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CHROMIUM-ALUMINIUM ORTHOPHOSPHATES, III. ACIDITY
AND CATALYTIC PERFORMANCE IN CYCLOHEXENE AND CUMENE
CONVERSIONS ON $CrPO_4$-$AlPO_4$ (20-50 wt.% $AlPO_4$) CATALYSTS
OBTAINED IN AQUEOUS AMMONIA

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The modification of $CrPO_4$-A catalyst with $AlPO_4$ leads to
$CrPO_4$-$AlPO_4$ (CrAlP-A) catalysts exhibiting not only an in-
creased total acidity but also an increased number of
strongest Lewis acid sites as compared to $CrPO_4$ and $AlPO_4$
catalysts. Besides, surface acidity is slightly influ-
enced by $AlPO_4$ loading (5-50 wt.%). This increased sur-
face Lewis acidity is responsible for the improved cata-
lytic activity in cyclohexene skeletal isomerization and
cumene dehydrogenation processes. Moreover, the catalytic
activity results can be well interpreted through differ-
ences in the number and strength of acid sites, measured
gas-chromatographically, in terms of pyridine and 2,6-
dimethylpyridine chemisorbed at different temperatures
(573-673 K).

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INTRODUCTION

In a previous paper [1] we have shown that the incorpora-
tion of $AlPO_4$ into $CrPO_4$ afforded $CrPO_4$-$AlPO_4$ catalysts with
better textural properties and higher surface acidities than
pure $CrPO_4$ [2, 3]. Moreover, in order to learn more about the
promotion of $CrPO_4$ catalysts by the incorporation of $AlPO_4$, in
the preceding paper [4] we showed that the surface area and
pore volume increase, at any calcination temperature below
1273 K, with the rise in $AlPO_4$ content from 20 wt.%. At the
same time, $AlPO_4$ speeds up the transformation of amorphous
$CrPO_4$ to crystalline β-$CrPO_4$.

In the present work we study the effect of $AlPO_4$ amount of
both surface acidity and catalytic performance of $CrPO_4$-$AlPO_4$
(CrAlP-A, 20-50 wt.% $AlPO_4$) for cyclohexene skeletal isomeriza-
tion (CSI) and cumene conversion (CC). The results obtained are
compared with those found previously for pure $CrPO_4$ [3] and
$AlPO_4$ catalysts [5].

EXPERIMENTAL

Catalysts

Three $CrPO_4$-$AlPO_4$ catalysts were used. Their compositions
were: $CrPO_4$:$AlPO_4$, 80:20 (CrAlP-A-20); 70:30 (CrAlP-A-30) and
50:50 (CrAlP-A-50) wt.%. All they were calcined for 3 h at 773,
923 and 1073 K to obtain three thermal products for every com-
position. The calcination temperature (in K) follows the sample
designation directly. Details of their preparation have been
previously reported [1, 4].

Methods

The surface acidity (sum of Brönsted and Lewis sites) was
measured in a dynamic mode by means of the gas-phase adsorption
(573 and 673 K) of pyridine (PY) and 2,6-dimethylpyridine
(DMPY) using a pulse-chromatographic technique [6, 7]. The
pulse size was in the range corresponding to 0.1-0.5 monolayers
so as to approach conditions of gas-chromatographic linearity.

The catalytic properties of CrAlP-A catalysts in CSI and CC (craking. CK, and dehydrogenation, DH) reaction processes were studied by using a microcatalytic pulse reactor inserted between the sample inlet and the analytical column of a HP-589000 GC, according to a method previously described [6, 7]. Catalytic measurements were performed under the following conditions: (a) CSI, hydrocarbon pulse, $1 \mu l$; temperature, 523-623 K (at 50 K intervals); 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% poly(phenyl ether) (6-rings) and 5% squalane, both on Chromosorb G AW-DMCS 80/100 at 323 K. (b) CC, hydrocarbon pulse, $1 \mu l$; temperature, 573-773 K (at 50 K intervals); carrier gas, nitrogen (20 mL min^{-1}). GC with FID and 2 m column (1/8", stainless steel) packed with 5% poly(phenyl ether) (6-rings) on Chromosorb G AW-DMCS 80/100 at 373 K.

The reaction products, characterized by GC-MS (HP-5970 MSD-detector; 60 m SPB-1 capillary column at 308 K), were 1- and 3-methylcyclopentenes (1- and 3-MCPE) for CSI and α-methylstyrene for CC.

Cyclohexene and cumene (from Merck) were used after distillation and purification with a column of alumina previously calcined at 573 for 3 h.

RESULTS AND DISCUSSION

Surface acid properties

The acidity of each CrAlP-A sample investigated was determined by measuring the amount of base retained (at saturation) on the surface at two temperatures (573 and 673 K). The gaseous adsorption method permitted surface acidity measurements under conditions close to those of catalytic reactions but is unable to distinguish Brönsted and Lewis acid sites unless specific basic probes were used. Thus, two basic probes were used:

pyridine (PY), that is adsorbed on both Brönsted and Lewis acid
sites [8], and 2,6-dimethylpiridine (DMPY) (more basic than PY
according to their pK_a values) and, in principle, able to be
selectively adsorbed on Brönsted acid sites [9, 10] but not on
Lewis ones because of the steric hindrance of two methyl groups.
The amount of base retained at 573 K is assumed to be a measure
of the total number of acid sites while the base retained at
673 K is a measure of only stronger acid sites.

The distribution of acid sites on the different CrAlP-A
catalysts is given in Table 1, where the results found previ-
ously for $CrPO_4$-A [3], $AlPO_4$ [5], CrAlP-A-5 and CrAlP-A-10 [1]
catalysts are also collected.

As was expected, the surface chemical interaction in all
CrAlP-A catalysts was determined by the adsorption temperature.
Besides, it is evident from Table 1 that CrAlP-A catalysts ex-
hibited not only an increased total acidity but also an increased
number of strongest acid sites (titrated at 673 K) compared to
$CrPO_4$ and $AlPO_4$ catalysts. The results of Table 1 also indicate
that the site energy distribution and the number of strong acid
sites on the CrAlP-A catalyst are slightly influenced by $AlPO_4$
loading, independently of the calcination temperature. Moreover,
the amount of adsorbed PY and DMPY decreased with the increase
in calcination temperature. Adsorption still remained at 1073 K
but, on treatment at 1273 (results not shown here), the acidity
disappeared completely. This fact is due to $CrPO_4$ and $AlPO_4$
crystallization [4]. As compared to pure $CrPO_4$-A catalysts [3],
CrAlP-A catalysts displayed increased acidity, especially at
higher calcination temperatures.

Furthermore, the quantitative estimations summarized in
Table 1 showed that for CrAlP-A catalysts calcined at 773-1073 K,
and independently of $AlPO_4$ loading, there was no significant
difference between the amounts of DMPY at 573 and 673 K. This
should indicate that these catalysts had dominantly strong
Brönsted acid sites. However, preliminary IR results of PY and
DMPY adsorption [11] indicate the absence of Brönsted acidity

Table 1

Surface acidity (μmol g^{-1}) and apparent rate constants
for cyclohexene skeletal isomerization (kK$_{SKI}$)
and cumene dehydrogenation (kK$_{CDH}$) on CrPO$_4$-AlPO$_4$ catalysts

CATALYSTS	PY[a]		DMPY[b]		kK$_{SKI}$	σ[c]	kK$_{CDH}$
	573 K	673 K	573 K	673 K	(mol/atm g s)		(mol/atm g s)
CrAlP-A-5-773	40	35	21	21	77.5	3.2	2.4
CrAlP-A-5-923	25	14	13	13	86.3	3.1	2.9
CrAlP-A-5-1073	10	4	3	2	48.6	2.6	2.2
CrAlP-A-10-773	37	27	20	20	106.3	3.4	3.4
CrAlP-A-10-923	26	26	8	8	126.6	3.1	2.3
CrAlP-A-10-1073	17	13	7	7	46.9	3.3	1.3
CrAlP-A-20-773	42	43	14	14	84.6	3.0	2.4
CrAlP-A-20-923	27	22	6	6	90.3	3.1	1.7
CrAlP-A-20-1073	23	12	5	5	43.6	2.9	1.9
CrAlP-A-30-773	41	38	34	29	103.3	3.0	3.2
CrAlP-A-30-923	38	37	17	10	93.2	3.2	2.6
CrAlP-A-30-1073	22	23	11	10	60.2	2.8	1.7
CrAlP-A-50-773	75	59	25	25	129.7	3.2	4.3
CrAlP-A-50-923	76	26	15	15	76.3	3.0	4.1
CrAlP-A-50-1073	48	22	11	11	60.6	2.9	1.5
AP-A-923	15	-[d]	4	-[d]	3.2	1.3	0.2
CrP-A-773	36	24	9	-[d]	68.2	3.0	3.3
CrP-A-923	18	17	8	-[d]	70.3	3.0	1.1
CrP-A-1073	17	12	<1	-[d]	54.5	2.8	1.9

[a] PY: pyridine

[b] DMPY: 2,6-dimethylpyridine

[c] Ratio of the fractional conversion of 1-MCPE to 3-MCPE (X_1/X_3)

[d] Not measured

(absence of bands at 1544 and 1636 cm^{-1} due to Brönsted-bound
PY [8] and DMPY [9, 10], respectively). Thus, DMPY adsorption
measured the number of more accessible strong Lewis acid sites
on CrAlP-A catalysts. In that sense, the absence of cumene
cracking in cumene conversion (see below) strengthens the Lewis
nature of surface acid sites.

Catalytic activity measurements

In the absence of diffusional influences, the conversion of
cyclohexene and cumene (which were maintained below the 20%
level) follows the requirements of Bassett-Habgood kinetic
treatment [12] for first order kinetic processes.

For all CrAlP-A catalysts Table 1 compiles the apparent
rate constants (kK) at a reaction temperature of 673 K, from
linear plots of $\ln[1/(1-X)]$ vs. F^{-1}, for the CSI (kK_{SKI}) and
cumene dehydrogenation (kK_{CDH}) reaction processes. A least-
squares regression analysis shows in all cases correlation co-
efficients above 0.99. All values were reproducible to within
about 8%. Table 1 also showed kK_{SKI} and kK_{CDH} values previously
obtained for $CrPO_4$-A [3], $AlPO_4$-A [5], CrAlP-A-5 and CrAlP-A-10
[1] catalysts.

Results in Table 1 showed that CrAlP-A catalysts exhibited
increased activity (at all $CrPO_4/AlPO_4$ weight ratios and treat-
ment temperatures) in CSI and CDH as compared to $CrPO_4$-A and
$AlPO_4$-A catalysts, strengthens the increase in surface acidity
(see above) by $AlPO_4$ loading. Also, the surface acid sites on
CrAlP-A catalysts ought to be Lewis type since they are unable
to catalyze cumene cracking.

Moreover, the catalytic activity of CrAlP-A catalyst is
slightly influenced by $AlPO_4$ loading although it decreases as
calcination temperature increases up to 1073 K. Activity dis-
appeared for treatment temperatures of 1273 K due to $CrPO_4$ and
$AlPO_4$ crystallization. So, the change in activity with the
change in both $AlPO_4$ loading and calcination temperature was
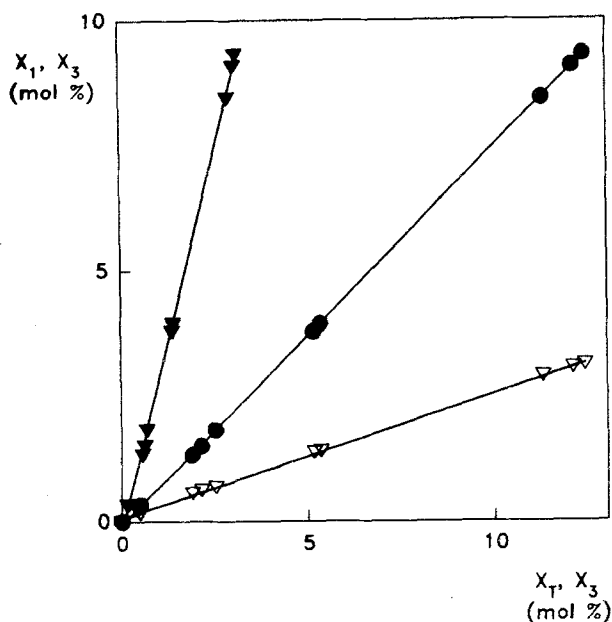similar to the change in acidic characteristics measured by

Fig. 1. OPE curves [X_1 (●) and X_3 (▽) vs. X_T] and Wheeler
selectivity [X_1 vs. X_3 (▼)] for the CSI on
CrAlP-A-50-923 catalyst

PY and DMPY adsorption. The results suggested that the differ-
ences between the activities of various samples arise from the
different Lewis acidity of these catalysts.

Furthermore, with regard to the selectivity of the CSI reac-
tion, we have applied the Wheeler criterion [13] on the kinetic
selectivity factor (σ) for first order processes by plotting
(Fig. 1) fractional conversion to 1-MCPE (X_1) vs. that to 3-MCPE
(X_3). Besides, we have also constructed the OPE curves by plotting
X_1 and X_3 against the total conversion (X_T) for different weight
ratios of catalyst with respect to cyclohexene introduced (Fig. 1)
as described by Ko and Wojciechowski [14].

The results obtained (straight lines at origin in all cases) showed that, in the range of the conversions studied, 1- and 3-MCPE were stable primary reaction products coming from cyclohexene through a parallel process with first order kinetics. The σ selectivities (Table 1) were measured at different reaction temperatures and found to be invariant as expected for a mechanism involving a carbenium ion intermediate. Also, Cr-AlP-A catalysts exhibited increased selectivity to 1-MCPE as compared to $CrPO_4$-A and $AlPO_4$-A catalysts. Moreover, σ values remained practically unchanged on increasing calcination temperature up to 1073 K.

Thus, the parallel carbenium ion reaction pathways previously proposed for $AlPO_4$ [5] and $CrPO_4$ catalysts [3] can also be applied for $CrPO_4$-$AlPO_4$ catalysts through the action of reaction intermediates with a carbocationic character higher than that of $AlPO_4$ and $CrPO_4$ catalysts.

In summary, Cr-AlP-A catalysts displayed higher surface acidity and hence, better catalytic performance in cyclohexene skeletal isomerization and cumene dehydrogenation as compared to $CrPO_4$-A and $AlPO_4$-A catalysts. Moreover, a slight influence of $AlPO_4$ loading (5-50 wt.%) was found.

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