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A Kinetic Study of the Water–Gas Shift Reaction over Rh/Al_2O_3 Catalysts

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An investigation of the water–gas shift reaction on Rh/Al_2O_3 catalysts showed that light oxidation of an inactive catalyst triggered a transient in activity. The stability of the transient was enhanced by lengthened O_2 exposures although extensive oxidations were detrimental to both activity and stability. The rate of deactivation is accelerated by exposure to H_2 or increases in temperature but is not sensitive to changes in CO partial pressure. Reaction rate parameters measured during the transient showed the reaction to be nearly zero order in P_{CO} and slightly positive order in P_{H_2O} with an activation energy of 23 ± 2 kcal/mol.

INTRODUCTION

The use of catalytic converters to improve automotive emissions has redirected the importance for water–gas shift (WGS) activity from an H_2-producing reaction to a means of reducing CO emissions. This is particularly important under fuel-rich conditions where the availability of O_2 for direct CO oxidation is limited. Schlatter and Mitchell studied the transient catalytic behavior of noble metal catalysts in simulated automobile exhaust by operating a packed bed reactor in a CO-rich feedstream, switching in a lean (O_2-rich) feed for several minutes, and returning to the CO-rich feedstream (*1*). CO conversion by water–gas shift was enhanced for several minutes following reintroduction of the rich feed to Rh-containing catalysts. The authors concluded that lightly oxidized Rh was active for WGS, and the catalyst deactivated as a result of reduction by the CO-rich environment. Additional work by Herz and Sell showed that WGS augments CO conversion in exhaust feeds over Pt/Rh and Pt/Rh/Ce catalysts (*2*). Enhanced CO conversion associated with WGS was observed in rich excursions following lean excursions of short duration. Kim demonstrated that the water–gas shift activity of Pt–Pd–Rh three-way catalysts can be enhanced by adding CeO_2 to the catalyst (*3*).

This current investigation was undertaken to gain a better understanding of the steady-state and transient behavior of the water–gas shift reaction over supported Rh catalysts. Special attention has been paid to factors influencing the triggering of the activity transient as well as to those factors affecting the deactivation of this transient.

EXPERIMENTAL

Nine mass flow controllers were used to construct two compositionally different reactor feedstreams which could individually be passed through the reactor. A tenth mass flow controller supplied He to a saturator containing distilled water; the resultant wet gas was connected directly to the reactor inlet. The reactor effluent passed through a water-cooled condenser before being analyzed by a mass spectrometer. The differentially pumped, rapid response interface between the effluent stream and the mass spectrometer has been described elsewhere (*4*).

A 23-cm-long, 0.95-cm-o.d. quartz tube was used as the reactor. The inlet side of the tube was comprised of quartz beads contained by quartz wool plugs. A heating

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tape was wrapped about this section of the tube. The heat generated in this region was convectively carried downstream to a bed of catalyst beads also contained by quartz wool. Both regions of the tube were insulated. A thermocouple was placed centrally at the exit of the catalyst bed.

The 0.01% Rh/Al_2O_3 catalysts used in these experiments were prepared using a nonaqueous impregnation technique on Grace low-density θ-Al_2O_3 beads (3.2 mm diameter; 113 m^2/g). Rhodium was added to the catalyst by adsorbing $(n\text{but}_4N)_2Rh_2(CO)_2Br_8$ dissolved in acetone. This procedure was used to confine the rhodium within a thin band at the periphery of the catalyst beads and has been described in detail elsewhere (5). Following the impregnation, catalysts were dried at room temperature overnight and later calcined in air at 500°C for 2 h. Electron probe analyses of fresh and used catalysts indicated that the rhodium was principally contained in the outer 50-μm shell of the catalyst beads.

All further catalyst pretreatments were done in the presence of ca. 10% H_2O. Typical experimental conditions were as follows: 900 Torr, 500°C, 1% CO, 10% H_2O, 0.5% Ar (reference). The space velocity was normally ca. 210,000 h^{-1}. At this flow rate the WGS activity of (unimpregnated) blank Al_2O_3 was immeasurably low.

RESULTS

The transient activity of the catalyst following overnight oxidation in 5% O_2/10% H_2O at 500°C is shown in Fig. 1 by the curves for CO_2 and H_2 production. Several features of this figure should be noted. The CO_2 and H_2 signals are not coincident because of their differences in detection efficiency by the mass spectrometer. However, the ratio of the CO_2 and H_2 signals remains constant throughout the transient except for the moment immediately following the switch, when CO reacts with residual O_2 from the catalyst pores. The ratio of CO_2 to H_2 in the effluent, determined by calibrating the mass spectrometer, was consistently within 5–10% of unity. Additionally, the introduction of CO causes the bed temperature to increase 4–6°C because of the sudden generation of heat from reaction. This temperature transient disappears within 2–3 min. It is clear from Fig. 1a that an extensively oxidized Rh/Al_2O_3 catalyst has significant WGS activity, and the activity decreases to immeasurable levels within 20 min of introducing CO. In an attempt to restore activity, the catalyst was reexposed to the 5% O_2/10% H_2O stream for 10 s at the same temperature and total pressure of reaction. As seen in Fig. 1b, the catalyst demonstrated both higher activity and stability following reintroduction of CO than was originally observed after overnight heating in 5% O_2/10% H_2O.

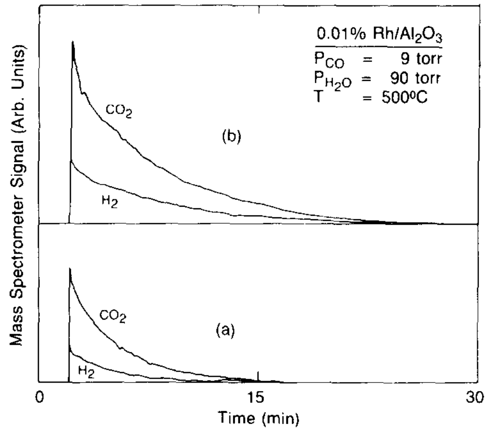

FIG. 1. Water–gas shift activity (a) following overnight oxidation in 5% O_2, 10% H_2O, 500°C and (b) following subsequent 10-s pulse of O_2 under the same conditions.

An attempt was made to quantify the amount of O_2 that was needed to restore activity to the deactivated catalyst. This was done in two ways. The first method was done by intermittently switching between a 2% CO/10% H_2O feed and a 0.1% O_2/10% H_2O feed. Figure 2 shows the results of this experiment. It can be seen

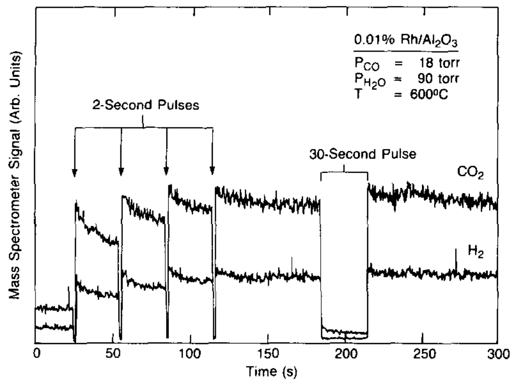

FIG. 2. Water–gas shift activity measured before and after injection of O_2 pulses. Pulses comprised of 0.1% O_2, 10% H_2O.

from this figure that both the WGS activity and the stability increase following successive 2-s pulses of O_2. However, it remained unclear as to how little O_2 was necessary for creating significant increases in activity.

The other experiment used to investigate the levels of O_2 needed for enhancing shift activity involved direct injection of small quantities of air through a septum placed upstream of the reactor. Significant enhancement of the water–gas shift reaction was observed following the first dose of 4 μl of air. This single dose introduced 6.5 × 10^{-8} mol O atoms to a catalyst bed of 2.6 × 10^{-7} mol Rh atoms. Early experiments such as these led us to modify the gas manifold to eliminate dead volumes that could potentially harbor small concentrations of O_2.

The data presented above suggest that (1) extensive oxidation of Rh/Al_2O_3 results in rapid loss of WGS activity, and (2) small O_2 pulses do not enhance the stability as well as large (or more numerous) pulses. The data therefore suggest that there is some intermediate oxidation treatment that gives the greatest stability to the water–gas shift reaction. An investigation into this behavior was made, and the results are given in Fig. 3. The time it takes for the H_2 signal to decay to half of the value observed immediately following the O_2 treatment is $t_{1/2}$. An intermediate treatment of ca. 1000 s in 5% O_2 provided the greatest stability for the water–gas shift reaction under the reaction conditions specified. With the exceptions of the transients following overnight oxidations, the initial rates of H_2 formation were all within 13% of one another. The maximum rates following overnight oxidations were typically 40% lower than those following the shorter pulses.

The data in Fig. 2 suggested that sequential pulses of the same duration continue to enhance the activity and stability of the shift reaction. This is illustrated in Fig. 4 for experiments at a higher termperature (600°C). The first peak in Fig. 4 shows the catalytic activity following overnight oxidation, and the two other peaks show the enhancement in activity resulting from 10-s pulses of 5% O_2. The activity following the pulses is greater than that following the overnight treatment—consistent with the above results. It can also be seen from the peak widths that the activity following the second pulse decays more slowly than that following the first, and both decay more slowly than the activity following overnight oxidation. It should be noted

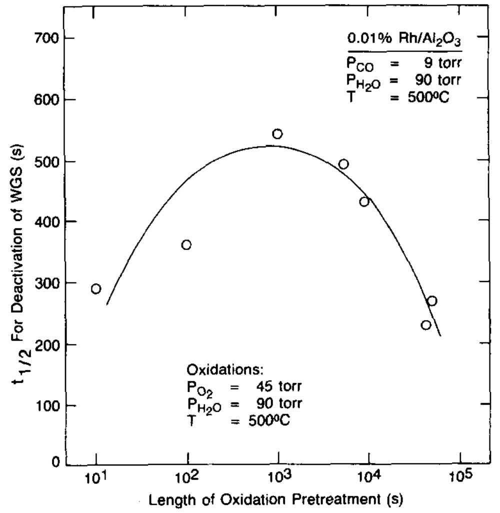

FIG. 3. Stability of catalytic activity following several oxidation pretreatments. $t_{1/2}$ is the time it takes to lose 50% of the activity measured immediately following introduction of CO.

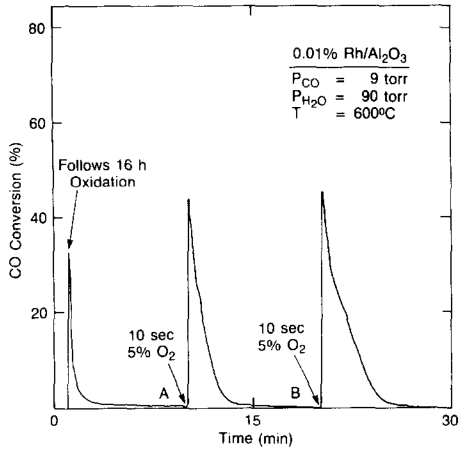

FIG. 4. Activity observed following overnight oxidation and two subsequent pulses of 5% O_2, 10% H_2O.

that the activity fell to immeasurable levels before either of the O_2 pulses were made. The catalyst's response to the second O_2 pulse was clearly influenced by the first pulse. That is, the first pulse had a lasting effect on the catalyst that was not reflected in the activity (immeasurable at point B).

The influence of overnight reduction in 5% H_2/10% H_2O was investigated by introducing a CO/H_2O feedstream immediately following the overnight treatment. In all instances, negligible activity was observed following reduction. However, following a single, 10-s pulse of 5% O_2, the WGS activity immediately rose to values greater than those observed earlier for the preoxidized catalysts. The stability of the oxygen-induced transients following overnight reduction was much greater than that observed with catalysts that had previously been oxidized overnight. The initial transient induced on the H_2-treated catalyst decayed over >90 min whereas that of the O_2-treated catalyst took less than 30 min to fully decay. Additional pulses of oxygen enhanced the stability of the transient, consistent with the results shown above for the preoxidized catalysts.

Nitric oxide, a strongly oxidizing exhaust gas component, was briefly tested as a substitute for O_2 in promoting the transient WGS activity. A 20-s pulse of 1% NO activated the catalyst as expected; no quantitative comparison was made between the effects of O_2 and NO.

An investigation was made of the reaction parameters influencing catalyst deactivation. The results in Fig. 5 show that the catalyst continues to deactivate when He and H_2O are substituted for the reaction mixture, and the rate of deactivation appears to be uninfluenced by the change in gases. Attempts to accelerate the deactivation were made by substituting 5% CO or 5% H_2 mixtures (in 10% H_2O) for the 1% CO reaction gas. The 5% CO mixture did not influence the rate of deactivation, yet the 5% H_2 atmosphere clearly enhanced the rate. As seen in Fig. 6, the CO_2 and H_2 signals are significantly lower following the H_2 treatment than what is expected from extrapolation of the initial deactivation curves. The influence of temperature was also investigated by substituting He for CO during deactivation, raising the reactor temperature from 500 to 575°C for several minutes, cooling back to 500°C, and reintroducing CO. The discontinuity in the deactivation curves was similar to that shown in Fig. 6 for the H_2 treatment.

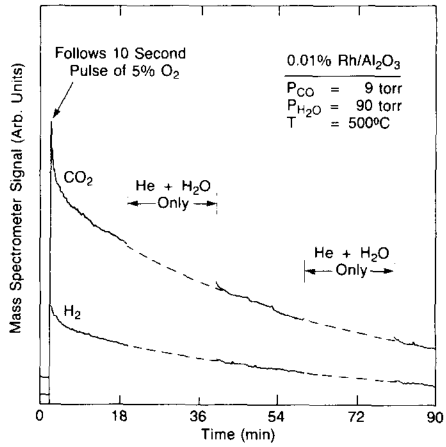

FIG. 5. Decline in catalytic activity both in the presence of reactants and in the absence of CO.

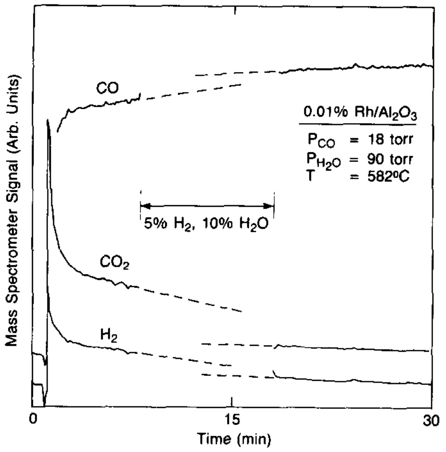

FIG. 6. Catalyst deactivation interrupted by purge with 5% H_2. H_2 appears to accelerate the deactivation process.

The rate of deactivation was often slow enough at temperatures equal to or below 500°C to allow measurement of the kinetic parameters. The reaction rate was found to be weakly dependent on both H_2O and CO partial pressures, the dependence on CO approaching zero order in the range of 18–45 Torr. A positive reaction order of approximately 0.4 was observed for H_2O. The measured activation energy was 23 ± 2 kcal/mol.

DISCUSSION

The results of these experiments show that the water–gas shift reaction over Rh/Al_2O_3 catalysts only proceeds on surfaces previously exposed to oxygen. Overnight oxidation at 500°C, which is thought to produce supported Rh_2O_3, yields a catalyst that has high shift activity but deactivates rapidly. On the other hand, extensive reduction of the catalyst, which presumably leads to Rh^0/Al_2O_3 or Rh^{1+}/Al_2O_3, produces a catalyst that is inactive for the water–gas shift reaction. The catalyst with the greatest activity and stability is that which has first been reduced and then exposed to small quantities of O_2. The brief exposures to O_2 may be viewed as causing a light surface oxidation of rhodium crystallites or perhaps a creation of sporadic islands of adsorbed O atoms on top of rhodium metal surfaces.

Either of these views of "light" oxidation would necessarily imply that the reaction rate is in some manner proportional to the amount of oxygen on the catalyst surface. Yet as seen in Fig. 4, the absence of activity does not merely imply the absence of adsorbed oxygen because identical O_2 pulses given to the same inactive catalyst create activity transients that vary in stability. In other words, there is a difference between the states of the catalyst at points A and B in Fig. 4 that is not reflected in the activity, the activity at both points being immeasurably low. A second factor (in addition to oxidation) appears to play a role in the activation/deactivation phenomena.

It is suggested here that the activity for the water–gas shift reaction may be influenced by facile rearrangement of rhodium atoms on the alumina surface, or what one might call a sintering–redispersion behavior. Prins and co-workers (*6*) and Haller and co-workers (*7*) have used EXAFS to show that Rh–Rh bond distances (supported catalysts) are lengthened by adsorption of CO at room temperature. It is reasonable to suspect that this phenomenon might occur with even greater facility at elevated temperatures in a CO/H_2O system.

We have found that the infrared spectra of CO adsorbed on a 0.475% Rh/Al_2O_3 catalyst are altered by the introduction of H_2O to a system containing 1% CO. As water is added, there is a marked decrease in the absorbances of the dicarbonyl bands. The absorption band for linear CO remains nearly constant, and the intensity of a broad band representing bridge-bonded CO increases. This influence of H_2O on the infrared spectrum of CO on Rh/Al_2O_3 had first been observed in the early work of Yang and Garland (*8*). Since the dicarbonyl bands are generally attributed to isolated rhodium atoms (or 1+ ions) and the bridged CO species requires adjacent rhodium atoms for bonding, the disappearance of the dicarbonyl bands and appearance of the band for bridge-bonded CO suggest that the rhodium atoms on the catalyst surface are coalescing under the influence of H_2O. A model such as this is not unlike the "breathing raft" picture given by Yates and co-workers (*9, 10*). Additional work is clearly warranted to determine whether rhodium atoms do migrate under reaction conditions.

The primary mode of catalyst deactivation may be through reduction of the lightly oxidized catalyst. The continuing deactivation observed in the absence of CO (Fig. 6) would thus suggest that the oxide decomposes in the absence of a strong oxidizer:

$$Rh_2O_3 \rightarrow 2Rh + 3/2\ O_2.$$

The deactivation process is not accelerated by CO, perhaps because the adspecies present in a CO/H_2O environment impart stability to the oxide surface. H_2, which presumably clears the surface of all but hydroxyl groups, accelerates the deactivation. It is clear that the deactivation is not due to carbon deposition since H_2 treatments reduce activity, activity declines in the absence of CO, and the rate of deactivation is not accelerated by increasing the CO partial pressure.

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