NOTES

Effect of Cu^{2+} on Alumina, Silica, and Silica–Alumina in Methylphenothiazine Cation Formation

The formation of 10-methylphenothiazine cation (MPTZ$^+$) over Cu-doped catalysts (alumina, silica, and silica–alumina) was studied by the ESR technique at room temperature. It was observed that on doping the catalysts with Cu ions, the concentration of MPTZ$^+$ ions on the catalyst surface increased in the sequence

silica–alumina > silica > alumina.

However, it was noted that all paramagnetic Cu^{2+} were not electron accepting sites for the formation of MPTZ$^+$. There were other electron accepting sites in the support which were not affected by Cu ions. The presence of three types of paramagnetic Cu^{2+} on the Cu-doped catalysts and the role of Lewis acid and Brønsted acid sites for the formation of MPTZ$^+$ are discussed. © 1988 Academic Press, Inc.

INTRODUCTION

The ESR technique is widely used to characterize the active sites on the surface of a catalyst by the formation of carbonium ions (cations or anions). It was believed that Lewis sites are responsible for the formation of cation radicals on the surface of silica–alumina catalyst (1–5). However, Wozniewski et al. (6) demonstrated that Brønsted acid sites were also responsible for cation formation. These sites have significant application in chemical industry. On doping the surfaces of the alumina with metal ions one changes the surface characteristics. Highly dispersed metal particles on a suitable support find major applications in several industrial processes. Differences between the catalytic properties of various supports can be due to a number of factors apart from metal–support interaction. Hirschler (7) has demonstrated that adding metal ions to silica–alumina replaced the strong acid sites with weak acid sites. Richardson (8) found that Cu^{2+} and Ni$^+$ ions had the highest electron affinity in zeolites. Few papers have been published about the acidic properties of metals in zeolite (7–10). Some work also has been reported about the nature of metals on silica–alumina (2, 11, 12). In this paper we describe the effect of Cu ion on the electron accepting sites of alumina, silica–alumina, and silica, and also the existence of various types of Cu^{2+} in the dispersed form on the surface.

EXPERIMENTAL

The techniques for the ESR measurement and preparation of samples under vacuum are given in earlier papers (13, 14, 15). Silica, silica–alumina (Al$_2$O$_3$, 14.6%), and γ-alumina I and II were supplied by Strem Chemical Co. The surface areas of these solids are given in Table 1. The extrudates were ground and only a 60–70 mesh fraction was used in the present study. The CuO–M catalysts (where M is for alumina, silica–alumina, and silica) were prepared by the conventional impregnation method (14) using copper nitrate (Fischer certified) solution. The catalysts were calcined at 400°C after drying over a hot water bath. The total concentration of Cu was always 2%. The weight of the catalyst in the ESR tube was ≤0.1 g. The ESR tube containing the catalyst was heated at 400°C for 0.5 h and then cooled to room temperature prior to use. Most of the experiments were carried in the presence of oxygen (air) unless

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TABLE 1

MPTZ$^+$ Radicals on M Catalysts

M catalysts	Surface area[a] (m^2/g)	Spins/g	Spins/m^2
γ-Alumina I	100	1.5×10^{16}	1.5×10^{14}
γ-Alumina II (high activity)	160	0.5×10^{16}	0.3×10^{14}
Silica–alumina	400	47.0×10^{16}	11.75×10^{14}
Silica	340	26×10^{16}	7.64×10^{14}

[a] Supplied by Strem Chemical Co.

mentioned otherwise. A solution of 10-methylphenothiazine (MPTZ, 0.5 ml of 0.015 M; Eastman–Kodak Corp.) in benzene was always used.

RESULTS

Silica–alumina, silica, and alumina I and II did not give any ESR signal in the absence or presence of benzene. However, a very weak signal with alumina II was detected at $g = 2.003$. This could be due to some impurity.

Figure 1 shows the ESR signal of 10-methylphenothiazine cation radical (MPTZ$^+$) on silica–alumina in the presence of benzene. The color of the MPTZ$^+$ was pink. The ESR spectrum of MPTZ$^+$ was similar to that observed on alumina (16). However, in this system the hyperfine lines of (MPTZ$^+$) are well defined. Similar spec-
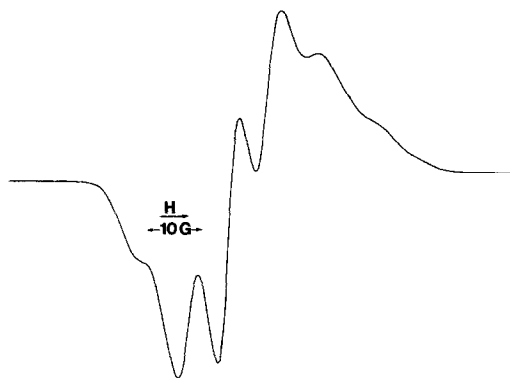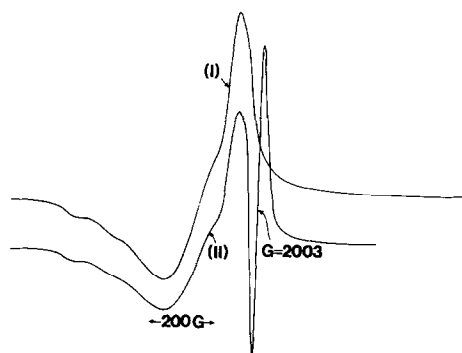

FIG. 2. (I) ESR spectra of Cu^{2+} in 2% Cu silica–alumina. (II) ESR spectra of 2% Cu silica–alumina and MPTZ solution in benzene.

tra were observed with silica and alumina. Although the hyperfine lines were well resolved with silica they were poorly resolved with silica and alumina under similar conditions. In the case of both aluminas, I and II, the hyperfine lines of MPTZ$^+$ were broad. The number of spins/g in different catalysts are given in Table 1. It is seen from Table 1 that the affinity of MPTZ$^+$ formation is maximum for silica–alumina. The electron accepting centers or sites for the formation of MPTZ$^+$ on different surfaces are in the sequence

silica–alumina > silica
$$> \gamma\text{-alumina I} > \gamma\text{-alumina II} \quad (1)$$
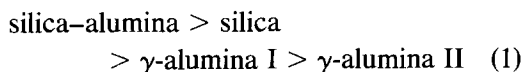
which is in the same order as that obtained in the phenothiazine cation formation on various catalysts (17). It seems, from Eq. (1), that the highly active alumina II has less affinity for the formation of MPTZ$^+$ than alumina I which has less surface area. The ESR spectrum of MPTZ$^+$ was also measured in the absence of air by degassing the sample at 400°C. But no appreciable change in the intensity or shape was observed. However, in the case of silica–alumina, the intensity increased slightly ($\sim$4%).

Figure 2 (I) shows the ESR spectra of Cu^{2+} (18) on silica–alumina. No appreciable effect of benzene on Cu^{2+} ESR spectra was observed. Similar spectra were also ob-

FIG. 1. 10-Methylphenothiazine cation radical (MPTZ$^+$) on silica–alumina.

TABLE 2

Distribution of Cu^{2+} on CuO–M Catalysts (Cu = 2%) before and after Adding MPTZ Sol[n]

CuO–M catalyst	Cu^{2+} spins/g	
	Before	After
Alumina I	2.4×10^{17}	2.29×10^{17}
Alumina II	11.3×10^{17}	10.6×10^{17}
Silica–alumina	33.3×10^{17}	25.5×10^{17}
Silica	13.6×10^{17}	11.9×10^{17}

FIG. 3. ESR spectra of MPTZ$^+$ on 2% Cu silica–alumina.

served with other CuO–M catalysts. A slightly well-resolved hfs structure was observed in the case of Cu^{2+} on silica–alumina and silica. The g values of all Cu^{2+} on CuO–M catalysts were nearly the same. The distribution of Cu^{2+} on various CuO–M catalysts is given in Table 2. The concentration of Cu^{2+} (spins/m^2) on the catalysts has been found in the sequence

silica–alumina > alumina II

$$> \text{silica} > \text{alumina I.} \quad (2)$$

It is clear from the sequence in Eq. (2) that CuO–silica–alumina has a higher activity for Cu^{2+} formation. Alumina II has less surface area than silica but has a higher affinity for Cu^{2+} formation. It appears from sequences (1) and (2) that all electron accepting sites are not responsible for the formation of Cu^{2+} and that there are other types of sites which could also act as sites for Cu^{2+} formation.

The presence of benzene did not show any significant change in the spectra of Cu^{2+} in CuO–M catalysts. However, the intensity of Cu^{2+} increased slightly in all CuO–M catalysts. When 10-methylphenothiazine solution in benzene was added to the CuO–M catalysts, a new ESR line at $g = 2.003$ appeared, the intensity of which depended on the catalyst surface. This new line is due to MPTZ$^+$ (16). The ESR spectra of the CuO–M–MPTZ system is shown in Fig. 2 (II). The same spectra for the MPTZ system with the ESR line in a narrow field scan is shown n Fig. 3. Similar
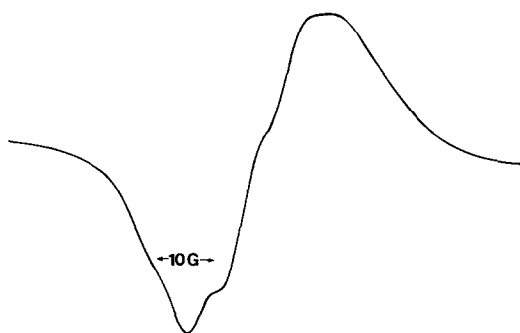
spectra were observed with all CuO–M catalysts. The number of spins due to MPTZ$^+$ are given in Table 3. The sequence for the MPTZ$^+$ formation on CuO–M catalysts is

CuO–silica–alumina > CuO–silica

$$> \text{CuO–alumina I, II.} \quad (3)$$

This sequence is similar to sequence (1). It is clear from Table 2 that, on addition of MPTZ solution in benzene, the Cu^{2+} concentration on supports slightly decreased. This could possibly be due to the MPTZ$^+$ formation on these particular Cu^{2+} sites. On comparison of the data in Tables 1 and 3 it is clear that the presence of Cu^{2+} on silica–alumina increased the affinity for the formation of MPTZ$^+$. However, in the case of silica and alumina I and II, the presence of Cu^{2+} decreased the affinity.

DISCUSSION

The formation of 10-methylphenothiazine cation radical on the surface of alumina and Dowex 50 has been discussed in

TABLE 3

MPTZ$^+$ Cations on CuO–M Catalysts (2% Cu)

M catalyst	No. of spins/g (MPTZ$^+$)
Alumina I	6.1×10^{14}
Alumina II	2.8×10^{15}
Silica–alumina	2.3×10^{18}
Silica	2.6×10^{16}

the literature (*17*, *19*). It is clear from Table 1 that the silica–alumina surface has more affinity for the formation of MPTZ$^+$ than silica or alumina I and II. Sato *et al.* (*20*) studied the surface hydroxyls on silica, alumina, and silica–alumina catalysts by using several kinds of organometallic compounds. They demonstrated that hydroxyl groups on silica–alumina are different from those on alumina or silica. Scokart *et al.* (*21*) studied the adsorption of pyridine and CD$_3$CN (Compon. 0–100%) by IR spectroscopy and demonstrated that Lewis sites increased smoothly from 0 to 75% Al$_2$O$_3$. On the other hand, the number of Brønsted sites reached maximum at 30–50% alumina and was zero for pure oxides. Also, the ratio of the number of Brønsted sites to Lewis sites changed with the composition of silica–alumina. This ratio was highest for the samples containing 30–50% Al$_2$O$_3$ and zero for pure alumina.

Flockhart and Pink (*3*) studied the oxidizing properties of silica–alumina catalysts and suggested that Lewis acid sites are responsible for cation formation. Hirschler (*7*) suggested that the catalyst proton affects the formation of triphenylcarbonium ion on the silica–alumina surface. Although Wu and Hall (*22*) generally supported Hirschler's theory, they gave the following mechanism for the triphenylcarbonium ion formation on the silica–alumina surface,

$$Ph_3CH + Cat.H^+ \rightarrow C_6H_5 + Ph_2C^+H \quad (i)$$

$$Ph_2C^+H + Ph_3CH \rightarrow Ph_2CH_2 + Ph_3C^+ \quad (ii)$$
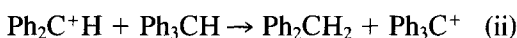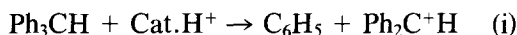
Hall and Dollish (*23*) suggested that in many cases oxygen molecules in the catalysts act as the electron acceptor. McVicker *et al.* (*24*, *25*) suggested that cation radicals of paraffins may decompose into hydrogen and carbenium ion during the conversion of isobutane over solid acids (such as silica–alumina and halided Al$_2$O$_3$). Wozniewski *et al.* (*6*) studied the perylene adsorption on a series of silica–alumina in the presence of oxygen. They suggested that the shape of ESR signal is influenced by the type of centers (Lewis and Brønsted acid sites) on the surface and not by the concentration of paramagnetic species (*26*, *27*). While the Lewis acid site is responsible for the broad ESR line, the Brønsted acid site is responsible for the hyperfine structure. Wozniewski (*27*, *28*) demonstrated that an alumina sample after suitable activation exhibits not only oxidizing sites but also an approximately equal number of reducing sites. These results confirm the previously reported findings of Flockhart *et al.* (*29*). Muha (*30*) raised the question of the formation of the two types of perylene radical, i.e., anion and cation on silica–alumina and the possibility of their subsequent reaction with each other. But Wozniewski *et al.* (*31*) demonstrated that the paramagnetic species of perylene developed after the adsorption of oxygen on the surface of aluminosilicate cannot be anion radicals. They (*6*) also proposed a hypothesis concerning the role of acidic, protic, and aprotic sites as well as oxygen in the formation of paramagnetic species from perylene over aluminosilicate. This hypothesis is not generally valid for surfaces of all solids.
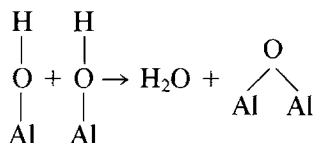
No quantitative data have been reported about the radical formation over alumina, alumina–silica, and silica. In the present study we have observed that silica–alumina has a greater affinity for the formation of MPTZ$^+$ than either silica or alumina (Table 1). In addition, a well-defined hyperfine structure of MPTZ$^+$ was observed on silica–alumina and silica. In the case of alumina we observed a hfs of MPTZ$^+$ which was not well defined. The results of the present study indicate that the MPTZ$^+$ formation on the studied solid surface is in the order

$$silica–alumina > silica$$
$$> alumina\ I,\ alumina\ II. \quad (4)$$
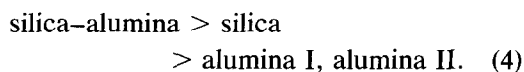
This sequence is about the same as the one we reported earlier on phenothiazine cation formation on these solids (*17*). The results of the present study indicate that not

only Lewis acid sites are responsible for the formation of MPTZ$^+$ but Brønsted acid sites are also taking part as suggested by Wozniewski et al. (6). It could also be just possible that there are other types of centers which might be responsible for MPTZ$^+$ formation on the surface of these solids. It is not necessary that these centers have an acidic character. These type of centers may be possible only in silica and silica–alumina.

In the case of alumina, on its dehydration two neighboring OH$^-$ ions combined to give water and left a strained oxygen,

$$\begin{array}{ccccc} H & H & & & O \\ | & | & & & / \backslash \\ O & + & O & \rightarrow H_2O + & Al \quad Al \\ | & | & & & \\ Al & Al & & & \end{array}$$

The combination of two adjacent OH$^-$ is now considered to leave behind an exposed Al atom, which because of its electron-deficient character behaves as a Lewis site. These sites could be responsible for MPTZ$^+$ formation on alumina.

In the case of 2% Cu on alumina, silica–alumina, and silica, it was observed that the paramagnetic Cu^{2+} formation was maximum in silica–alumina (Table 2). It is reported (22) that although nearly all copper in the CuO–alumina system contributed to the magnetic susceptibility, only 2% contributed to the ESR signal. It is also reported that in the CuO–alumina system copper complexes are formed (12) with Cu^{3+}, Cu^{2+}, and Cu$^+$ depending on the composition and thermal treatment (32). Cu^{2+} complexes are grouped into clusters on the support surface (33). This could be true for other supports also. The spectra of Cu^{2+} was nearly similar for all studied systems. However, in the case of the low surface area alumina (II) a broad signal for Cu^{2+} with a not very well-defined hfs was observed. This signal could be due to the Cu^{2+} clusters and its broadness may be due to dipole–dipole interaction.

When MPTZ in benzene was added to the Cu-doped supports, the ESR line due to MPTZ$^+$ was observed for all systems, indicating the affinity of the system for the formation of MPTZ$^+$. In the case of silica–alumina, the concentration of MPTZ$^+$ was maximum (Table 3). However, Cu^{2+} decreased in the presence of MPTZ solution.

For Cu-doped silica and alumina, the formation of MPTZ$^+$ spins slightly decreased in the presence of Cu ions. The decrease in MPTZ$^+$ spins is not equal to the decrease in Cu^{2+} spins. In silica–alumina the formation of MPTZ spins increased several times when it was doped with Cu ions. However, the decrease in Cu^{2+} spins is not equal to the increase in MPTZ$^+$ spins. It seems that in silica–alumina new sites were generated when silica–alumina was doped with Cu. It could be Cu^{3+} complex (32), which may react as

$$Cu^{3+} + 2MPTZ \rightarrow Cu^+ + 2MPTZ^+$$
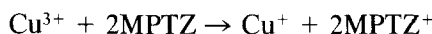
It seems that few Cu^{2+} complexes sit on solids. These are responsible for the formation of MPTZ$^+$. The decrease in Cu^{2+} could possibly be explained by the reaction

$$MPTZ + Cu^{2+} \rightarrow Cu^+ + MPTZ^+$$
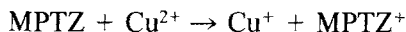
The concentration of MPTZ$^+$ ion on Cu-doped supports has the same activity (concentration) sequence as the electron donating sites of undoped supports (sequence (1)).

CONCLUSION

It can be concluded from the present investigation that the formation of paramagnetic cation radical (MPTZ$^+$) does not depend mainly on Lewis or Brønsted sites. There could be other sites which have a slightly different environment. There could be at least three types of Cu^{2+} on CuO–M supports which are responsible for the ESR signal, namely (i) did not accept electrons given by MPTZ, (ii) did accept electrons and formed MPTZ$^+$, and (iii) did accept electrons but formed a nonparamagnetic complex with MPTZ. In the case of silica–alumina the electron accepting sites for the

formation of MPTZ⁺ increased several times when it was doped with Cu ions. The results of the present study indicate that the formation of MPTZ⁺ on a solid surface is in the sequence

silica–alumina $>$ silica $>$ alumina.

This is similar to the sequence observed for Cu-doped solids.

ACKNOWLEDGMENT

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