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Synergism between Pt/Al_2O_3 and Au/TiO_2 in the low temperature oxidation of propene

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CO impedes the low temperature (<170 °C) oxidation of C_3H_6 on supported Pt. Supported Au catalysts are very effective in the removal of CO by oxidation, although it has little propene oxidation activity under these conditions. Addition of Au/TiO_2 to Pt/Al_2O_3 either as a physical mixture or as a pre-catalyst removes the CO and lowers the light-off temperature (T_{50}) for C_3H_6 oxidation compared with Pt catalyst alone by ~54 °C in a feed of 1% CO, 400 ppm C_3H_6, 14% O_2, 2% H_2O.

KEY WORDS: Pt/Al_2O_3, Au/TiO_2, CO oxidation, C_3H_6 oxidation, synergism, physical mixture.

1. Introduction

Hydrocarbons (HC) in the lower atmosphere are one of the major factors leading to smog generation. Therefore, their emission from a combustion source is strictly regulated. Hydrocarbon emissions from urban sources are typically at low temperature, as is exhaust of diesel engines. For gasoline engine exhausts, it is well established that the majority of the HC are emitted during cold-start. Thus, effective treatments of these exhausts could benefit from good, low temperature HC and CO oxidation catalysts. Typically, noble metal catalysts are used for such applications because of their high activities in the low-temperature oxidation of HC and CO. A supported Pt catalyst is one of the most active systems for the low-temperature oxidation of C_3H_6. However, it is a well known phenomenon that its oxidation activity is strongly suppressed by the presence of carbon monoxide [1,2]. Thus, removal of carbon monoxide from the feed stream should enhance the Pt catalytic activity significantly. It is known that supported Au catalysts are possibly the most active catalysts for low-temperature CO oxidation [3]. Therefore, an integrated catalytic system containing a Au component to remove CO and a Pt component to remove C_3H_6 appears to be ideal for low-temperature removal of HC and CO. Thus, the objective of this study is to test this concept. Specifically, the effect of the presence of a supported Au catalyst on the low-temperature C_3H_6 oxidation activity of supported Pt catalysts was investigated.

2. Experimental

2.1. Catalyst preparation

Au/TiO_2 was prepared by a deposition–precipitation method similar to that of Haruta et al. [4]. $HAuCl_4$ was hydrolyzed at pH 7 and 70 °C and was then added to a suspension of mesoporous TiO_2 (Aldrich, ~1000 $m^2\ g^{-1}$). The suspension of Au and TiO_2 was stirred for 1 h, filtered, washed with deionized distilled room temperature water two times and 50 °C deionized distilled water once. After the final wash, the filtrate contained no Cl^- as verified by Quantab chloride paper (Fisher Scientific). The catalyst was calcined at 350 °C for 4 h. The Au loading was 1.93 wt% as determined by ICP and the average Au particle size was 12 nm as determined by TEM (average of 200 particles). In spite of the high surface area of the support, the particle size of Au was significantly larger and the activity lower than one prepared with conventional P_{25} TiO_2 [5]. Au/γ-Al_2O_3 was prepared also by the deposition–precipitation method similar to that of Au/TiO_2 and the Au loading was 0.14% as determined by ICP. γ-Al_2O_3 was prepared by hydrolysis of aluminum isopropoxide in the presence of 2-methyl 2,4-pentanediol as reported previously [6]. The Pt/Al_2O_3 catalyst was prepared by impregnation with a platinum nitrate precursor. The Pt loading was 2%, and the Pt dispersion, as measured by CO chemisorption at 35 °C, was 40.8%.

2.2. Reaction tests

The catalysts were tested in a U-shape fused silica micro-reactor. The catalyst bed, consisted of the catalyst and SiC mixture, was 1.7 cm in diameter and approximately 1 cm in height. The volumes of the

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reactor upstream and downstream of the catalyst bed were 20 and 3.8 mL, respectively, and they were filled with quartz chips to reduce the void space. Unless specified, the catalysts were mixed with 0.5 g SiC for more efficient removal of heat generated in the oxidation reaction. Temperature was measured with a thermocouple located in the catalyst bed. When studying the simultaneous oxidation of CO and C_3H_6, the feed composition was 1% CO, 400 ppm C_3H_6, 14% O_2, 2% H_2O and balance He. When studying the oxidation of CO or C_3H_6 individually, the same feed composition was used except that the other reductant was omitted and replaced with He. The catalyst weight and flow rate were adjusted to obtain a W/F of either 1.33×10^{-3} or 6.67×10^{-4} g min mL^{-1}. The conversions were calculated from the disappearance of the reductant. The measure of efficacy used here is the light-off temperature, T_{50}, or temperature at which 50% of the relevant reactant is converted. The carbon balance was within ±2% in all experiments. It was calculated as follows:

$$\{[3 * C_3H_6 + CO]_{in} - [3 * C_3H_6 + CO + CO_2]_{out}\} \times 100/[3 * C_3H_6 + CO]_{in}]$$

3. Results and discussion

Figures 1**a** and **b** show the C_3H_6 and CO oxidation activities over Pt/Al_2O_3 when the components were present individually and when they were present in a mixed feed. It can be seen that the presence of 1% CO severely suppressed C_3H_6 oxidation (Compare curves a figures 1**a** and **b**). The T_{50} for propene was shifted higher by nearly 90 °C. On the other hand, the presence of C_3H_6 in the feed did not affect the CO oxidation activity (compare curves b figures 1**a** and **b**). Changing the concentration of CO in the feed had a strong impact on the CO oxidation activity; reducing the CO in the feed from 1% to 0.25% lowered the T_{50} by about 40 °C (not shown).

Figure 2 shows the effects of water and W/F on C_3H_6 oxidation over Pt/Al_2O_3. Water has a slightly positive effect on C_3H_6 conversion (curves a and b). This effect was reported for a Pt catalyst prepared with a chloride precursor, but was not seen for a catalyst prepared with dinitrodiamine platinum precursor [7]. The catalyst in this study was prepared with a nitrate precursor, and the positive effect of water was observed. Decreasing W/F by a factor of two (curve c), raised T_{50} by 18 °C.

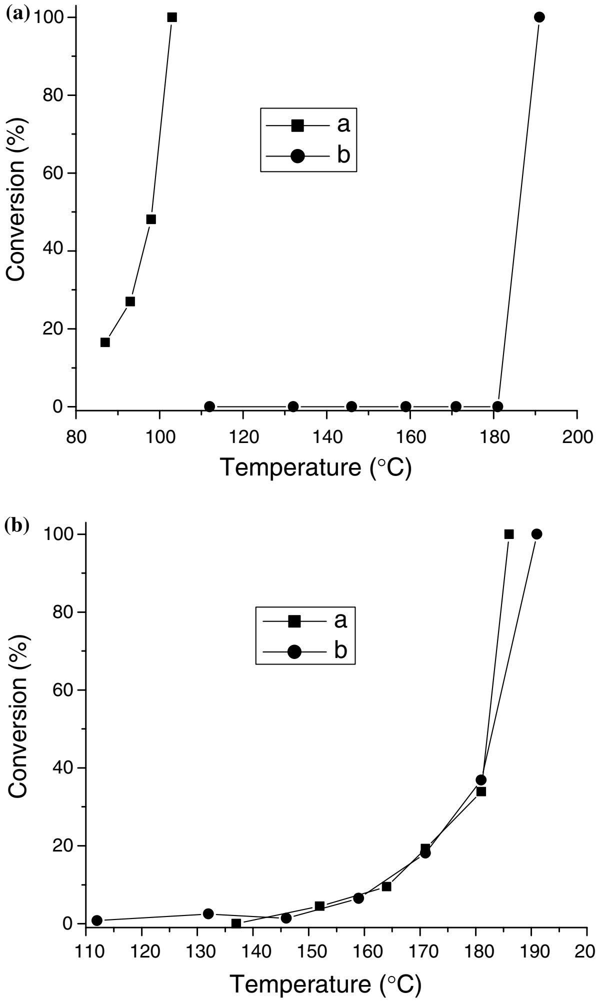

Figure 1. C_3H_6 conversion (**a**) and CO conversion (**b**) over Pt/Al_2O_3 in a feed of: (a) 400 ppm C_3H_6, 14% O_2, 2% H_2O, (b) 1% CO, 400 ppm C_3H_6, 14% O_2, 2% H_2O; W/F = 1.33×10^{-3} g min mL^{-1}.

Figure 3 compares the simultaneous oxidation of CO and C_3H_6 over two Au/TiO_2 catalysts prepared in the same manner. Considering the fact that the activity of a supported Au catalyst is very sensitive to small variations in the synthesis conditions [8], the results from the two preparations were quite reproducible. The catalyst with the better low temperature CO oxidation activity (sample a) also appeared to be a little more active for C_3H_6 oxidation. The presence of C_3H_6 severely poisons the CO oxidation activity of supported Au catalyst. Figures 4**a** and **b** compare the simultaneous oxidation of CO and C_3H_6 over a Au/TiO_2 catalyst in the presence and absence of water. As seen in figure 4**a**, the presence of water significantly enhanced the oxidation of CO (compare curves a and b). The T_{50} was 110 °C lower in the presence of water. The effect of water was not due to the water gas shift reaction as the water gas shift activity only began to appear above 200 °C (curve c). Enhancement of CO oxidation over supported Au catalysts by water has been reported [9,10] and the dependence of this enhancement on the concentration of water in the stream varied with the type of supported Au catalysts as well as the temperature of operation. It is also possible that water can displace C_3H_6 that is poisoning the CO oxidation active site.

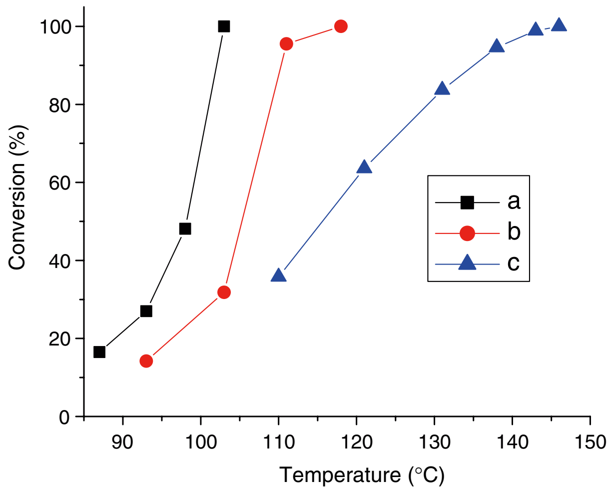

Figure 2. C_3H_6 conversion over Pt/Al_2O_3 (a) in a feed of 400 ppm C_3H_6, 2% H_2O and 14% O_2 ($W/F = 1.33\times10^{-3}$ g min mL^{-1}), (b) in a feed of 400 ppm C_3H_6 and 14% O_2 ($W/F = 1.33\times10^{-3}$ g min mL^{-1}), and (c) in a feed of 400 ppm C_3H_6, 2% H_2O and 14% O_2 ($W/F = 6.67\times10^{-4}$ g min mL^{-1}).

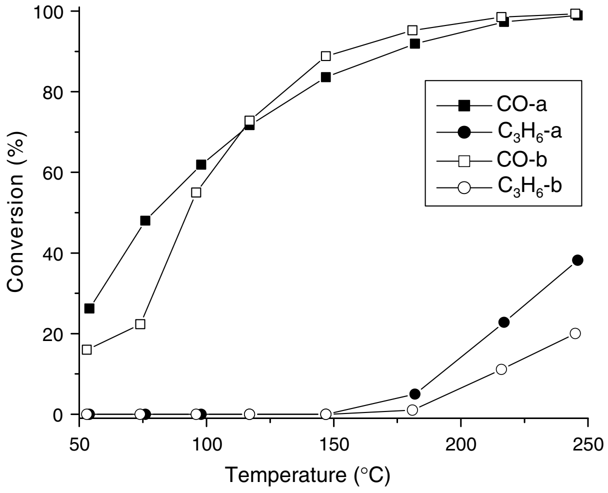

Figure 3. CO and C_3H_6 conversion over two different Au/TiO_2 catalysts (a, b) in a feed of 400 ppm C_3H_6, 1% CO, 14% O_2 and 2% H_2O, $W/F = 6.67\times10^{-4}$ g min mL^{-1}.

Figure 4**b** shows that the effect of H_2O on propene conversion is insignificant.

The simultaneous oxidation of CO and C_3H_6 were tested with Pt/Al_2O_3 and Au/Al_2O_3 in different configurations. The results are shown in figure 5 and 6. For comparison, the CO oxidation activity (Figure 5) over 0.1 g Pt/Al_2O_3 (curve a) and 0.1 g Au/TiO_2 (curve b) are also shown. Curve c shows the results of a physical mixture of 0.1 g Au/TiO_2 and 0.1 g Pt/Al_2O_3 and curve d is for a configuration of two reactor beds arranged in series with 0.1 g Au/TiO_2 upstream of 0.1 g Pt/Al_2O_3. The T_{50} for CO

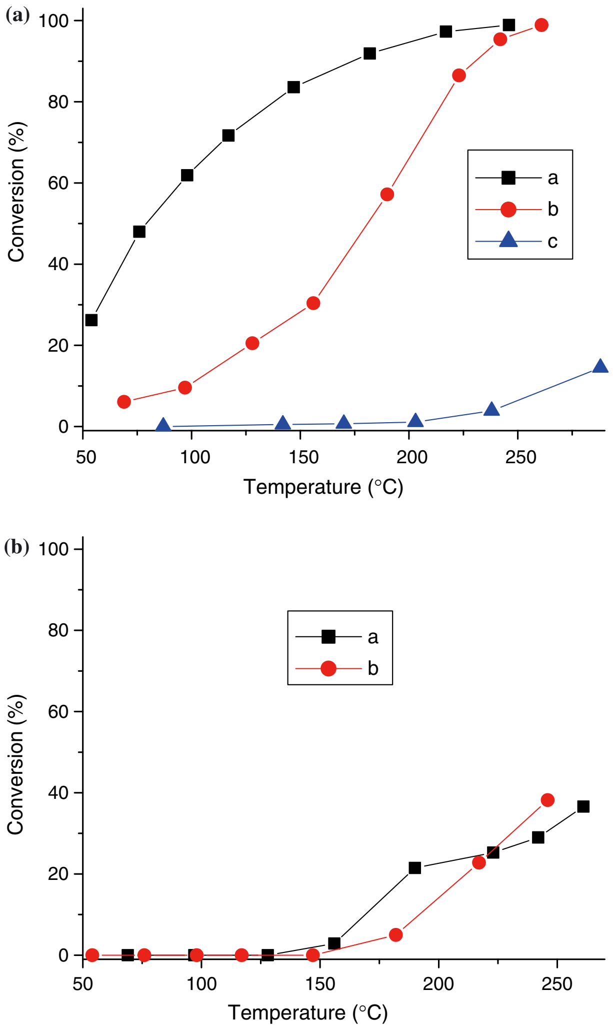

Figure 4. Conversion of CO (**a**) and C_3H_6 (**b**) over a Au/TiO_2 catalyst in a feed of (a) 1% CO, 400 ppm C_3H_6, 14% O_2, 2% H_2O, (b) 1% CO, 400 ppm C_3H_6, 14% O_2 and (c) 1% CO, 2% H_2O; flow rate 120 mL min^{-1}.

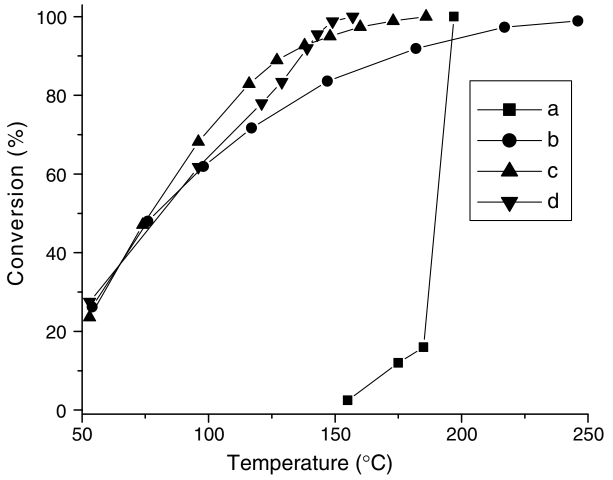

Figure 5. CO conversion over (a) 0.1 g Pt/Al_2O_3, (b) 0.1 g Au/TiO_2, (c) a physical mixture of 0.1 g Pt/Al_2O_3 and 0.1 g Au/TiO_2, and (d) two beds in series with 0.1 g Au/TiO_2 upstream of 0.1 g Pt/Al_2O_3. Feed condition:1% CO, 400 ppm C_3H_6, 14% O_2, 2% H_2O, 120 mL min^{-1}.

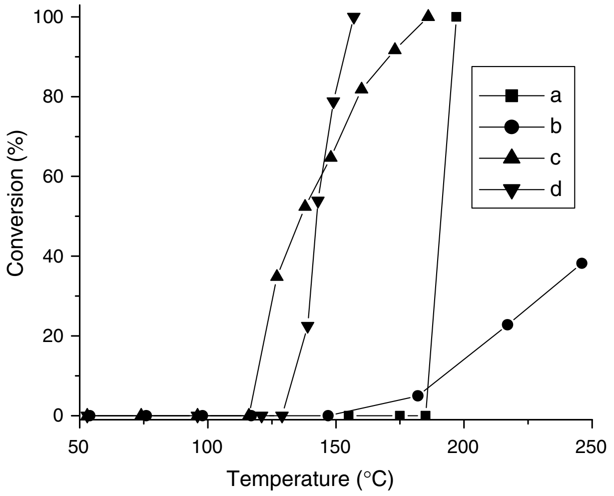

Figure 6. C_3H_6 conversion over (a) 0.1 g Pt/Al_2O_3, (b) 0.1 g Au/TiO_2, (c) a physical mixture of 0.1 g Pt/Al_2O_3 and 0.1 g Au/TiO_2, and (d) two beds in series with 0.1 g Au/TiO_2 upstream of 0.1 g Pt/Al_2O_3. Feed condition: 1% CO, 400 ppm C_3H_6, 14% O_2, 2% H_2O, 120 mL min^{-1}.

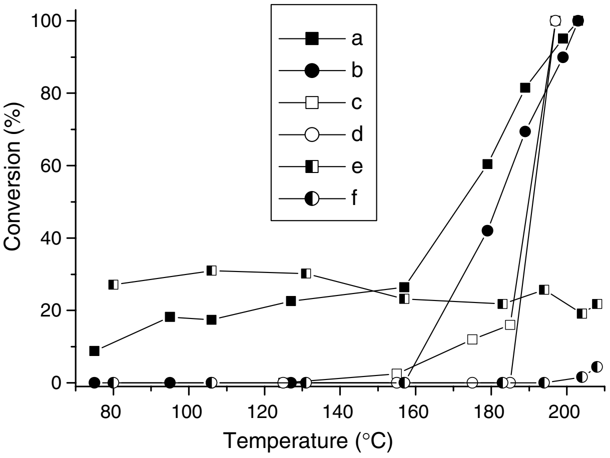

Figure 7. CO conversion (a) and C_3H_6conversion (b) over a physical mixture of 0.1 g Au/Al_2O_3 and 0.1 g Pt/Al_2O_3. CO conversion (c) and C_3H_6conversion (d) over 0.1 g Pt/Al_2O_3. CO conversion (e) and C_3H_6conversion (f) over 0.1 g Au/Al_2O_3. Feed condition: 1% CO, 400 ppm C_3H_6, 14% O_2, 2% H_2O, 120 mL min^{-1}.

oxidation over Au/TiO_2 was lower than that for Pt/Al_2O_3 by 110 °C, and the T_{50} for physical mixture of the two catalysts and for the two-reactor bed configuration were similar to that for Au/TiO_2. The conversions for the two-reactor configuration above 100 °C were somewhat higher than Au/TiO_2 because of contribution from Pt/Al_2O_3. As mentioned earlier, the T_{50} for CO oxidation on this Pt/Al_2O_3 decreased by about 40 °C when the CO concentration in the feed was decreased from 1% to 0.25%. Thus, Pt/Al_2O_3 began to contribute to CO oxidation at about 100 °C because of the oxidation (removal) of CO by Au/TiO_2.

The beneficial effect of a combination of Au/TiO_2 and Pt/Al_2O_3 on C_3H_6 conversion was much more obvious, as shown in figure 6. When used individually, Pt/Al_2O_3 was more active than Au/TiO_2 (curves a and b). When a physical mixture of 0.1 g Au/TiO_2 and 0.1 g $Pt/Al_2O_3$was used, the T_{50} for C_3H_6 conversion was ~54 °C lower than Pt/Al_2O_3 (curve c), when 70–80% of the CO was converted. A similarly lowered T_{50} was observed with the two-bed reactor configuration (curve d). That this improvement in C_3H_6 oxidation was observed for the two-catalyst system, regardless of whether the catalysts were in physical contact or separated, suggests that the increased activity is not due to local heating caused by the oxidation of CO over Au/TiO_2. It is also not due to migration of metallic components from one support to another to form bimetallic clusters.

There were subtle differences in the activity-temperature profiles depending on whether the two catalytic components were physically mixed or separated. The activity was more sensitive to temperature for the two-bed configuration. In the physical mixture, gas phase CO would decrease as the gas feed traverses the catalyst bed because of oxidation by the Au catalyst. When the gas phase CO concentration was reduced sufficiently in the latter part of the catalyst bed, the Pt/Al_2O_3 would contribute to the CO oxidation and further accelerate the depletion of CO. In this portion of the bed, C_3H_6 oxidation over Pt would occur. The higher the temperature, the sooner this happens. For the two-catalytic bed configuration, as long as the CO concentration is reduced to a sufficiently low level by the Au/TiO_2 bed, the entire bed of Pt/Al_2O_3 could participate in the reaction. Hence, the change in C_3H_6 and CO conversions as a function of temperature was steeper.

That the observed enhancement in C_3H_6 conversion with the Au/TiO_2–Pt/Al_2O_3 system is due to effective removal of CO by Au/TiO_2 can be further illustrated by comparison with the Au/Al_2O_3-Pt/Al_2O_3 system. Au/Al_2O_3 is an active CO oxidation catalyst; its reactivity is comparable to that of Au/TiO_2 at room temperature [11]. However, its activity did not increase with temperature (Figure 7, curve e) in the presence of C_3H_6, and the CO conversion remained below 30% over the temperature range investigated. Hence, when it was used in a mixture with Pt/Al_2O_3, the T_{50} for propene oxidation decreased by less than 20°C.

4. Conclusion

The light-off temperature for C_3H_6 over Pt/Al_2O_3 is significantly lower than for CO. However, in a C_3H_6 and CO mixture, the presence of CO greatly suppresses the oxidation of C_3H_6. The extent of suppression depends on the concentration of CO in the gas feed, since CO was adsorbed strongly on Pt and inhibited its oxidative activity. Au/TiO_2 was significantly less active than Pt/Al_2O_3 for C_3H_6

oxidation. However, it has a high CO oxidation activity. Therefore, over a mixture of these two catalysts, the partial pressure of CO is lowered by oxidation over Au/TiO_2, reducing its suppression of C_3H_6 oxidation over Pt/Al_2O_3. Consequently, the C_3H_6 oxidation activity can be enhanced substantially. A similar enhancement can be observed when the two catalysts are placed in series in a two reactor-bed configuration, with the Au/TiO_2 up-stream of Pt/Al_2O_3. Thus, a good strategy for improving the light-off characteristics for automotive catalysts is to use catalysts that contain both Au and Pt active sites. The challenge will be to make a catalyst containing Au that is durable in automotive exhaust conditions.

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