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CHROMIUM-ALUMINIUM ORTHOPHOSPHATES, II. EFFECT OF $AlPO_4$ LOADING ON STRUCTURE AND TEXTURE OF $CrPO_4$-$AlPO_4$ (20-50 wt.% $AlPO_4$ CATALYSTS OBTAINED IN AQUEOUS AMMONIA

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The $AlPO_4$ content in $CrPO_4$-$AlPO_4$ (CrAlP-A) systems has a marked influence on thermal behavior, speeding up the transformation of amorphous $CrPO_4$ to crystalline β-$CrPO_4$. Thus, XRD analysis showed that amorphous systems are formed at $AlPO_4$ loadings less than 50 wt.% and calcination temperatures below 1273 K. Moreover, on 50 wt.% $AlPO_4$ developed crystalline β-$CrPO_4$ in CrAlP-A systems for every calcination temperature. Besides, at 1273 K crystalline systems (β-$CrPO_4$ and tridimite-$AlPO_4$) are formed for every composition. Moreover, surface area at any calcination temperature increases with the rise in the $AlPO_4$ content. Also, a surface area decrease on increasing calcination temperature is shown. Furthermore, CrAlP-A catalysts thermally treated below 1273 K only exhibited hydrogen bonded hydroxy groups ($\nu_{O-H} \approx 3450$ cm^{-1}).

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INTRODUCTION

In previous papers we have shown that stoichiometric $CrPO_4$ is able to catalyze cyclohexene skeletal isomerization and cumene conversion reaction processes [1, 2]. Besides, the catalytic performance of $CrPO_4$ is largely influenced by the gelation agent and the treatment temperature further to preparation [2].

Moreover, the incorporation of low amounts (5-10 wt.%) of $AlPO_4$ leads to $CrPO_4$-$AlPO_4$ catalysts whose physicochemical properties and catalytic performance for the above reaction processes are improved in relation to those of the single components [3].

In order to learn more about the promotion of $CrPO_4$ catalysts by the incorporation of $AlPO_4$, the present paper deals with the effect of $AlPO_4$ amount (up to 50 wt.%) on structure and textural properties of $CrPO_4$-$AlPO_4$ (CrAlP-A, 20-50 wt.% $AlPO_4$) catalysts, obtained with aqueous ammonia as gelation agent, with reference to their thermal behavior and crystal structure at various temperatures (773-1273 K). Gas-phase surface acidity, infrared spectroscopy of adsorbed bases as well as the catalytic activity of CrAlP-A catalysts in cyclohexene and cumene conversions will be reported in a forthcoming paper [4].

EXPERIMENTAL

Catalysts

CrAlP samples of varying composition (20-50 wt.% $AlPO_4$) were obtained by adding $CrPO_4$ (obtained by precipitation with aqueous solution of chromium nitrate and H_3PO_4) to a reaction medium where the precipitation of $AlPO_4$, from aluminium nitrate and H_3PO_4 aqueous solutions, was initiated by the addition of aqueous ammonia (pH=4). Afterwards, the total precipitation of $AlPO_4$ was carried out by addition of aqueous ammonia. After filtration, washing with water and, then, with isopropanol and drying at 390 K, the solids were calcined at 773, 923, 1073 and 1273 K for 3 h.

The samples are designated by CrAlP followed by a letter that indicates the precipitation medium (A: ammonia) and by the calcination temperature (CrAlP-A-20-773, CrAlP-A-50-923, and so on).

Methods

Surface area and pore size information were obtained from nitrogen adsorption/desorption isotherms at 77 K, using a Micromeritics ASAP 2000 analyzer. Assessment of possible microporosity was made from t-plot constructions, using the Harkins-Jura correlation for t as a function of p/p_o. Parameters were fitted to a low-area, nonporous silica. Mesopore size distributions were calculated using the Barrett, Joyner and Halenda (BJH) method, assuming a cylindrical pore model [5].

X-ray investigation of the thermal products was carried out using a Siemens D-500 diffractometer provided by a control and data acquisition automatic system (DACO-MP). The patterns were run with Ni-filtered CuK_α radiation (λ=1.5405 Å) at 35 KV and 20 mA; the diffraction angle 2Θ ($10° < 2\Theta < 70°$) was scanned at a rate of 2° min^{-1}.

Diffuse reflectance FTIR (DRIFT) Spectra [Bomem MB-100 with an "environmental chamber" (Spectra Tech)] were recorded at 573 K (absorbance mode with a resolution of 8 cm^{-1} and a gain factor of 1) in the wavenumber range 4000-400 cm^{-1}. DRIFT spectra have been recorded for all the calcined catalysts previously dried at 400 K for 24 h under vacuum [6].

RESULTS AND DISCUSSION

X-ray investigation of the 773-1273 K calcination products

As shown in Fig. 1 the incorporation of $AlPO_4$ up to 30 wt.% developed amorphous CrAlP-A catalysts with treatment temperatures lower than 1073 K since only a very broad hump in the range of 20-30° (2Θ) was found. At 1073 K a small degree of crystallinity begins to appear while at 1273 K both $AlPO_4$ and $CrPO_4$ crystallized leading to highly crystalline CrAlP-A catalysts.

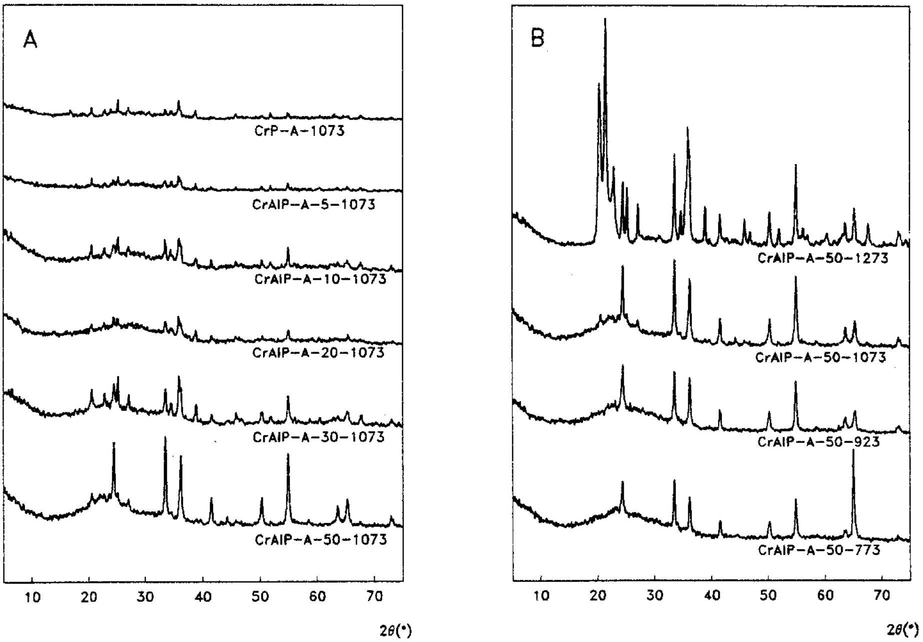

Fig. 1. XRD patterns (CuK$_\alpha$ radiation) of the different CrAlP-A samples

$CrPO_4$ crystallizes in the β-$CrPO_4$ structure [1, 3], while the $AlPO_4$ structure corresponded to the pseudohexagonal one of tridymite [7], with bands at d=4.35 (2Θ=20.4°), d=4.13 (2Θ=21.5°) and d=3.87 (2Θ=22.9°), although the relative intensities differed slightly from those reported by Florke [7]. This is due to the presence of structural defects in some part of the crystal as a result of tetrahedral sheet placement (structure in two sheets instead of three sheets).

Furthermore, the presence of $AlPO_4$ in a 50 wt.% developed crystalline β-$CrPO_4$ in CrAlP-A catalysts for every calcination temperature (Fig. 1B). Thus, the $AlPO_4$ content in $CrPO_4$-$AlPO_4$ catalysts has a marked influence on thermal behavior, speeding up the transformation of amorphous $CrPO_4$ to crystalline β-$CrPO_4$.

DRIFT measurements

The DRIFT spectra of CrAlP-A catalysts, treated at temperatures below 1273 K (Fig. 2, as example) show a broad band around 1100 cm^{-1} due to triply degenerate P-O stretching vibration [ν_3 of tetrahedral $(PO_4)^{3-}$] and a broad absorption around 500 cm^{-1} due to triply degenerate O-P-O bending vibration [ν_4 of $(PO_4)^{3-}$ tetrahedra]. Calcination at 1273 K, develops crystalline β-$CrPO_4$ and tridymite-$AlPO_4$ and the DRIFT spectra show several bands below 1000 cm^{-1} due to the presence of mixed motions which involve both PO_4 tetrahedra and CrO_6 octahedra, as was described by Baran et al. [8] for β-$CrPO_4$. Besides, the band around 710 cm^{-1} is due to stretching vibrations of Al-O bonds in combination with P-O bonds. Moreover, the bands at 1620, 1830 and 2220 cm^{-1} probably reflect combinations or overtones of lattice vibration. Furthermore, CrAlP-A catalysts only exhibited hydrogen bonded hydroxy groups ($\nu_{O-H} \simeq 3450$ cm^{-1}).

Textural properties

Nitrogen adsorption isotherms for all CrAlP-A catalysts thermally treated up to 1073 K are type IV in the BDDT classification [9] with closed hystheresis (H1 loops) corresponding to mesoporous solids [10]. Besides, t-plots from the adsorption branch of the isotherm showed the absence of microporosity. Moreover, after heating at 1273 K all CrAlP-A-1273 catalysts displayed reversible type II isotherms that corresponded to non-porous adsorbents. Surface areas and pore volumes are compiled in Table 1 together with the mean pore radius. Results for CrAlP-A-1273 catalysts were not included (surface area lower than 1 m^2g^{-1}). The agreement between the S_{BET} and ΣS_p, as well as the agreement between the cumulative volume, ΣV_p, and the total volume V_p, indicates the correct choice in the method of pore analysis. Pore size distributions are also shown in Table 1.

Inspection of Table 1 reveals that the surface area at any calcination temperature increases with the rise of $AlPO_4$ content from 20 wt.%. It is also seen that the surface areas of

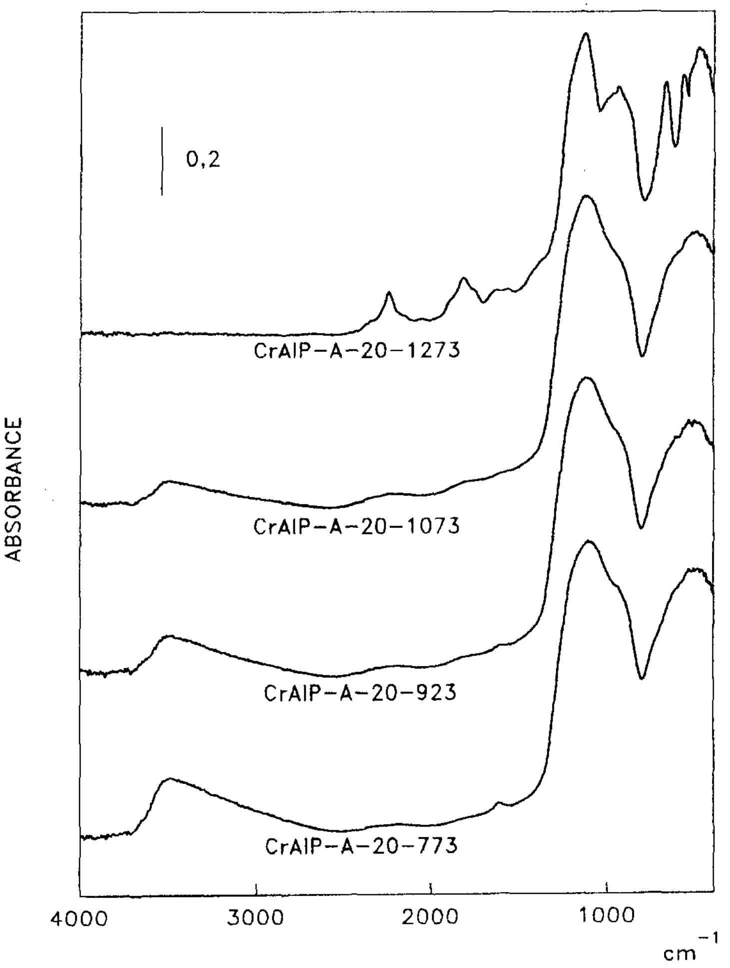

Fig. 2. DRIFT spectra of the CrAlP-A-20 samples calcined at 773, 923, 1073 and 1273 K.

All CrAlP-A catalysts showed similar DRIFT spectra

all samples decrease with increasing calcination temperature from 773 to 1273 K, indicating a sintering process in the solid beyond 1073 K. This sintering is accompanied by $CrPO_4$ and $AlPO_4$

Table 1

Textural properties of CrAlP-A (20-50 wt.% $AlPO_4$), AP-A and CrP-A catalysts calcined at different temperatures

Catalysts	S_{BET}	V_p	r_p	Pore size distribution (vol. %)*			
	($m^2\ g^{-1}$)	($mL\ g^{-1}$)	(nm)	>20 nm	10-20	5-10	2-5
CrAlP-A-20-773	18	0.10	11.8	68.0	13.7	11.7	6.6
CrAlP-A-20-923	9	0.08	18.4	80.9	12.4	5.5	1.1
CrAlP-A-20-1073	8	0.06	16.2	87.1	7.3	4.5	1.1
CrAlP-A-30-773	22	0.10	8.8	65.3	15.2	12.2	7.3
CrAlP-A-30-923	13	0.10	17.6	77.1	13.9	7.4	1.6
CrAlP-A-30-1073	10	0.09	17.0	87.2	6.4	4.7	1.7
CrAlP-A-50-773	44	0.22	9.8	68.3	14.7	10.6	6.4
CrAlP-A-50-923	40	0.20	10.0	70.2	13.5	9.5	6.8
CrAlP-A-50-1073	27	0.22	16.6	84.0	9.2	4.5	2.3
AP-A-773	114	0.49	8.5	3.7	7.2	28.8	60.3
AP-A-923	109	0.48	8.8	4.6	8.1	32.6	54.7
AP-A-1073	81	0.46	11.4	5.6	10.0	42.3	42.1
CrP-A-773	9						
CrP-A-923	8						
CrP-A-1073	<1						

* From the adsorption branch of the isotherms using the BJH method and cylindrical pore system

crystallization (see above). Moreover, the decrease in progressive surface area versus calcination temperature is smaller as the $AlPO_4$ content of the catalyst increases. Furthermore, pore analysis indicates that the decrease in surface area is accompanied by a decrease in total pore volume and increase in the pore size (Table 1). Also, pore size distribution is displaced to larger pores.

In conclusion, as compared to pure $CrPO_4$ catalysts [1], the most striking feature of the results shown in Table 1 is that the presence of $AlPO_4$ leads to CrAlP catalysts with surface areas higher than pure $CrPO_4$. Moreover, as compared to pure $AlPO_4$ [11], CrAlP catalysts exhibited smaller surface areas and pore volumes but, however, they displayed an increase in the most frequent pore radius as well as higher surface acidities [4], so that $CrPO_4$-$AlPO_4$ catalysts show better catalytic performance in cyclohexene skeletal isomerization (reaction that requires the presence of strong acid centers) to be shown in a forthcoming paper [4].

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