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N_2 Adsorption Method for Measuring Certain Acid–Base Sites on Alumina

Surface acidity of gamma alumina is complex and highly dependent on the pretreatment drying conditions. Alumina dried below 400°C probably contains some weak Lewis acid–base sites able to isomerize olefins and dehydrate alcohols at temperatures in the range of 25–300°C (*1*). Brønsted acidity possibly only exists in a very weak form and is not capable of protonating either ammonia or pyridine (*2, 3*) or inducing color changes in Brønsted indicator dyes (*1*). On increasing the drying temperature above 400°C, alumina becomes increasingly active for a number of reactions (*4*) including a variety of H/D exchanges occurring at different temperatures (*5, 6*). Selective poisoning of some of these reactions can occur with such molecules as NH_3, CO_2, and H_2S (*2, 6, 7*). Furthermore, the increased predrying produces IR observable sites for adsorbed CO, CO_2, and NH_3 (*2, 8, 9*). The correspondence between the number of such sites and the activity of the reactions is not always clear.

An interpretation of some of the changes occurring on predrying has been provided by a model of the alumina surface based on random dehydroxylation to produce both OH groups and Al-oxide ion pairs of differing nearest neighbor configurations (*10*). Certain of these Al-oxide ion pairs with strained linkages have been termed alpha sites. They form very reactive centers and can have particular significance for industrial processes using alumina-based catalysts running above 400°C.

Recently we have found that sites closely associated, if not actual alpha sites, will strongly adsorb molecular N_2 just below room temperature. This note reports results found with three different commercial aluminas and relates the observations to similar adsorptions of CO and adsorbed CO_2 characterized by an IR band near 2360 cm^{-1}. In addition, the results of coking reactions conducted on these aluminas are reported.

The three aluminas used in this study were obtained from Engelhard, Cyanamid, and Kaiser. Properties are listed in Table 1. Each alumina was ground and sieved to a 14- to 20-mesh size before use.

The adsorption measurements were carried out in a pulse chromatographic apparatus consisting of a He flow system, a gas sampling valve with 0.25-cm^3 loop, a quartz U-tube for holding the sample, and a thermal conductivity detector. The He carrier gas (Matheson's UHP grade) was further purified by passing through a trap of well-dried alumina at liquid N_2 temperature. It was found essential to eliminate all traces of water and N_2 from the flow gas.

The procedure consisted of weighing out 0.5–1.0 g of sample into the quartz reactor and pretreating at the required temperature for at least 3 h in flowing He. Desorption of water could be monitored during this period by the thermal conductivity cell and, when the base line returned to normal and water was no longer detected, the sample tube was cooled to −20°C. The sample was then exposed to 0.25-cm^3 pulses of a 5% mixture of N_2 in He until the sample was saturated and a break-through was observed. The temperature of adsorption, −20°C, was selected because lower temperatures produced no further adsorption. A check on the amount adsorbed was made after every run by temperature programming the sam-

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TABLE 1

Properties of Aluminas Used

Alumina	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Impurities (ppm)											
			Ca[a]	Cr[a]	Cu[a]	Fe[a]	Mg[a]	Mn[a]	Na[a]	Ni[a]	S[b]	Si[a]	Zn[a]	Cl[a]
Engelhard RD	360	0.40	<1000	<200	<10	<300	<200	nd	nd	nd	50	100	nd	3000
Cyanamid Aero 1000	240	0.54	<1000	<200	<10	<300	<200	nd	70	<1000	60	nd	nd	nd
Kaiser SAS	272	0.94	<1000	nd	<10	400	200	nd	nd	nd	30	300	nd	nd

Note. nd: not detected.

[a] By Edax.

[b] By high-temperature oxidation.

ple at 50°C/min rate and measuring the desorption. Only one peak was observed at a peak temperature of 130°C.

A similar procedure was used for the adsorption experiments with CO, but in this case pulses of 10% CO in He were used and adsorptions were carried out at 0°C. The CO pulses passing through the aluminas were considerably broadened out compared with the equivalent N_2 peaks, and therefore the measurements of adsorption were obtained from the desorption peak.

Procedures for obtaining both the IR data and coking rates have been discussed previously (*8, 11*).

Table 2 gives the complete set of results obtained from the three aluminas predried at 500 and 700°C for the N_2 and CO adsorptions, the integrated IR absorbance peaks at 2360 cm^{-1} for adsorbed CO_2, and the relative coking rates obtained with naphtha feed at 504°C and 100 psig. Figures 1 and 2 respectively show the IR spectra and the coking rates obtained. Differences between the aluminas correspond well for all three adsorptive tests. However, close inspection of the data shows some significant discrepancies. Comparison of the results at 500 and 700°C pretreatment shows a large difference for N_2 adsorption (almost two or-

TABLE 2

Adsorption, IR, and Coking Rates Results on Three Aluminas

Alumina	Predrying temp. (°C)	N_2 adsorption at −20°C[a]		CO adsorption at 0°C[b]		Integrated IR adsorbance CO_2 at 2360 cm^{-1}	Coking rates[c] (mg min^{-1} g^{-1} × 10^5)
		(cm^3 g^{-1} × 10^3)	(sites cm^{-2} × 10^{-10})	(cm^3 g^{-1} × 10^3)	(sites cm^{-2} × 10^{-10})		
Engelhard	500	7.5	5.1	40	27.2	2.3	43.3
RD	700	150	102	220	150	6.0	
Cyanamid	500	1.2	1.2	18	18.4	1.2	16.7
Aero 1000	700	90	92	110	112	3.3	
Kaiser	500	—	—	—	—	—	0.83
SAS	700	12.5	11.3	50	45.2	1.4	

[a] Obtained by pulse adsorption.

[b] Obtained from desorption peak.

[c] Run on aluminas pretreated at reaction temperature (504°C).

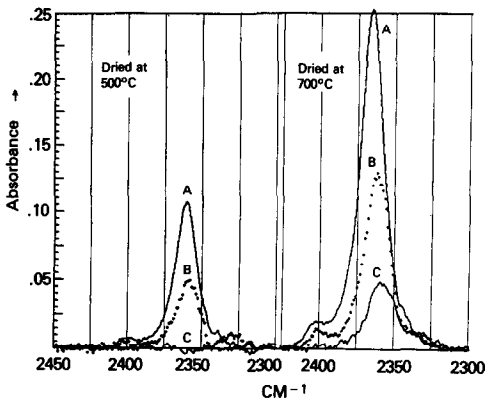

FIG. 1. Spectra of CO_2 adsorbed on three aluminas at two different temperatures. Aluminas: (A) Engelhard RD, (B) Cyanamid Aero 1000, (C) Kaiser SAS. Calcined at temperatures indicated for 1 h. CO_2 adsorbed and evacuated for 5 min at room temperature. Background subtracted by computer.

ders of magnitude for the Engelhard alumina) while this difference is much smaller for the other adsorptions; furthermore, the amount of N_2 adsorbed is less than the CO adsorbed. Evidently N_2 goes on a smaller number of sites than CO and presumably CO_2. It is probable that N_2 goes on only the most highly active or highly strained dual ion pair sites. However, after a 700°C treatment the differences in amount adsorbed are small.

Peri and later Della Gatta *et al.* have shown that CO can adsorb on various aluminas at two IR identifiable bands ascribed to strongly and weakly held CO on dual sites (*9, 12*). If N_2 goes only to sites equivalent to the strongly held CO, this would not be surprising since the reactivity of N_2 is considerably less than CO or CO_2. It is, however, surprising that N_2 adsorbs at all. Possibly N_2 with its quadrupole can interact with the large dipole of these dual sites; O_2, which has no quadrupole, did not adsorb at these conditions. Reports of N_2 chemisorption on transition metals are not unknown (*13*), and IR evidence has been presented of adsorbed N_2 on alpha hematite (*14*).

Differences between the Engelhard and Cyanamid aluminas are readily explained by the difference in surface areas; however, the low adsorption results on the Kaiser alumina are not easily understood. Impurities of trace elements shown in Table 1 give no indication for this difference. Possible differences in the method of manufacture could lead to differences in the morphology of the surface and thus produce a different population of strained alpha sites.

The values obtained for the population of sites per square centimeter of surface are lower than previous results obtained by poisoning experiments by factors of 2–5 (*6, 8, 9, 12*). Some doubt may exist with values obtained by poisoning because this represents an upper limit, since other sites may adsorb poison molecules. A recent paper by Quanzhi and Amenomiya shows that the poisoning effect of CO_2 is a nonlinear function of the equilibration reaction between CD_4 and CH_4, which was used as a probe for these sites (*15*). However, as shown in this work, aluminas are different and this could be another possible explanation.

The coking rates observed with the aluminas appear to relate generally with the adsorption measurements despite the pretreatment and conditions of reaction occurring only around 500°C, when the population of these type sites cannot be large; furthermore, no extraordinary effort was made to keep the reaction conditions entirely water-free as in the case of the ad-

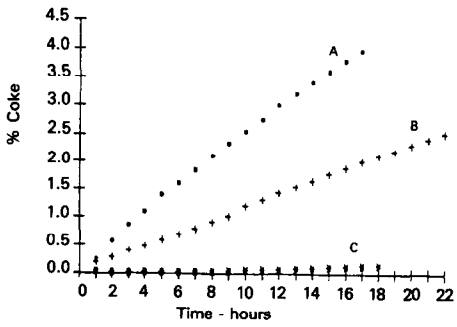

FIG. 2. Coking rates on three aluminas. Aluminas: (A) Engelhard RD, (B) Cyanamid Aero 1000, (C) Kaiser SAS. Reaction conditions: naphtha feed 4 WHSV, 100 psig, 3/1 H_2/hydrocarbon, 504°C.

sorption measurements. It is possible that these potential sites can be sufficiently active to cause coking even when still hydroxylated. Whatever the nature of these actual or potential sites, they represent an important property of alumina and alumina-containing catalysts. In conclusion, the method of measuring "irreversible" adsorbed N_2 is a simple technique that allows a relative measure of the dual acid–base ion pair or alpha site population. Its main advantage is that it can be used when other reactive components are present on the alumina that would otherwise adsorb more reactive probe molecules.

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