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^{121}Sb Nuclear Gamma-Ray Resonance Study of Crystal Chemical Structures in U–Sb–O Acrylonitrile Catalysts

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^{121}Sb Nuclear-gamma-ray resonance measurements have been made at 77°K on USb_3O_{10}, $USbO_5$ and on a commerical supported catalyst preparation 60 wt% $USb_{4.6}O_x$–40 wt% SiO_2. The NGR spectrum of $USbO_5$ is consistent with a single Sb site. The spectrum of USb_3O_{10} is interpreted as resulting from more than one Sb site. In both materials, the covalency of the Sb sites is greater than that in pure Sb–O phases such as Sb_2O_4 and Sb_2O_5. The NGR data are consistent with both $USbO_5$ and USb_3O_{10} being catalytically active and with previous conclusions based on kinetic data that differences in the selectivity of $USbO_5$ and USb_3O_{10} result from differences in atomic topologies and geometries.

INTRODUCTION

The U–Sb–O catalyst (*1*) used in the synthesis of acrylonitrile from propylene, ammonia, and oxygen (air), according to the reaction

$$C_3H_6 + NH_3 + \tfrac{3}{2}O_2 \rightarrow C_3H_3N + 3H_2O,$$

has been the topic of several ex post facto investigations into the fundamental basis of its catalytic activity (*2–5*). While there was some confusion initially concerning the compositions of the U–Sb–O phases present in the catalyst (*1–6*), there is little doubt that the U–Sb–O phases are $USbO_5$ and USb_3O_{10}. USb_3O_{10} is believed to be the phase that is catalytically active in the formation of acrylonitrile from propylene and ammonia (*3*).

Some tentative suggestions have been made as to the structural and crystal chemical basis for the activity of the USb_3O_{10} phase (*3,5*); but the absence of a definitive structure for this phase, due to the lack of single crystal, behooves us to seek further confirmation of these speculations. In our studies, we have been primarily concerned with and have used a technique that is particularly sensitive to the following aspects of this catalyst: (1) the kinds and relative quantities of Sb-containing phases in the commerical catalyst, (2) the valence state of the Sb ion in these phases, and (3) the nature of the bonding of the Sb ions in the catalytically active and selective USb_3O_{10}.

Aspects (1) and (2) of our studies have been treated in the previously reported investigation (*3*) and our measurements were made and are reported on here because of the greater precision and accuracy of nuclear gamma-ray resonance (NGR) technique for these specific determinations. In addition, our determinations are more direct and less hampered by non-Sb-containing impurities than magnetic susceptibility measurements which have been used previously to infer the oxidation state of Sb (and therefore of U). Our results are also in agreement with previous conclusions regarding the different antimony-containing phases in the commercial catalysts; we are able, however, to provide a reliable quantitative estimate of the relative quantities of Sb_2O_4 and USb_3O_{10} that are present.

Further, our results are *consistent* with there being *only one* equipoint set for Sb in $USbO_5$ and *more than* one equipoint set for Sb in USb_3O_{10}. Alternatively, our results are consistent with there being one Sb site in both $USbO_5$ and USb_3O_{10} but with there being a greater distortion of the Sb site in USb_3O_{10} than in $USbO_5$. At any rate, the symmetry and number of inequivalent Sb sites in $USbO_5$ are not higher than those of the Sb sites in USb_3O_{10}.

EXPERIMENTAL

A sample of a commercial catalyst having the composition 60% $USb_{4.6}O_x$ and 40% SiO_2 support material was obtained from the Standard Oil Company Research Department, Cleveland, Ohio. While not identified as such, this appears to be the same supported catalyst reported on extensively in Ref. (*1*).

USb_3O_{10} and $USbO_5$ were prepared according to the methods of Grasselli, Suresh, and Knox (*2*). These were confirmed to be single phase using X-ray powder diffraction. $USbO_5$ was prepared by decomposing USb_3O_{10} at 1100°C in air for 1 hr. Measurements were also made on a sample prepared by heating USb_3O_{10} at 1020°C in air for 1 hr. This sample contained both USb_3O_{10} and $USbO_5$.

TABLE 1

Lattice Constants of $USbO_5$ and USb_3O_{10}

Phase	a_0 (nm)	b_0 (nm)	c_0 (nm)	Ref.
USb_3O_{10}	0.7352	1.263	1.533	[a]
	0.7352	1.263	1.5306	[b]
$USbO_5$	0.7346	1.272	1.540	[c]
	0.753	0.649	1.577	[a]
	0.7540	0.6478	1.5782	[b]
	0.753	1.304	1.580	[c]

[a] Present study.
[b] Ref. (*6*).
[c] Ref. (*3*).

The ^{121}Sb NGR spectra were obtained using a $BaSnO_3$ source. Both the source and the absorber were cooled to 77°K. The experimental apparatus and treatment of the data have been described previously (*8*).

RESULTS

The lattice constants for the two pure U–Sb–O phases are given in Table 1; they are in good agreement with those reported previously. No attempt was made to estimate from the X-ray diffraction data the relative amounts of USb_3O_{10} and $USbO_5$ in the multiphase material. The ^{121}Sb NGR spectra are shown in Fig. 1. The filled circles are the experimental data and the lines are the result of fitting a single, lorentzian line to each of the absorption lines. The appearance of two absorption lines in the spectrum for the catalyst is worthy of note. Only one line was apparent in the spectra of $USbO_5$, USb_3O_{10}, and the multiphase $USbO_5$–USb_3O_{10} sample. The result is of significance in the latter case since it relates to the mode of decomposition of USb_3O_{10}. The parameters corresponding to the solid line fits to the data are given in Table 2.

It is quite likely that the *apparent* single lines in the spectra of Fig. 1 are not intrinsic single lines, and this is certainly the case for the low-velocity line in the commercial catalyst. But the lines for USb_3O_{10} and $USbO_5$ are sufficiently symmetric to make a deconvolution of the pattern unreliable, as discussed previously (*7*). The isomer shifts of a fit resulting from fitting a multiple-line pattern, such as a quadrupole split pattern, will not be significantly different from the line positions in Table 2. Such fits will also not permit a distinction to be made for USb_3O_{10} between a spectrum resulting from several crystallographically inequivalent Sb atoms and a spectrum re-

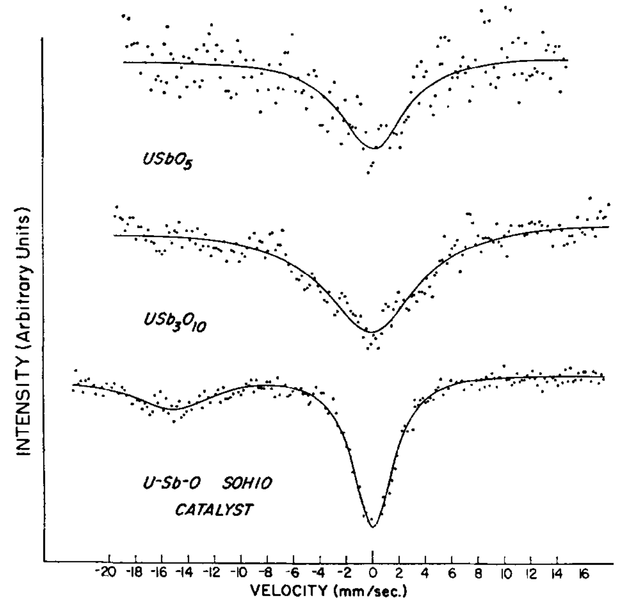

FIG. 1. ^{121}Sb NGR spectra of pure U–Sb–O phases and of a supported catalyst preparation. The points are the experimental data and the solid lines are the least-mean-squares fit of a single lorentzian line to each absorption line. The supported catalyst has the composition 60 wt% $USb_{4.6}O_x$–40 wt% SiO_2.

sulting from a single Sb atom with a large quadrupole splitting.

DISCUSSION

The principal motivation for the present NGR study of the U–Sb–O catalysts is the strong sensitivity of the ^{121}Sb isomer shift to the actual charge state of Sb and the opportunity that the sensitivity provides in delineating any correlations between Sb–O bond strengths and topologies and the relative activities of $USbO_5$ and USb_3O_{10}. For example, in each of the compounds $KSbF_6$, $NaSbF_6$, Sb_2O_5, and $SbCl_5$, the Sb ion has an oxidation number of +5; yet the isomer shift varies from −3.7 mm/sec with respect to $BaSnO_3$, for $SbCl_5$, to +3.7 mm/sec for $KSbF_6$.

The isomer shift is determined by the s electron density at the nucleus according to the relationship

$$\delta_{Is} = R^2(\delta R/R)(|\Psi(0)|_a^2 - |\Psi(0)|_s^2),$$

where δR is the difference between nuclear radii in the gound and excited states, e.g., $R_{ex} - R_{gd} = \delta R$; and $|\Psi(0)|_a^2$ and $|\Psi(0)|_s^2$ are the electron densities at the absorber and source nuclei, respectively. For ^{121}Sb, $\delta R/R$ is $\sim -22 \times 10^{-4}$ *(9)* and therefore for a given source, δ_{Is} decreases as the electron density at the antimony nucleus increases. Despite the fact that changes only in s electron density are measured directly, it has been demonstrated *(10)* that changes in the isomer shift correlate very

TABLE 2

^{121}Sb NGR Parameter of U–Sb–O Phase at 77°K

	Line position[a] (mm/sec)	Linewidth (mm/sec)
$USbO_5$	−0.53 ± 0.15	3.19 ± 0.22
USb_3O_{10}	−0.57 ± 0.03	4.28 ± 0.13
SOHIO catalyst	+0.38 ± 0.03	3.62 ± 0.10
	−14.68 ± 0.2	7.74 ± 0.2
USb_3O_{10}–$USbO_5$–Sb_2O_4 mixture	−0.54 ± 0.02	7.14 ± 0.2

[a] Relative to $BaSnO_3$/^{121}Sn source.

well with changes expected from electronegativity, covalency, and overlap considerations. That is, the isomer shift decreases as the covalency increases or as the electronegativity difference decreases. Thus, the changes in the isomer shift as one goes through the series $KSbF_6$, $NaSbF_6$, Sb_2O_5, and $SbCl_5$ are in good agreement with the increasing covalency and decreasing electronegativity difference in the series.

If the previous studies (*3–5*) of the catalytic activity $USbO_5$ and USb_3O_{10} are correct in the implication that incipient in the equilibrium crystal chemistry of USb_3O_{10} and $USbO_5$ are the crystal chemical structures that are active during the catalysis of the ammoxidation of propylene, then we might expect to see differences in the bonding of Sb in these two phases.

First of all, we observe in Table 2 and Fig. 1 that only Sb^{5+} is present in USb_3O_{10} and $USbO_5$; there is no ambiguity in this conclusion, and previous indirect conclusions as to the oxidation state of Sb are proved correct (*3,6*). Similarly, the absence of any Sb^{3+} in the mixture resulting from the partial decomposition of USb_3O_{10} indicates that USb_3O_{10} decomposes to give $USbO_5$ and "Sb_2O_5," i.e.,

$$USb_3O_{10} \rightarrow USbO_5 + \text{“}Sb_2O_5\text{.”}$$

Sb_2O_4 and Sb_2O_3 are not produced. The somewhat large linewidth of the USb_3O_{10}–$USbO_5$–Sb_2O_5 mixture, (Table 2) apparently results from the poor crystallinity of the Sb_2O_5 phase. The difference in the isomer shifts of Sb_2O_5, USb_3O_{10}, and $USbO_5$ would result in a line broadening of only 1.5 mm/sec and not the observed 3 mm/sec. A mixture of USb_3O_{10} and $USbO_5$ would not show line broadening to the extent exhibited in this sample since the positions of the lines and their widths are rather similar.

There are some questions regarding the existence of an "Sb_2O_5" phase (*11*). It is clear, however, that it is possible to synthesize from aqueous media an Sb–O phase that contains only Sb^{5+}. For our purposes here, the existence of an Sb–O phase that contains only Sb^{5+} is the essential requirement, and its precise composition is only of secondary importance.

In the case of the commercial catalyst, the presence of an Sb^{3+}-containing phase is clearly indicated by the line at −14.68 mm/sec. This phase is identified as Sb_2O_4 in accord with the NGR parameter derived in previous studies (*7,11*). From the relative integrated intensities, the Sb_2O_4/USb_3O_{10} ratio is calculated as 1.4. This result, which corresponds to approximately 42% USb_3O_{10} and 58% Sb_2O_4, confirms a more recent qualitative estimate of 50% Sb_2O_4 and USb_3O_{10} obtained from X-ray diffraction analysis (*11*).

In terms of the crystal chemistry/catalytic activity correlation for USb_3O_{10} and $USbO_5$, it is clear from the very similar isomer shifts of Sb in USb_3O_{10} and $USbO_5$ that differences in their catalytic activity and selectivity cannot be ascribed to differences in the covalence of the Sb–O bonds. In fact, since the structures of $USbO_5$ and USb_3O_{10} are probably quite similar and since the Sb–O bonds are also similar, it might be expected that they would have similar activities. In fact, USb_3O_{10} and $USbO_5$ do indeed have rather similar *overall* activities (*4,5*).

$USbO_5$ and USb_3O_{10} do differ significantly, however, in their selectivities. The ^{121}Sb NGR linewidths of the two phases are different and may provide some clues to the difference in catalytic selectivity. It has been suggested that in $USbO_5$ there is only one Sb site but that there are two Sb sites in USb_3O_{10}; the larger linewidth of the ^{121}Sb NGR spectrum of USb_3O_{10} is *consistent* with this suggestion, since the larger width of the *apparent* single-line spectrum can result from the superposition of slightly different absorption lines arising from at least two inequivalent Sb sites. The larger linewidth of the spectrum of USb_3O_{10} could also result from a large electric quadrupole interaction but there is no asymmetry in the line to suggest this and no other independent evidence for this latter interpretation.

Thus, the difference in catalytic activity of $USbO_5$ and USb_3O_{10} is not due primarily to a difference in the strength of the Sb–O bonds (assuming that the bond strength is proportional to the degree of covalency). In fact, the covalency of the Sb–O bond in USb_3O_{10} and $USbO_5$ is rather high, especially when allowance is made for the fact that the oxygens are also bonded to other pentavalent ions. For example, the ^{121}Sb isomer shifts in Sb_2O_5 and Sb_2O_4 are 0.65 and 0.61 mm/sec, respectively, and tend more toward the value in $KSbF_6$, suggesting a saturation of the covalence of the oxygen ions. The isomer shift of Sb in the U–Sb–O phases, however, is about 1 mm/sec *lower* than those for Sb_2O_5 and Sb_2O_4 and tends toward a value typical of more covalent compounds such as $SbCl_5$. The difference in the degree of saturation of the oxygen covalence in the Sb–O and U–Sb–O phases results in all likelihood from the fact that U is an actinide element for which a crystal field description of the bonding, with its low degree of covalence, is appropriate.

On initial consideration, it might be supposed that the high covalence of Sb–O bonds might be in opposition to a high catalytic activity. However, it is not unreasonable that the strong covalence would facilitate electron transfer between the Sb ions and its environment and therefore enhance its catalytic activity vis-à-vis the pure Sb–O phases.

Therefore, it is clear that the relative covalence of the Sb–O bonds in $USbO_5$ and USb_3O_{10} cannot account for the higher activity of USb_3O_{10} relative to $USbO_5$. Structural differences and synergistic participation of uranium must be important. The high covalence of the Sb–O bonds does raise some questions, however, regarding an oxidation mechanism which requires extensive mobilization of oxygen ion within the lattice. It is interesting in this regard that extensive diffusion of oxygen from the bulk of the solid to the surface does not take place easily for $USbO_5$ and USb_3O_{10}; and in the oxidation reactions catalyzed by these materials, the proposal that primarily surface oxygen ions are involved receives support from the NGR measurements (*4*). In addition, the high covalence of the Sb–O bonds makes the generation of Sb^{3+} ions, as proposed in the oxidation mechanisms, more feasible.

In our discussion, we have assumed that the equilibrium crystal chemistry of stoichiometric U–Sb–O phases is important in understanding their catalytic activities. This is certainly a useful approach, as demonstrated in this study and in previous ones (*3–5*). Clearly, however, the special character of the surfaces and role of defects are important, too, and our study has provided little in the way of direct proof or disproof of the defect structures proposed on the basis of indirect kinetic evidence (*3–5*).

In summary, the covalency of the Sb–O bonds in $USbO_5$ and USb_3O_{10} is higher than that in pure Sb–O phases and this difference in bonding is suggested as being important in accounting for the higher activity as oxidation catalyts of the U–Sb–O phases. This is believed to be due to the ease with which Sb^{5+} can be reduced reversibly to Sb^{3+} as a result of the considerable electron transfer from O to Sb^{5+} already present in the highly covalent bonds. The suggestion that there is one Sb site in $USbO_5$ and at least two Sb sites in USb_3O_{10} receives further support from the present study. The results of this study (especially the isomer shifts) suggest that the difference in the activities of $USbO_5$ and USb_3O_{10} arises more from differences in atomic topologies, geometries, and possibly synergistic effects involving uranium than from differences in local bonding properties of Sb. Last, the ^{121}Sb NGR technique is an easily applied technique for quantitative determinations of the relative amounts of different Sb phases in a multiphase mixture when the antimony exists in different valence states in the different phases. A similar conclusion was also reached in a study directed specifically at the quantitative analysis of multiphase Sb–O materials (*12*).

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