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# Oxide Acid–Base Reactions Relating to the Inhibition of Vanadium Attack on REY Zeolite Catalysts

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Certain materials, especially Sn, passivate the rare earth-exchanged Y zeolite (REY) used in petrochemical fluid-cracking catalysts against vanadium degradation caused by V impurities in the feed oil. The mechanism of passivation was investigated here from the standpoint of high-temperature oxide acid–base reaction; i.e., where the controlling factors were considered to be Lewis acid–base reactions between $V_2O_5$, the RE oxides, $SnO_2$, etc. Molten salt tests at 680°C showed $SnO_2$, presumably because of its acidic nature, to be essentially nonreactive with $V_2O_5$ or $Na_2O$–$V_2O_5$ compounds. A hypothesis was developed to explain how the passivation effect by Sn might result from the unique resistivity of $SnO_2$ to reaction with $V_2O_5$. © 1991 Academic Press, Inc.

## INTRODUCTION

Many thousands of tons per year of rare earth-exchanged Y zeolite (REY) are used in the fluid-cracking catalysts (FCC) employed in petrochemical refining (*1*). Zeolites have a negatively charged aluminosilicate framework, where the amount of negative charge depends on the ratio of $AlO_2^-$ to $SiO_2$ groups. Charge-compensating cations such as $Na^+$ are required within the zeolite pore network to obtain electrical neutrality and structural stability. To produce REY zeolite, mixtures of RE cations (usually as the chloride) are exchanged to replace about 60 to 85% of the original cations occurring in the zeolite. The RE chlorides are prepared from mineral ores, and routinely have an RE composition of cerium (about 50%), lanthanum (30%), neodymium (15%), praseodymium (5%), and other (1–5%). Addition of the RE cations improves the catalytic properties of the zeolite, and also stabilizes the zeolite crystal structure against thermal and hydrothermal degradation during catalyst regeneration.

However, REY zeolite is degraded by the vanadium contained in many petroleum crudes, and serious problems arise when these oils are refined. Vanadium reacts with REY zeolite, causing destabilization and destruction of the zeolite crystal structure and loss of catalytic activity. Many aspects of the vanadium attack are still uncertain, but it is generally accepted that: (i) vanadium-containing organic compounds are deposited on the catalyst during the catalytic cracking process; (ii) these compounds are converted to $V_2O_5$ (mp 690°C) during the regeneration of the catalyst where temperatures can reach 750–900°C; and (iii) the $V_2O_5$ segregates to the zeolite particles in the catalyst, where it reacts destructively with the zeolite (*2*). The compound $CeVO_4$ has been identified on degraded REY, indicating a removal of Ce from the zeolite structure by reaction with $V_2O_5$ (*3*). Other work suggests that a low-melting RE–vanadate phase is formed by the $V_2O_5$ reaction, with oxygen being extracted from the zeolite framework in the vanadate formation process so as to cause collapse of the zeolite crystalline structure (*4*). An alternative theory is that $V_2O_5$ reacts with steam in the catalyst regenerator to produce vanadic acid ($H_3VO_4$), which destroys the zeolite $Al_2O_3/SiO_2$ framework by acid hydrolysis (*5*).

A number of inhibitors have been devel-

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oped to alleviate vanadium attack on REY zeolite catalysts. These include magnesium oxide-containing vanadium scavengers such as sepiolite, $Mg_8Si_{12}O_{30}(OH)_4$, which remove V from the feed stock by magnesium vanadate formation (*3*). Other materials such as Sb, Bi, Sn, Sn–Sb compounds, Ba, P, and B (*3*), as well as Al, Ti, Li, and W (*6*), have also been reported to inhibit vanadium attack. Tin in particular is said to be effective against vanadium. How tin and the other cited elements inhibit vanadium attack has been unknown, except for the general assumption that they caused formation of "inert compounds" on the FCC surface (*3*). Recently however, Occelli and co-workers (*6–9*) have made a detailed investigation of the vanadium poisoning of FCC catalysts and the inhibition effect of tin. From Mossbauer, electron paramagnetic resonance, and luminescence data, they conclude (*7*) that tin is oxidized to $Sn^{4+}$, and that a complex of $Sn^{4+}$, $V^{5+}$, and oxygen forms that leads to the passivation of vanadium when deposited on the zeolite. They speculate that the complex may be a compound like $V_2SnO_7$ (i.e., $SnO_2 \cdot V_2O_5$) or similar higher molecular weight species.

The temperatures and conditions involved in the vanadium degradation of REY zeolite are similar, in many ways, to those encountered in vanadate attack on $ZrO_2$ thermal barrier coatings (TBC) in engines burning V-containing fuel. For TBC usage, zirconia must be stabilized in a tetragonal crystal structure by addition of 5–20 w/o of such oxides as $Y_2O_3$ or $CeO_2$, to prevent the catastrophic tetragonal-to-monoclinic structure transformation that would otherwise occur during the engine thermal cycling. When the engine intake contains both vanadium and sodium (Na is ubiquitous), these are oxidized in combustion, and depending on the Na/V ratio, produce low-melting sodium vanadate deposits as shown in the phase diagram by Kolta *et al.* (*10*). These deposits destroy the zirconia TBC by leaching out the stabilization oxide by $YVO_4$ or $CeVO_4$ formation, e.g.,

$$2CeO_{2\,(a<1)} + V_2O_{5\,(a<1)} = 2CeVO_{4\,(a=1)} + \tfrac{1}{2}O_2, \quad (1)$$

where $CeO_2$, by virtue of being in solid solution, and $V_2O_5$, by compound formation or solution, may both have activities well below 1. The reaction between vanadium compounds and ceramic oxides appears to be largely controlled by the relative Lewis acid–base nature of individual oxides (*11*). This is demonstrated in Fig. 1, where classic acid–base behavior is exhibited; i.e., acids react with bases, and vice versus, but there is little reaction when the Lewis acidities of the ceramic and corrodent oxides are nearly "matched." It is important to note that the point of minimum reactivity is marked by a transition in acid–base reaction behavior. For example, $NaVO_3$ in Fig. 1 reacts as an acid with basic $Y_2O_3$ to yield $YVO_4$, but as a base with acidic $Ta_2O_5$ to yield $Na_2Ta_4O_{11}$. A similar behavior has been shown by Rapp and co-workers (*12*) for the reaction of transition metal oxides with molten $Na_2SO_4$ of varying $Na_2O$ (or $SO_3$) activity. Insight of this type has led to the identification of $Sc_2O_3$ (more acidic than $Y_2O_3$) as a promising vanadate-resistant stabilizer for $ZrO_2$ (*13*).

Because of the unique zeolite structure, one may question whether the exchanged RE cations and inhibitors such as Sn can be

—INCREASING ACIDITY→

| INCREASING ACIDITY ↓ | $Na_3VO_4$ | $NaVO_3$ | $V_2O_5$ |
|---|---|---|---|
| $Y_2O_3$ | NR | $YVO_4$ | $YVO_4$ |
| $CeO_2$ | NR | NR | $CeVO_4$ |
| $ZrO_2$ | NR | NR | $ZrV_2O_7$ (BUT SLOWLY) |
| $GeO_2$ | $Na_4Ge_9O_{20}$ | $Na_4Ge_9O_{20}$(*) | NR |
| $Ta_2O_5$ | $NaTaO_3$ | $Na_2Ta_4O_{11}$ | $\alpha$-$TaVO_5$ |

NR = NO REACTION
(*) AS PPT FROM $H_2O$ SOL'N

FIG. 1. Acid–base reaction behavior between ceramic oxides and vanadium compounds of different $V_2O_5$ activity. Reprinted, by permission of The Electrochemical Society, Inc., from Ref. (*11*).

considered to react as oxides. Indeed, the rare earth cations are thought to form polynuclear hydroxy complexes within the sodalite cages of the zeolite structure (*1*). However, the RE cations tend to be removed from the zeolite structure as hydrated rare earth oxides ($RE_2O_3 \cdot 3H_2O$) during hydrothermal treatment (*1*). Also, the rare earths, as well as Sn and the other reported inhibitors (e.g., Al, Ti, W), are oxygen active and form oxides which are stable to 900°C and above at oxygen partial pressures lower than $10^{-10}$ bar. It seems a reasonable assumption therefore that, at some point in the 600–900°C treatment of REY zeolite, the RE cations, Sn, and other inhibitors may react essentially as oxides. Sodium oxide is also a probable reactant, resulting either from residual Na in the REY zeolite, or Na in the feed stock as the result of poor desalting (*14*).

Following the reasoning above, we have applied Lewis acid–base oxide reaction concepts from the field of ceramic hot corrosion to possibly explain Sn passivation of vanadium attack on REY catalyst. Although primary interest was with Sn (or $SnO_2$), our investigation included $Sb_2O_3$ and $Bi_2O_3$, since Sb and Bi represent other examples of "nonvanadium scavenging" inhibitors.

## EXPERIMENTAL METHODS

Thoroughly ground mixtures of $SnO_2$ (mp 1630°C), $Sb_2O_3$ (mp 656°C), or $Bi_2O_3$ (Tr 704°C, mp 860°C), with $V_2O_5$ or various sodium vanadates (Table 1) were prepared and heated at 680°C in a Pt boat under flowing air (200 ml/min) in a quartz-lined furnace. After 20–24 h, the mix was removed from the furnace and boat, reground, and X rayed for evidence of reaction. Stoichiometric ratios of oxide to vanadium compound were used, except for certain cases where up to 1 × excess of vanadate was employed. The oxides were of 99.9% or higher purity, and the $V_2O_5$, $NaVO_3$, and $Na_3VO_4$ were Fisher certified or purified reagents. A number of duplicate tests were made at 630°C (below the $Sb_2O_3$ mp) and at 800°C, but these yielded no difference in results. The XRD analyses were made with a Norelco X-ray diffractometer using Cu radiation and graphite monochromation.

TABLE 1

Reaction Behavior of Selected Inhibitor Oxides with $V_2O_5$ and Sodium Vanadates of Decreasing $V_2O_5$ Activity at 680°C

| Vanadium Compound | Inhibitor Oxide | | |
|---|---|---|---|
| | $SnO_2$ | $Sb_2O_3$ | $Bi_2O_3$ |
| $V_2O_5$ | NR | $SbVO_4$ | HT $BiVO_4$ |
| $Na_2V_{12}O_{31}$ | NR | NR(?) | HT $BiVO_4$ |
| $NaV_3O_8$ | NR | UP | HT $BiVO_4$ |
| $NaVO_3$ | NR | $(Na,Sb)Sb_2O_7$ | UP |
| $Na_3VO_4$ | NR | $NaSbO_3$ | UP |

*Note.* NR, no reaction; UP, unidentified product; HT, high temperature.

## RESULTS AND DISCUSSION

Table 1 summarizes the results of our experiments. No reaction was found between $SnO_2$ and $V_2O_5$, or any of the sodium vanadates, at the experimental 680°C temperature. This judgment was based not only on the fact that no new compound peaks could be identified, but also that the $SnO_2$ pattern remained strong, indicating little or no consumption of $SnO_2$. Reaction between $SnO_2$ and $Na_2O$-rich $Na_3VO_4$ was expected since compounds such as $Na_2SnO_3$ (formed by heating $Na_2CO_3$ with SnO) are known, but no evidence of reaction was found in three separate tests at 630, 680, and 800°C.

The strong resistance of $SnO_2$ to high-temperature reaction with $V_2O_5$ or $V_2O_5$-rich vanadates shown in Table 1 is consistent with DTA measurements where $V_2SnO_7$ was found to decompose to $SnO_2$ and $V_2O_5$ below 450°C (*15*). Evidently the Gibbs free energy of formation for $V_2SnO_7$ is small and becomes positive at relatively low temperatures. This low tendency to reaction presumably results from the close matching of the Lewis acidities of $SnO_2$ and $V_2O_5$, but other bonding factors cannot be ruled out.

The reaction series for antimony oxide in Table 1 shows $Sb_2O_3$ forming $SbVO_4$ with $V_2O_5$, but then converting from basic to acidic behavior, and thus having a minimum in reactivity, at a $Na_2O$–$V_2O_5$ composition of about $Na_2V_{11}O_{31}$. (The notation "NR?" is used because, although a strong $Sb_2O_3$ pattern remained, some unidentified peaks were present.) The $Na_2V_{12}O_{31}$ composition corresponds, in the practical sense, to $V_2O_5$ containing some small amount of $Na_2O$. On the other hand, $Bi_2O_3$ reacts as a base down to $NaV_3O_8$, and its minimum reactivity likely lies at a $Na_2O$–$V_2O_5$ composition near $NaVO_3$ or lower. Thus as the $V_2O_5$ content of the vanadate is reduced, the $V_2O_5$ activity is lowered to levels at which $SbVO_4$ and $BiVO_4$, respectively, cease to be stable at 680°C. No chemical reaction of $Sb_2O_3$ or $Bi_2O_3$ then occurs, at 680°C or higher, unless the $V_2O_5$ activity is lowered farther, and the $Na_2O$ activity of the vanadate increases to the point where $Na_2O$ itself begins to react with $Sb_2O_3$ and $Bi_2O_3$.

There appears to be essentially little difference between the vanadate reactions of $Sb_2O_3$ and $Bi_2O_3$ and those of $SnO_2$, except that the $SnO_2$ "reaction minimum" is broader, and perhaps centered at a different site on the $Na_2O$–$V_2O_5$ composition scale, than those of $Sb_2O_3$ and $Bi_2O_3$. A behavior similar to $SnO_2$ has been found by Shi and Rapp (*12, 16*) for $SiO_2$, which shows no chemical reactivity over several orders of magnitude of $Na_2O$ activity in $SO_3$-rich $Na_2SO_4$ melts.

The results in Table 1 indicate that $SnO_2$ probably does not passivate vanadium attack by forming inert residues with $V_2O_5$. Inert compounds are normally those produced from reagents which have an exceptionally high affinity for interaction. Rather, it appears to be the resistance of $SnO_2$ to Lewis acid–base reaction with $V_2O_5$ that is important.

An explanation of the inhibitive effect of $SnO_2$, based on this idea, might go as follows: The rare earths (Ce, La) are exchanged into the zeolite as aqueous cations, but calcining, at 540°C and higher, dehydrates the RE cations and converts them to oxide or hydroxide-like species which stabilize the zeolite. During the regeneration thermal cycle, and perhaps predominantly during the ca. 730°C steaming treatment, the vanadium-containing organic matter on the catalyst is converted to a mobile, molten phase which, because of Na impurities, is probably not actually pure $V_2O_5$, but rather a low-melting $Na_2O$–$V_2O_5$ mixture. This vanadate species segregates to the REY zeolite phase of the FCC catalyst and reacts *preferentially* with $CeO_2$ (*3*) to form $CeVO_4$, the Ce possibly having been converted from hydroxyl-like lattice bonding to "free" $CeO_2 \cdot 3H_2O$ during steaming (*1*). The $CeVO_4$ produced is a stable compound, and its formation may in fact be the driving force for the segregation of $V_2O_5$ to the REY zeolite phase. Removal of Ce causes destabilization of the REY zeolite, and thereby loss of its crystal structure and catalytic activity.

Since $La_2O_3$ is the more basic oxide (*17*), it would be expected to react with $V_2O_5$ before $CeO_2$ does. The fact that $CeVO_4$ is formed preferentially thus implies that the activity of $La_2O_3$ (or La) has been reduced, presumably because it is bound more strongly than Ce to the acidic aluminosilicate zeolite framework. On the other hand, when the zeolite is stabilized only by La, reaction with $V_2O_5$ produces $LaVO_4$ readily (*3*). This suggests that a number of bonding sites with different energy levels, or of different degrees of accessibility as proposed by Stencel (*3*), are involved in the stabilization process, and that removal of cations (or oxides) from even the lower bonding energy sites can initiate REY zeolite destabilization.

Therefore $SnO_2$ may be effective because it has the appropriate acidity and other bonding characteristics (i) to resist reaction with $V_2O_5$, and (ii) to replace Ce (or other RE) lost from the weaker stabilization sites by vanadate formation, and so augment the overall RE stabilizing effect as to preserve the zeolite structure in the presence of

$V_2O_5$. Such $SnO_2$ action may be occurring, for example, in the experiments of Anderson *et al.* (*9*) on the Sn passivation of Eu-exchanged Y zeolite (EuY). Under $V_2O_5$ attack, a certain amount of $EuVO_4$ was formed, with Eu thus being evidently removed from the RE stabilization sites, even in the presence of Sn. However, the EuY crystallinity was preserved, perhaps because $SnO_2$ replaced the Ce (or $CeO_2$) lost from the weak stabilization sites and thus maintained the zeolite crystallinity.

Our research therefore suggests that Sn is an effective passivator because it is nonreactive with $V_2O_5$. On the other hand, Ocelli *et al.* (*6–9*) consider that Sn is effective because it reacts to form an $Sn^{4+}$–O–$V^{5+}$ complex on the zeolite surface which minimizes V-zeolite interactions and preserves zeolite crystallinity (*9*). Since our results show no chemical reaction between bulk $SnO_2$ and $V_2O_5$, at the temperatures involved, we believe any tendency to form inert compounds or complexes between just Sn, V, and O is likely to be small. However, a "three-way" complex between $SnO_2$, $V_2O_5$ and the zeolite surface might be possible even if $SnO_2$ and $V_2O_5$ do not react directly. Suib *et al.* (*7*) have observed changes in Mossbauer and luminescence spectra which they generally describe as indicating complex formation between Sn and V oxides *on* the zeolite surface, but it may be that the spectra changes actually indicate complex formation between Sn and V oxides *and* the zeolite surface. The critical question appears to hinge on how much, or in what way, the reaction chemistry between tin and vanadium oxides may be affected when these oxides are adsorbed, or otherwise bound, onto a zeolite structure. The fact that $EuVO_4$ was formed during vanadium attack on EuY (*9*), even when Sn was present and the $Sn^{4+}$–O–$V^{5+}$ complex presumably produced, implies that a $V_2O_5$ activity exists in equilibrium with the $Sn^{4+}$–O–$V^{5+}$ complex which is sufficient to allow the reaction,

$$Eu_2O_{3\,(a<1)} + V_2O_{5\,(a<1)} = 2EuVO_{4\,(a=1)}.$$

Further investigation is needed of the thermodynamic activity relationships between the different oxides and possible complexes. It might be feasible, for example, to determine the $V_2O_5$ activity associated with the $Sn^{4+}$–O–$V^{5+}$ complex by gas phase equilibrium or other techniques.

Stabilized zirconia oxides are dense ceramics produced generally at 1400°C and above, and where the stabilizing oxide exists in solid solution in the $ZrO_2$ matrix. They differ greatly in structure from the highly porous REY zeolites, where the stabilizing RE cations are exchanged from aqueous solution into the unique cage structure of the zeolite framework. Nonetheless, our findings here suggest that vanadium attack on REY zeolite, just as on stabilized zirconia TBCs, is largely controlled by high-temperature Lewis acid–base oxide reactions. Our results also appear to provide an explanation for the inhibitive effect not only of Sn, but of other acidic oxide forming elements such as Sb and Bi.

## CONCLUSIONS

The degradation of REY zeolite by vanadium during petrochemical refining occurs under conditions much like those encountered in the vanadate hot corrosion of RE oxide-stabilized zirconia. It is reasonable therefore that the oxide acid–base reaction concepts that help explain the vanadate corrosion of ceramic oxides should also be applicable to REY degradation.

Study of the 680°C reaction behavior of $SnO_2$, $Sb_2O_3$, and $Bi_2O_3$ (oxides of elements reported, esp. Sn, to passivate REY against V attack) with $V_2O_5$ and the different sodium vanadates (Table 1) indicates $SnO_2$ in particular to be highly resistant to reaction with $V_2O_5$ or $Na_2O$–$V_2O_5$ compounds.

The passivation effect of Sn and the unique resistivity of $SnO_2$ to $V_2O_5$ reaction are almost certainly related. Because of its resistance to $V_2O_5$ reaction, it seems unlikely that Sn passivates REY zeolite against vanadium degradation by forming "inert compounds" with $V_2O_5$ on the zeolite surface. Rather, it may be that, by virtue of its nonreactivity, $SnO_2$ is able to remain on (or in) the zeolite essentially in competition with $V_2O_5$, and to augment the overall RE stabilization effect and preserve the zeolite crystal structure by occupying low-energy stabilization bonding sites vacated, e.g., of Ce by $CeVO_4$ formation. Similar functions may be served by $Sb_2O_3$ and other acidic oxide inhibitors if the $V_2O_5$ contains certain amounts of $Na_2O$.

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