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Fluoride treatment of $AlPO_4$–Al_2O_3 catalysts. II. Poisoning experiments by bases for cyclohexene conversion and cumene cracking

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Brønsted acid sites on fluoride-modified $AlPO_4$–Al_2O_3 (2.5 wt% F; APAl-P-2.5F) catalyst are poisoned by the presence of 2,6-dimethylpyridine (DMPY) and hexamethyldisilazane (HMDS), thus decreasing the catalytic activity for cyclohexene and cumene reaction processes, while the effect of pyridine (PY) was scarce. Besides, the drop in activity for cyclohexene conversion was accompanied by a change in reaction selectivity so that hydrogen transfer sites are much more sensitive to base poisoning (getting greater as the poisoning effect increased) than isomerization sites. Moreover, surface trimethylsilyl (TMS) complexes (formed by covalent reaction of HMDS with surface hydroxyls) decomposed and thus, the activity progressively increased at increasing time intervals, thus reaching greater values (at ca. 4 h) than the unpoisoned APAl-P-2.5F catalyst. So, DMPY was more suitable than PY and HMDS for the poisoning of Brønsted acid sites on APAl-P-F catalyst.

Keywords: $AlPO_4$–Al_2O_3; fluoride ion loading; surface acidity; cyclohexene conversion; cumene cracking; poisoning by bases; pyridine; 2,6-dimethylpyridine; hexamethyldisilazane

1. Introduction

In a previous paper [1] we showed that $AlPO_4$–Al_2O_3 (APAl-P) catalysts developed increased acidity upon incorporation of fluoride anion. The increase in both the number and strength of acid sites resulted in a better catalytic performance for cyclohexene conversion and cumene cracking reaction processes. Moreover, at difference of the $AlPO_4$ or $AlPO_4$–Al_2O_3 ones, the increased acidity gives to APAl-

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P-F catalysts the ability to exhibit both skeletal isomerization (SKI) and hydrogen transfer (HT) activities in cyclohexene conversion although the former always predominated. Furthermore, APAl-P-F catalysts exhibited a maximum in catalytic activity for a 2.5 wt% fluoride ion.

On the other hand, DRIFT measurements of adsorbed PY and DMPY give rise to pyridinium and 2,6-dimethylpyridinium cations respectively, produced by the reaction of PY and DMPY with surface Brønsted acid sites (bands at 1544 and 1636 cm^{-1}, respectively). Besides, Lewis-bound pyridine decreases significantly faster than the Brønsted-bound pyridine, so that at 573 K only Brønsted-bound pyridine remained evident. Moreover, simultaneously with the appearance of these bands, the bands at 3786 and 3647 cm^{-1} (ν_{O-H} stretching vibration of Al–OH and P–OH, respectively, with Al and P atoms in tetrahedral coordination) disappeared [1]. Furthermore, the changes in the normalized peak area of $DMPY^+$ (at 1636 cm^{-1}) with fluoride content showed a maximum (highest Brønsted acidity) at a fluoride loading of 2.5 wt%, the catalyst that exhibited the highest catalytic activity in cyclohexene and cumene conversions.

In the present paper, we study the effect of the poisoning of the APAl-P-2.5F protonic acid sites with pyridine (PY), 2,6-dimethylpyridine (DMPY) and hexamethyldisilazane (HMDS) on its catalytic performance in cyclohexene and cumene conversion processes. The activity poisoning results have indicated that the Brønsted acid sites of APAl-P-2.5F catalyst participated in both reaction processes, thus strengthening the carbenium ion reaction pathway.

2. Experimental

2.1. CATALYST PREPARATION

$AlPO_4$–Al_2O_3 (25 wt% Al_2O_3) was obtained in the presence of propylene oxide and calcined at 923 K for 3 h as it was previously described [2]. Fluorinated $AlPO_4$–Al_2O_3 catalyst containing a 2.5 wt% fluoride ion (APAl-P-2.5F) was prepared by impregnation until incipient wetness using an aqueous ammonium fluoride solution. After soaking the catalyst in this solution for 1 h, the impregnated $AlPO_4$–Al_2O_3 catalyst was dried at 393 K for 24 h and then calcined at 773 K for 3 h [1]. The characterization of this catalyst, including XRD, DTG-DTA, XPS, SEM, ^{27}Al and ^{31}P MAS-NMR, TPD of water, N_2 adsorption and DRIFT (catalyst and PY and DMPY adsorption), has been described elsewhere [1].

2.2. REACTION STUDIES

The catalytic performance measurements of APAl-P-2.5F catalyst in cyclohexene and cumene reaction processes were carried out in a microcatalytic pulse reactor according to a method previously described [1,2] and by using the Bassett–Habgood equation for first order processes [3]:

$$\ln[1/(1-X)] = kKRT(W/F),$$

where X is the total conversion, k the rate constant of the surface process, K the adsorption constant of the substrate on the catalyst, W the catalyst weight and F the flow rate of the carrier gas. A least squares regression analysis shows, in all instances, correlation coefficients over 0.99. A t-test of significance, performed on the regression coefficients, shows that these are significant at levels over 1%. This is a measurement of data fit, in all experimental conditions, by the linear plots of $\ln[1/(1-X)]$ versus F^{-1}. At least three measurements were used to calculate each kK. All values were reproducible to within about 8%.

The catalytic measurements were performed under the following conditions:

(a) *Cyclohexene conversion*: hydrocarbon pulse, 1 μl; temperature, 623 K; carrier gas, nitrogen (40 ml min^{-1}). GC with FID and two columns (1/8″, stainless-steel, 2 m each) in series packed with, respectively, 5% polyphenylether (6-rings) and 5% squalane both on Chromosorb G AW-DMCS 80/100 at 323 K. Reaction products, 1- and 3-methylcyclopentenes (1- and 3-MCPE), methylcyclopentane (MCPA) and cyclohexane (CHA).

(b) *Cumene conversion*: hydrocarbon pulse, 1 μl; temperature, 673–733 K; carrier gas, nitrogen (20 ml min^{-1}). GC with FID and a 2 m column (1/8″ stainless-steel) packed with 5% polyphenylether (6-rings) on Chromosorb G AW-DMCS 80/100 at 373 K. Reaction products, propylene, benzene (BZ) and α-methyltyrene (MS).

In order to characterize the reaction products, GC-MS (HP-5890II GC and HP-5970 MSD quadrupole mass spectrometer) was used. The reaction products were 1- and 3-MCPE, MCPA and minor amounts of CHA, for cyclohexene conversion and propylene, benzene and α-methylstyrene for cumene cracking.

Cyclohexene and cumene (from Merck) were used after distillation and purification with a column of alumina previously calcined at 573 K for 3 h in order to remove oxygen and peroxides.

2.3. POISONING EXPERIMENTS

The pulse poisoning technique, based on the selective poisoning of stronger acid sites with PY and DMPY, was used for both reactions. In some cases, hexamethyldisilazane (HMDS) was also used as the poison [4,5]. Catalyst poisoning experiments were carried out by pulses of either pure base or that in cyclohexane solution.

PY (Aldrich, Gold-label 99.9%), DMPY (Merck, 99%) and HMDS (Merck, 99%) were used without purification.

3. Results and discussion

Previous to any poisoning experiment by base probe, we have studied the catalyst deactivation versus pulse number. Thus, we have found that the initial activity

remained at the same level after several pulses (25–30) of cyclohexene or cumene. So, there is no evidence of coking of the APAl-P-2.5F catalyst. Besides, reaction selectivities remained almost unchanged with pulse number.

Moreover, in order to obtain information on the poisoning of the APAl-P-2.5F acid catalyst, PY, DMPY and HMDS were used as basic probes. While PY is bonded to Brønsted and Lewis sites [6,7], DMPY [6–9] and HMDS [4,5] are specifically bonded to 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 [4,5], i.e. a covalent bond rather than the acid–base reaction characteristic of PY or DMPY probe.

3.1. CYCLOHEXENE CONVERSION

The poisoning of the active sites on APAl-P-2.5F catalyst in the cyclohexene reaction was performed through the previous saturation of the acid sites with PY, DMPY or HMDS according to the following procedure. After measuring the activity of the fresh catalyst at 623 K (in triplicate; $\sim$ 8% error), the reaction temperature was lowered to 523 K. At this temperature, the catalyst was saturated with the probe reagent (PY, DMPY or HMDS) in the nitrogen stream. After saturation, the reaction temperature was increased to 623 K and then, the bed was flushed with nitrogen at 623 K (1 h) to remove all traces of unreacted probe reagent. Then, the activity of the catalyst was measured again. Pulses of cyclohexene were injected at different time intervals.

The poisoning effect of PY, DMPY and HMDS on cyclohexene conversion has been demonstrated on APAl-P-2.5F catalyst through the changes obtained in the apparent rate constants for isomerization (kK_{SKI}) and hydrogen transfer (kK_{HT}) as well as in the hydrogen transfer selectivities (S_{HT}, mol%) on pulsed cyclohexene. The results obtained on the influence of probe reagents in catalytic activities and hydrogen transfer selectivities of APAl-P-2.5F catalyst are shown in tables 1 and 2.

It can be seen that basic reagents suppressed the activity for cyclohexene conversion although the effectiveness of DMPY was greater than that of PY, as corresponded to its higher basicity. DMPY can interact with weak and strong Brønsted acid sites. So, the DMPY treatment lowered the activity (4–22 h) of the catalyst to about 25%, whereas PY caused a decrease to about 14%.

The drop in activity after poisoning was accompanied by a change in the hydrogen transfer selectivity (getting greater as the poisoning effect increased) as it can be seen in table 2, where the initial and poisoned activities appeared together with the S_{HT} selectivities. These data indicate that the hydrogen transfer sites are much more sensitive to base poisoning than isomerization sites. Thus, the DMPY treatment decreased the kK_{HT} to about 62% whereas, in kK_{SKI}, DMPY caused a decrease to about 25% after 22 h.

Table 1
Apparent rate constants (kK_{SKI}; error: ~ 8%) for the cyclohexene skeletal isomerization on APAl-P-2.5F catalyst deactivated with pyridine (PY), 2,6-dimethylpyridine (DMPY) or hexamethyldisilazane (HMDS). Reaction temperature: 623 K

Time interval (h)	kK_{SKI} 10^6 (mol/atm g s)		
	DMPY	PY	HMDS
0	203.7	202.6	202.4
1	75.9	80.4	160.8
1.5	86.0	80.6	225.2
3	142.6	120.1	244.9
4	141.8	136.5	307.2
5	145.2	151.7	300.2
6	150.0	167.3	293.2
7	146.1	184.9	304.1
8	148.1	180.2	286.8
22	156.1	175.5	296.5

Moreover, although in table 1 it is also evident that at first HMDS affected the catalytic activity and selectivity of the APAl-P-2.5F catalyst for cyclohexene conversion, notwithstanding, at increasing time intervals, the kK_{SKI} progressively increased thus reaching greater values (at ca. 4 h) than the unpoisoned APAl-P-2.5F catalyst. This indicated decomposition of the surface trimethylsilyl (TMS) complexes. In this sense, qualitative DRIFT measurements (fig. 1) indicated that a new hydroxyl group (ν_{O-H}: 3739 cm^{-1}) was created for HMDS adsorption on the APAl-P-2.5F catalyst. In this respect, experiments are in progress in order to understand the exact nature (Si–OH band?) of the newly developed surface hydroxyl group as well as the promotion of surface acidity by the adsorption of HMDS at a high temperature.

Table 2
Apparent rate constants (kK_{HT}; error: ~ 8%) and selectivities (S_{HT}) for the cyclohexene hydrogen transfer on APAl-P-2.5F catalyst deactivated with pyridine (PY), 2,6-dimethylpyridine (DMPY) or hyxamethyldisilazane (HMDS). Reaction temperature: 623 K

Time interval (h)	DMPY		PY		HMDS	
	kK_{HT} 10^6 (mol/atm g s)	S_{HT} (mol%)	kK_{HT} 10^6 (mol/atm g s)	S_{HT} (mol%)	kK_{HT} 10^6 (mol/atm g s)	S_{HT} (mol%)
0	11.5	6.2	12.0	6.2	12.0	6.2
1	1.7	2.4	1.0	1.3	0.8	0.6
1.5	2.0	2.4	3.5	4.4	3.2	1.8
4	3.1	2.8	7.8	5.9	4.5	2.3
6	4.0	3.0	9.5	6.0	6.7	2.9
8	5.7	4.2	11.2	7.0	8.0	3.5
22	5.2	3.9	13.8	7.0	11.1	4.8

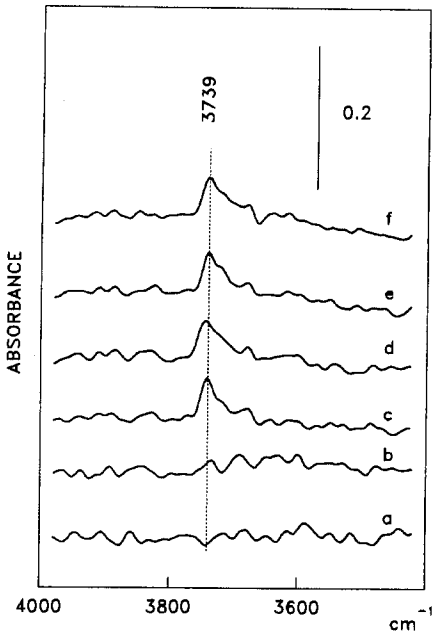

Fig. 1. DRIFT spectra (4000–3500 cm^{-1}) of adsorbed HMDS: spectra of HMDS–APAl-P-2.5F which was treated at 373 K under nitrogen (20 ml min^{-1}), after adsorption of HMDS, for 1 h (a). Then, the temperature was increased to 473 K and the catalyst remained, in the nitrogen stream at 473 K for an additional hour (b). Then, the temperature was increased to 573 K, the catalyst remaining at that temperature for 30 min (c), 1 h (d), 2 h (e), 4 h (f). Spectra are displaced for presentation.

Also, table 1 clearly showed that kK_{SKI} for PY and DMPY decreased at first but later on (ca. 3 h) remained almost unchanged (up to at least 22 h) showing that the Brønsted acid sites are occupied by irreversibly adsorbed PY or DMPY at 673 K. So, PY and DMPY were more suitable than HMDS for the characterization of surface acidity as well as the poisoning of fluoride-treated APAl-P catalysts.

In summary, these poisoning data indicate that the Brønsted acid sites of APAl-P-F catalysts participated in cyclohexene conversion, thus strengthening the carbenium ion reaction pathway.

3.2. CUMENE CRACKING

The poisoning of the active sites on the APAl-P-2.5F catalyst in the cumene cracking reaction was also performed using PY, DMPY and HMDS probes. Two procedures were used:

(a) In the first procedure, the acid sites were poisoned by saturating them with pyridine irreversibly adsorbed at 723 and 753 K. Upon increasing the adsorption temperature only the strongest acid sites were able to retain the adsorbed pyridine. Thus, only the acid sites which were weaker than those blocked by the base at the saturation temperature were available for the reaction of the poisoned catalyst. In this case, the desorption of the PY adsorbed from the poisoned catalyst during the

Table 3
Apparent rate constants (kK_{CK}; error: ~ 8%) and selectivities (S_{CK}) for cumene cracking on APAl-P-2.5F catalyst deactivated with pyridine (PY)

Poison	T_{ADS} [a] (K)	T_{REAC} [b] (K)	$kK_{CK}\ 10^6$ (mol/atm g s)	S_{CK} [c] (mol%)
–	–	673	3.7	100
PY	723	673	1.9	100
PY	753	673	2.3	100
–	–	723	11.9	100
PY	753	723	12.0	100

[a] Temperature of PY adsorption.
[b] Reaction temperature.
[c] Ratio of the fractional conversion of benzene to α-methylstyrene.

activity test was prevented by carrying out the reaction at a temperature (673 or 723 K) lower than the lowest temperature at which the acid sites were blocked with irreversibly adsorbed PY. The results obtained are compared to those by using the catalyst without poisoning.

The poisoning effect of pyridine on cumene cracking (CK) for the APAl-P-2.5F catalyst is given in table 3, where the apparent rate constant (kK_{CK}) and selectivity (S_{CK}) values appeared on the fresh catalyst as well as after its poisoning with PY (at two adsorption temperatures).

As can be seen in table 3, the catalytic activity of the APAl-P-2.5F catalyst for cumene cracking (CK) decreased with the decrease in the temperature at which the catalyst was saturated with irreversibly adsorbed PY, i.e. when more acid sites were blocked. However, the CK activity of the poisoned APAl-P-2.5F catalyst remained appreciable after PY poisoning.

(b) In the second procedure, the acid sites were poisoned with pyridine, 2,6-dimethylpyridine or hexamethyldisilazane (adsorbed at saturation) at 523 K. After adsorption, the weakly held probe molecule was removed by flowing nitrogen for 1 h at 723 K. Furthermore, catalytic experiments were carried out at that temperature.

Table 4
Apparent rate constants (kK_{CK}; error: ~ 8%) and selectivities (S_{CK}) for cumene cracking on APAl-P-2.5F catalyst [a] deactivited with pyridine (PY), 2,6-dimethylpyridine (DMPY) or hexamethyldisilazane (HMDS). Reaction temperature: 723 K

Poison	$kK_{CK}\ 10^6$ (mol/atm g s)	S_{CK} [b] (mol%)
–	11.9	100.0
PY	11.2	99.5
DMPY	9.7	99.0
HMDS	0.6	90.1

[a] Third pulse of cumene after poisoning by base.
[b] Ratio of the fractional conversion of benzene to α-methylstyrene.

Table 5
Cumene cracking (kK_{CK}; error: ~ 8%) on APAl-P-2.5F catalyst deactivated with hexamethyldisilazane

Time interval (h)	kK_{CK} 10^6 [a] (mol/atm g s)	Time interval (h)	kK_{CK} 10^6 [a] (mol/atm g s)
0	11.3	5	4.7
0.5	0.2	6	5.1
1	0.6	7	5.5
2	1.5	8	6.1
3	2.5	21	19.0
4	3.3		

[a] Reaction temperature: 673 K.

As regards this second poisoning procedure, table 4 collected the kK_{CK} values on the fresh APAl-P-2.5F catalyst as well as after its poisoning with PY, DMPY or HMDS (third pulse of cumene after poisoning by base).

As can be seen in table 4 the presence of DMPY or HMDS lowered the catalytic activity while the PY effect was scarce (9%). It appeared, therefore, that DMPY and HMDS blocked surface Brønsted acid sites. The effectiveness of DMPY, however, was much less than that of HMDS. The DMPY treatment lowered the activity of the catalyst to 80% whereas HMDS caused a decrease to 95%. From the foregoing, we could conclude that DMPY and HMDS were more specific poisons for Brønsted acid sites although, as in the cyclohexene reaction (see above), the catalyst treated with HMDS increasingly developed activity (table 5), thus reaching greater values (at 21 h) than the unpoisoned APAl-P-2.5F catalyst. So, its use as a specific poison in $AlPO_4$ and $AlPO_4$–Al_2O_3 catalysts was restricted.

4. Conclusions

In summary, in the cyclohexene and cumene reaction processes on fluorided $AlPO_4$–Al_2O_3 catalysts, DMPY poisoned surface active sites, which were therefore Brønsted acidic and readily accessible, because even a large molecule such as HMDS has been found to react easily. Moreover, the poisoning effect of DMPY was more pronounced on cumene cracking, a reaction that required stronger Brønsted acid sites than cyclohexene conversion.

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References

[1] F.M. Bautista, J.M. Campelo, A. Garcia, D. Luna, J.M. Marinas, A.A. Romero, J.A. Navio and M. Macias, J. Catal., in press.
[2] J.M. Campelo, A. Garcia, D. Luna, J.M. Marinas and M.I. Martinez, Mater. Chem. Phys. 21 (1989) 409.
[3] D. Bassett and H.W. Habgood, J. Phys. Chem. 64 (1960) 769.
[4] A.J. van Roosmalen and J.C. Mol, J. Chem. Soc. Chem. Commun. (1980) 804.
[5] A.J. van Roosmalen, M.C.G. Hartmann and J.C. Mol, J. Catal. 66 (1980) 112.
[6] H.A. Benesi, J. Catal. 28 (1973) 176.
[7] A. Corma, C. Rodellas and V. Fornes, J. Catal. 88 (1984) 374.
[8] L.L. Murrell and N.C. Dispenziere, J. Catal. 117 (1989) 275.
[9] S. Sato, M. Tokomitsu, I.T. Sodesawa and F. Nozaki, Bull. Chem. Soc. Japan 64 (1991) 1005.