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Effect of Quaternary Ammonium Compounds on the Physicochemical Properties of Amorphous Silica–Alumina

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Quaternary ammonium compounds were used in the preparation of amorphous silica–alumina containing 88% silica. The acidities of the samples were characterized by IR spectroscopy using three probes: pyridine, ammonia, and carbon monoxide. The morphology and structural details were examined respectively by TEM and MAS NMR. All of these characterizations reveal that the use of the quaternary ammonium compounds affect physicochemical properties such as surface area, particle size, acidity, and tetrahedral-to-octahedral ratio of aluminium in amorphous silica–alumina and catalytic activity toward vapor-phase synthesis of pyridine bases from acetaldehyde and ammonia.

INTRODUCTION

Amorphous silica–alumina is a known solid acid utilized in organic reactions involving carbonium ion mechanisms like polymerization, isomerization, cracking, alkylation, and cyclodehydrogenation (*1*, *2*). However, because of its wide spectrum of pore size distribution amorphous silica–alumina is lacking in selectivity toward the desired product. Work has been reported on amorphous silica–alumina which has catalytic properties similar to those of zeolites but without zeolitic pore restrictions (*3*). Zeolites, by virtue of their regular pore geometry, are shape selective catalysts for many acid-catalyzed reactions.

Earlier amorphous silica–alumina containing 88% silica was found to be suitable for vapor-phase synthesis of light pyridine bases through cyclodehydrogenation reaction of acetaldehyde and ammonia (*2*). In order to optimize the yield, an attempt has been made to modify the properties of amorphous silica–alumina through the use of quaternary ammonium compounds (QACs) like tetramethylammonium hydroxide, tetrapropylammonium hydroxide, and tetrabutylammonium bromide. The object of this paper is to report changes in physicochemical properties such as surface area, particle size, acidity, and structural aspects and ultimately the impact on catalytic activity as a result of use of the above compounds.

EXPERIMENTAL

The sources of reagents used and their purities are indicated in Table 1.

H_2SO_4 (4.2 *M*) was added slowly with vigorous stirring to 300 ml of hot solution of 2.4 *M* $Na_2SiO_3 \cdot 5H_2O$ until the pH reached 7 and the gel was formed. The gel was aged for 1 h, filtered, and washed to free it from sulfate ions.

NH_4OH (1 : 1) was added with vigorous stirring to 100 ml 0.6 *M* $Al_2(SO_4)_3 \cdot 18\ H_2O$ until the pH reached 7–8 and the gel was formed. The gel was aged for 1 h and then filtered and washed to free it from sulfate ions.

Each of the above gels, silica as well as alumina, was dissolved in a mixture of 66 ml 10.0 *M* NaOH and 70 ml 1.21 *M* quaternary ammonium compound solutions under heating and stirring. To either of the solutions 5.0 M HCL was added until the gelation occurred at pH 9. The gel was allowed to age for 24 h, filtered, washed to free it from chloride ions, and then left for 24 h,

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TABLE 1

Details of Reagents Used

Reagent	Source	Concentration or purity
Na–Silicate	Loba Chemie L.R	99.9%
$Al_2(SO_4)_3 \cdot 16H_2O$	Loba Chemie G.R.	98%
NaOH	Sarabhai M Chemicals G.R	98%
TMA–OH	EMERCK	10% in aqueous solution
TPA–OH	FLUKA	20% in aqueous solution
TBA–Br	FLUKA	99%
H_2SO_4	BDH L.R.	97%
HCl	Glaxo A.R.	Minimum assay 35.4% Sp gr 1.18

for syneresis to occur. The gel was then dried in an air oven maintained at 393 K for 3 h. The semidried coke was base-exchanged with 2.0% NH_4Cl solution, again dried in an air oven at 393 K and finally calcined at 723 K for 3 h in a muffle furnace.

Identical conditions except for the addition of quaternary ammonium compound were maintained for the preparation of sample A. While sample B was prepared by use of TMA–OH as PRA, samples C and D were prepared by use of TPA–OH and TBA–Br as PRAs, respectively.

All the amorphous silica–alumina samples thus prepared were found to be X-ray amorphous. The particle size in the samples was evaluated by JEOL 100 CX TEM. Before electron microscopic examination the samples were ultrasonically dispersed in ethanol. Structural aspects of the samples were studied by Bruker CXP-300 MAS NMR.

The acidity of the samples was measured by IR spectroscopy using three probes: pyridine, ammonia, and carbon monoxide. The spectra were recorded on IR-75 Specord spectrophotometer by use of thin self-supporting rectangular wafers (10–15 mg/cm^2) prepared from samples under pressure in a hydraulic press. Beer-Lambert law in integrated form was applied for the measurement of concentration of acid sites (*4*). The details of the method as well as the infrared cells used for the study are described elsewhere (*5*).

Activity of the prepared catalysts for the cyclodehydrogenation reaction of acetaldehyde and ammonia to produce alkyl pyridines was evaluated in a fixed bed continuous flow reactor under atmospheric pressure at a wide range of temperatures, 623–723 K. The activities of different silica–alumina samples were compared under identical conditions, viz., at the reaction temperature of 700 K and NH_3/CH_3CHO (mole) = 1.0. The products, consisting of 2-picoline, 4-picoline, and pyridine, were identified and estimated by IR spectroscopy by use of the bands at 791, 749, and 700 cm^{-1}, respectively. The total amounts of pyridine bases were also determined by the standard method of perchloric acid titration (*6*).

RESULTS AND DISCUSSION

The morphological aspects of samples A, B, C, and D are described in the electron micrographs of Fig. 1. Micrograph 1A reveals that sample A consists of aggregates of irregular size formed from primary particles of average size ~5 nm. The morphology changes when quaternary ammonium compounds are used. In B small globules between 50 and 80 nm in size are observed together with amorphous aggregates formed from 5- to 10-nm primary particles. Growth in the size of the globules is found to be greater in catalyst C. Sample D predominantly consists of big globules ~150 nm in size. Thus, each of the samples B, C, and D has its own morphology, which is quite distinct from that of A, the sample that was prepared without any quaternary ammonium compound. A trend in the morphology from irregular-sized aggregates to spherical globules is observed as we go from A to D. This gradual change in morphology, i.e., the growth of globules, may be attributed to charge and size of the carbon present during the synthesis of silica–alumina. Table 1 shows that in the case of samples prepared with TMA–OH, TPA–

OH, and TBA–Br, the surface area is found, in parallel with the observation made by Manton and Davidtz (*3*), to be greater in the case of TPA–silica–alumina. However, in contrast to their observation, we have observed a decrease in surface area after the use of quaternary ammonia compounds. This is probably due to such differences in preparation methods as the nature of source materials, product concentration, and pH, which affect the surface area to some extent. While the ratios of silica to alumina and pH used by Manton and Davidtz are 79–80 and 5, respectively, we have maintained a $SiO_2 : Al_2O_3$ ratio of 88 : 12 and a pH of 9 during gelation. Moreover, we have used different source materials.

The distributions of surface acid sites in the samples measured by use of pyridine, ammonia, and carbon monoxide as test molecules are presented in Table 2. With carbon monoxide as probe, two Lewis sites L(1) and L(2) at frequencies 2190 and 2225 cm^{-1}, respectively, in the infrared spectrum are observed. The concentrations of both the Lewis acid sites are included in the table. The concentrations of Lewis and Brønsted sites in the samples as measured from ammonia adsorption are much higher than those from pyridine adsorption. This can be explained by the fact that ammonia, being a strong base and a relatively small molecule (kinetic diameter 2.62 Å), has access to more acid sites. It is observed that the concentration of acid sites is maximum for sample C, which is prepared with tetrapropylammonium hydroxide.

The use of QACs also affects the structure. ^{27}Al MAS NMR of the samples reveals two peaks at about 50 and 0 ppm which are assigned to Al atoms in tetrahedrally and octahedrally coordinated sites. Table 2 reports the *T*/*O* peak ratio in different samples. The results clearly indicate that the *T*/*O* ratio depends on the preparation procedures of the samples. A similar view was also expressed by Welsh *et al.* (*7*). It is observed that the *T*/*O* ratio falls when QACs are used. The ^{29}Si MAS NMR spectra show a broad line with peak centering around −110 ppm, suggesting only amorphous structure in the samples.

The catalytic activities of different samples have been compared under identical conditions of temperature, mole ratio of reactants, and contact time, and the results are given in Table 3. From the table it is evident that pore-regulating agents have modified the catalytic activity of silica–alu-

TABLE 2

Characteristics of Amorphous Silica–Alumina Measured by Use of IR and NMR Spectroscopic Techniques

Sample	Surface area (m^2/g)	Concentration of Lewis acid sites ($\mu mol/m^2$)			Concentration of Brønsted acid sites ($\mu mol/m^2$)		Tetrahedral-to-octahedral ratio (*T*/*O*) of ^{27}Al	^{29}Si NMR shift (ppm)
		C_6H_5N	NH_3	CO	C_6H_5N	NH_3		
A	326	0.34	1.29	(1) 0.26 (2) 0.16	0.08	0.61	2.00	−107.8
B	148	0.32	1.35	(1) 0.13 (2) 0.12	0.10	0.88	1.2	−108.4
C	168	0.51	1.82	(1) 0.23 (2) 0.19	0.13	1.13	1.3	−106.2
D	143	0.21	1.14	(1) 0.13 (2) 0.08	0.12	1.12	1.3	−109.1

Note. Data for surface area and acidity are from Ref. (*5*).

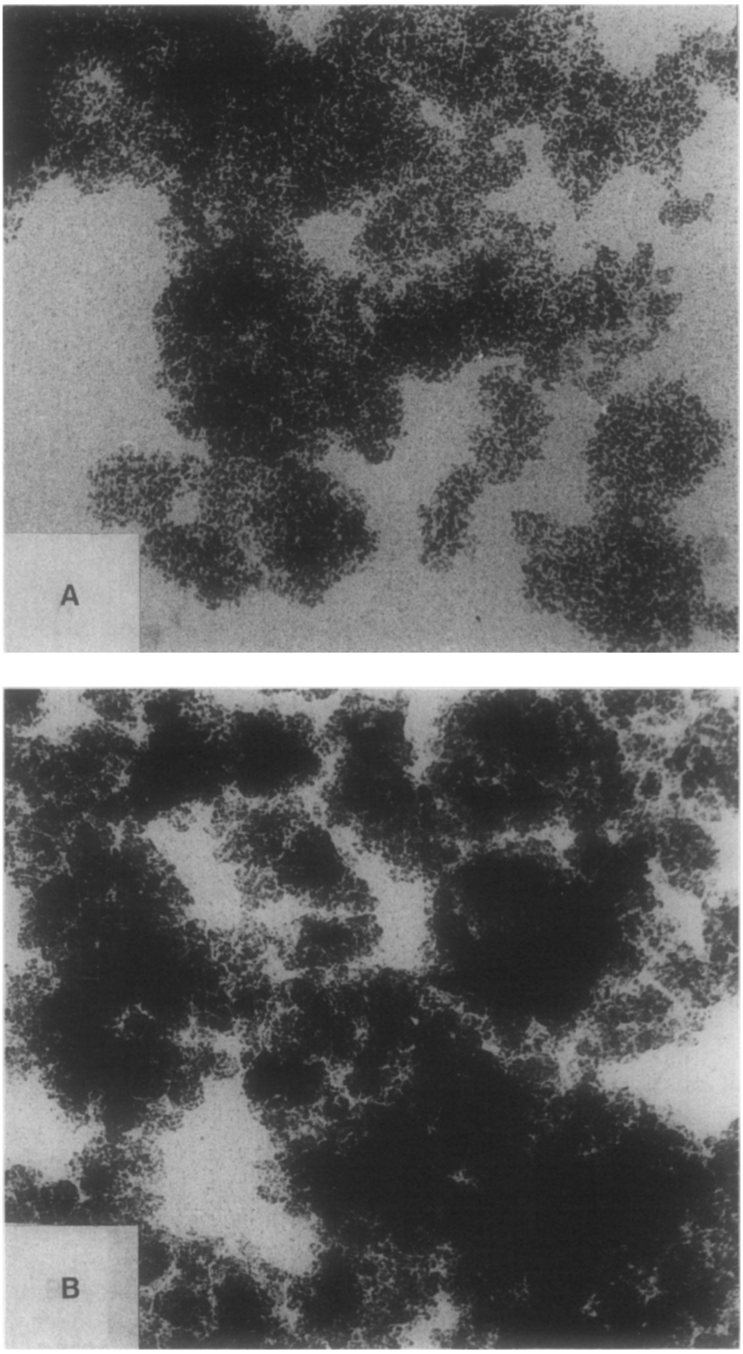

FIG. 1. Transmission electron micrographs A, B, C, and D displaying particle sizes in amorphous silica–alumina samples A, B, C, and D, respectively. Scale: 1 cm = 100 nm.

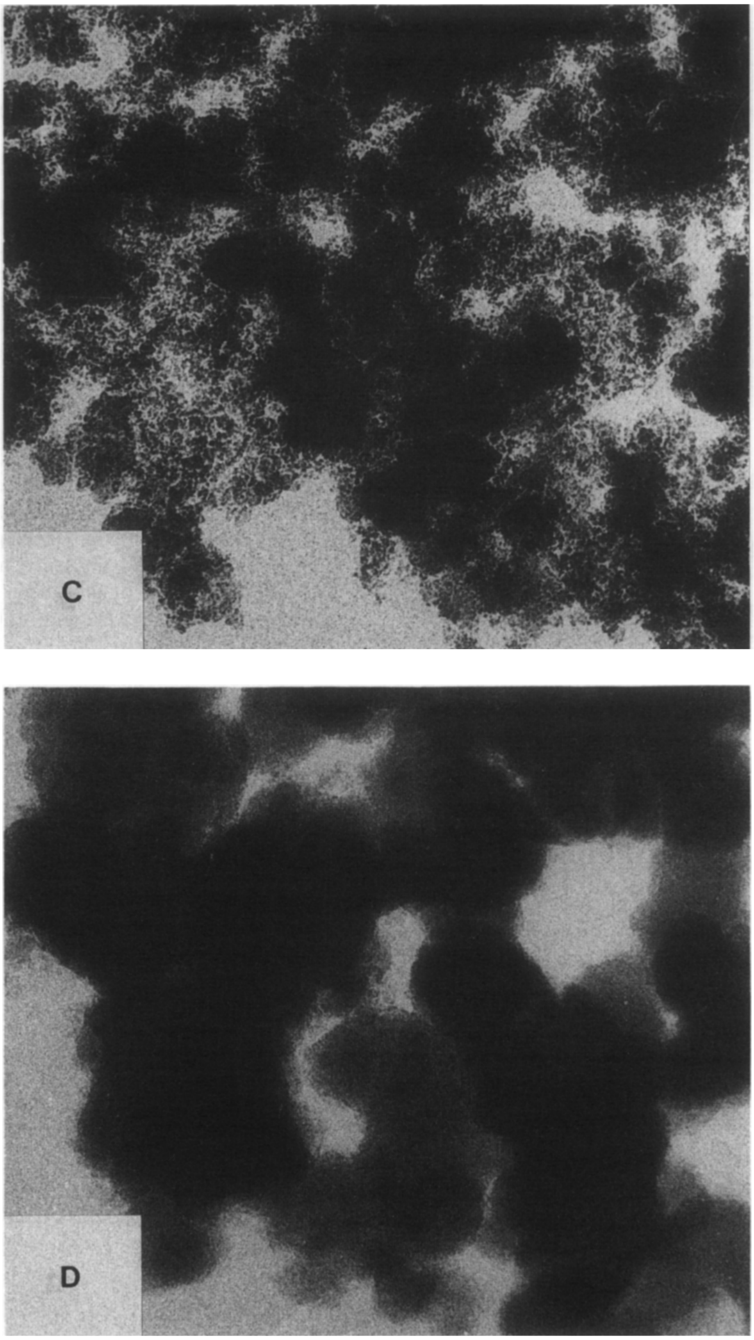

FIG. 1—*Continued*

TABLE 3

Variation in Catalytic Activity of Amorphous Silica–Alumina with Pore Regulation by Different Quaternary Ammonium Compounds

Catalyst	Conversion to pyridine bases (mol%)				
	4-Picoline	2-Picoline	Pyridine	Higher pyridine bases	Total pyridine bases
A	16.00	17.15	1.35	19.10	53.60
B	11.86	12.38	0.88	26.88	52.00
C	16.64	14.26	Trace	34.78	65.68
D	14.03	12.07	2.52	19.55	48.17

mina for cyclodehydrogenation reaction of actaldehyde and ammonia to pyridine bases. Among all the catalysts, the one prepared with TPA–OH exhibits the highest activity. Higher acidity in this sample might have enhanced its catalytic activity.

CONCLUSION

QACs can modify the physicochemical properties of amorphous silica–alumina. The modified properties may enhance its catalytic activity depending upon the cation used in the preparation. It may be noted that silica–alumina prepared with different QACs exhibited different activity during synthesis of pyridine bases. Silica–alumina prepared with TPA–OH showed highest activity.

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