Conversion of 2-propanol over chromium aluminum orthophosphates

Felipa M. Bautista, Juan M. Campelo [1], Angel Garcia, Diego Luna, Jose M. Marinas, Antonio A. Romero and Maria R. Urbano

Department of Organic Chemistry, Sciences Faculty, Cordoba University,
Avda. S. Alberto Magno, s/n^o, E-14004 Cordoba, Spain

Received 28 February 1995; accepted 20 June 1995

The catalytic conversion (dehydration/dehydrogenation) of 2-propanol on a series of $CrPO_4$–$AlPO_4$ (CrAlP) catalysts, which were differently prepared and thermally treated at 773–1073 K, has been studied by microcatalytic pulse reactor technique at different temperatures (473–573 K). Kinetic parameters for conversion of 2-propanol to propene have been obtained by analysis of the data through the Bassett–Habgood equation for first-order reaction processes. The influence of the reaction temperature upon alcohol conversion and product selectivities was also investigated. Catalytic performance was affected by the precipitation agent. Catalysts obtained in propylene oxide–aqueous ammonia showed the highest activity towards propene compared to other catalysts. Calcination at increasing temperatures caused a decrease in the activity due to the decrease in surface acid character. The results of dehydration to propene can be well interpreted through the differences in the number and strength of acid sites, which were gas-chromatographically measured using pyridine and 2,6-dimethylpyridine chemisorbed at different temperatures (573 and 673 K). Dehydrogenation to 2-propanone occurred to a small extent at all reaction temperatures and, besides, its conversion changed slightly with reaction temperature. Propene selectivity strongly increased with increasing reaction temperature.

Keywords: chromium orthophosphate ($CrPO_4$); $CrPO_4$–$AlPO_4$; surface acidity; 2-propanol conversion; activity; selectivity; poisoning by bases; pyridine; 2,6-dimethylpyridine; hexamethyldisilazane

1. Introduction

In a previous paper [1] we showed that the modification of $CrPO_4$ catalysts with small amounts of $AlPO_4$ considerably influences the surface properties. The most striking feature is the increase in the surface acidity by $AlPO_4$ loading. Besides, the precipitation of $CrPO_4$–$AlPO_4$ in a mixed medium (aqueous

---

[1] To whom correspondence should be addressed.

ammonia–propylene oxide) leads to catalysts that exhibit better textural properties (surface area and pore volume) as well as a higher number and strength of acid sites as compared to the catalysts exclusively obtained in aqueous ammonia. Also, they exhibited improved catalytic activity for cyclohexene skeletal isomerization and cumene cracking processes. Moreover, the catalytic activity results can be well interpreted through the differences in the number and strength of acid sites (gas-chromatographically measured using pyridine (PY) or 2,6-dimethylpyridine (DMPY) chemisorbed at different temperatures (573–673 K)).

In this work the decomposition of 2-propanol has been chosen as a model reaction for the investigation of the activity of $CrPO_4$–$AlPO_4$ catalysts and selectivity toward dehydration–dehydrogenation as a function of the preparation method and thermal treatment of them in order to understand the correlation with the acid–base properties. It is generally accepted that dehydration to propene occurs on acidic sites whereas the base and/or redox sites are responsible for dehydrogenation to 2-propanone [2–6]. However, Lahousse et al. [7] 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, did not produce any dehydrogenation product.

2. Experimental

2.1. CATALYSTS

$CrPO_4$–$AlPO_4$ (CrAlP) samples of varying composition (5–50 wt% $AlPO_4$) were obtained according to the scheme outlined in fig. 1. Details of the method of preparation as well as of characterization of all catalysts have been previously described [1,8,9]. The surface areas are shown in table 1. The samples are designated by CrAlP followed by a letter that indicates the precipitation medium (A, ammonia; PA, propylene oxide–ammonia) and by two numbers that indicate, respectively, the $AlPO_4$ amount (wt%) and the calcination temperature (CrAlP-A-5-773, CrAlP-PA-10-923, etc.).

2.2. METHODS

Surface acid–base properties measured in a dynamic mode by means of the gas-phase adsorption (573 and 673 K) of PY, DMPY and phenol (PH) using a pulse chromatographic technique [1,10] are also shown in table 1. The pulse size was in the range corresponding to 0.1–0.5 monolayers so as to approach the conditions of gas-chromatographic linearity. For comparative purposes $CrPO_4$-PA and $CrPO_4$-A catalysts [11] were also included.

The catalytic properties of CrAlP catalysts in the 2-propanol conversion (dehydration and dehydrogenation) process were studied by using a pulsed microcataly-

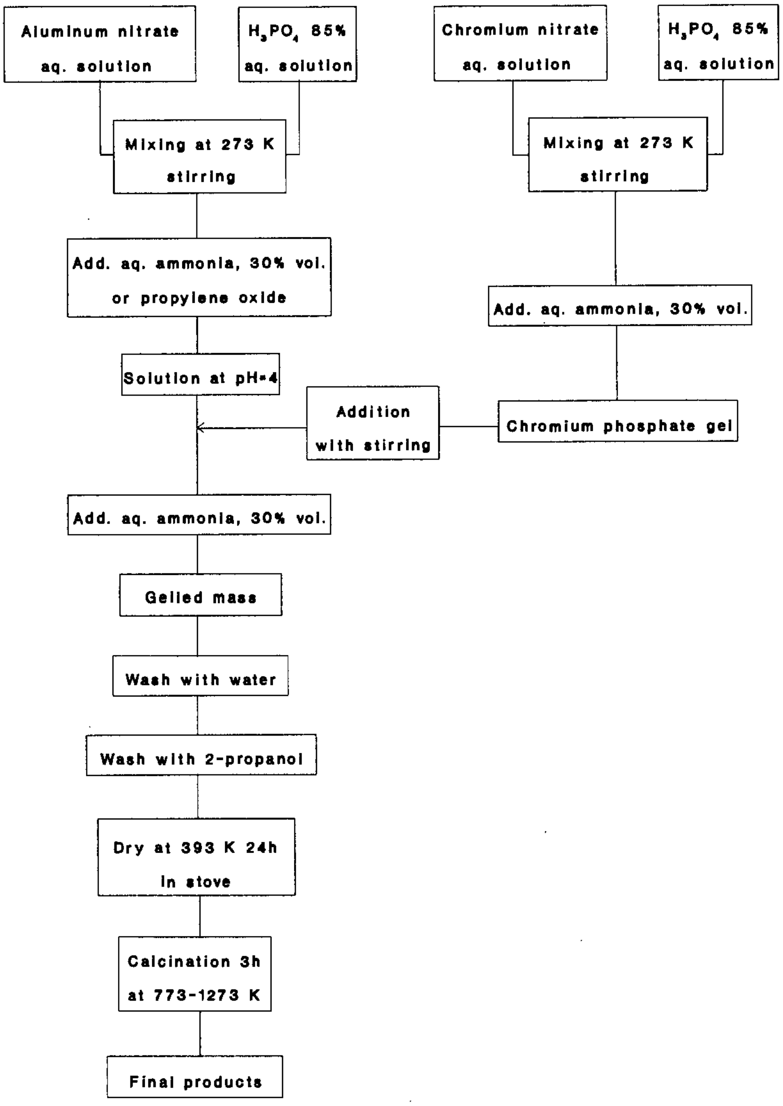

Fig. 1. Schematic drawing of the preparation schedule for $CrPO_4$–$AlPO_4$ (CrAlP) catalysts.

tic fixed-bed reactor inserted between the sample inlet and the analytical column of a 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 the adsorption isotherm. Thus, catalytic measurements were performed under the following conditions: 2-propanol (liquid) volume/pulse size 1 µl; reaction temperature, 473–573 K (at 25 K intervals); catalyst weight, 20–40 mg in powder form: flow rate of nitrogen carrier gas, 30 ml min^{-1}. A fresh catalyst was used on each run, and before use, the catalyst was pretreated by in situ heating under nitrogen (30 ml min^{-1})

Table 1
Surface area and acid–base properties (μmol/g) of $CrPO_4$ and $CrPO_4$–$AlPO_4$ catalysts

Catalyst	S_{BET} (m^2/g)	Acidity versus				Basicity versus PH[c]	
		PY[a]		DMPY[b]		573 K	673 K
		573 K	673 K	573 K	673 K		
CrP-PA-773	28	99	91	57	52	114	89
CrP-PA-923	23	70	52	58	58	128	82
CrP-PA-1073	19	44	33	37	27	94	54
CrP-A-773	9	36	24	9	–	104	86
CrP-A-923	8	18	17	8	–	44	44
CrP-A-1073	1	17	12	1	–	18	15
CrAlP-PA-5-573	62	93	51	77	55	140	85
CrAlP-PA-5-923	55	91	56	61	50	126	68
CrAlP-PA-5-1073	35	63	42	55	45	64	64
CrAlP-PA-10-773	58	86	63	60	54	133	84
CrAlP-PA-10-923	38	85	64	54	40	127	76
CrAlP-PA-10-1073	31	50	40	44	34	64	57
CrAlP-A-5-773	28	40	35	21	21	66	49
CrAlP-A-5-923	16	25	14	13	13	41	37
CrAlP-A-5-1073	7	10	4	2	2	9	9
CrAlP-A-10-773	19	37	27	20	20	52	52
CrAlP-A-10-923	16	26	26	8	8	40	40
CrAlP-A-10-1073	13	17	13	7	7	9	9
CrAlP-A-20-773	18	42	43	14	14	65	65
CrAlP-A-20-923	14	27	22	6	6	25	25
CrAlP-A-20-1073	8	23	12	5	5	11	11
CrAlP-A-30-773	22	41	38	34	29	63	62
CrAlP-A-30-923	13	38	37	17	10	23	23
CrAlP-A-30-1073	10	22	23	11	10	14	7
CrAlP-A-50-773	44	67	59	25	25	71	71
CrAlP-A-50-923	40	59	26	15	15	43	28
CrAlP-A-50-1073	27	48	22	11	11	10	10

[a] PY: pyridine.
[b] DMPY: 2,6-dimethylpyridine.
[c] PH: phenol.

for 1 h at 473 K. The reaction products were analyzed in a Hewlett-Packard 5890 II gas chromatograph with a flame ionization detector. The column was 2 m long (1/8″, stainless-steel) packed with 5% celanesse-ester on Chromosorb G AW-DMCS 80/100 at 323 K. These reaction products, characterized by GC-MS (HP-5970 MSD-detector, 25 m HP-101 capillary column at 523 K) were propene, 2-propanone and minor amounts of diisopropylether. A blank test showed that there occurred insignificant thermal reaction in the absence of the catalyst.

3. Results and discussion

The conversion of 2-propanol on CrAlP catalysts was found to proceed via two different paths, namely dehydration to propene (with minor amounts of diisopropylether) and dehydrogenation to 2-propanone. Fig. 2 shows the 2-propanol conversion over CrAlP-A-5, CrAlP-A-10, CrAlP-PA-5 and CrAlP-PA-10 catalysts (thermally treated at 923 K) as a function of reaction temperature. The experimental results show an increase in both 2-propanol conversion and propene selectivity accompanied by a decrease in 2-propanone selectivity when the reaction temperature increases from 473 to 573 K, irrespective of the preparation method used. Diisopropylether selectivity never reached over 2 mol%.

In the absence of diffusional influences and with pulse size always within the linear range of adsorption isotherm, the conversion of 2-propanol to propene (below 20%, where the equilibrium reaction can be neglected) satisfies the requirements of Bassett–Habgood kinetic treatment [12] for first-order reactions in which the reactant partial pressure is low and the adsorption rate is faster than the rate of surface reaction, the latter being the rate determining step. The Bassett–Habgood equation is in the form:

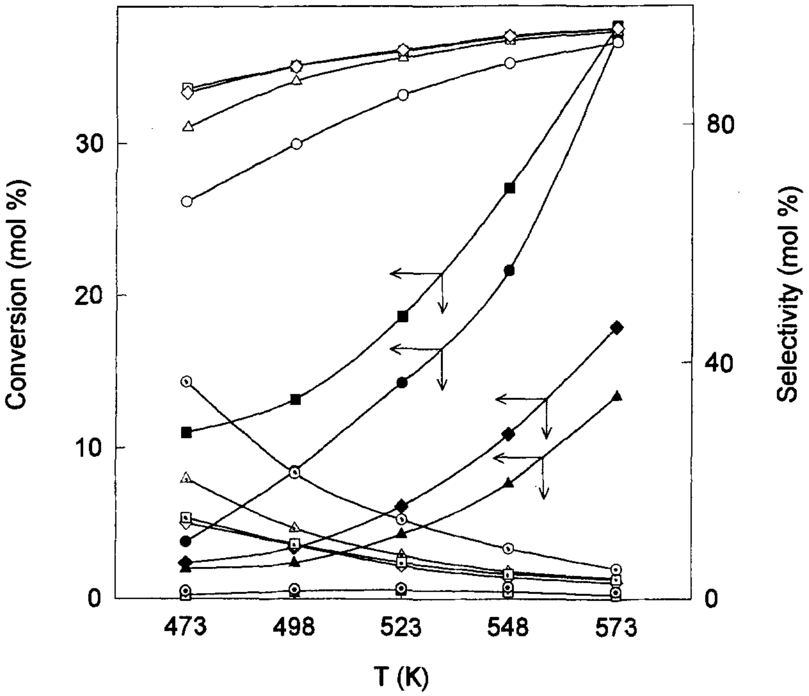

Fig. 2. Effect of the reaction temperature on the conversion and selectivity for 2-propanol conversion over CrAlP-PA-5 (■), CrAlP-PA-10 (●), CrAlP-A-5 (▲) and CrAlP-A-10 (◆) catalysts thermally treated at 923 K. Conversion of 2-propanol (■ ● ▲ ◆), selectivity to propene (□ ○ △ ◇), to 2-propanone (⊡ ⊙ △ ◇) and to diisopropylether (⊞ ⊕).

$$\ln[1/(1-X)] = RTk_a(W/F)\,, \tag{1}$$

where X is the conversion of 2-propanol to propene, k_a the apparent rate constant of the surface dehydration process, W the catalyst weight and F the flow rate of carrier gas.

A plot of $\ln[1/(1-X)]$ vs. F^{-1} or W gave satisfactory straight lines that passed through the origin indicating that the dehydration of 2-propanol to propene on CrAlP catalysts is a first-order reaction. The first-order kinetics holds at all reaction temperatures between 473 and 573 K (25 K intervals) for 2-propanol conversions less than 20 mol% where the equilibrium reaction can be neglected. This agrees with previous investigations where the conversion of 2-propanol was found to be of the first order-kinetics [13–15].

Table 2 gives, for all CrAlP catalysts, the apparent rate constants (k_a, at a reaction temperature of 573 K), from linear plots of $\ln[1/(1-X)]$ vs. F^{-1}, for the 2-propanol dehydration reaction process generating propene. Table 2 also includes apparent activation energies, E_a, and preexponential factors of Arrhenius equation, $\ln A$, from linear plots $\ln k_a$ vs. T^{-1}.

The 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, performed on the regression coefficients, showed that these are significant at levels over 98%. This is a measure of data fit, in all experimental conditions. At least three measurements were used to calculate each k_a, value, all of them being reproducible to within ca. 8%.

The results from fig. 2 and table 2 indicate that the incorporation of $AlPO_4$ to $CrPO_4$ developed catalysts that exhibited increased activity (at all $CrPO_4/AlPO_4$ weight ratios) in the 2-propanol conversion to propene as compared to $CrPO_4$ catalysts [11], irrespective of the calcination temperature in the range 773–1073 K.

Moreover, the precipitation agent also affects the catalytic performance of CrAlP-catalysts. Thus, CrAlP-PA catalysts always are more active than CrAlP-A ones. Furthermore, the catalytic activity of the CrAlP catalyst also varied with $AlPO_4$ loading. Thus, while the activity remained almost unchanged for $AlPO_4$ loadings in the range 5–20 wt%, above this loading the activity increased with $AlPO_4$ loading. On the other hand, the activity is decreased on increasing the calcination temperature up to 1073 K. Furthermore, activity disappeared in all cases at 1273 K due to β-$CrPO_4$ crystallization [1].

These results are fully consistent with the results of the acidity measurements here and with previous catalytic tests employed as an indirect method of acidity measurement. Thus, CrAlP-PA catalysts exhibit not only an increased total acidity but also an increased number of acid centres (titrated at 673 K) compared to CrAlP-A catalysts. Moreover, the results in table 1 also indicate that the site energy distribution and the number of strong acid sites on CrAlP catalysts are slightly influenced by $AlPO_4$. Furthermore, the diffuse reflectance infrared spectra of adsorbed DMPY (results not shown) also indicate a higher Brønsted acid sites

Table 2

Apparent rate constants at 573 K (k_a; error: ~8%) and activation parameters (E_a, ln A) for the conversion of 2-propanol to propene on $CrPO_4$ and $CrPO_4$–$AlPO_4$ catalysts

Catalysts	$k_a \times 10^6$ (mol/atm g s)	E_a (kcal/mol)	ln A [a]
CrP-A-773	158.6	17.8 ± 0.2	6.9
CrP-A-923	96.6	14.8 ± 0.3	3.7
CrP-A-1073	25.8	19.1 ± 0.4	6.3
CrP-PA-773	338.3	23.3 ± 0.3	12.5
CrP-PA-923	273.6	16.0 ± 0.1	5.9
CrP-PA-1073	171.6	12.1 ± 0.3	2.0
CrAlP-PA-5-773	626.0	15.9 ± 0.2	6.6
CrAlP-PA-5-923	465.5	8.8 ± 0.1	0.1
CrAlP-PA-5-1073	416.7	11.2 ± 0.2	2.0
CrAlP-PA-10-773	639.9	13.2 ± 0.2	4.2
CrAlP-PA-10-923	434.0	12.8 ± 0.1	3.5
CrAlP-PA-10-1073	450.1	11.5 ± 0.2	2.4
CrAlP-A-5-773	194.6	11.4 ± 0.1	1.4
CrAlP-A-5-923	136.0	12.7 ± 0.4	2.2
CrAlP-A-5-1073	55.4	7.3 ± 0.3	−3.4
CrAlP-A-10-773	220.8	12.3 ± 0.1	2.4
CrAlP-A-10-923	181.1	12.0 ± 0.2	2.0
CrAlP-A-10-1073	55.8	16.7 ± 0.7	4.9
CrAlP-A-20-773	183.6	11.7 ± 0.2	1.6
CrAlP-A-20-923	123.4	13.4 ± 0.2	2.8
CrAlP-A-20-1073	68.8	10.6 ± 0.4	−0.3
CrAlP-A-30-773	198.7	14.8 ± 0.2	4.5
CrAlP-A-30-923	166.1	13.2 ± 0.2	2.9
CrAlP-A-30-1073	97.0	13.2 ± 0.3	2.4
CrAlP-A-50-773	360.5	13.3 ± 0.2	3.8
CrAlP-A-50-923	285.1	14.8 ± 0.6	4.8
CrAlP-A-50-1073	163.3	10.0 ± 0.4	0.1

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

[b] At 573 K.

number in CrAlP-PA catalysts. So, the change in dehydration activity with the change in both precipitation medium and calcination temperature agrees with the change in the acidic characteristics shown in table 1, and is similar to that previously obtained for cyclohexene isomerization and cumene cracking [1,9]. Besides, taking into account that 2-propanol dehydration is a less acid demanding reaction than both cyclohexene isomerization and cumene cracking, it is natural that it exhibited higher apparent rate constants.

Moreover, the poisoning effect of PY, DMPY and hexamethyldisilazane (HMDS) on 2-propanol conversion has been demonstrated on CrAlP catalysts through the changes obtained in the apparent rate constants and hence, in product selectivities. The poisoning of the active acid sites on CrAlP catalysts with PY, DMPY and HMDS was performed according to the following procedure. After measuring the activity of the CrAlP catalyst at 573 K (in triplicate: ~8% error) the catalyst was saturated with pulses of pure base. After saturation, the catalyst was maintained in nitrogen at 523 K (30 min) to remove traces of unreacted base, and the activity of the catalyst was again measured at that temperature [16]. 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 3 for CrAlP-A-10-923 and CrAlP-A-50-923 catalysts, the remaining catalysts showed similar behaviours.

As can be seen from table 3 the reagents strongly suppressed the activity for 2-propanol dehydration but the effectiveness of PY and DMPY was much lower than that of HMDS, corresponding to their basicity, thus poisoning part of the acid sites. Moreover, the HMDS treatment lowered the activity to about 93%. In this way, 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 [17,18], i.e., a covalent bond rather than the acid–base reaction characteristic of PY or DMPY probe.

Furthermore, as the dehydrogenation activity to acetone slightly decreases by base poisoning, a drop in dehydration activity is accompanied by a change in product selectivities, getting greater as the poisoning effect increases (table 3).

On the other hand, there is a relationship between the values of E_a and $\ln A$ for propane formation as can be seen in fig. 3. This relationship, known as "compensation effect" [19–25], may be ascribed to the existence of a linear free energy relationship.

$$\ln A = \ln \alpha + E_a/\theta R\,, \tag{2}$$

where R is the gas constant and θ is a constant termed "isokinetic temperature" at

Table 3
Poisoning experiments in 2-propanol conversion over $CrPO_4$–$AlPO_4$ catalysts

Catalyst	Poison	T (K)	$k_{C=C} \times 10^{6\,a}$	$k_{-O-} \times 10^{6\,a}$	$k_{C=O} \times 10^{6\,a}$	$S_{C=C}$	S_{-O-}	$S_{C=O}$
CrAlP-A-10-923	–	523	65.9	1.2	44.0	59.3	1.0	39.7
	PY	523	19.2	–	38.7	33.1	–	66.9
	DMPY	523	12.7	–	37.4	25.2	–	74.8
	HMDS	523	4.8	–	36.4	11.7	–	88.3
CrAlP-A-50-923	–	523	82.4	2.8	20.4	77.6	2.7	19.7
	PY	523	32.7	1.0	19.1	61.6	2.0	36.4
	DMPY	523	27.1	0.8	18.3	59.0	1.6	39.4
	HMDS	523	4.9	–	17.8	21.8	–	78.2

[a] All k values are expressed in mol/atm g s (C=C, propene; –O–, diisopropylether; C=O, propanone).

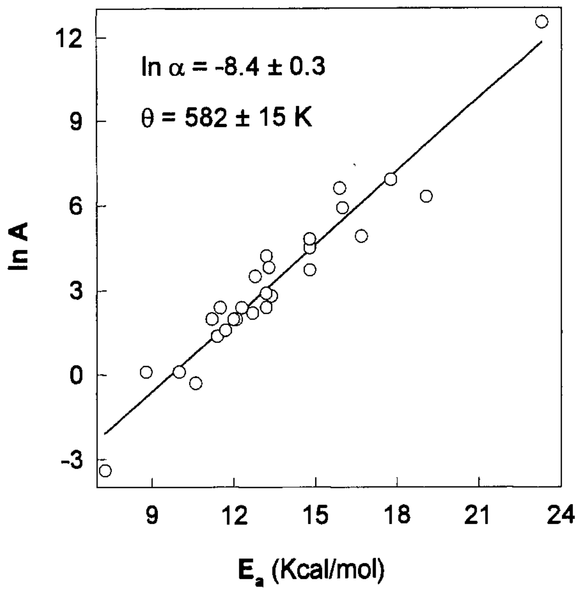

Fig. 3. Compensation effect between E_a and ln A for different catalysts in the dehydration of 2-propanol to propene. Uncertainties are determined for a 98% confidence limit.

which identical values of reaction rate constant $k_a = \alpha$ are obtained. In fact, the plot of ln A, vs. E_a for propene formation indicates a linear correlation (with regression coefficients over 0.96) and significant data at levels over 98% (Students' t-test) for all CrP and CrAlP catalysts. θ and α are obtained from the slope and intercept in eq. (2) and shown in fig. 3. Uncertainties are determined for a 98% confidence limit.

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 [19–25].

The effect is interpreted essentially as a consequence of the heterogeneity of acidic sites [24] due to the fact that the catalytic reaction involved adsorbed species and that the surface heterogeneity of the catalysts affects the reaction activation energy. Thus, the distribution of acid strength determines the energy barrier for the reaction to occur; the number of acid sites is also very important. So, the global rate will be the sum of the individual rates on each kind of acid site, every one acting with a different activation energy.

In this way, the differences in the reaction rate originate from the changes in the energetics and number of reactive species. Moreover, the number of the sites which are active for a given reaction depends mainly on the activation energy [25]. Thus, strong acid sites are characterized by a lower activation energy while the relative abundance of such acid sites can be related to the relative activity.

So, the differences between the activities of CrAlP catalysts are due to the differences in the number and strength of acid sites. Thus, the balance between (i) the amount of acidic sites, that mainly affects the frequency factor values, and (ii) their activity, that mainly affects the activation energy, determines the sequence of catalytic activity in CrAlP catalysts.

As far as the 2-propanol dehydrogenation reaction process is concerned, the conversion of 2-propanol to 2-propanone never surpasses a 3 mol% at the highest reaction temperature (573 K) where 2-propanol total conversion as high as 35 mol% can be achieved. Although high 2-propanone selectivities are found at lower reaction temperature, the 2-propanol conversion never attained a 3 mol% at this temperature. Moreover, only a very slight increase in 2-propanone yield on increasing reaction temperature was found. This behaviour results in a remarkable drop in 2-propanone selectivity upon increasing the reaction temperature to 573 K (fig. 2). Thus, comparison between samples exhibiting very different activities is difficult since reaction temperatures considerably affect the relative rates of 2-propanone and propene formation, propene being always favoured at high temperatures. Thus, as Vedrine et al. [26] indicate, the selectivity which depends on temperature cannot be used to calculate a number of basic sites as proposed by several authors [27,28].

On the other hand, poisoning of basic sites by phenol adsorption did not influence 2-propanol to 2-propanone conversion and thus, the dehydrogenation reaction process ought to be related to the redox properties of the $CrPO_4$ catalysts. Thus, as Lahousse et al. recently indicate [7], 2-propanol dehydrogenation requires an additional redox ability since basic oxides like MgO or magnesium aluminates do not catalyse 2-propanol dehydrogenation. However, they act as catalysts in the 2-methyl-3-butyn-2-ol decomposition into 2-propanone and acetylene, and this reaction has been proposed for the total basicity measurements [26]. Previous results on 2-methyl-3-butyn-2-ol conversion on $CrPO_4$ and $CrPO_4$–$AlPO_4$ catalysts [27] indicated that surface acid and basic sites indeed take part in such alcohol conversion.

4. Conclusions

CrAlP catalysts are active and selective catalysts for the 2-propanol decomposition and their activity and selectivity towards propene and 2-propanone formation were greatly influenced by reaction temperature. Thus at 573 K CrAlP catalysts are highly active and selective for dehydration to propene. Catalysts obtained in propylene oxide–aqueous ammonia showed the highest activity towards propene as compared to other catalysts. Calcination at increasing temperatures caused a decrease in the activity due to the decrease in surface acid character. Thus, the change in dehydration activity with the change in both precipitation medium and calcination temperature was similar to the change in acidic characteristics and was also similar to that previously obtained for cyclohexene isomerization and cumene cracking [1]. Moreover, 2-propanone was scarcely found at all reaction temperatures and its formation does not correlate with basicity measurements.

Acknowledgement

MRU is indebted to the Consejeria de Educacion y Ciencia (Junta de Andalucia, Spain) for a doctoral fellowship. The authors acknowledge the subsidy received from the DGICYT (Project PB92/0816), Ministerio de Educacion y Ciencia, and from Consejeria de Educacion y Ciencia (Junta de Andalucia), Spain.

References

[1] F.M. Bautista, J.M. Campelo, A. Garcia, D. Luna, J.M. Marinas and M.R. Urbano, J. Mater. Chem. 4 (1994) 311.
[2] R. Rudam and A. Stockwell, in: *Catalysis*, Vol. 1, Specialist Periodical Reports (The Chemical Society, London, 1977) p. 87.
[3] J. Cunningham, B.K. Hodnett, M. Ilyas, E.L. Leahy and J.L.G. Fierro, Faraday Discussions Chem. Soc. 72 (1981) 283.
[4] H. Pines, in: *The Chemistry of Catalytic Hydrocarbon Conversions* (Academic Press, New York, 1981) p. 127.
[5] B. Grzybowska-Swierkosz, Mater. Chem. Phys. 17 (1987) 121.
[6] J. Kijenski and A. Baiker, Catal. Today 5 (1989) 1.
[7] C. Lahousse, J. Bachelier, J.C. Lavalley, H. Lauron-Pernot and A.M. Le Govic, J. Mol. Catal. 87 (1994) 329.
[8] F.M. Bautista, J.M. Campelo, A. Garcia, D. Luna, J.M. Marinas, A.A. Romero and M.R. Urbano, React. Kinet. Catal. Lett. 53 (1994) 45.
[9] F.M. Bautista, J.M. Campelo, A. Garcia, D. Luna, J.M. Marinas, A.A. Romero and M.R. Urbano, React. Kinet. Catal. Lett. 53 (1994) 55.
[10] J.M. Campelo, A. Garcia, D. Luna and J.M. Marinas, React. Kinet. Catal. Lett. 47 (1992) 263.
[11] F.M. Bautista, J.M. Campelo, A. Garcia, D. Luna, J.M. Marinas, A.A. Romero and M.R. Urbano, React. Kinet. Catal. Lett., in press.
[12] D. Bassett and H.W. Habgood, J. Phys. Chem. 64 (1960) 769.
[13] M. Richter and G. Ohlmann, Appl. Catal. 36 (1988) 81.
[14] F. Pepe, C. Angeletti and S. de Rossi, J. Catal. 118 (1989) 1.
[15] B.Z. Wan, R.G. Anthony, G.Z. Peng and A. Clearfield, J. Catal. 101 (1986) 19.
[16] J.M. Campelo, A. García, J.F. Herencia, D. Luna, J.M. Marinas and A.A. Romero, J. Catal. 151 (1995) 307.
[17] A.J. van Roosmalen and J.C. Mol, J. Chem. Soc. Chem. Commun. (1980) 804.
[18] A.J. van Roosmalen, M.C.G. Hartmann and J.C. Mol, J. Catal. 66 (1980) 112.
[19] A.K. Galwey, Catal. Rev. 26 (1977) 247.
[20] A.K. Galwey and M. Brown, J. Catal. 60 (1979) 335.
[21] M. Boudart, in: *Kinetics of Chemical Processes* (Prentice-Hall, Englewood Cliffs, 1968).
[22] W.C. Conner Jr., J. Catal. 78 (1982) 238.
[23] W. Linert, R.W. Soukup and R. Schmid, Comput. Chem. 6 (1982) 47.
[24] A. Corma, F. Llopis, J.B. Monton and S. Weller, J. Catal. 142 (1993) 97.

[25] R.W. Maatman, Adv. Catal. 9 (1980) 51.
[26] A. Ouqour, G. Coudurier and J.C. Vedrine, J. Chem. Soc. Faraday Trans. 89 (1993) 3151.
[27] T. Yasima, H. Suzuki and N. Hara, J. Catal. 30 (1973) 362.
[28] K.T. Seo, S.C. Kang, H.J. Kim and S.K. Moon, Korean J. Chem. Eng. 2 (1985) 163.
[29] H. Lauron-Pernot, F. Luck and J.M. Popa, Appl. Catal. 78 (1991) 213.
[30] F.M. Bautista, J.M. Campelo, A. Garcia, D. Luna, J.M. Marinas and M.R. Urbano, unpublished.