Characterization of Acid Surfaces by Adsorption of 2,6-Dimethylpyridine

A. CORMA,* C. RODELLAS,† AND V. FORNES†

*Instituto de Catálisis y Petroleoquímica, CSIC, Serrano 119, and †Instituto de Físicoquímica Mineral, CSIC, Serrano 115dup, Madrid-6, Spain

2,6-Dimethylpyridine has been adsorbed on different samples of γ-Al_2O_3, fluorinated γ-Al_2O_3, and decationated Y zeolites. The ir spectra of the adsorbed base have been obtained after desorption at different temperatures. It has been shown that the 2,6-dimethylpyridine cannot differentiate among different types of Lewis sites (Na^+, tricoordinated aluminum, AlO^+, etc.). The 1618-cm^{-1} absorption band appearing in γ-Al_2O_3 is related to weak Brønsted sites, and its frequency increases when the acid strength is increased by fluorination. This band has not been observed on NaHY zeolites for which the Brønsted acid strength is higher.

INTRODUCTION

The chemisorption of bases such as pyridine, piperidine, ammonia, quinoline, and aliphatic amines is frequently used to characterize solid acid catalysts and to correlate their catalytic activity with the concentration of a particular type of acid site. Pyridine has been the most widely used base for acid characterization purposes, due to its possibility of interacting with both Brønsted and Lewis sites, giving specific ir absorption bands (*1–5*). Recently (*6*) it has been shown that chemisorption measurements of sterically hindered dimethyl and terbutyl pyridines can be very useful probe molecules to characterize acid surfaces. The most important features of these molecules, compared with pyridine, are their basicity (the pK_a is 6.7 for 2,6-dimethylpyridine and 5.2 for pyridine) and their specificity for protonic centers.

In the case of an acid catalyst such as fluorinated γ-Al_2O_3, where both Brønsted and Lewis acid sites exist, pyridine fails in titrating the Brønsted acidity due mainly to the low surface concentration of these sites capable of interacting with it. In this case, dimethylpyridine has revealed itself as a more convenient probe molecule, although there is some controversy in the literature on the assignment of the ir bands of the chemisorbed dimethylpyridine (*7, 8*). In this work, dimethylpyridine has been chemisorbed in a wide range of experimental conditions on γ-Al_2O_3, fluorinated γ-Al_2O_3, and a series of HNaY zeolites with different degrees of exchange, and the ir spectra of the adsorbed molecules are discussed from the point of view of their interaction with the different types of acid sites present on these surfaces.

EXPERIMENTAL

Materials

The materials used in this study were γ-Al_2O_3 (Girdler, T-126) with a BET surface of 193 m^2/g, fluorinated alumina, and partially decationated samples of NaY (SK-40) zeolite. The fluorinated γ-alumina samples with nominal fluorine contents of 0.5, 2.5, 4.0, and 50 g per 100 g of alumina, were prepared by the pore volume impregnation method: the alumina, previously calcined at 823 K during 5 h, was treated with aqueous ammonium fluoride solutions for 15 h at room temperature. Subsequently the sample was dried at 383 K, heated for 2 h in air at 648 K, and finally calcined at 823 K for 5 h. The zeolite samples were prepared through exchange of the starting material in a solution of ammonium acetate up to dif-

374

ferent levels: 20, 60, and 80%. Pyridine and 2,6-dimethylpyridine (Merck) were vacuum-dried and then stored in the presence of 3-Å molecular sieve.

Procedure

Adsorption experiments were carried out in a greaseless Pyrex-glass vacuum system, in which a dynamic vacuum of 10^{-5} Torr could be maintained. Wafers 10 mm in diameter and 10 mg in weight were placed into a conventional Pyrex ir cell, fitted with CaF_2 windows, connected to the vacuum line by means of a ground joint with a Viton O-ring. The samples were heated under 10^{-5} Torr of dynamic vacuum at 673 and/or 773 K during 16 h, and the background spectra were recorded at room temperature in the range 4000–1300 cm^{-1}. Then, dimethylpyridine (3 Torr) was adsorbed at room temperature and spectra were recorded after 1 h desorption at different temperatures (295, 423, 523 K) under dynamic vacuum. The competitive adsorption experiments were made on a sample of γ-Al_2O_3 pretreated at 673 K in the same way and by adsorbing first the pyridine at room temperature, evacuating at 323 K for 1 h, adding the second base at room temperature, and degassing during 1 h at 323 K.

RESULTS

Figure 1 shows the ir spectra of the alumina pretreated at 673 K, before (a) and after adsorbing dimethylpyridine and desorbing it at 10^{-5} Torr and 295 (b), 423 (c), 523 K (d). Spectrum (a) shows absorption bands at 3680, 3740 cm^{-1} and a shoulder at 3780 cm^{-1} which according to the literature (9, 10) have been related to different types of OH groups on the surface of alumina. Spectrum (b) shows the characteristic absorption bands of dimethylpyridine coordinated to Lewis sites at 1465, 1580, and 1605 cm^{-1} (7, 8), two bands at 1630 and 1650 cm^{-1} ascribed to Brønsted sites, and a band at 1618 cm^{-1} characteristic of dimethylpyridine adsorbed on γ-alumina, which has been assigned by Matulewicz et al. (8) to Lewis sites. Simultaneously with the appearance of these bands, the 3740- and 3780-cm^{-1} OH bands disappear, while the 3680-cm^{-1} band decreases only slightly, if at all. When the desorption temperature is raised (spectra c and d), the Lewis-associated ir bands disappear, the Brønsted-asso-
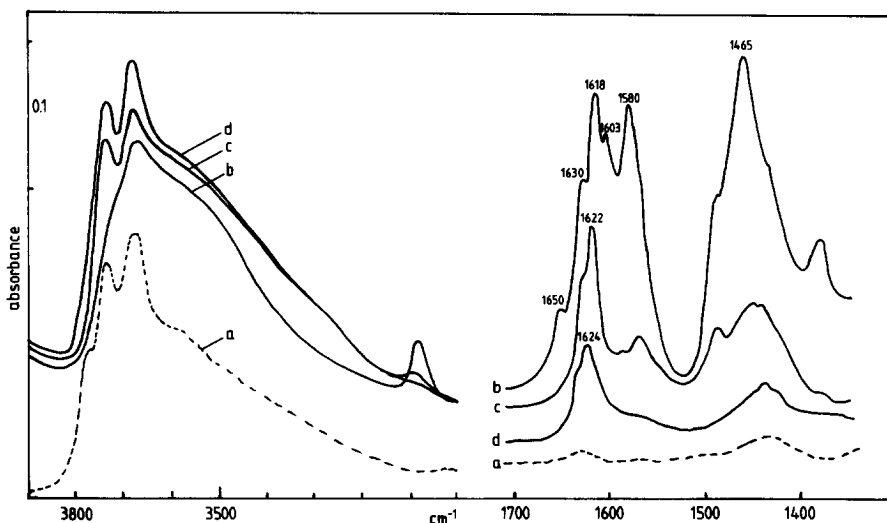

FIG. 1. Infrared spectra of γ-Al_2O_3 pretreated at 673 K: (a) before adsorbing dimethylpyridine; (b), (c), and (d) after adsorption and desorption at 295, 423, and 523 K, respectively.
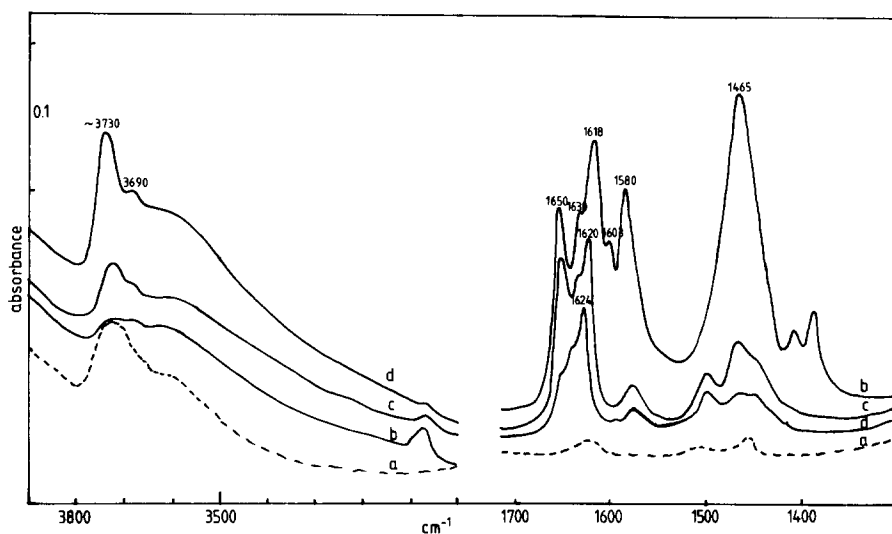
FIG. 2. Infrared spectra of γ-Al₂O₃ pretreated at 773 K: (a) before adsorbing dimethylpyridine; (b), (c), and (d) after adsorption and desorption at 295, 423, and 523 K, respectively.

ciated ir bands decrease (mainly the 1650-cm⁻¹ band), and the 1618-cm⁻¹ band shifts to higher wavenumbers (up to 1624 cm⁻¹). At 523 K, only a massif of two bands (1624 and 1630 cm⁻¹) is left. On the other hand, and parallel to this, the 3740- and 3680-cm⁻¹ OH bands increase with desorption temper-

ature up to 523 K becoming even slightly higher than in the background spectrum (a).

In Fig. 2 the same experimental procedure has been followed but with the γ-Al₂O₃ sample pretreated at 773 K. In this case, the background spectrum (a) shows the presence of a broad band at ~3730 cm⁻¹ which
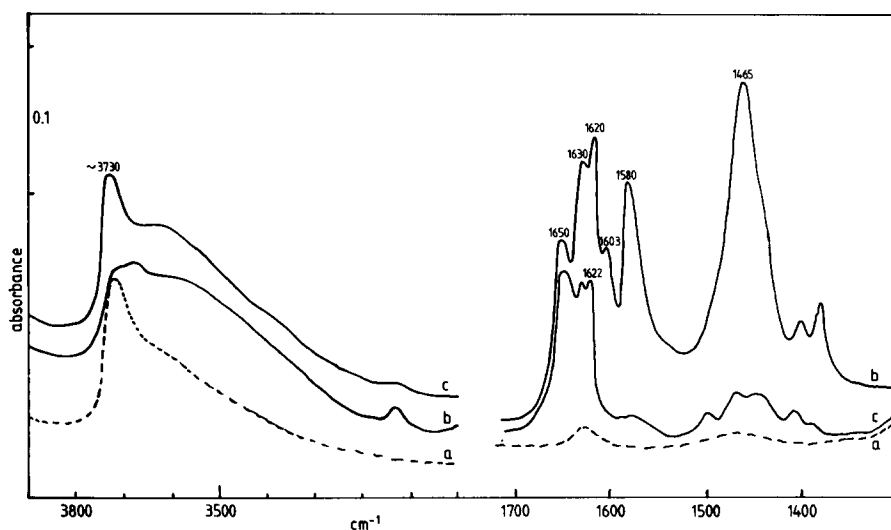

FIG. 3. Infrared spectra of a fluorinated γ-Al₂O₃ (2.5% fluorine) pretreated at 673 K: (a) before adsorbing dimethylpyridine; (b) and (c) after adsorption, and desorption at 423 and 523 K, respectively.
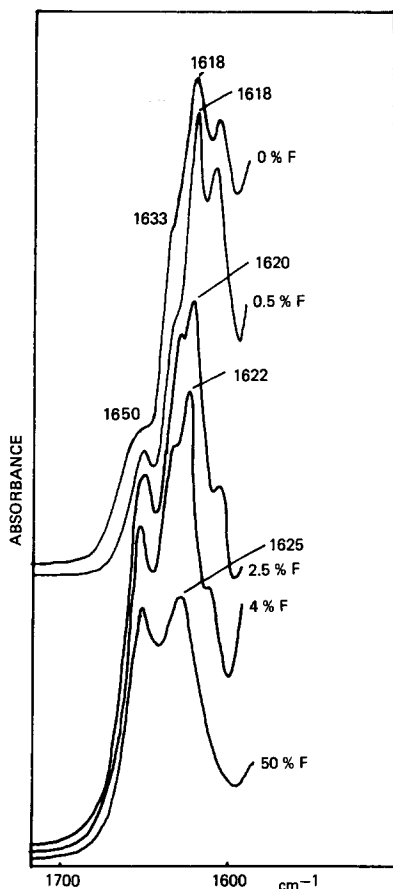
FIG. 4. Infrared spectra of fluorinated γ-Al₂O₃ with increasing nominal content in fluorine: (a) 0, (b) 0.5, (c) 2.5, (d) 4, (c) 50%.

spectra of the dimethylpyridine adsorbed on the fluorinated γ-Al₂O₃ with increasing fluorine contents (Fig. 4) shows a shift of the 1618-cm⁻¹ band toward higher wavenumbers.

Competitive adsorption experiments among pyridine and dimethylpyridine have been carried out at 323 K and the resulting spectra are given in Fig. 5.

DISCUSSION

Figure 1 shows that OH groups absorbing at 3740 and 3780 cm⁻¹ in γ-alumina are acid enough to interact with dimethylpyridine, while those absorbing at 3680 cm⁻¹ are practically unaffected by the presence of the base. Simultaneously the Lewis (1465, 1580, and 1605 cm⁻¹) and the Brønsted (1630 and 1650 cm⁻¹) ir bands appear. The same results are found when dimethylpyridine is adsorbed on partially exchanged zeolites (Fig. 6). However, a band at 1618 cm⁻¹ is detected in alumina but not in zeolites. This band was already observed by Matulewicz *et al.* (8) on alumina and, based
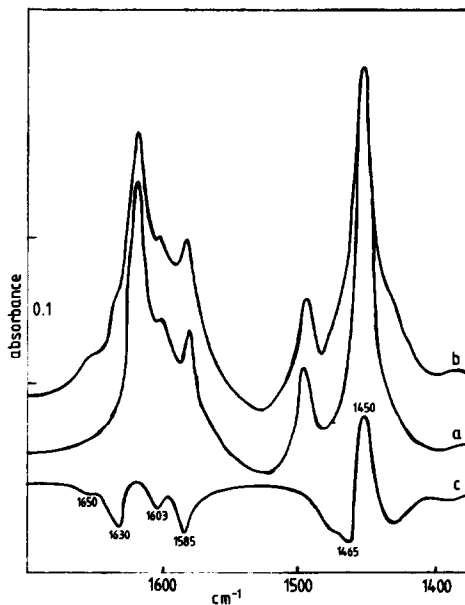
disappears when dimethylpyridine is adsorbed (spectrum b), while the bands at 1618, 1630, and 1650 cm⁻¹ appear, together with the Lewis-associated ir bands. It is noticeable that the 1630- and 1650-cm⁻¹ bands are higher than in the sample pretreated at 673 K. Identical behavior with desorption temperature is observed for the two samples outgassed at 673 and 773 K.

The spectra of the fluorinated γ-alumina outgassed at 673 K (Fig. 3) is qualitatively similar to that of the alumina outgassed at 773 K, i.e., only a broad band at about 3730 cm⁻¹ is observed. After interaction with dimethylpyridine the same bands appear, the 1630- and 1650-cm⁻¹ bands being more intense than in the case of γ-alumina. The

FIG. 5. Competitive adsorption of pyridine and dimethylpyridine on γ-Al₂O₃ at 323 K: (a) after pyridine adsorption, (b) after adsorption of dimethylpyridine on sample (a), (c) difference spectrum ((a)–(b)).
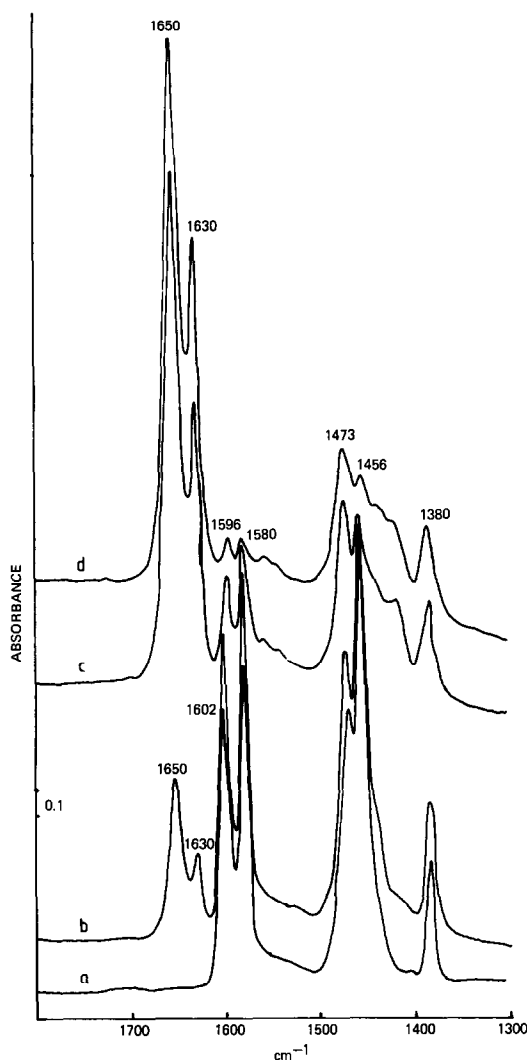
FIG. 6. Infrared spectra of dimethylpyridine adsorbed on NaHY zeolites with increasing proton exchange, after desorption at 295 K: (a) NaY, (b) 20% H, (c) 60% H, (d) 80% H.

on the assumption that this material has no Brønsted acidity it was assigned to Lewis sites. The absence of this band in zeolites was interpreted by attributing the bands reported by Jacobs and Heylen (7) to physically adsorbed, instead of coordinatively bonded dimethylpyridine. The first assumption must be ruled out, since Dunken et al. (11) with ammonia, Dewing et al. (5) with 2,6-di-tert-butylpyridine, and our own work (Fig. 1) have demonstrated the existence of Brønsted sites on γ-alumina. Moreover,

Fig. 7 shows that after desorbing at 423 K under vacuum the dimethylpyridine adsorbed on zeolites, the bands described before are still present, indicating that they do not correspond to physically adsorbed dimethylpyridine. From all this we consider that the assignment of the 1618-cm^{-1} absorption band has to be further discussed.

In order to consider an alternative assignment of this band, we discuss below the influence on the behavior of the 1618-cm^{-1} band, of dimethylpyridine desorption temperature, of the pretreatment temperature and the degree of fluorination of the γ-alumina, and of the competitive adsorption of pyridine and dimethylpyridine.

1. Influence of Desorption Temperature

When the desorption temperature is raised (Fig. 1c), the Lewis-associated bands practically disappear, the bands at
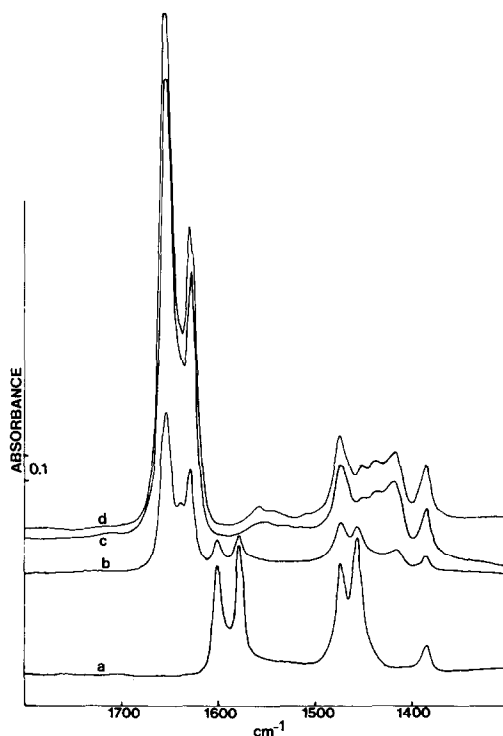

FIG. 7. Infrared spectra of dimethylpyridine adsorbed on NaHY zeolites with increasing proton exchange after desorption at 423 K: (a) NaY, (b) 20% H, (c) 60% H, (d) 80% H.

1618, 1630, and 1650 cm^{-1} decrease, and the 3740-cm^{-1} OH band is partially restored. At higher desorption temperature we observe the same behavior (Fig. 1d), and consequently a direct relation between the high frequency hydroxyl groups and the bands of dimethylpyridine at 1618, 1630, and 1650 cm^{-1} can be established to a first approximation. However, there is a fact which must be pointed out: the 1618-cm^{-1} band shifts to higher frequencies, approaching the position of the known Brønsted-associated ir band at 1630 cm^{-1}. Knözinger et al. (12) have shown that adsorbed pyridine can react on the surface of alumina at temperatures above 623 K to give a pyridone which presents a strong ir band at 1635 cm^{-1}. We do not think that this reaction is taking place in our case, since we are carrying out the desorption experiments at temperatures much lower than 623 K. Moreover, dimethylpyridine is much less reactive than pyridine, due to the two methyl groups which act as electron-releasing substituents (12). We think that this result can be explained considering a wide distribution of OH groups with different acid strengths. In these conditions, the increase of temperature provokes the desorption of dimethylpyridine, starting from the weakest (lower frequencies) acid centers and shifting the 1618-cm^{-1} band toward higher frequencies (strongest acid centers).

2. Influence of the Pretreating Temperature

An increase in the outgassing temperature of alumina (from 673 to 773 K) (Fig. 2), gives rise to a rearrangement of the surface hydroxyl groups. Indeed, only a broad band at ~3730 cm^{-1} is observed. These OH groups are able to interact with dimethylpyridine (spectrum b); the alumina outgassed at 773 K has a higher number of Brønsted sites corresponding to stronger acidity (1630–1650 cm^{-1}), and a smaller number of weaker Brønsted sites (1618–1625 cm^{-1}).

3. Influence of Fluorination of Alumina

The spectrum in the OH region of a fluorinated alumina (2.5%) shows (Fig. 3a) a broad band at ~3730 cm^{-1} indicating that the effect of fluorination is similar to the increase of pretreating temperature. Figure 4 presents the spectra of fluorinated samples treated with dimethylpyridine, showing that increase in fluorine provokes a shift in the position of the 1618-cm^{-1} band toward higher wavenumbers, approaching the position of the 1630-cm^{-1} band. It is known (13) that when γ-alumina is fluorinated, the hydroxyl groups are substituted by F$^-$ ions, starting with the weakest protonic groups, while enhancing the acidity of the remaining. According to this, a band associated with weak Brønsted acid sites would have a behavior similar to that shown by the 1618-cm^{-1} band for increasing fluorine content.

4. Competitive Adsorption Experiments

Based on their studies on competitive adsorption of pyridine and 2,6-di-tert-butylpyridine, Dewing et al. (5) have suggested the presence in γ-alumina of Brønsted sites and of "special" Lewis sites for which the hindered pyridines would not show steric hindrance. Knözinger et al. (14) have discussed this work and have shown that in their experiments, a competitive adsorption among pyridine and 2,6-di-tert-butylpyridine is not observed. Furthermore, they conclude that the interaction of the OH groups of alumina with the base is of the OH . . . π bond type, and that a protonation of the adsorbed base on the alumina surface is hardly probable. In Fig. 5c, we present the difference spectrum of dimethylpyridine adsorbed on pyridine-treated γ-alumina, showing a very small displacement of coordinatively bound pyridine (1450 cm^{-1}) and the appearance of dimethylpyridine Lewis (1465, 1585, 1603 cm^{-1}) and Brønsted (1650, 1630 cm^{-1}) ir bands; however, no variations are observed in the region 1615–1620 cm^{-1}. Conse-

quently, in our case, the 1618-cm^{-1} band cannot be ascribed to the presence of Lewis sites for which the sterically hindered dimethylpyridine can compete with pyridine. Moreover, the presence of Brønsted-associated ir bands shows that dimethylpyridine is able to be protonated by acid sites which are not acidic enough to protonate the less basic pyridine and di-*tert*-butylpyridine.

The results presented here allow us to conclude that the 1618-cm^{-1} absorption band observed in γ-alumina after adsorption of dimethylpyridine cannot be associated with Lewis sites, but rather with the presence of weak protonic centers.

According to Jacobs and Heylen (7) the spectrum of dimethylpyridine adsorbed on a NaY zeolite (Fig. 6a) only presents the Lewis-associated ir bands at 1602, 1580, 1473, and 1456 cm^{-1}. When the sodium zeolite is partially exchanged by protons, the spectra (Figs. 6b, c, and d) show, besides the Lewis-associate bands, two absorptions at 1650 and 1630 cm^{-1}, ascribed, as said above, to Brønsted sites (7). It is noticeable that in all cases the 1618-cm^{-1} absorption band is absent.

One may try to explain the difference between the spectra of NaHY and alumina by considering that the bands observed in the case of the zeolite correspond to the interaction of dimethylpyridine with Na$^+$, while the 1618-cm^{-1} band is associated with the base bonded to tricoordinated aluminum atoms present on the surface of γ-alumina. To discuss this possibility, the NaHY samples have been heated at 1023 K for 6 h in order to dehydroxylate the sample and to generate tricoordinated aluminum atoms on the surface of the zeolite (15), and then dimethylpyridine was adsorbed. The spectra obtained show the same ir bands at the same frequencies as the original samples but they are more intense. These results indicate not only that it is not possible to distinguish between different types of Lewis centers (cations, tricoordinated aluminum atoms, AlO$^+$) by adsorption of dimethylpyridine but also that the 1618-cm^{-1} band

should not be assigned to Lewis sites, but rather to weak Brønsted sites present on γ-alumina. These sites are not observed on NaHY zeolites because the protonic centers in acid zeolites are stronger than those present in the samples of alumina studied here.

CONCLUSIONS

1. The OH groups on γ-Al$_2$O$_3$ absorbing at 3780 and 3740 cm^{-1} are acid enough to interact with dimethylpyridine, while those absorbing at 3680 cm^{-1} are practically unaffected by the presence of the base.

2. The absorption band appearing at 1618 cm^{-1} after adsorbing dimethylpyridine on alumina must be attributed to weak Brønsted centers.

3. An increase in the pretreatment temperature of the γ-Al$_2$O$_3$ in the range 673–773 K at 10^{-5} Torr provokes an increase in the number of the stronger Brønsted sites and a decrease of the weaker ones, as measured by dimethylpyridine adsorption.

4. An increase in fluorine content causes a shift to higher frequencies of the 1618-cm^{-1} band.

5. It is not possible to distinguish between different types of Lewis acid sites by adsorption of dimethylpyridine.

REFERENCES

1. Peri, J. B., and Hamman, R. B., *J. Phys. Chem.* **64**, 1526 (1960).
2. Parry, E. P., *J. Catal.* **2**, 371 (1963).
3. Basila, M. R., and Kantner, T. R., *J. Phys. Chem.* **71**, 467 (1967).
4. Hughes, T. R., and White, H. M., *J. Phys. Chem.* **71**, 2193 (1967).
5. Dewing, J., Monks, G. T., and Youll, B., *J. Catal.* **44**, 226 (1976).
6. Benesi, H. A., *J. Catal.* **28**, 176 (1973).
7. Jacobs, P. A., and Heylen, C. F., *J. Catal.* **34**, 267 (1974).

8. Matulewicz, E. R. A., Kerkhof, F. P. J. M., Moulijn, J. A., and Reitsma, H. J., *J. Colloid Interface Chem.* **77**, 110 (1980).

9. Knözinger, H., and Ratnasamy, P., *Catal. Rev. Sci. Eng.* **17**, 31 (1978).

10. Scokart, P. O., Selim, S. A., Damon, J. P., and Rouxhet, P. G., *J. Colloid Interface Chem.* **70**, 209 (1979).

11. Dunken, H., Fink, P., and Pily, E., *Chem. Tech.* **18**, 400 (1966).

12. Knözinger, H., Krietenbrink, H., Muller, H. D., Schultz, W., *in* "Proceedings, 6th International Congress on Catalysis, London, 1976" (G. C. Bond, P. B. Wells, and F. C. Tompkins, Eds.), Vol. 1, p. 183. The Chemical Society, London, 1976.

13. Peri, J. B., *J. Phys. Chem.* **69**, 220 (1965).

14. Knözinger, H., Krietenbrink, H., and Ratnasamy, P., *J. Catal.* **48**, 436 (1977).

15. Ward, J., *in* "Zeolite Chemistry and Catalysis" (J. A. Rabo, Ed.), ACS Monograph 171, p. 140. Amer. Chem. Soc., Washington, D.C., 1976.