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Electrical Conductance of Catalysts in Contact with Gaseous Reactants

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Electrical conductivities were measured for several catalytic materials during reactions of industrial interest. It is shown that conductivity changes can be used to monitor both the composition of gaseous reactants in contact with catalysts and how catalysts are altered by the reactants. Most significant is the result that certain commercial supported metal catalysts, in which the major component is an insulating oxide such as SiO_2 or Al_2O_3, exhibit large differences in conductivity when contacted with oxidizing and reducing gases. This phenomenon is illustrated for supported Ni and Co catalysts in monitoring catalyst metal/oxide composition in O_2 and H_2 and also the effect of H_2S during the reaction of H_2 and CO. In addition, it is shown that coke deposited on insulating catalysts such as those used in hydrodesulfurization greatly increases the catalysts' conductivity and this can be used to observe the removal of coke by an oxidizing gas. Results for three semiconductor catalysts are presented in order to further illustrate the concept of electrical sensitivity of catalytic materials. These include descriptions of the effect of H_2S on ZnO, the changes in promoted Fe_2O_3 during the conversion of ethylbenzene to styrene, and the response of bismuth molybdate to propene/oxygen mixtures.

INTRODUCTION

One approach commonly taken in interpreting observations made in heterogeneous catalysis is to make use of the electronic theory of catalysis. Generally this involves attempts to correlate observed catalytic activities with bulk electronic properties. Such treatment of catalytic phenomena has been applied to pure metals (*1*), alloys (*2*), and semiconductor (*3, 4*) materials.

For semiconductor catalysts, much work has been done to relate catalyst activities to collective electronic properties such as ferromagnetism, ferroelectricity, conductivity, and position of the Fermi level and band gaps. Examples of this approach can be found in the literature for NiO (*5*), Fe_3O_4 (*6*), ZnO (*7*), MoO_3 (*8*), $CoFe_2O_4$ (*9*), and SnO_2–Sb_2O_4 (*10*). In addition, a review has been published on utilizing electrical properties in some cases to study transient response in heterogeneous catalysis (*11*).

Conductivity measurements done on catalysts under reaction conditions are described in a number of the references listed above. Such measurements carried out on polycrystalline powder samples do not provide intrinsic bulk values of the material but rather give an estimate of the main charge carrier concentration. Quantitative correlation with catalyst activity is difficult because of the uncertainty in interpretation of intergranular resistance and mobility changes. In addition, the higher surface areas of catalytic materials relative to sintered samples result in surface effects predominating. Therefore, conductivity changes of catalysts in contact with gaseous reactants are generally useful for qualitative description of events rather than as a basis for quantitative comparison with theory (*7*).

We used such a qualitative approach to *in situ* conductivity measurements in order to investigate a number of industrially important catalyst systems. Our purpose has

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been not to obtain a complete picture of electrical transport properties, but more practically, to demonstrate that conductivity measurements can be usefully correlated with catalytic phenomena. Some possible models for the conductivity changes in real catalyst pellets are, however, discussed and related to the structure of supported catalyst material.

While this paper describes results for a single-pellet reactor, our long-range goal is to show that in a typical fixed-bed reactor several catalyst tablets acting as sensors along the bed could provide input information for a monitor system which could be used to continuously control reaction conditions for maximum product formation.

Some of the catalysts were investigated more completely in order to obtain information on the nature of the charge transport in the catalysts. A brief discussion on the physical basis for the electrical conductivity changes is therefore also given.

EXPERIMENTAL

Conductivity measurements were done in a stainless-steel cell constructed of two Balzers high-vacuum flanges (1.33 in.). The top flange held two $\frac{1}{8}$-in. stainless-steel tubes as gas inlet and outlet. The bottom flange had a Feldmühle oxide–ceramic ultrahigh-vacuum current feedthrough welded in place.

A goldplated copper gasket was used to seal the cell. The base of the bottom flange was goldplated and it served as the bottom contact of the catalyst sample. The top contact was a stiff goldplated tungsten wire connected to the insulated electrode. Both the reactor base and wire electrode were in contact with thick gold films which were evaporated onto the sample prior to use. Proper contact between electrodes and sample is an important consideration in making conductivity measurements on granular materials. Our usual test of contact was to check the linearity of the current versus voltage response at conditions where the catalyst was fairly conducting.

Direct current measurements were done by applying 1 V from a B3000 Ultronix power supply across the catalyst in series with a decade resistor and measuring the voltage drop across the decade resistor (1–100 kΩ).

The decade resistor, r_d, was always chosen to give a voltage drop across it, V_d, much smaller than 1 V (≤ 50 mV). During these conditions the conductance of the catalyst sample is given by

$$G\ (\mathrm{mS}) = (V_d\ (\mathrm{mV})/r_d\ (\mathrm{ohm}).$$

Ar, H_2, O_2, CO, C_3H_6, and 1% H_2S/Ar were obtained in cylinders from Alfax AB and used without further purification. Ethylbenzene and *n*-heptane were of reagent grade from Merck and were passed over the catalyst by saturating an Ar carrier gas at room temperature. Catalyst activities were measured by injecting the reactor effluent at intervals from a Carle sampling valve into a Perkin–Elmer 800 gas chromotograph equipped with a flame detector. For propene oxidation, reaction products were also introduced into a Micromass Q 200 mass spectrometer by means of a capillary so that CO_2 concentrations could be measured.

All reactions were done at atmospheric pressure. We report gas velocities and catalyst weights under Results although the concept of space velocity is not very meaningful for a one-pellet reactor. Temperature was measured by means of a chromel–alumel thermocouple connected to the external reactor wall. The reactor was placed upright in a resistively heated furnace during the experiments.

Catalysts used were obtained from the following manufacturers: Harshaw, United Catalysts Inc., Shell, Nalco, Linde, and Ketjen. The samples were $\frac{3}{16}$- or $\frac{1}{8}$-in. tablets and $\frac{1}{8}$- or $\frac{1}{16}$-in. extrudates. We also prepared our own α-$2Bi_2O_3 \cdot 3MoO_3$ oxidation catalyst (*12*) and ZnO sulfur removal material (*7*) according to procedures described elsewhere. The calcined powders were

TABLE I

Catalyst	Description	Conductance, 20°C	Response to H_2–O_2
Ketjen Al_2O_3	No metal	1 nS	No
UCI G62RS	32% Co/Al_2O_3	1 nS	Yes
Harshaw Ni-3210T	35% Ni/proprietary	15 mS	No
Harshaw Ni-0104T	60% Ni/SiO_2		
	$\frac{3}{16}$ in.	0.3 mS	Yes
	$\frac{1}{8}$ in.	0.3 mS	Yes
	$\frac{3}{16}$ in. repacked	1 mS	No
Harshaw Ni-1404T	68% Ni/proprietry	5 mS	No
Nalco Nm 504	4% Ni, 13% Mo/Al_2O_3	1 nS	No

Note. nS = $10^{-9}\ \Omega^{-1}$, μS = $10^{-6}\ \Omega^{-1}$, mS = $10^{-3}\ \Omega^{-1}$.

compacted at 400 kg/cm^2 in order to obtain suitable samples.

RESULTS

We describe here six different systems where we observed changes in catalyst conductance as a function of reaction conditions. In addition, we mention two systems where we expected to observe some response but did not.

Response of Supported Ni and Co to O_2–H_2 Mixtures

Supported catalysts containing Ni and Co are sold commercially for hydrogenation reactions such as methanation, finishing of fats and oils, conversion of benzene to cyclohexane, and others. Generally these catalysts contain 20–70 wt% metal and 80–30% oxide support (SiO_2 or Al_2O_3) and often are supplied in a prereduced form, stabilized with adsorbed CO_2, so that activation is accomplished by heating to 200–300°C in an inert atmosphere.

Certain members of this catalyst group were observed to exhibit a change in conductance upon being oxidized and reduced at elevated temperatures. As shown in Table I, two members of the group available to us ranging from Ketjen γ-Al_2O_3 (0% metal) to Harshaw's Ni-1404 (68% Ni) were active electrically. As shown in the table, the two electrically active catalysts, UCI's G62RS and Harshaw's Ni-0104T, were quite different in metal content.

The manner of response of the two active catalysts was also quite different. G62RS was insulating at 20°C at our most sensitive scale (1 nS) and maintained its insulating character when heated in Ar (to desorb CO_2) and also in H_2. In O_2 it became quite conducting. We show in Fig. 1 that the catalyst's conductivity can be used to follow its apparent degree of oxidation in different O_2–H_2 mixtures. The data were obtained using a computerized gas mixing apparatus to systematically control a flow of Ar, O_2, and H_2 over the catalyst at 400°C (*13*). During the experiment the H_2 content of the flow was 1.5% and the O_2 content was varied linearly (25-min on, 5-min off intervals) from 0.4 to 2.0%. Total gas flow was constant at 200 cm^3/min. As shown in the figure, each higher O_2 addition to the flow resulted in an increase in the catalyst's conductance. During the 5-min O_2-off period the catalyst returned to its original insulating condition. We found the conductance to be 80 μS in pure O_2 and 40 nS in pure H_2. We checked the contribution of thermoelectric power to the data by removing the 1 V applied across the sample and found it to be about 2% (*9*).

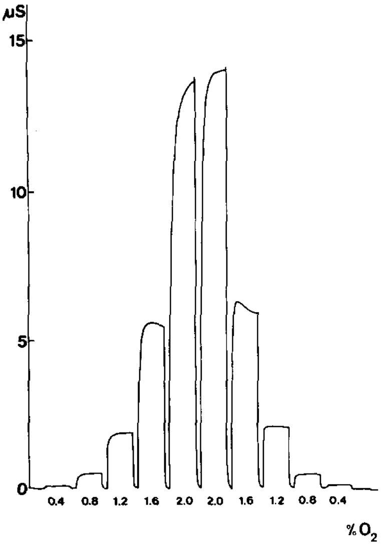

FIG. 1. Response of G62RS at 400°C to a gas stream composed of a constant 1.5 vol% H_2 and O_2 content varied as shown along the X axis, diluted in Ar. For each concentration, O_2 was on for 25 min and off for 5 min.

The other electrically active catalyst, Harshaw's Ni-0104T, behaved quite differently. After being heated to elevated temperature in Ar, Ni-0104T remained very conducting both in Ar and in pure H_2. A number of treatments in O_2 and H_2 were required to condition the catalyst so that it would respond to O_2 in a similar manner as G62RS. In Fig. 2 we show a typical treatment sequence at 425°C necessary to transform the catalyst ($\frac{3}{16}$-in.) into a sensor condition (1 min O_2, Ar flush, H_2 cycles). It is important to note that the other Harshaw catalysts listed in Table I, Ni-3210T and Ni-1404T, could not be changed from their conducting state using the same procedure described in Fig. 2.

We also tested tablets from another preparation batch of Ni-0104T ($\frac{1}{8}$-in) and found them to be similarly electrically active. This would seem to indicate good reproducibility in the manufacturing process with regard to the electrical properties of the catalysts. However, when we pulverized some $\frac{3}{16}$-in. tablets and repacked them at 400 kg/cm^2, the ability to respond to H_2–O_2 even after the treatment cycles was lost.

It should also be noted that these measurements were done on tablets cut in half so that one electrode was in contact with the center of the catalyst. Oftentimes, tablets have a hard outer skin which may have some influence on the observed electrical properties.

Response of Supported Ni and Co to H_2S during CO + H_2 Reaction

A serious problem in a number of catalytic processes, such as upgrading of coal-derived synthesis gas, is the deactivation of the catalyst by sulfur compounds present in the feed. A number of papers have described such catalyst deactivation (*14–17*), and work is continuing in an effort to understand the mechanism of both sulfur poisoning and regeneration for methanation and Fischer Tropsch catalysts.

The catalysts described in the previous section as responding to O_2–H_2 mixtures were also observed to change conductance upon the introduction of H_2S into a mixture of H_2 and CO passing over the catalyst. In Fig. 3 we show the change in conductivity of Ni-0104T (previously pretreated as described in Fig. 2) when H_2S was added to the system. A mixture of 24 cm^3/min H_2 and 5.5 cm^3/min CO was passed over a 70-mg pellet at 275°C and the hydrocarbon prod-

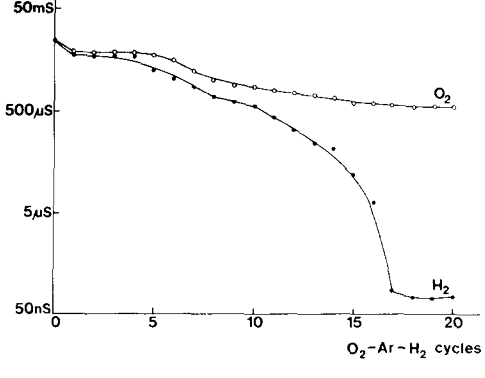

FIG. 2. Pretreatment of Ni-0104 at 425°C in alternating O_2 and H_2 streams necessary to transform the catalyst into a sensing state.

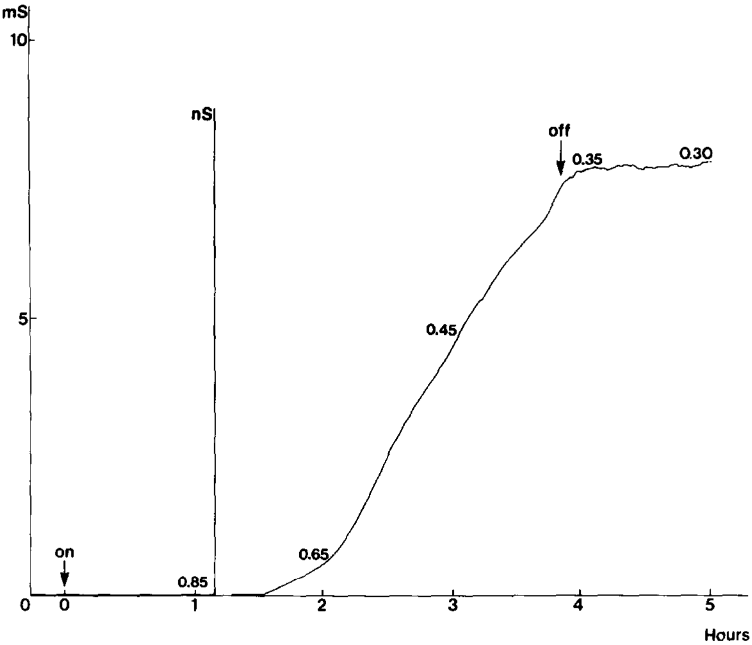

FIG. 3. Response of Ni-0104 at 275°C to 200 ppm H_2S (in at $t = 0$) in a stream of H_2 and CO. Numbers along the curve represent hydrocarbon product normalized to the production at $t = 0$. Initial response to H_2S after 1 hr was recorded on the nanosiemens scale.

uct was measured at intervals by the FID detector. After 1 to 2 hr to establish a steady-state product formation H_2S was introduced into the reaction stream at ~200 ppm ($t = 0$ in Fig. 3). The catalyst continued to be insulating for about 1 hr, but then exhibited a sharp response to the H_2S on the nanosiemens scale. We then followed the conductance increase on the 10-mS scale for several hours. The hydrocarbon production normalized to 1 at $t = 0$ is shown as numbers along the curve.

As shown in the figure, catalyst deactivation was observed before the first indication of change in conductance. The increase in conductance was halted by stopping the H_2S input to the reactants. The final conductance level reached in Fig. 3 was stable in flowing H_2 overnight. However, raising the temperature to 375°C caused it to decrease (Fig. 4), but not back to its original highly resistive state.

G62RS exhibited a similar response to H_2S under the same reaction conditions. It

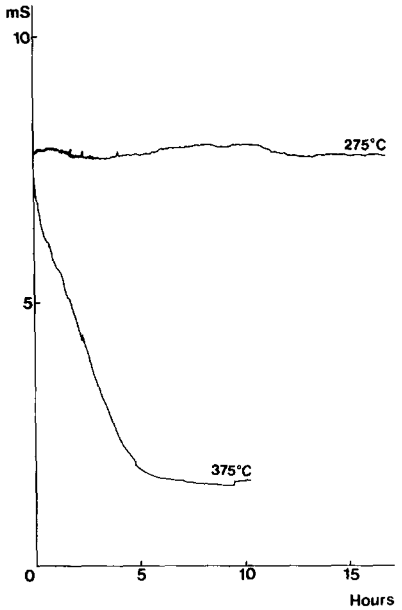

FIG. 4. Response of Ni-0104 poisoned by H_2S as described in Fig. 3 to treatment in pure flowing H_2 at 275°C and then later at 375°C.

did not deactivate to the same level as Ni-0104T for 200 ppm H_2S in the feed, but again the highly conducting state caused by the H_2S was stable in H_2 at 275°C. However, G62RS could be returned to its original highly insulating state by further treatment in H_2 at 350°C.

In light of the fact that the usual concentration of H_2S discussed in the literature for poisoning the CO + H_2 reaction is 1–10 ppm (*15*), it is perhaps necessary to mention what we observed regarding the sensitivity to H_2S of the catalysts investigated. Although we did not adequately explore the H_2S partial pressure–temperature relationship of the systems, it was clear that lower temperatures favored higher sensitivity. First response to H_2S on our most sensitive scale was observed for G62RS at 275°C after 1–2 hr in ~200 ppm H_2S, after 3–4 hr in ~80 ppm H_2S, and after about 14 hr in ~40 ppm H_2S.

The slow response suggests that a special-purpose thin-film sensor of the catalysts could be an interesting alternative as a faster monitor for the poisoning of the catalyst.

Conductance of Coke on Hydrotreating Catalysts

A $\frac{1}{16}$-in. extrudate of Nalco NM 504 hydrotreating catalyst (4 wt% Ni, 13 wt% Mo on Al_2O_3 support) which was insulating at 20°C was found to exhibit no response to H_2 or O_2 at 400°C. Several extrudates were separately exposed to a gas mixture of 5% C_2H_2 in Ar at 400°C for 2 hr and cooled in flowing Ar. Catalyst weight gain was about 14%. These were then tested in the conductivity cell and its was observed that after the C_2H_2 treatment the catalysts exhibited a conductance level of 1–10 μS in Ar at 400°C and that the conductance could be decreased to as low as 10 nS by 30 min treatment in 1–5% O_2 in Ar. We attribute this decrease in conductance to the removal of some coke from the catalyst (an initial increase in conductance was observed upon first exposure to O_2 because of the reaction exothermicity).

However, by determining the weight loss of several samples after further treatment at 550°C in air, it was found that the observed decrease in conductance down to the level of an uncoked, fresh catalyst was caused by a loss of only 10–20% of the total coke on the catalyst. Thus one must be careful in interpreting such data, since if the coke removal had been done at 550°C a direct relationship between total coke removal and loss of conductance would have been inferred, whereas it appears that the conductance level of the coked catalysts relative to the clean is actually due to only a fraction of the coke present (which is removable at 400°C).

Unfortunately we were not able to observe coke buildup on the catalysts because the C_2H_2 decomposition reaction also deposited coke across the insulating ceramic of the electrode in the reactor cell which resulted in false conductance levels. On the other hand, this indicates that the buildup of coke is generally possible to detect by electrical measurements.

Response of ZnO to H_2S in H_2

Pure ZnO in extrudate form is used to purify gas streams such as natural gas and naphtha containing H_2S. Sulfur removal is accomplished by converting the oxide to sulfide and it is thus not a catalytic process. The usual configuration is to place the extrudates in trays with the gas entering the top of the reactor. Operating conditions are up to 50 psig and 400°C.

As has already been mentioned, much work has been done on investigating the electrical properties of ZnO under catalytic reaction conditions (*7*). We also observed that when ZnO is exposed to H_2S in a reducing environment, the apparent accumulation of S in the solid can be observed by monitoring the change in conductivity. In Fig. 5 we show this result. A 70-mg pellet of ZnO at 325°C was found to have a conduc-

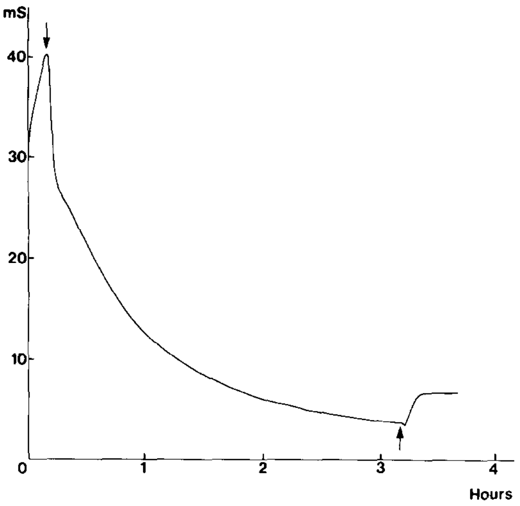

FIG. 5. Response of ZnO at 325°C to 300 ppm H_2S in H_2 carrier gas.

tivity level of 10 μS in O_2. In 75 cm^3/min H_2 the conductance level increased to 50 ms, but addition of 300 ppm H_2S into the gas flow ($t = 0$) caused a decrease in the conductivity as shown in the figure. When H_2S was removed, there was an initial small increase in conductivity to a constant level for 6 hr, followed by a slow increase to 50 ms after 20 hr.

Response of Promoted Fe_2O_3 during Styrene Production

An important reaction in the petrochemical industry is the dehydrogenation of ethylbenzene to styrene. The most effective styrene catalysts are promoted iron oxides. The reaction is run at about 600°C, 1 atm pressure, and with a high molar ratio (>10) of steam to ethylbenzene (EB). The steam in the reaction stream serves several purposes. As a diluent it shifts the equilibrium-controlled system to higher styrene conversion, it removes coke from the surface, supplies heat for the endothermic reaction, and as an oxidant equilibrates the catalyst to an oxidation state most effective for styrene production.

An extensive review describing iron oxide catalysts has been published by Lee (*18*). He described several aspects of the dehydrogenation reaction, including the electronic factor with respect to promoter ions in the lattice. Contact potentials were measured for catalysts containing different alkali and alkaline earth cations after exposure to a reaction mixture at 600°C and quenching in Ar. In an earlier note, Lee also described Seebeck emf measurements at 600°C on compacted powders of Zn and Zr containing catalysts (*19*).

Shell 105 (7% K_2O, 2% Cr_2O_3, 91% Fe_2O_3) is one of the commercial catalysts used for styrene production. For this type of catalyst it has been shown that Fe_2O_3 is in fact converted to Fe_3O_4 during use. Water vapor added to the system and H_2 from the reaction equilibrate the catalyst:

$$Fe_2O_3 \underset{H_2O}{\overset{H_2}{\rightleftharpoons}} Fe_3O_4 \underset{H_2O}{\overset{H_2}{\rightleftharpoons}} FeO.$$

Catalysts are more active and selective for styrene production after they have "aged" (become reduced), and oftentimes prereduction with H_2 or NH_3 is done on a new catalyst charge.

We followed such catalyst improvement with time by observing the conductance change of Shell 105 during exposure to an H_2O/EB/Ar mixture (10/1/80 molar, 30 cm^3/min total flow) at 600°C. Products were introduced into the gas chromatograph from a heated sampling valve and separated on a 6-ft DC-200, 15% on Chrom W column at 80°C. One can see in Fig. 6 that the wt% styrene in the reactor effluent relative to ethylbenzene, benzene, and toluene increased as the catalyst conductivity increased. At 600°C the conductivity level was 0.5 mS in O_2 and 40 mS in H_2. A short circuit in our system is 120 mS (due to contact resistances etc.), which indicates that the reduced catalyst is almost a metallic conductor in agreement with Lee (*18*).

One other styrene catalyst, UCI's G-64 (20% K_2CO_3, 2.5% MoO_3, 5% CeO_2, 60% Fe_2O_3), exhibited a similar response to oxidation and reduction.

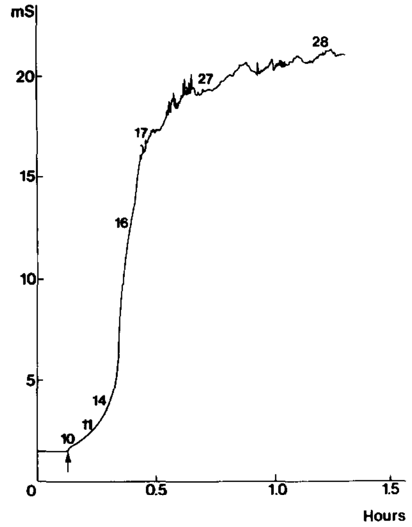

FIG. 6. Response of Shell 105 at 600°C during the conversion of ethylbenzene to styrene. Numbers along the curve represent the wt% styrene product relative to ethylbenzene, benzene, and toluene in the reactor effluent.

Response of Bismuth Molybdate to Propene–O_2 Mixtures

Another important reaction in the petrochemical industry is the selective oxidation of olefins to aldehydes and acids. The discovery of bismuth molybdate-based catalysts for the selective (amm) oxidation of propene (*20*) has been followed by numerous other mixed oxide systems. It is generally agreed that the reactions proceed by incorporation of lattice oxygen in the olefin followed by reoxidation of the lattice from the gas phase (*21*). Such a redox mechanism has been proven for bismuth molybdate in that the catalyst will oxidize propene in the absence of gas-phase oxygen and the oxygen so removed in the reaction can be quantitatively replaced.

Peacock *et al.* have published a study of the electrical conductivity of the bismuth molybdate system upon exposure to various propene–oxygen mixtures (*22*). We included our own data here in order to emphasize how rapidly one can continuously monitor changes in the lattice oxide for this system.

We show in Fig. 7 the conductivity changes associated with O_2/propene/Ar flows (cm^3/min) of 24/6/70, 15/6/79, and 6/6/88 over a 70-mg pellet of α-$2Bi_2O_3 \cdot 3MoO_3$ at 475°C. The data were recorded on the 10-μS scale. As a comparison, the conductance level of the catalyst in propene/Ar was 50 mS. We added additional catalyst to the reactor (0.5 g total) to obtain sufficient product for analysis. Acrolein formation was about 10 wt% by FID and did not significantly change with gas composition. Carbon dioxide formation was monitored by mass spectrometry, and the relative peak heights for different gas compositions (normalized to that at O_2/propene = 4) are shown in the figure.

No Response of Ni–Mo Hydrotreating Catalyst to H_2S in H_2

A $\frac{1}{16}$-in. extrudate of Nalco NM504 hydrotreating catalyst was heated to 375°C in Ar. At this temperature the catalyst exhibited no electrical response to O_2 or H_2. A gas stream of Ar/H_2S/H_2 (cm^3/min) (50/0.5/25) flowing over the catalyst for several hours caused no change in the conductivity.

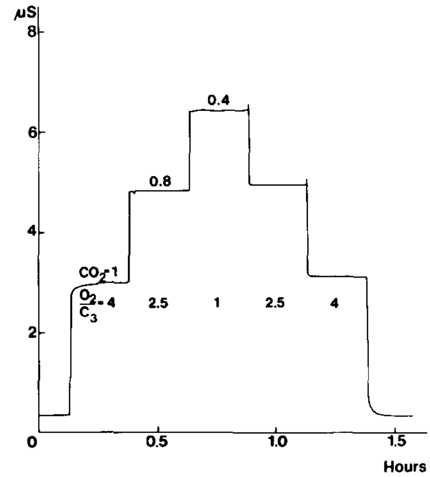

FIG. 7. Response of bismuth molybdate at 475°C to an Ar carrier gas containing different oxygen/propene volume ratios. Normalized CO_2 formation is shown for each case.

No Response of REY Zeolite to Carbon Buildup during n-Heptane Cracking

A $\frac{1}{16}$-in. extrudate of Linde SK-500 REY zeolite which was insulating at ambient conditions was heated to 475°C in Ar. The zeolite exhibited no response to O_2 or H_2. *N*-Heptane in Ar carrier was passed over the catalyst for several hours, and while deactivation of cracking was observed by GC, there was no change in conductivity due to carbon buildup on the catalyst.

Several extrudates were treated at 400°C in 5% C_2H_2/Ar so that weight gain from coke deposition was about 14%. However, these extrudate exhibited a conductance level (nS) essentially the same as uncoked extrudates when heated to 400°C in Ar.

Temperature Dependence of Conductivity

The temperature dependence of the conductivity was also investigated for some of the catalysts and the results are shown in Figs. 8 and 9.

In Fig. 8 it is shown that the activation energy for conductance is larger in H_2 than in O_2 for G62RS. H_2S-poisoned catalysts exhibited very little temperature dependence. It was also noted that the conductivity in H_2 of G62RS was very similar to that for the pure support Al_2O_3.

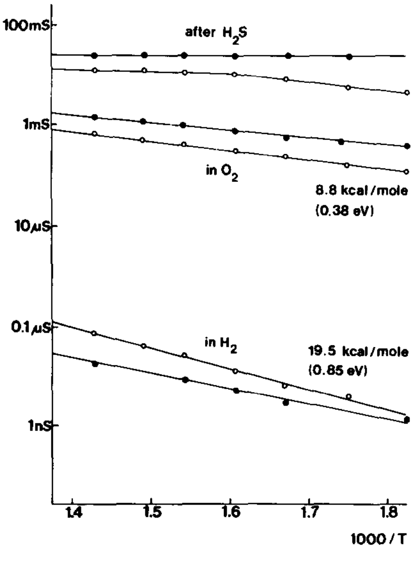

FIG. 8. Temperature dependence of the conductance of G62RS in H_2, in O_2, and in 1% H_2/Ar after H_2S poisoning. Pairs of points for each case represent the observed spread in the data.

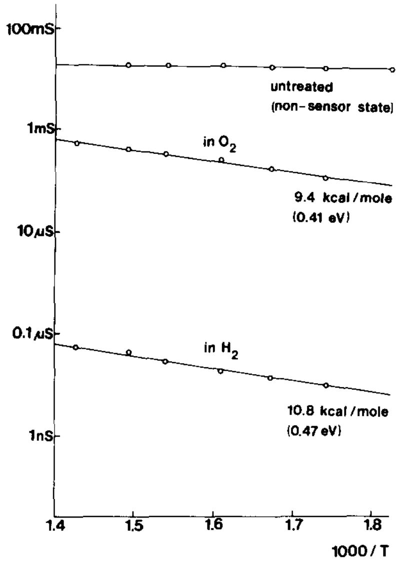

FIG. 9. Temperature dependence of the conductance of Ni-0104 in the as prepared form (untreated) and in H_2 and O_2 after the pretreatment described in Fig. 2.

Ni-0104 catalyst exhibited no temperature dependence in its untreated nonsensor state (Fig. 9). This same behavior was observed for Ni-3210, which, however, could not be transformed into a sensing state. After the treatment described in Fig. 2, Ni-0104 exhibited similar activation energies for conduction in both the oxidized and reduced forms.

It should be mentioned that the temperature of the catalysts varies with reaction conditions described in Figs. 1–7 and this certainly contributes to the data. Our procedure of measuring only the external reactor temperature was done for convenience and an internal probe on the catalyst surface would have been better. However, even then it is questionable if the pellet surface temperature is the same as at internal points. We do not feel that it is possible to explain the data by temperature changes. The conductance changes observed are too large and in all cases (except Fig. 1) in the opposite direction to what is expected from temperature change due to the reaction proceeding on the catalyst surface.

DISCUSSION

We will limit our discussion mostly to the data concerning the supported metal catalysts. Many of the references listed in the introduction describe conductivity measurements on semiconducting catalysts. For a material like ZnO it is obvious that changes in composition and/or adsorbed gas species will change the electrical properties. Such metal oxides are commonly used as sensors for gases (*23–25*). We also point out that, as TiO_2 is of current interest as a support material (*26, 27*), one can observe a similar effect of H_2S on TiO_2 as that shown for ZnO in Fig. 5.

Morrison has shown how the oxidation state ("Fermilevel") of metal–oxide catalysts can be inferred from the electrical properties of TiO_2 used as a support for the catalysts (*28*). In this case the number of available charge carriers in the semiconducting support (TiO_2) depends on the Fermilevel of the catalyst, which thus determines the conductance of a pellet made of the impregnated TiO_2. For such a system it is possible to use normal semiconductor physics to describe the changes in conductivity (for example, in its temperature dependence) upon oxidation and/or absorption (*28*).

The situation is more complicated for catalysts supported on insulating materials. Both the macroscopic (granularity) and microscopic (metal dispersion) structure will determine the electrical properties of a pellet. The possible significance of changes in the electrical conductivity of supported metal catalysts was discussed by Thomson and Harvey about ten years ago (*29*). They showed that the activation energy for conduction in supported noble metal catalysts was altered after reduction. No change in conductivity was observed upon oxidation and reduction for the low loadings (<5 wt% metal) used. They especially pointed out the possibility of charge transport between a catalytic metal particle and an adsorbate on the support.

We observed large differences in conductivities of oxidized and reduced forms of certain catalysts of higher metal content. The temperature dependence of the conductivity was also investigated for the catalysts and the results are summarized in Figs. 8 and 9. The following was observed for the Co catalyst, G62RS. The activation energy for conduction was larger in the reduced than the oxidized state. The H_2S-poisoned samples exhibited very little temperature dependence. The prefactor G_0 of the conductance (assuming $G = G_0e^{-E/RT}$) was rather similar for the oxidized, reduced, and poisoned samples. This suggests that the rate-limiting step in the conductance is actually an energy barrier and not the supply of charge carriers. This could indicate that it is species adsorbed on or between metal clusters which are responsible for the change in conductance. Furthermore, the change in conductance (Fig. 1) depends strongly on the oxygen pressure, which indicates a nonlinear mechanism behind the conductance changes. The nonlinearity can, for example, be due to a competition between hydrogen and oxygen for the same adsorption sites. Another suggestion consistent with the oxygen pressure dependence and the change in activation energy is given at the end of this section.

The nickel catalyst (Fig. 9) exhibited temperature-insensitive conductivity in its untreated nonsensor state. After treatment with H_2 and O_2, Ni-0104 showed a low conductivity in its reduced form compared with the oxidized form. However, in this case, the activation energies for conduction are about the same, which means that the prefactors (G_0) are quite different for the oxidized and reduced states. This fact indicates that for this particular catalyst oxidation increases the mobility and/or the number of available charge carriers.

One can take the point of view that catalyst G62RS can be thought of as being made up of p-type Co_3O_4 (30 wt% Co) and Al_2O_3. It is well known that p-Co_3O_4 becomes more conducting in oxidizing and less conducting in reducing gases (*23*). However, when one considers the supported Co catalyst (which is approximately 10 vol% Co) it is difficult to describe the nature of the conducting pathway which yields the data in Fig. 8 for a material which is 90 vol% insulating Al_2O_3. This is particularly puzzling when one considers that Ni-3210 with 35 wt% metal behaves so differently.

Our conclusion is, not surprisingly, that each catalyst material manufactured has its own special properties which are a function of the preparational parameters employed. There are only a limited number of publications on how preparation affects final catalyst properties for catalysts in our metal content range. What has been reported is that metal surface area passes through a maximum at 30–50 wt% metal (minimum in crystallite size) (*30*). For metal loadings greater than 5 wt% the crystallite size distribution is broad and even binodal (*31*). Thus the important microscopic properties of G62RS, results for which are shown in Fig. 8, and Ni-0104, results shown in Figs. 2 and 9, are poorly understood.

An observation which may be of general interest in this context was recently reported by Ruckenstein and Chen (*32*). They observed a change in the size of supported metal crystallites during alternating heating in oxygen and hydrogen. One conclusion was that Pd crystallites on alumina films generally became larger in oxygen. The activation energy for conduction between small metal clusters is known to depend on the size of the clusters (*33, 34*). Therefore the change of size of supported metal clusters can be a general reason why the activation energy should be smaller for the oxidized form. Furthermore, if electronic tunneling is also involved in the charge transport, the distance between the supported crystallites is an important parameter.

One could also apply the results of Ruckenstein and Chen to explain the behavior of Ni-0104. This catalyst could be viewed as having a Ni metal crystallite distribution after its preparation and reduction, which causes the catalyst to be very conducting and electrically stable upon first exposure to H_2 (Fig. 2). However, several cyclic treatments with O_2 and H_2 alter the original crystallite distribution so that the catalyst behaves like G62RS after the treatments. Sintering could result in an increase in distances between crystallites in the reduced form and thus the resulting insulating behavior. Ni-3210 and 1404 resist such sintering perhaps because of special additives.

With regard to H_2S poisoning, the concept of surface versus bulk properties of the catalysts must be included in the picture. It is generally agreed that poisoning of Co and Ni catalysts by H_2S results in a surface-bonded sulfide which is much more stable than bulk sulfides (*14–17*). We are unfortunately unaware of what species is responsible for the data shown in Figs. 3 and 4. At the rather high H_2S partial pressures used it is quite possible that bulk Co_9S_8 is forming in the catalyst (*35*). We do not claim in Fig. 3 that the conductivity change observed is directly related to the poisoning of surface catalytic sites, but rather wish to present the idea that catalyst conductance can be used to monitor the accumulation of sulfur, a poison which can either lower activity or alter selectivity (*16, 35, 36*). Furthermore, although G62RS could be returned to its originally insulating state by treatment in pure H_2 at 350°C, its original catalytic activity was not restored.

The final poison which was monitored by conductivity changes was carbon. Metal–oxide semiconductors have long been known to function as smoke detectors (*23*). In our study even materials totally unresponsive to O_2, H_2, or H_2S at elevated temperatures, such as Al_2O_3 or NM504 hydrotreating catalyst, increased their conductivity when carbon was deposited on their surface. It appears that maximum conductivity obtainable and temperature dependence of the conductance are very dependent on the metal content and pretreatment of the catalyst (*37*). An interesting example of this is the fact that zeolite SK-500 exhibited no conductance change after coking, perhaps because most of the carbon was concentrated in the zeolitic cages and had no possibility to form a connective network through the solid. For such materials we suggest that ac-impedance measurements can be an interesting technique to use. Changes in the conductivity in local areas can be observed as an ac capacitance and conductance change if the measurement frequency is sufficiently high.

FURTHER APPLICATIONS

In addition to the already described sensor uses, the electrical properties described for catalysts of the type listed in Table I may have further applications. Because of the high conductance observed for some of the catalysts listed they could possibly be used as electrodes in batteries or fuel cells, such as the CO–air cell shown in Fig. 11.85 of Ref. (*38*). For such application the conductance, surface area, porosity, and activity would be important in determining electrode efficiency.

Certain catalysts exhibit improved performance after they have been oxidized and reduced several times prior to use. It is often speculated that such pretreatment alters the surface area or texture of the catalyst. One could take this approach further by considering the data in our Fig. 2. The several oxidation/reduction cycles necessary to transform Ni-0104 to a sensor state can also be used as a pretreatment procedure to sequentially change the catalyst from a conducting to an insulating material (stable in H_2 at the end of each cycle). Thus a single catalyst could exhibit a range of activities for hydrogenation reactions because its conductance can be varied in a carefully controlled manner.

CONCLUSIONS

We have shown how the electrical properties of supported and unsupported catalysts can be used to monitor their physical state and therefore also their efficiency for certain reactions. We have also found that not all supported catalysts can be used in this way. Some, which do not show any electrical response initially, can, however, be transformed into a "sensing" state.

The observed phenomena can be used in a practical way for process control and to monitor, for example, sulphur poisoning of catalysts. Specially prepared thin films of such catalytic materials may furthermore be possible for use as chemical sensors in general.

Although we have some understanding about the processes behind the conductance changes much more work has to be done to correlate them with the macroscopic and microscopic properties of the catalysts.

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