether and no hydrocarbons were formed. Also, no formaldehyde was found. Moreover, *tert*-butanol generates only isobutene. Besides, no oligomerization of isobutene was found. Furthermore ethanol and 2-propanol were converted almost exclusively into dehydration products: diethyl ether and ethene (mostly diethyl ether) in the case of ethanol and diisopropyl ether and propene (mostly propene) in the case of 2-propanol. Besides, ethanol dehydrogenation to acetaldehyde was never obtained, while 2-propanol dehydrogenation to 2-propanone was scarcely found (selectivities never reached 4 mol%).

Because of the different alcohol reactivities, reactions on $AlPO_4$ catalysts were carried out at different temperatures: methanol and ethanol (523–673 K) and 2-propanol (473–598 K), at 25-K intervals in the three cases, and *tert*-butanol (398–473 K) at 10-K intervals.

The influence of the reaction temperature on the conversion products of ethanol over $AlPO_4$ catalysts is displayed in Fig. 2. The experimental results show an increase in both ethanol conversion and ethene selectivity when the reaction temperature increases from 523 to 673 K; however, diethyl ether always predominates. Thus, the production of diethyl ether over $AlPO_4$ catalysts is several orders of magnitude higher than that of ethene.

In the conversion of 2-propanol (results not shown) an increase in the reaction temperature (473–598 K) was accompanied by an increase in both 2-propanol conversion and propene selectivity as well as by a decrease in the selectivities to diisopropyl ether and 2-propanone. However, for all catalysts and reaction temperatures propene was always the major reaction product so that reaction selectivities varied between 91–95 mol% for propene, 5–3 mol% for diisopropyl ether, and 4–2 mol% for 2-propanone.

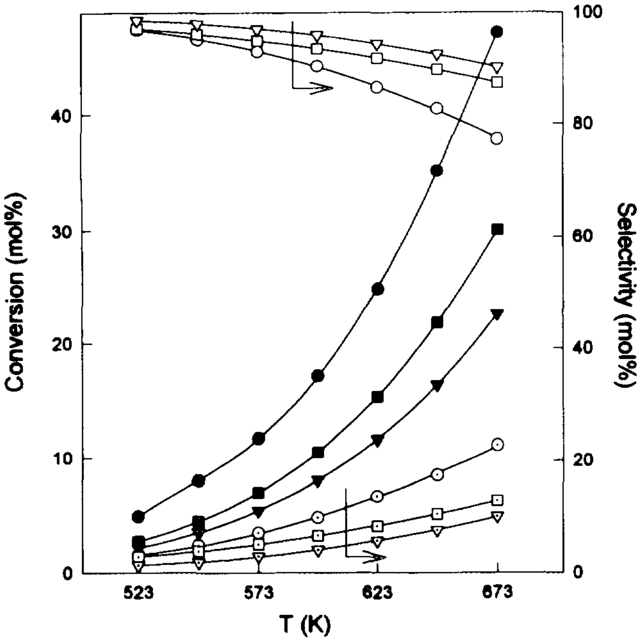


FIG. 2. Effect of reaction temperature on conversion and selectivity for ethanol reaction over $AlPO_4$–CE (circles), $AlPO_4$–CP (squares), and $AlPO_4$–CA (inverted triangles) catalysts. Closed, open, and dotted symbols denote ethanol conversion, diethyl ether, and ethene selectivities, respectively.

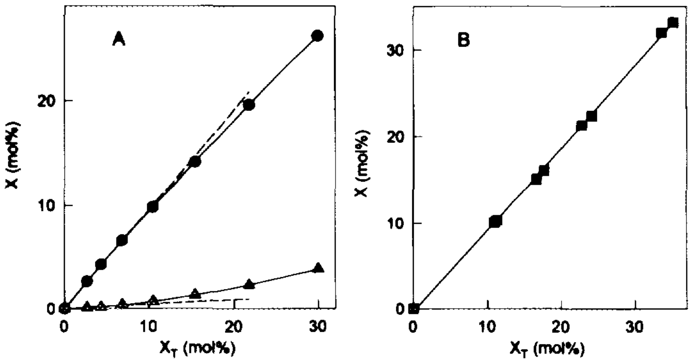
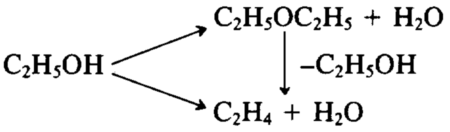


FIG. 3. OPE curves for ethanol (A) and 2-propanol (B) conversion. Fractional conversion at a particular reaction product (X) versus alcohol conversion (X_T) for APAl-E catalyst. (●), Diethyl ether; (▲), ethene; (■), propene.

As far as the selectivity behaviour of products in ethanol and 2-propanol conversions is concerned, we have developed the corresponding optimum performance envelope (OPE) curves by plotting the fractional conversion (X) to each of the reaction products against the total conversion (X_T) for different weight ratios of the catalyst to the alcohol introduced, as described by Ko and Wojciechowski (38). The OPE curves represent conventional selectivity behaviour of active sites present on a fresh catalyst and whose slope at origin represents the initial selectivity for those products. In these OPE curves for obtaining the product distribution as a function of the conversion we have included experiments performed using different weights so that conversions as high as 40–50 mol% can be achieved. However, for kinetic analysis (see below) only the data for 3–20 mol% total conversion were used.

The product profiles for ethanol dehydration on $AlPO_4$–CP catalyst (Fig. 3A) show that both diethyl ether and ethene are present from the onset of the reaction, indicating that both reaction products are formed by direct dehydration; i.e., they are primary reaction products coming from ethanol through a parallel reaction network. A primary product is defined as that which is produced from the reactant no matter how many surface intermediates may be involved in its formation. However, diethyl ether is an unstable product since a downward deviation from the straight line at origin is obtained due to the fact that it also participates in the formation of ethene. So, ethene is a primary plus secondary stable reaction product. A secondary product is formed from a primary product no matter how many surface intermediates may be involved in its formation. The same occurs on the remaining AlPO$_4$ catalysts. Thus, the pathway of the formation of diethyl ether and ethene from ethanol dehydration on AlPO$_4$ catalysts is a combination pathway of parallel and consecutive reactions:



$$\begin{tikzcd} & C_2H_5OC_2H_5 + H_2O \arrow[d, "-C_2H_5OH"] \\ C_2H_5OH \arrow[ur] \arrow[dr] & \\ & C_2H_4 + H_2O \end{tikzcd}$$

The same thing occurs in 2-propanol conversion (Fig. 3B), although in this case the selectivity to propene in all cases remained higher than 90 mol% and a little dehydrogenation was also found. Therefore, propene is primary plus secondary reaction product while diisopropyl ether is a primary unstable product. As for the dehydrogenation product, 2-propanone, it seems to be a primary stable product, although in all cases its selectivity never surpassed 4 mol%. Thus, a parallel consecutive reaction pathway also operates in 2-propanol conversion.

So, in ethanol and 2-propanol conversions the selectivity to a given reaction product is determined by alcohol structure (primary or secondary), reaction temperature, and surface acidity of the catalyst.

Apparent Rate Constants

The alcohol conversion reaction data in all AlPO$_4$ catalysts were found to fulfill the Bassett–Habgood rate equation (39) for first-order reactions in which the partial reactant pressure is low and the adsorption rate is faster than the rate of surface reaction, the latter being the rate determining step. In this sense, only the data for 3–20 mol% total conversion were used for the calculation. The Bassett–Habgood (39) equation was in the form

$$\ln [1/(1\text{-}X)] = k_a RT (W/F), \qquad [1]$$

where X is total conversion, k_a the apparent rate constant of surface process, W the catalyst weight, and F the flow rate of carrier gas.

The $\ln [1/(1\text{-}X)]$ vs F^{-1} plots, according to Eq. [1], for the conversion of alcohols on AlPO$_4$ catalysts at various flow rates of the nitrogen carrier gas (20–40 ml min^{-1}) and different reaction temperatures are linear and also pass through the origin, indicating a good fit of the data to Eq. [1] and, therefore, the first-order process in the alcohol conversion. Also, the data for different catalyst particle sizes below 0.7 mm lie on the same plot; i.e., the reactions are not influenced by internal diffusion for catalyst particle sizes $\leq$0.7 mm. Furthermore, the catalytic runs have also been carried out at different weight ratios of catalyst from the alcohol introduced, showing that the fractional conversion of a pulse of reactant to products was independent of the pressure, which determined the first-order reaction process. This behaviour also ensured linear chromatography in the pulse mode, i.e., ensuring equilibrium chromatography.

The apparent rate constants, k_a, obtained from the slopes of the linear plots of $\ln [1/1\text{-}X)]$ vs F^{-1} for X less than 20 mol%, where the equilibrium reaction can be neglected, are collected in Tables 2 and 3.

Position of the 98% confidence limit lines and the value of the coefficient of determination (always over 0.99) for the regressions are used to check the adequacy of the data. A students' t-test of significance showed that these are significant at levels over 1%. At least three measurements were used to calculate each value of k_a. All values are reproducible to within about 7%.

In the comparison of Tables 2 and 3, it was found that the apparent rate constants of the dehydration of alcohols follow the sequence

$$\text{MeOH} < \text{EtOH} < \text{2-PrOH} < t\text{-BuOH}.$$

Basicity of t-BuOH is stronger than that of primary and secondary alcohols because the substitution of the methyl group in place of hydrogen enhances the basicity. Then, because of the strong basicity, a weak acid seems to be enough for the acid-catalyzed reaction.

Moreover, as can also be seen from the data in Tables 2 and 3, the rate constants of catalysts for the conversion of alcohols also depend on the precipitation method. Thus, the catalytic activities are greater when catalyst is

TABLE 2

Apparent Rate Constants (k_a) and Activation Parameters (E_a and ln A) for Methanol and *tert*-Butanol Conversion on AlPO$_4$ Catalysts

Catalyst	k_a 10^6 (mol/atm g s)	E_a (Kcal/mol)	ln A[a]
	MeOH → dimethyl ether		
AlPO$_4$–CE	482.3[b]	7.0 ± 0.3	−0.2
AlPO$_4$–CP	336.4[b]	10.6 ± 0.4	0.6
AlPO$_4$–CA	305.2[b]	7.8 ± 0.4	−1.8
	t-BuOH → isobutene		
AlPO$_4$–CE	3405.3[c]	6.2 ± 0.3	1.7
AlPO$_4$–CP	2362.3[c]	3.7 ± 0.2	−1.6
AlPO$_4$–CA	1522.1[c]	7.0 ± 0.2	1.9

[a] A is expressed in mol/atm g s.

[b] At a reaction temperature of 623 K.

[c] At a reaction temperature of 423 K.

TABLE 3

Apparent Rate Constants at 573 K (k_a) and Activation Parameters (E_a and ln A) for Ethanol and 2-Propanol Conversion on $AlPO_4$ Catalysts

Catalyst	k_a 10^6 (mol/atm g s)	E_a (Kcal/mol)	ln A[a]
	EtOH → diethyl ether		
$AlPO_4$–CE	209.5	9.3 ± 0.4	−0.3
$AlPO_4$–CP	120.6	10.2 ± 0.3	−3.8
$AlPO_4$–CA	94.6	9.9 ± 0.5	−0.6
	EtOH → ethene		
$AlPO_4$–CE	14.5	18.9 ± 0.4	5.5
$AlPO_4$–CP	6.2	17.2 ± 0.5	3.2
$AlPO_4$–CA	2.7	19.9 ± 1.0	5.5
	2-PrOH → propene		
$AlPO_4$–CE	983.8	11.8 ± 0.3	3.5
$AlPO_4$–CP	719.8	9.6 ± 0.4	1.2
$AlPO_4$–CA	490.0	12.4 ± 0.5	3.3
	2-PrOH → di-isopropyl ether		
$AlPO_4$–CE	47.8	5.7 ± 0.6	−4.9
$AlPO_4$–CP	30.9	4.8 ± 0.7	−2.3
$AlPO_4$–CA	22.7	10.2 ± 0.6	−1.7

[a] A is expressed in mol/atm g s.

obtained with ethylene oxide ($AlPO_4$–CE) than when they are prepared in propylene oxide ($AlPO_4$–CP) or in aqueous ammonia ($AlPO_4$–CA). This is attributed to the Brønsted acidity of the surface P–OH groups on calcined $AlPO_4$ catalysts. The greater Brønsted acidity of $AlPO_4$–CE catalyst is also manifested in a greater retention of base at increasingly higher temperatures (see Table 1), measured by pyridine and 2,6-dimethylpyridine chemisorption.

In this way, it is well known that the dehydration of alcohols to the corresponding olefins proceeds on acid catalysts via carbenium-like intermediates. This reaction is considered to be a monomolecular elimination of the β-hydrogen atom. The dehydration to the corresponding ether is also possible. Even the nominally weak acidic OH groups in alkali cation exchanged faujasites catalyze 2-propanol dehydration (6).

The irreversible poisoning by nitrogen bases, such as PY, DMPY, and hexamethyldisilazane (HMDS), the latter being more Brønsted selective, as well as the hydrogen–deuterium exchange reaction of the alcohol, only in the hydroxyl group, and in the formed alkenes, using D_2O-pretreated $AlPO_4$ catalysts, are other facts which indicate that conversion of alcohols over $AlPO_4$ catalysts involves Brønsted acid sites.

Poisoning Measurements

The poisoning of the active sites of $AlPO_4$ catalysts in the 2-propanol conversion was performed through the previous saturation of the acid sites with PY, DMPY, and HMDS according to the following procedure. After measuring the conversion activity of the $AlPO_4$–CE catalyst at 523 K (in triplicate: ~7% error) the catalyst was saturated with the probe reactant (pulses of pure base) in the nitrogen stream. After saturation, the bed was flushed with nitrogen at 523 K (30 min) to remove all traces of unreacted reagent, the activity of the $AlPO_4$–CE catalyst was measured again at that temperature. In this way, while PY is bonded to Brønsted and Lewis sites (29, 30), DMPY (29–32) and HMDS (40, 41) are specifically bonded to the Brønsted sites. The method using HMDS was slightly different from the method using PY and DMPY. The silylating agent reacts easily and quantitatively with Brønsted acidic hydroxyl groups, with the formation of stable trimethylsilyl (TMS) ethers (40, 41), i.e., a covalent bond rather than the acid–base reaction characteristic of PY or DMPY probe. In this way, DRIFT spectra of adsorbed HMDS (results not shown) indicated that the silylating agent reacts easily and quantitatively with Brønsted acidic hydroxyl groups so that Al–OH and P–OH stretching vibrations in $AlPO_4$ catalysts disappeared almost completely. Besides, the adsorbed HMDS remained on the surface at 573 K so that the OH bands were not regenerated.

The poisoning effect of PY, DMPY, and HMDS on 2-propanol conversion has been demonstrated on $AlPO_4$–CE catalyst through the changes obtained in the apparent rate constants and, hence, in product selectivities. The results obtained on the influence of probe reagents in catalytic activities and product selectivities at a reaction temperature of 523 K are shown in Table 4. As can be seen from Table 4, the reagents strongly suppressed the activity for the 2-propanol dehydration but the effectiveness of PY and DMPY was much lower than that of HMDS, corresponding to their lower basicity, thus poisoning part of the acid sites. So, the PY treatment lowered the activity of the catalyst to about 50%, whereas HMDS decreased the activity to only about 7%. The decrease in activity by DMPY poisoning was intermediate (ca. 62%).

As the dehydrogenation activity practically does not change by base poisoning, a drop in dehydration activity is accompanied by a change in product selectivities, getting greater as the poisoning effect increases (Table 4). These data indicate that 2-propanol dehydration occurs on Brønsted acid sites of $AlPO_4$ catalysts, thus strengthening the carbenium ion reaction. In this sense, it is noteworthy to indicate that at 523 K HMDS completely poisoned $AlPO_4$–CE catalyst acid sites for methanol and ethanol conversions.

H–D Exchange Reaction

In regard to the hydrogen–deuterium exchange reaction of the alcohol, the surface of the $AlPO_4$–CE catalyst

TABLE 4

Poisoning Experiments in 2-Propanol Conversion over $AlPO_4$–CE Catalyst

Poison	T^a (K)	$k_{C=C}$ ($\times 10^6$)^b	k_{-O-} ($\times 10^6$)^b	$k_{C=O}$ ($\times 10^6$)^b	$S_{C=C}$ (mol %)	S_{-O-} (mol %)	$S_{C=O}$ (mol %)
—	523	366.1	17.9	15.2	91.9	4.7	3.9
PY	523	174.0	12.1	15.4	84.1	7.2	8.6
DMPY	523	136.1	8.3	14.8	83.1	6.2	10.6
HMDS	523	27.9	1.3	14.4	61.7	3.3	35.0

[a] Temperatures of both nitrogen base adsorption and reaction process.

[b] All k values are expressed in mol/atm g s (C=C, alkene; –O–, ether; C=O, 2-propanone).

was saturated with D_2O, as described by Baumann *et al.* (42), and afterwards the 2-propanol conversion was carried out in the pulse method using a GC connected with a VG-AUTOSPEC. As separation column we used an SPB-1 capillary column 60 m × 0.32 mm, film thickness 0.25 μm, from Supelco. The deuterium uptake indicates that 2-propanol dehydrates to form carbenium ion-like intermediates (oxonion or carbenium ions) prior to desorbing as olefin products. The carbenium ion cannot revert to the alcohol, hence deuterium exchange occurs during the second step, causing deuterium uptake into the alkene. Thus the primary interaction between the alcohol and the catalyst may be assumed to be the proton transfer at the P–OH sites and so the sequence of alcohol reactivity can be explained according to their proton affinities (43). Therefore, 2-propanol and *tert*-butanol are much more reactive than the primary alcohol because of the increased stability of the secondary and tertiary ions that they can form.

Activation Parameters

The temperature dependence of apparent rate constants, k_a, for the conversion of alcohols has been studied according to the Arrhenius equation. Tables 2 and 3 set out the results of apparent activation energies, E_a, and pre-exponential factors of Arrhenius equation, ln A, from linear plots ln k_a vs T^{-1}. A least-squares regression analysis always shows correlation coefficients over 0.99. Also, students' t-test indicates that these are significant at levels over 1%. This is a measurement of fit data, under all experimental conditions, for the linear plots of ln k_a vs T^{-1}. All values are reproducible to within about 9%.

On the other hand, there is a relationship between the values of ln A and E_a according to the expression for the compensation effect or isokinetic relationship (44–49)

$$\ln A = \ln \alpha + E_a/\theta R,$$

where R is the gas constant and θ is the isokinetic temperature at which identical values of reaction rate constant $k_a = \alpha$ are obtained. In fact, such plots of ln A vs E_a for the alkene formation in ethanol, 2-propanol, and *tert*-butanol indicate a linear correlation (with regression coefficients over 0.99) for every one of the three $AlPO_4$ catalysts. θ and α are obtained from the slope and intercept. When a compensation effect holds for a reaction occurring on a series of homologous catalysts, a single common interaction mechanism and, consequently, a common transition state intermediate can be expected for all catalysts (44–49).

The effect is interpreted essentially as a consequence of the heterogeneity of acidic sites (48) due to the fact that the catalytic reaction involved adsorbed species and that the surface heterogeneity of the catalysts affects the activation energy for the reaction. Thus, the distribution of acid strength determines the energy barrier for the reaction to occur; the number of sites is also important. So, the global rate will be the sum of the individual rates on each type of site, each one proceeding with a different activation energy.

In this way, the differences in reaction rate originate in changes in the energies and number of reactive species. Moreover, the number of sites which are active for a given reaction depends mainly on the activation energy (49). Thus, strong acid sites are characterized by a lower activation energy while the relative abundance of such sites can be related with the relative activity.

So, the differences between the activities of $AlPO_4$ catalysts are due to differences in the number and strength of acid sites. Thus, the balance between the factor of (*i*) the amount of acid sites, which mainly affected the frequency factor values, and (*ii*) their activity, which mainly affected the activation energy, determines the sequence of catalytic activity in $AlPO_4$ catalysts. In this way, the $AlPO_4$ catalyst obtained in ethylene oxide in general produces a higher number of acid sites than the catalyst obtained in propylene oxide. However, according to their increased values in activation energy ought to be less active.

CONCLUSIONS

The conversion of alcohols in α-methylated series (methanol, ethanol, 2-propanol, and *tert*-butanol) on $AlPO_4$ catalysts follows the requirements of the Bassett–Habgood kinetic for first order reaction processes. Activity increases as a function of surface acidity of the $AlPO_4$ catalyst as well as with the α-substitution in the alcohol. Besides, ethanol and 2-propanol follow a combination pathway of parallel and consecutive reactions. Moreover, a good correlation between the results of dehydration conversion and acid properties, measured through the irreversible adsorption of pyridine and 2,6-dimethylpyridine vapours, is observed. Furthermore, DMPY and HMDS poisoned surface active sites, which were therefore Brønsted acidic and readily accessible, because even a large molecule such as HMDS has been able to react easily.

ACKNOWLEDGMENTS

We gratefully acknowledge the subsidy received from the Dirección General de Investigatión Científica y Técnica (DGICYT), Ministerio de Educación y Ciencia de España (Project PB92/0816), and from the Consejería de Educación de la Junta de Andalucía.

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