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Characterization of acidity in $AlPO_4$–Al_2O_3 (5–15 wt% Al_2O_3) catalysts using pyridine temperature-programmed desorption

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Abstract

TPD of pyridine desorbed from the surface of $AlPO_4$–Al_2O_3 catalysts, with different Al_2O_3 loadings (5–15 wt%), yields a complex desorption curve consisting of three overlapped peaks which are ascribable to weak ($T_m \approx 460$ K), medium ($T_m \approx 530$ K) and strong ($T_m \approx 590$ K) acid sites (Brönsted and Lewis). There is a homogeneous distribution of acid strength and an increase in alumina loading leads to an increase in the number of pyridine-adsorbing sites, even though there is no change in the strength distribution when catalysts are calcined at 773–1073 K. Furthermore, calcination at 1273 K reduces both the number and strength of the acid sites as the alumina content increases. The overall number of acid sites decreases continuously as the temperature of the pyridine adsorption increases.

Keywords: Acidity; $AlPO_4$–Al_2O_3; Pyridine; TPD

1. Introduction

In a previous paper [1], an investigation of the surface acidity of $AlPO_4$–Al_2O_3 (APAl-A) catalysts with different alumina loadings (5–25 wt% Al_2O_3) using pyridine and 2,6-dimethylpyridine adsorption followed by gas chromatography and diffuse-reflectance FT-IR spectroscopy, it was shown that the nature (Brönsted and Lewis) and number of the acid sites depends on the alumina content and thermal pretreatment of the APAl-A catalyst. The catalytic activity of the APAl-A catalyst in cyclohexene

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skeletal isomerization [1], cumene cracking [1], and toluene methylation [2] can also be explained in terms of differences in acidity.

In this way, Marcelin [3] emphasized that the characterization of acid sites should be done using a multitechnique approach, with each technique best suited for characterizing a particular acid site. Many techniques have been used for the acidic characterization of catalysts, thermal desorption, infrared spectroscopy and probe reactions being the most important. In recent years there has been increasing interest in the application of thermal desorption to problems involving adsorption molecules on catalytically active centers [4–9]. Ammonia and pyridine are the most commonly used probe molecules in the study of active acid sites. More recently, aliphatic amines have also been used as probe molecules [10, 11]. Evaluation of the desorption spectra provides the temperatures of the maximum rate of desorption (strength) and the relative population (number) of the respective sites.

The aim of the present paper was to characterize by pyridine thermodesorption the strength of the acid sites on $AlPO_4$–Al_2O_3 catalysts in order to arrive at a complete description of their acid sites. The results are discussed with reference to those previously found by gas-phase adsorption of pyridine and 2,6-dimethylpyridine, including IR spectroscopy and rate measurements of acid-catalyzed reactions [1, 2].

2. Experimental

2.1. Materials

Three composite $AlPO_4$–Al_2O_3 catalysts were used. The compositions were: $AlPO_4$:Al_2O_3, 95:5 (APAl-A-5); 90:10 (APAl-A-10) and 85:15 (APAl-A-15). All catalysts were calcined for 3 h at 773, 923, 1073 and 1273 K. Details of their preparation and characterization have been reported elsewhere [1, 12]. The surface area S_{BET}, pore volume V_p, main pore radius r_p, and the surface acidity (sum of Brönsted and Lewis sites) measured in a dynamic mode (pulse-chromatographic technique) by means of the gas phase (473–673 K) adsorption of pyridine and 2,6-dimethylpyridine, are collected in Table 1.

2.2. Temperature-programmed desorption of pyridine

The apparatus used for pyridine adsorption/desorption was basically a gas chromatograph, modified by dispensing with the empty column before the catalyst tube which is connected directly to the detector so that the eluted band was recorded directly and peak retardation occurred only on the catalyst. The catalyst tube was made of a 100 mm × mm s.s. tube containing about 200 mg of catalyst packed between quartz wool plugs. Pure helium at a flow rate of 12 ml min^{-1} was used as the carrier gas. Before adsorption experiments were started, catalyst was pretreated in situ by passing pure helium, at a flow rate of 12 ml min^{-1}, for 323 to 723 K (rate 10 K min^{-1}) and remaining at 723 K for 10 min. After catalyst pretreatment, the temperature was

Table 1
Textural and surface acid properties of $AlPO_4$–Al_2O_3 (5–15 wt% Al_2O_3) catalysts

Catalyst	S_{BET}/(m^2g^{-1})	V_p/(ml g^{-1})	r_p/(nm)	Acidity/(μmol g^{-1}) vs. pyridine		
				473 K	573 K	673 K
APAl-A-5-773	192	0.77	8.0	168	41	16
APAl-A-5-923	189	0.66	7.0	119	33	12
APAl-A-5-1073	196	0.71	7.2	110	29	10
APAl-A-5-1273	165	0.55	6.7	91	23	6
APAl-A-10-773	194	0.59	6.1	165	57	19
APAl-A-10-923	182	0.49	5.3	151	50	16
APAl-A-10-1073	180	0.53	5.9	141	47	18
APAl-A-10-1273	59	0.17	5.7	62	23	7
APAl-A-15-773	279	0.74	5.3	216	79	48
APAl-A-15-923	267	0.77	5.9	156	61	29
APAl-A-15-1073	223	0.79	7.1	144	52	30
APAl-A-15-1273	33	0.15	9.2	21	8	3

lowered to the temperature at which the adsorption experiment was carried out (usually 323 K), maintaining the helium flow.

Adsorption experiments were carried out in the temperature range 323–523 K. After adsorption at the desired temperature (323, 373, 423, 473 or 523 K), the weakly held pyridine was then eluted from the catalyst by continuing the stream of helium for an additional 1 h at the temperature at which the adsorption takes place. Then the temperature was lowered to 323 K and thermal desorption experiments carried out from 323 to 723 K at a rate of 10 K min^{-1}, remaining at 723 K for 10 min. Desorption was measured by a FID.

The GC signal due to pyridine was proportional to the partial pressure above the catalyst surface, which is directly proportional to the desorption of pyridine, because the flushing speed was constant. The integral of the rates was therefore proportional to the amount of pyridine desorbing from one adsorption site.

Repeated adsorption/TPD experiments using the same sample did not show any change in the desorption curve.

3. Results and discussion

The thermodesorption of pyridine from APAl-A catalysts resulted in a number of overlapping peaks, generating complex thermodesorption spectra which depend on the initial coverage, activation and adsorption temperatures. Fig. 1, curve a shows characteristic pyridine thermal desorption profiles obtained after adsorption of pyridine at 323 K on APAl-A-5-773 catalyst with a heating rate of 10 K min^{-1}.

These TPD experiments started with complete coverage of the APAl-A samples with pyridine. To improve the resolution of the TPD spectra, a further series of desorption

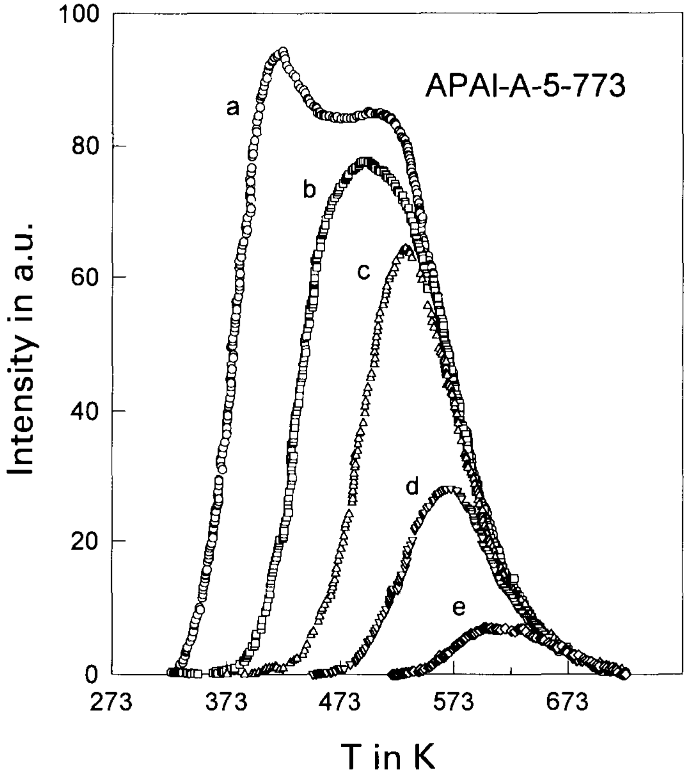

Fig. 1. TPD curves for different amounts of pyridine on the APAl-A-5-773 catalyst. Pyridine adsorption temperature: a, 323 K; b, 373 K; c, 423 K; d, 473 K; e, 573 K.

experiments was undertaken with samples that were initially loaded with different amounts of pyridine. Thus, Fig. 1, curves b–e show TPD curves for the APAl-A-5-773 catalyst after preadsorption of different amounts of pyridine by changing the pyridine adsorption temperature. As the pyridine adsorption temperature is raised from 323 to 523 K, the total amount of pyridine decreased and the onset of pyridine desorption shifted to higher temperatures. From 373 K, only a desorption peak of pyridine is found in the TPD profile. However, this peak is not symmetrical. These profiles indicate the presence of centers of different acid strength on APAl-A catalyst.

Complex TPD profiles after pyridine adsorption at 323 K were resolved into independent parallel desorption steps. When the TPD spectra were deconvoluted, four independent types of parallel desorption processes were revealed, and thus the theoretical desorption curves of the individual peak components summed to an overall contour that was well-correlated to the experimental data.

Fig. 2A shows the experimental data for sample APAl-A-5-773, the individual components as the result of deconvolution, and the theoretical spectrum obtained by

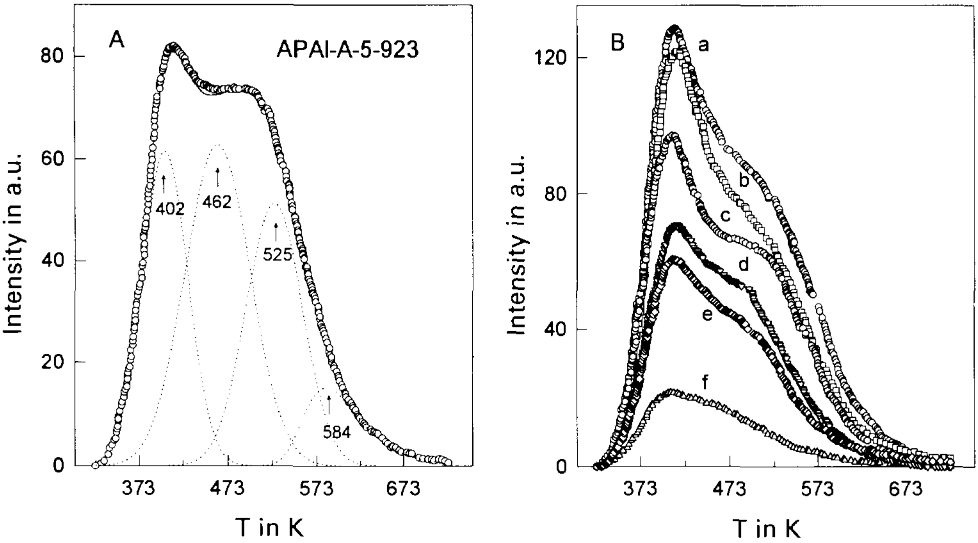

Fig. 2. A. TPD spectrum of PY desorbed from APAl-A-5-923 catalyst: experimental data (○); calculated curves for desorption from different types of sites (···); theoretical curve of overall desorption (—). B. TPD spectra of PY desorbed from a, APAl-A-15-773; b, APAl-A-15-923; c, APAl-A-10-1073; d, APAl-A-5-1273; e, APAl-A-10-1273; f, APAl-A-15-1273.

summing the individual peaks. Superposition of the individual components leads to a good fit of the experimental data, showing mean standard deviations of less than 3%. Analogous spectra were obtained for all APAl-A samples (Fig. 2B) except for APAl-A-15-1273 catalyst for which only three peaks were found (the highest temperature peak did not appear). The first peak at 402 K was assumed to be caused by physically bonded pyridine. This physisorption that can occur not only on the catalyst surface but also on various components of the experimental system may be minimized or eliminated by conducting the adsorption at 373 K. Thus, three types of adsorption sites were operative. The assignment of the TPD peaks was based on comparison with previous results of pyridine chemisorption [1] at temperatures in the range 473–673 K and IR results of pyridine adsorption at 373–573 K [1]. Thus IR results showed that pyridine molecules remained in interaction with both Brönsted and Lewis acid sites of APAl-A catalysts at adsorption temperatures of 573 K. Moreover, Brönsted acid sites are also accessible to 2,6-dimethylpyridine. Therefore, the low-temperature pyridine peak at around 460 K is attributable to weak acid sites, whereas the second and third peaks (around 530 and 590 K, respectively) are assumed to be due to medium and strong acid sites (Brönsted and Lewis). Almost all acid sites corresponding to the third peak are of Brönsted nature (absence of Lewis-bound pyridine in IR spectra).

The experimental data obtained from the TPD of pyridine for APAl-A catalysts with various Al_2O_3 loadings and calcined in the range 773–1273 K are given in Fig. 3 and Table 2. Thus, Fig. 3 shows the total peak areas as a function of the alumina loading and calcination temperature. Table 2 gives the temperatures of the peak maxima and

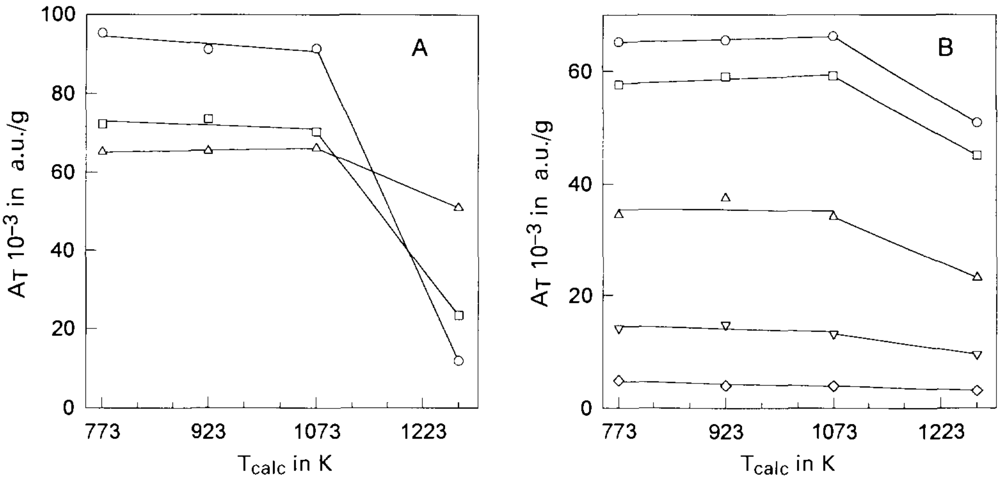

Fig. 3. Total peak areas as a function of the alumina loading and calcination temperature. Pyridine adsorption temperature, 323 K: △, APAl-A-5; □, APAl-A-10; ○, APAl-A-15. B. Total peak areas as a function of the pyridine adsorption temperature and calcination temperature for APAl-A-5 catalyst. Pyridine adsorption temperature: ○, 323 K; □, 373 K; △, 423 K; ▽, 473 K; ◇, 523 K.

Table 2
Temperature of the peak maxima and their contributions to the total area for pyridine-TPD profiles of APAl-A (5–15 wt% Al_2O_3) catalysts

Catalyst	pK_1		pK_2		pK_3	
	T_m/K	Area %	T_m/K	Area %	T_m/K	Area %
APAl-A-5-773	470	56.4	534	30.2	587	13.4
APAl-A-5-923	462	51.8	525	36.6	584	11.6
APAl-A-5-1073	463	55.1	528	32.5	582	12.4
APAl-A-5-1273	465	66.0	523	23.3	576	10.7
APAl-A-10-773	459	53.0	528	34.1	584	12.9
APAl-A-10-923	458	54.7	524	31.4	575	13.9
APAl-A-10-1073	462	54.5	527	34.6	582	10.9
APAl-A-10-1273	454	59.1	517	33.3	589	7.6
APAl-A-15-773	457	58.1	531	28.8	586	13.1
APAl-A-15-923	459	65.5	533	24.1	586	10.4
APAl-A-15-1073	456	67.1	534	23.5	589	9.4
APAl-A-15-1273	456	76.7	538	23.3	–	–

their contribution to the total area (A_T) for all APAl-A catalysts. In order to facilitate comparisons, areas under the experimental desorption spectra were normalized to catalyst weight. Table 2 and Fig. 3 show that the catalysts have different numbers of acid sites of different strengths depending on the Al_2O_3 loading and calcination temperature. However, the composition has no influence on the acid strength because no significant difference in peak maximum temperatures is evident in the three APAl-A catalysts thermally treated in the 773–1073 K range. This tends to indicate that the mean strength of each acid site does not change significantly as their number changes with alumina content and/or calcination temperature (773–1073 K). This is in agreement with a homogeneous distribution of acid strength.

Moreover, based on the TPD data reported above, the APAl-A catalysts can be arranged in order of increasing number of acid centers as

APAl-A-5 < APAl-A-10 < APAl-A-15

for catalysts treated in the 773–1073 K range. This increased acidity as the alumina content is increased was not accompanied by changes in acid strength distribution because the contributions of the three peaks to the total area of the pyridine-TPD profile were almost the same.

The total acidity, which includes both Brönsted and Lewis sites, remained almost unchanged as calcination temperature increased up to 1073 K but, however, a drop in the acidity was obtained increasing the calcination temperature to 1273 K and, besides, the loss of acidic centers depends on the alumina content. Pyridine-TPD profiles for APAl-A-1273 catalysts are shown in Fig. 2B where it can be seen that the acidity was notably reduced as the alumina content was raised from 5 to 15 wt%. These facts are due to the crystallization of $AlPO_4$ at 1273 K which increases as the alumina content increases [1], so that for a 15 wt% Al_2O_3, $AlPO_4$ is fully crystallized.

The comparison of desorption profiles for the APAl-A-15 sample calcined at 773 and 1273 K (Fig. 2B) clearly shows that the sample calcined at the lower temperature contains a significant amount of strong acid centers, whereas the sample calcined in more drastic conditions (1273 K) lacks such acid sites almost completely. This indicates that calcination at 1273 K reduces both the number of acid sites capable of pyridine adsorption and their strength, causing a shift towards relatively weaker sites.

From Fig. 3B, it can also be seen that the overall number of acid sites of APAl-A-5 catalyst decreases continuously as the temperature of the pyridine adsorption increases because only the strongest acid sites were able to retain the adsorbed pyridine. Moreover, a similar decrease in acidity with increasing adsorption temperature was found, irrespective of the increase in the calcination temperature to 1073 K; but, however, the acidity notably declined further when the calcination temperature was raised from 1073 to 1273 K. APAl-A-10 and APAl-A-15 exhibited a similar behavior but, as mentioned above, the decrease at 1273 K is faster as the alumina content increases, irrespective of the pyridine adsorption temperature (323–523 K).

4. Conclusions

Temperature-programmed desorption (TPD) of pyridine indicates the presence of three types of acid sites on APAl-A (5–15 wt% Al_2O_3) catalysts. From IR results, these sites are ascribable to weak, medium and strong (Brönsted and Lewis) acid sites. An important result is that the TPD spectra suggest that there is a homogenous distribution of acid strength. Also, the increase in alumina loading leads to an increase in the number of pyridine-adsorbing sites even though there is no change in the strength distribution when catalysts are calcined in the 773–1073 K range. This increased acidity was not accompanied by changes in strength distribution because contributions from the three peaks to the total area were almost the same. Moreover, calcination at 1273 K reduces both the number and strength of acid sites as the alumina content increases.

The TPD results are fully consistent with previous acidity measurements of pyridine adsorption using a pulse-chromatographic technique at temperatures in the range 473–673 K, and with catalytic tests employed as indirect acidity measurements. Thus for cyclohexene isomerization, cumene cracking and toluene alkylation with methanol, the catalytic activity was changed with alumina loading, and was maximized at an Al_2O_3 loading of 15 wt%, at which the amount measured by pyridine showed a maximum.

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