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$AlPO_4$–Al_2O_3 catalysts with low alumina content. III. Surface basicity of catalysts obtained in aqueous ammonia

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The amount of basic sites of $AlPO_4$–Al_2O_3 (APAl-A, 5–15 wt% Al_2O_3) catalysts at two basic strengths was measured by studying the liquid-phase adsorption of two acidic molecules (benzoic acid (BA, $pK_a = 4.2$) and phenol (PH, $pK_a = 9.9$) from cyclohexane solutions, through the application of a spectrophotometric method. The data obtained follow the Langmuir adsorption isotherm and the monolayer coverage at equilibrium (at 298 K), X_m, is assumed as the amount of basic sites corresponding to the specific pK_a of the acid used as titrant. The amount of basic sites of any $AlPO_4$–Al_2O_3 catalyst is higher than that of $AlPO_4$, but lower than that of Al_2O_3. Besides, an increase in the Al_2O_3 content from 10 wt% gradually increases the basicity of the APAl-A catalyst. Moreover, calcination at increasing temperatures does not practically affect the surface basicity of APAl-A-5 and APAl-A-10 catalysts. However, for $AlPO_4$ content higher than 10 wt% we observe a decrease in surface basicity, this decrease depends on alumina content, i.e. it is higher as the amount of alumina increases. The basic sites of APAl-A systems catalyze the Knoevenagel condensation of *p*-methoxybenzaldehyde and malononitrile at room temperature and in the absence of solvent.

Keywords: $AlPO_4$; $AlPO_4$–Al_2O_3; surface basicity; Langmuir adsorption; Knoevenagel condensation

1. Introduction

Our previous works [1–3] had already indicated that the incorporation of Al_2O_3 into $AlPO_4$ catalysts resulted in a mutual stabilization, thus maintaining the amorphous nature of $AlPO_4$ and the γ-structure of Al_2O_3. This was manifested by better thermal stability of the surface area of $AlPO_4$–Al_2O_3 and by a significant delay in the γ- to α-Al_2O_3 phase transformation. Thus, in all $AlPO_4$–Al_2O_3 cata-

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lysts, obtained by precipitation with aqueous ammonia, calcined at 1073 K the $AlPO_4$ remained mesoporous up to Al_2O_3 contents of 15 wt%. For a 5 wt% Al_2O_3, the catalyst calcined at 1273 K even is mesoporous. Besides, APAl-A catalysts exhibit improved surface acidity and, hence, better catalytic performances in cyclohexene isomerization and cumene cracking than $AlPO_4$ catalysts.

In addition, $AlPO_4$–Al_2O_3 catalysts showed surface basic sites [1,4] thus catalyzing liquid-phase reaction processes such as the retroaldolization of the diacetone alcohol [4], and the Knoevenagel condensation of carbonyl compounds with active methylene compounds [5].

The present work is devoted to an investigation of the changes in surface basic properties (amount and strength of the sites) brought about by both progressive Al_2O_3 loading (5–15 wt%) and heating (773–1273 K) of APAl-A catalysts recently described [2,3]. The results are compared with those previously found for $AlPO_4$[4], γ-Al_2O_3 [4] and $AlPO_4$–Al_2O_3 (25 wt% Al_2O_3) [1]. Furthermore, some preliminary results on Knoevenagel condensation of *p*-methoxybenzaldehyde and malononitrile, at room temperature and in the absence of solvent, were included.

2. Experimental

Catalysts

The preparation of APAl-A catalysts (5–25 wt% Al_2O_3) was described in previous papers [1–3]. They are designated by APAl-A followed by the Al_2O_3 loading and by the calcination temperature: APAl-A-5-773, APAl-15-1073, and so on. For comparative purposes $AlPO_4$ (AP-A) [4] and γ-Al_2O_3 (Al-A) [4] catalysts were also included. The surface areas of APAl-A, AP-A and Al-A catalysts are collected in table 1.

Methods

Surface basic properties (amount of basic sites at two basic strengths) of APAl-A catalysts, at different stages of heat treatment, were obtained through the irreversible adsorption (in the liquid-phase and at 298 K) of organic acid probes (benzoic acid (BA, $pK_a = 4.2$) and phenol (PH, $pK_a = 9.9$)) from cyclohexane solutions and by using a spectrophotometric method described elsewhere [1,4].

Benzoic acid and phenol were obtained from Merck and were purified prior to use. The cyclohexane solvent was spectroscopic grade (Merck).

Knoevenagel condensation: to a mixture of *p*-methoxybenzaldehyde (5 mmol) and malononitrile (5 mmol) mechanically stirred without solvent and at room temperature, the APAl-A catalyst (750 mg) was added. The system thus obtained was stirred for 15 min. Afterwards, reactants and reaction products were eluted with methylene dichloride and analyzed by GLC. GLC was done on a Hewlett-Packard 5890 II instrument using an OV-1 column (0.5 m) and nitrogen as carrier gas.

Response factors were determined from GLC analysis using mixtures of known concentrations of each product.

3. Results and discussion

The ability of the catalyst surface to interact specifically through its basic sites can be estimated by determining the adsorption capacity of organic acid probe molecules from a hydrocarbon solvent.

According to conventional wetting theory the interaction between two surfaces can be described in terms of the work of adhesion (W_{SL}) between the solid/liquid interface. This parameter can be divided into two separate parts, the London dispersion force component (W^D) and the specific or polar interactions (W^P), which can be generally described in base of the acid/base theory [6,7].

Since the van der Waals dispersion force interaction between different types of catalysts and the hydrocarbon will not differ significantly, the strength of the acid–base interaction will be the major factor distinguishing one solid support from another.

Thus, all the adsorption experiments were carried out from cyclohexane. This solvent was chosen because it can be assumed that it will interact with the catalyst surface or with the probe molecules only through dispersion forces, so that it will not affect the adsorption strength differently for different probes. Furthermore, the sorbate probes used in the study differ largely in pK_a, so that a basic site distribution can be established.

The adsorption data were analyzed by the Langmuir equation,

$$X/X_m = KC/(1+KC)\,, \tag{1}$$

where K is the Langmuir equilibrium constant and X is the amount of probe adsorbed on the surface per unit weight of catalyst. X_m represents the maximum amount of probe that can be adsorbed per unit weight corresponding to a *monolayer coverage* and C is the equilibrium concentration of probe in solution. In all cases, within the concentration ranges investigated, the adsorption data follow a Langmuir type behaviour reaching a plateau value. Also, a plot of C/X versus C showed straight lines. Nevertheless, the adsorption is supposed to be of complex character because the surface exhibits centres of different strength, and the consistency with the Langmuir isotherm (which assumes a homo-energetic surface) should be explained by formation of different bonds between the probe molecule and catalyst surface, which are, approximately, equivalent energetically, since a unique straight line is attained.

For APAl-A-10-923 catalyst the adsorption isotherms of benzoic acid and phenol, from cyclohexane solutions and at 298 K, are shown in fig. 1, where the adsorbed amount per gram of catalyst is plotted versus the equilibrium concentra-

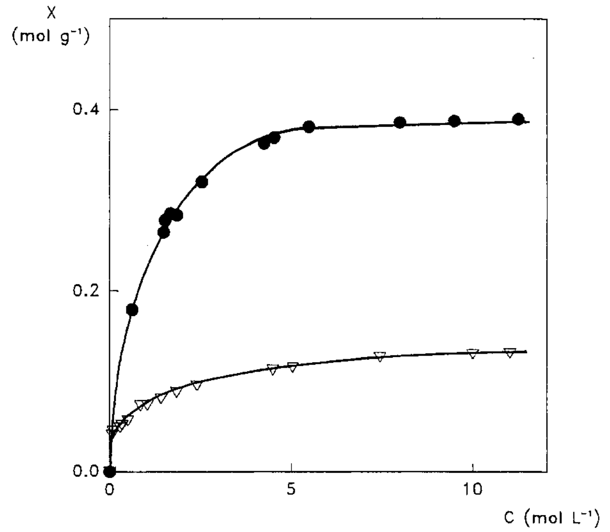

Fig. 1. Adsorption isotherms on APAl-A-10-923 catalyst: (●) BA; (▽) PH.

tion in the supernatant. As expected, the limiting amount of the base adsorbed on the surface is determined by the pK_a of the titrant used and thus, the amount of basic sites (X_m) decreased with increasing pK_a of the acid. So, for benzoic acid (with a strong acid functionality) fairly strong adsorption occurs.

The adsorption data (X_m, *monolayer coverage*), at two basic strengths, for APAl-A catalysts at various compositions and calcined at different temperatures

Table 1
Surface basic properties, equilibrium constants and adsorption free energies of $AlPO_4$–Al_2O_3 (5–25 wt% Al_2O_3), $AlPO_4$ and Al_2O_3 catalysts

Catalyst	S_{BET} (m^2/g)	BA (pK_a = 4.2)			PH (pK_a = 9.9)		
		X_m (μmol/g)	$K \times 10^{-4}$	$-\Delta G$ (kcal/mol)	X_m (μmol/g)	$K \times 10^{-4}$	$-\Delta G$ (kcal/mol)
APAl-A-5-773	192	420	9.4	6.8	113	18.9	7.2
APAl-A-5-923	189	411	10.6	6.8	115	17.5	7.1
APAl-A-5-1073	196	426	13.6	7.0	109	12.2	6.9
APAl-A-10-773	194	421	10.0	6.8	114	23.7	7.3
APAl-A-10-923	182	420	13.2	7.0	113	20.5	7.2
APAl-A-10-1073	180	437	15.9	7.1	115	10.2	6.8
APAl-A-15-773	279	494	6.9	6.6	183	8.9	6.7
APAl-A-15-923	267	488	5.4	6.4	157	9.3	6.7
APAl-A-15-1073	223	473	5.4	6.4	146	11.9	6.9
APAl-A-25-923	244	535	1.9	5.8	166	6.7	6.6
APAl-A-25-1073	242	354	2.3	5.9	124	6.7	6.6
AP-A-923	109	200	0.6	5.1	81	3.2	6.1
Al-A-923	151	556	13.2	7.0	194	24.0	7.3

(773–1073 K) are shown in table 1. Table 1 also includes the same values, selected for comparison, obtained for pure AP-A [4] and Al-A [4] catalysts. Generally the amount of adsorbed probe was reproducible within ±5%.

Results in table 1 show differences in adsorption capacity between catalysts. Thus, it is evident that the amount of basic sites of APAl-A catalysts, regardless of the Al_2O_3 content, is higher than that of AP-A catalysts. However, it is lower than that of Al-A catalyst irrespective of the titrant used.

Furthermore, some differences appear when comparing APAl-A catalysts with different alumina content. Thus, an increase in the alumina content from 10 wt% gradually increases the amount of basic sites. Moreover, calcination at increasing temperatures does not practically affect the surface basicity of APAl-A-5 and APAl-A-10 catalysts. However, for Al_2O_3 content higher than 10 wt% we observe a progressive surface base site decrease versus calcination temperature.

Since the linearization of the Langmuir isotherm assumes uniformity of sites, besides X_m, we can also use the Langmuir equilibrium constant, K, which depends on the interaction strength of the acid titrant with the basic sites, i.e. the site strength. However, these K values displayed a greater experimental error since they are obtained from the intercept at origin. Thus, the K values were reproducible to within about 15%. Besides, from eq. (1) the standard molar free energy of adsorption ΔG can be calculated from K using the equation

$$\Delta G = -RT \ln K . \qquad (2)$$

In table 1 values of the Langmuir equilibrium constants and adsorption free energies are presented.

From these data it can be seen that a small range of interaction strengths occur with the combination of different catalysts and probes. On increasing the alumina content a progressive small decrease in the interaction strengths with the different APAl-A catalysts can be observed; this decrease depends on probe molecule, i.e. it is higher for BA than for PH. Furthermore, calcination temperature does not appear to significantly affect interaction strengths, although a decrease in the amount of basic sites was found.

Furthermore, table 2 shows that basic sites on APAl-A systems catalyze the Knoevenagel condensation of *p*-methoxybenzaldehyde and malononitrile at room temperature and in the absence of solvent (dry reaction). The results, not optimized, showed an increase in activity with alumina content, i.e. with the surface basicity of the APAl-A catalyst.

4. Conclusions

In summary, the results indicate that the addition of alumina even in a small amount (5 wt%) could improve the surface basicity of $AlPO_4$ catalyst. The amount of basic sites varied with the alumina loading and, thus, it gradually increases as

Table 2
Knoevenagel condensation of *p*-methoxybenzaldehyde and malononitrile with $AlPO_4$–Al_2O_3 catalysts [a]

Catalyst	Yield (mol %)
APAl-A-5-1073	10
APAl-A-10-1073	15
APAl-A-15-1073	41
APAl-A-25-923	45

[a] *p*-methoxybenzaldehyde: 5 mmol; malononitrile; 5 mmol; catalyst; 750 mg; 15 min at room temperature.

the alumina content of the APAl-A catalyst increased (5–25 wt%). Moreover, a small range of interaction strengths (6–7 kcal/mol) occur with the combination of different catalysts and probes (BA and PH). Furthermore, basic sites catalyze the Knoevenagel condensation of *p*-methoxybenzaldehyde and malononitrile to *p*-methoxybenzylidene-malononitrile.

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