snow, is responsible for this rather unique occurrence of perennially frozen ground.

One important implication of this discovery is that the process by which snow is incorporated into dunes and the melting of temporary snow in the dune may provide a mechanism for large-scale contortion and brecciation. Large-scale deformation in ancient sandstone of supposed eolian origin (for example, the Navajo, Entrada, and Casper formations) has perplexed geologists for many years. As a result of observational and experimental work, McKee (*8*) has related small-scale deformation to lee-side avalanching on dunes and large-scale recumbent folding in cross-bedded sand to surface drag, but there is still no adequate explanation for contortions on a scale of several meters and more. In fact, the apparent lack of eolian processes capable of producing such deformation of cohesive sand masses has led some observers to cite it as evidence for subaqueous deposition.

Although I did not observe deformation as large as that in some ancient eolian deposits, the contortion associated with cornice sliding (5 m wide and 0.5 m in amplitude) (Fig. 2) and the zone of brecciation (2 m wide and 0.3 m high) associated with volume change due to the melting of interred snow are much larger than any previously reported for modern dunes. Apparently depositional conditions and processes in cold-climate dunes produce internal structures not observed in more commonly studied warm-climate dunes (*9*).

It is premature to relate large-scale deformation in ancient eolian sandstone to the incorporation and melting of snow in cold-climate dunes. Sufficient modern analogies have yet to be documented. Furthermore, other mechanisms capable of producing these structures should be sought in order to evaluate the potential of such occurrences as paleoclimatic indicators. In any case, large-scale deformation in sand should not be interpreted as definite evidence of subaqueous deposition.

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Exhaust Catalysts: Appropriate Conditions for Comparing Platinum and Base Metal

Abstract. *There are fundamental differences in the behavior of alumina-supported samples of a platinum and a copper-chromium catalyst for oxidation of carbon monoxide in a simulated automotive exhaust stream. Ignoring such differences can result in inappropriate comparisons between oxidation catalysts for automotive application.*

The requirement that carbon monoxide and hydrocarbons be virtually eliminated from the exhaust of 1975 and later model automobiles has generated considerable interest in the development of an oxidation catalyst suitable for this task. Precious metals, notably platinum and palladium, have been reported to be especially well suited for catalyzing oxidation reactions in the auto exhaust environment (*1*). However, the high cost and relatively short supply of these metals have caused the search to continue for an oxidation catalyst which is inexpensive, plentiful, and as effective as the metals of the platinum group. Our studies of platinum and base metal catalyst systems have shown that the fundamental differences in their behavior have direct implications for both laboratory comparisons and automotive exhaust applications since the choice of experimental conditions can determine the outcome of the comparison. In light of this result, recent comparisons of various automotive emission control catalysts (*2, 3*) deserve some attention.

The catalysts used to oxidize CO in our experiments were among the most active of their respective classes. The base metal catalyst was a combination of copper (~8 percent by weight) and chromium (~7 percent by weight) on an alumina support. Under the conditions of the experiments, these metals exist primarily in an oxidized form. The other catalyst, 0.3 percent by weight platinum on alumina, presumably retained the metallic state throughout the experiments. The catalysts were made by first impregnating 3-mm spheres of alumina with solutions of the appropriate metal salts and then drying and calcining.

Oxidation activity was measured in an integral flow reactor, with 7 cm^3 of catalyst placed in a 19-mm (inside diameter) stainless steel pipe enclosed in a tube furnace. A feedstream blended to simulate exhaust gas (typically 2 percent CO, 2 percent O_2, 0.05 percent C_3H_6, 10 percent H_2O, 10 percent CO_2, and the balance N_2) was passed at flow rates ranging from 3.5 to 19 liter/min through the catalyst bed as the furnace temperature was slowly raised. The exit stream was analyzed continuously for CO, O_2, and hydrocarbons. Conversion and catalyst bed temperature were recorded simultaneously as the temperature increased.

Data on the relation between conversion and temperature for various inlet gas compositions were fitted to integrated forms of several different rate equations to establish the concentration dependence of the CO oxidation reaction. The rate over the base metal catalyst is best described by the expression

$$-d[\mathrm{CO}]/dt = k_{\mathrm{bm}}[\mathrm{CO}]^{0.7} \qquad (1)$$

Symbols in brackets represent concentrations; t is time; and the coefficient k_{bm} is the rate constant. These kinetics are in reasonable agreement with those reported earlier for oxide catalysts (*4*) and are to be expected if the slow step in the reaction sequence is the extraction of an oxygen atom from the base metal oxide lattice by a CO molecule.

The rate over the Pt catalyst is best described by the expression

$$-d[\mathrm{CO}]/dt = k_{\mathrm{Pt}}[\mathrm{O}_2]/[\mathrm{CO}] \qquad (2)$$

This expression is also in agreement with previous work (*5*), and it is in

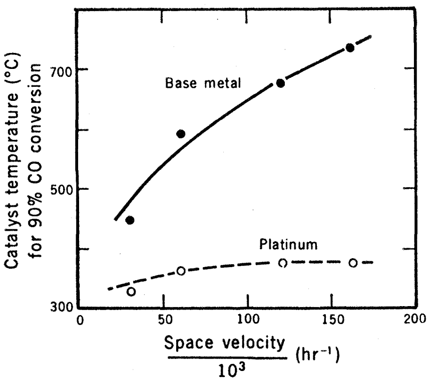

Fig. 1. Effect of space velocity (cubic centimeters of gas per cubic centimeter of catalyst per hour) on the temperature required to oxidize 90 percent of the CO in the "standard" inlet stream (2 percent CO, 2 percent O_2, 0.05 percent C_3H_6, 10 percent H_2O, 10 percent CO_2, and the balance N_2).

accordance with a rate-determining step that involves adsorption of oxygen on a surface nearly covered with CO.

The rate constants k_{bm} and k_{Pt}, although independent of CO and O_2 concentrations, are sensitive (to varying degrees) to changes in the concentrations of H_2O, CO_2, and propylene in the feedstream. Because of these interferences, the rate equations were derived with the use of the same concentrations of H_2O (10 percent), CO_2 (10 percent), and C_3H_6 (0.05 percent) in all experiments.

The rate equations apply until, at high temperatures, mass transfer rates begin to influence the conversion. Over Pt, the kinetics will also change when the CO concentration has been reduced considerably so that CO can no longer inhibit the adsorption of O_2; the reaction then becomes positive order in CO concentration (*6*).

Increasing the space velocity, that is, decreasing the contact time, was detrimental to the performance of the base metal catalyst. The Pt catalyst, on the other hand, maintained its efficiency remarkably well over more than a fivefold increase in gas flow rate (Fig. 1).

Carbon monoxide conversions as a function of the temperature of the gas slightly upstream from the catalyst are shown in Fig. 2. The curves for the two types of catalyst are different. Thus, the oxidation started at a lower temperature over the base metal, but the Pt catalyst yielded conversions near 100 percent (as required in the automotive application) at much lower temperatures than the base metal.

These results should be considered when oxidation catalysts of widely differing characteristics are compared. First, the kinetic expressions show that increasing the oxygen concentration increases the efficiency of a Pt catalyst, but does not affect the base metal's performance. Also in accordance with Eqs. 1 and 2, a high concentration of CO decreases the initial oxidation rate when Pt is the catalyst, but increases the rate when a base metal is the catalyst. These effects of reactant concentration, to say nothing of the interactions and inhibitions that occur when hydrocarbons, H_2O, and CO_2 are present at typical concentrations, make extrapolations from a pure reactant stream to automobile exhaust quite uncertain.

There are additional ways in which experimental conditions can influence catalyst comparisons. A relatively low space velocity of 20,000 hr^{-1} (Fig. 1) results in an apparently modest difference between the Pt and the base metal catalyst, whereas a space velocity of 160,000 hr^{-1} shows Pt to be considerably more effective in reaching 90 percent conversion.

The level of conversion chosen for the experiments can also influence the outcome of a catalyst comparison. For base metal and Pt oxidation catalysts (Fig. 2), the effectiveness of the latter becomes most obvious at high conversions. In general, the automotive application necessitates conversions above 90 percent to meet the legislated requirements.

Our results have a bearing on the recent work of Voorhoeve *et al.* (*2*), who reported that rare earth oxides of manganese and cobalt "rival platinum" for the treatment of CO in auto exhaust. We are not surprised that, as reported, under their experimental conditions all the catalysts they tested behaved similarly for CO oxidation; however, their test conditions were not relevant to the automotive emission control application. Their feedstream did not contain H_2O or CO_2, both of which are important components of exhaust gas and have significant effects on the catalytic oxidation of CO (*7*). More importantly, oxygen was not in excess, and the CO concentration was 20 to 100 times higher than that encountered in auto exhaust; these conditions would undoubtedly make platinum appear less effective in a comparison with an oxide catalyst.

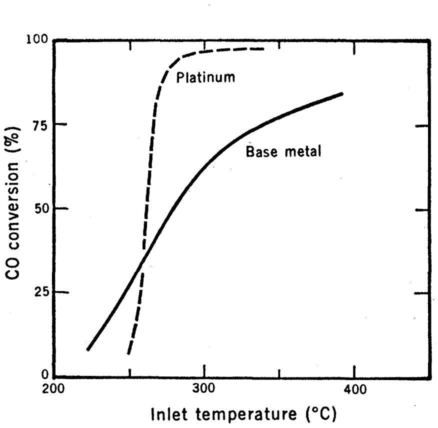

Fig. 2. Carbon monoxide conversion as a function of the temperature above the catalyst bed. Standard feedstream; 85,000 hr^{-1} space velocity.

The maximum space velocity reported by Voorhoeve *et al.* was about 900 hr^{-1} (30 cm^3 of gas per minute over 2 cm^3 of catalyst); that value is 20 to 200 times lower than the space velocities of interest for an automobile catalytic converter. Platinum's effectiveness at high space velocity (or, equivalently, small catalyst volume) is an important consideration for a practical catalyst because a small catalytic converter is best able to heat up quickly. Rapid catalyst warmup is essential if a system is to even approach future federal emission requirements.

The application requires conversions near 100 percent, but the maximum reported in (*2*) was 20 percent. The assumption that the ranking of the catalysts would not change with increasing conversion is not justifiable in view of the fundamental differences in the chemistry of the CO oxidation process over metal and oxide surfaces. Such differences are evident in our work reported here and in the kinetics reported by others (*4, 5*).

We have pointed out some of the uncertainties and biases that can occur when experimental results are applied to situations far removed from the actual laboratory conditions. We have shown why the extrapolation made by Voorhoeve *et al.* from their laboratory results to automotive application was not appropriate, nor was their reference to auto exhaust in the title. Libby's references to auto exhaust (*3*) were also not pertinent, since his feedstream contained only hydrogen and butenes.

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Lunar Surface Radioactivity: Preliminary Results of the Apollo 15 and Apollo 16 Gamma-Ray Spectrometer Experiments

Abstract. *Gamma-ray spectrometers on the Apollo 15 and Apollo 16 missions have been used to map the moon's radioactivity over 20 percent of its surface. The highest levels of natural radioactivity are found in Mare Imbrium and Oceanus Procellarum with contrastingly lower enhancements in the eastern maria. The ratio of potassium to uranium is higher on the far side than on the near side, although it is everywhere lower than commonly found on the earth.*

The Apollo 15 and Apollo 16 missions carried a group of orbiting geochemistry experiments, including an alpha-particle spectrometer (*1*), an x-ray spectrometer (*2, 3*), and a gamma-ray spectrometer (*4*). These instruments, located in the scientific instrument module bay of the service module, were operated in orbit during the lunar stay of each mission. This report is an account of the preliminary findings of the gamma-ray spectrometer experiment. A gamma-ray spectrometer was previously operated in lunar orbit aboard Luna 10 (*5*).

This experiment was designed to measure the concentrations of the most important natural gamma-ray emitters, Th, U, and K, in the surface layers of the region overflown. The instrument is also capable of measuring the concentrations of other elements which give rise to characteristic gamma-ray lines under cosmic-ray bombardment. The Apollo instrument consisted of a scintillation detector and a 511-channel pulse-height analyzer. The sensing element of the detector was a cylindrical scintillation crystal (7.0 by 7.0 cm) of NaI(Tl), coupled to a photomultiplier tube 7.6 cm in diameter. In order that the instrument reject signals produced by charged particles, the NaI(Tl) crystal assembly was surrounded by a plastic scintillator coupled to a photomultiplier tube 3.8 cm in diameter. The entire instrument was contained within a cylindrical thermal shield and mounted on a boom which was extended 7.6 m during prime periods of operation to remove the detector from the vicinity of gamma radiation produced in the spacecraft. The details of the instrumentation have been discussed elsewhere (*4*).

Prime data for this experiment could be collected only after the separation of the lunar module from the orbiting spacecraft, because of the presence of a radioisotope thermoelectric generator used to power surface experiments. During the Apollo 15 mission, 74 hours of lunar data were collected with the gamma-ray boom fully extended. Because of the comparatively high latitude of the landing site, the orbit of the spacecraft was inclined about 30°, which, in combination with the monthly rotation of the moon, allowed a considerable fraction of the lunar surface to be investigated. This instrument drifted in gain rather rapidly at first. We compensated for the total decrease in gain of 32 percent while in lunar orbit by commanding an increase in the high voltage supplied to the larger photomultiplier tube. The energy resolution (full width at half maximum) for the ^{137}Cs line at 0.662 Mev was 8.6 percent. The Apollo 16 mission covered a different region of the moon, with more intensive coverage of a smaller area. Useful lunar data were collected for 71 hours. The drift in gain was only 9 percent in lunar orbit; the energy resolution was also notably better, about 7.4 percent.

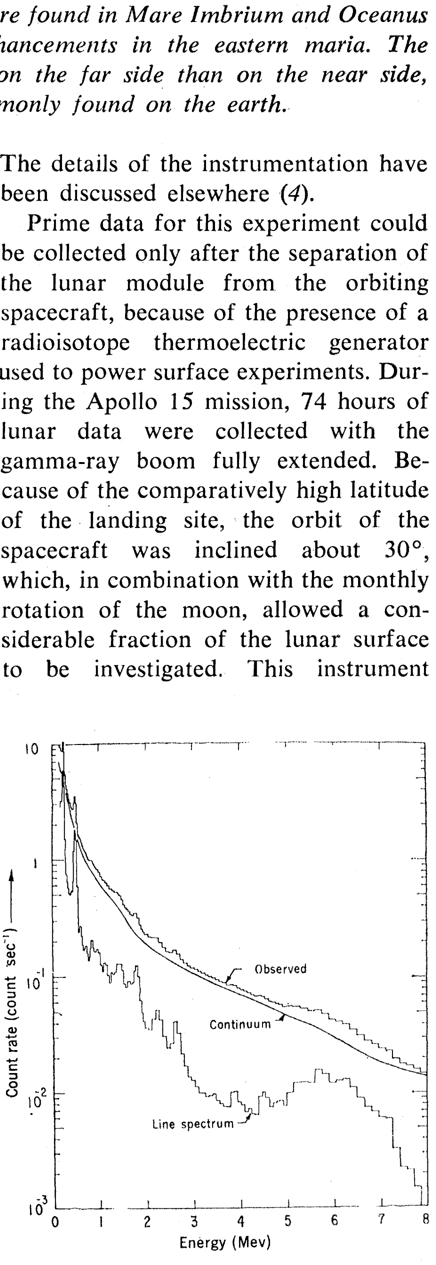

Fig. 1. Apollo 16 pulse-height spectrum, 270-minute accumulation, over 1° to 73°W. (Upper curve) Transmitted data; (middle curve) featureless continuum; (lower curve) net line spectrum.

The total areal coverage achieved on both missions was about 20 percent of the entire lunar surface at altitudes of 100 to 120 km. Regions at the east and west limbs were flown over on both missions, and data for these regions provide a cross-check of results.

A typical Apollo 16 pulse-height spectrum is shown in Fig. 1. The upper curve shows the transmitted spectrum; most of the events of the upper curve are part of a smooth continuum (middle curve) containing little useful chemical information. In the lowest spectrum of Fig. 1 our best present estimate for that continuum has been removed, and the line structure shows more clearly. The net line pulse-height spectrum must be unfolded (*6*) to obtain the incident photon spectrum from which concentrations can be calculated.

Quantitative values for the concentrations of the nine elements detected to date will not be reported here since the full matrix inversion analyses required are not yet complete. However, some major results are already available. In the energy region above the positron line at 0.51 Mev (which is attributable to many sources and contains little chemical information) up to and including the highest-energy line due to radioactivity, namely, the 2.61-Mev line due to Th, the regional *differences* in count rate are overwhelmingly attributable to the varying intensities of the lines of the radioactive elements Th, U, and K. This is a fortunate circumstance, since the statistical precision of the total count rate in this region (fixed in practice at 0.55 to 2.75 Mev) is excellent, and we can thus obtain the best possible areal resolution. At a nominal altitude of 100 km, the theoretical resolution of the system is of the order of 70 km or 2.5°, for cases of distinctive contrast (*6*). This resolution appears to be confirmed by the data. In the procedure