Selective Oxidation of Carbon Monoxide in the Presence of Butane and Maleic Anhydride

David R. Corbin and Cristobal Bonifaz

Central Research and Development,[1] DuPont Company, Experimental Station, P.O. Box 80262, Wilmington, Delaware 19880-0262

The selective oxidation of carbon monoxide in the presence of butane and maleic anhydride has been studied over platinum- and palladium-containing zeolites as well as palladium-on-silica (Pd/SiO$_2$) catalysts. The results show that although a zeolite support is needed in many systems to effect a kinetic control to improve selectivity, thermodynamic control using Pd(~2–4 ppm)/SiO$_2$ is sufficient to give the desired selectivities in this system. In addition, a palladium-containing vanadium-phosphate catalyst was prepared that showed complete oxidation of carbon monoxide, conversion of butane to maleic anhydride, and no observable decomposition of the maleic anhydride. © 1994 Academic Press, Inc.

INTRODUCTION

In the gas-phase oxidation of butane to maleic anhydride over a vanadium-phosphate (V/P/O) catalyst, significant amounts of carbon monoxide are produced as a by-product of the reaction (1, 2). To maximize the overall conversion of butane to maleic anhydride, recirculation of the product stream is necessary. The separation of maleic anhydride from the butane and CO is relatively easy compared to the separation of butane from CO. Without separation or removal of the CO, a potential explosion hazard could arise from the gradual accumulation of carbon monoxide. It would be most desirable to selectively eliminate the CO from this stream without incurring butane or maleic anhydride losses to undesirable oxidation products. This can be accomplished either by passing the product stream over a separate catalyst bed (Scheme 1) or preferably by eliminating the carbon monoxide in the main butane to maleic anhydride reactor by modifying the vanadium-phosphate catalyst (Scheme 2). Following the work of Chen and Weisz (3), we examined metal-supported zeolites and found that a site/shape selective support was not necessarily required. In this paper, we report a study of these and other supported metal catalysts for the selective oxidation of CO to CO$_2$ in the presence of butane or butane and maleic anhydride using both schemes.

EXPERIMENTAL

Catalyst Preparation (4)

Pt/Na–A zeolites. Samples of platinum containing zeolite A were prepared by variation of literature procedures (5). An example synthesis follows. A mixture containing NaAlO$_2$ (40.5 g), NaOH (75 g), H$_2$O (900 cm^3), and (NH$_3$)$_4$PtCl$_2$ · H$_2$O (0.100 g in 10 cm^3 H$_2$O) was added to Na$_2$SiO$_3$ · 5H$_2$O (31.8 g in 600 cm^3 H$_2$O) at 90°C. The mixture was stirred until crystalline as indicated by the powder X-ray diffraction pattern. After filtering, the sample was washed with distilled water and dried. Approximately 16 g of dried product was obtained. Chemical analysis gave a metal loading of 230 ppm. Other samples of lower metal loading were also prepared by appropriate reduction of the amount of (NH$_3$)$_4$PtCl$_2$ · H$_2$O added.

Pd/SiO$_2$ catalysts. Pd/SiO$_2$ catalysts were prepared by a variation of literature methods (6). An example synthesis follows. Silica gel (10 g, Davison Grade 952) was contacted with a solution of (NH$_3$)$_4$Pd(NO$_3$)$_2$ (0.03 g) in NH$_4$OH : H$_2$O (50 cm^3 : 150 cm^3) for 5 min. The mixture was filtered, washed with H$_2$O, and dried. Assuming total exchange (or adsorption) of the metal species on the silica gel, the palladium loading would be approximately 0.11% by weight. Other samples of lower metal loading were prepared by appropriate reduction of the amount of (NH$_3$)$_4$Pd(NO$_3$)$_2$ used.

Pd/V/P/O catalyst. The preparation of the V/P/O component of this catalyst comprises the following series of steps (7): synthesis of the V/P/O catalyst precursor, preparation of the 5 wt% SiO$_2$ solution of polysilicic acid, preparation and spray-drying of the V/P/O precursor–PSA slurry, calcination, and activation. The spray-dried V/P/O component was prepared by literature methods (8). The spray-dried V/P/O catalyst (20 g) was contacted with 300 ml of a 1.1 × 10^{-6} M solution of (NH$_3$)$_4$Pd(NO$_3$)$_2$ for 5 min with stirring. The slurry was filtered,

[1] Contribution No. 6497.
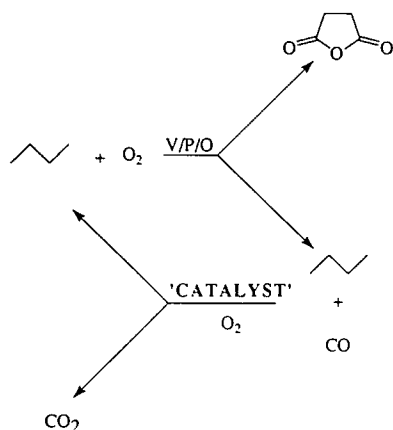
SCHEME 1

washed and dried. The calculated loading of Pd assuming complete ion-exchange is 1.8 ppm.

Silicalite. A mixture of ethylsilicate (40%, 235 g), tetrapropylammonium bromide (50 g) and distilled water (600 g) were loaded in an autoclave (2-L, Hastelloy C) at room temperature. The autoclave was sealed and heated to 180°C with agitation (200 rpm). After 125 h, the autoclave was cooled to room temperature. X-ray powder diffraction indicated the material to be crystalline. The crystalline silica thus synthesized was then filtered, dried, and calcined for 4 h at 550°C. The calcined silica (56 g) was analyzed to contain 5 ppm Al.

Na,Pd-silicalite. A solution containing 1.5 g of Na_2PdCl_6, 35 g concentrated HCl, 30 g tetrapropylammonium bromide, and 410 g H_2O was added to a solution containing 40 g of waterglass and 300 g H_2O. This mixture was placed in a polypropylene bottle and heated at 100°C for 7 days. The resulting material was filtered, washed, and dried. The product was calcined in air by raising the temperature 50°C h^{-1} and heating the material at 540°C for 10 h.

H,Pt-silicalite. A solution containing 2 g of H_2PtCl_6, 35 g concentrated HCl, 30 g tetrapropylammonium bromide, and 410 g of H_2O was added to a solution containing
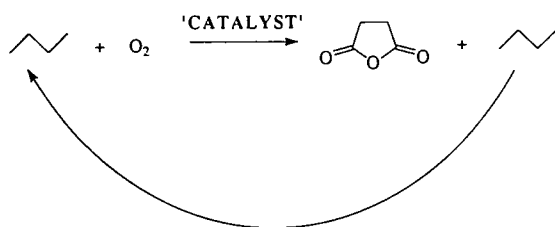
SCHEME 2

240 g of waterglass and 300 g H_2O. This mixture was placed in a polypropylene bottle, heated at 100°C for 8 days, and then filtered, washed, and dried. The product was calcined in air by raising the temperature 50°C h^{-1}, and heating the material at 540°C for 10 h. The calcined material was then contacted three times with a 10% NH_4NO_3 solution and filtered, washed, and dried. The product was then calcined in air by raising the temperature 50°C h^{-1} and heating the material at 540°C for 10 h.

Reactor

Experiments were performed in glass-lined U-tube reactors capable of holding 0.5 to 4 cm^3 of catalyst. The reactors were heated to the desirable temperatures by means of a sandbath contained in a laboratory barricade. Carbon monoxide and oxygen were fed from cylinders with flows controlled by use of automatic Brook's rotameters. Butane and maleic anhydride were fed to the reactors using Isco liquid pumps. Pumps were filled with butane liquid at dry ice temperatures and uniform flow of butane to the reactor was achieved by use of two Grove micropressure regulators in series. The first pressure regulator maintained uniform liquid flow of butane under pressure, which then in turn evaporated in line. The second regulator controlled and maintained uniform gas flow. Gas products from the reactor were analyzed on-line via a gas chromatograph.

Temperature (370–440°C) and gas flow conditions to the reactor were chosen to simulate actual recycle conditions in a butane to maleic anhydride reactor (2). Helium was used instead of carbon dioxide. Flowrates used were 1.68 cm^3/min of CO, 121.6 cm^3/min of He, and 10.9 cm^3/min of O_2. Butane was fed at a rate of 0.66 liquid cm^3/hour. Contact times were established at 1 s.

RESULTS AND DISCUSSION

The use of zeolites as catalysts and catalyst supports in shape selective catalysis is well known (9). For example, platinum-containing sodium mordenite has been shown

TABLE 1

Effect of Pt Loading in Zeolite A on Selective Oxidation at 410°C

Pt loading (~ppm)	CO to CO_2 (%)	C_4H_{10} to CO_2 (%)
230[a]	100	55
120[b]	100	40
12[b]	100	36
2.3[b]	100	3

[a] ICP analysis.
[b] Estimated based upon above.

to selectively hydrogenate ethylene in propylene streams (3) and nickel-containing zeolite A selectively hydrogenates acetylene in the presence of butadiene and ethylene (10). Based upon the known activity of Pt metal to catalyze the oxidation of organic molecules, it was assumed by Chen and Weisz (3) that a shape-selective catalyst was required for the selective oxidation of CO in the presence of butane. Since the kinetic diameters of butane and CO are 4.3 and 3.76 Å, respectively (11), they chose a small-pore zeolite to study and showed using a Pt-containing zeolite A that carbon monoxide is selectively oxidized compared to butane when fed as separate streams at 427 to 540°C.

Since the known soluble Pt^{2+} species are larger than the pore opening of a small pore zeolite (<5 Å), ion exchange is not possible so the platinum-containing species must be added in the synthesis gel in order to incorporate the metal within the zeolite pores (3). We prepared a series of platinum-containing zeolite A catalysts with varying metal loadings and examined them for the selective oxidation of CO in the presence of butane. The reactor results given in Table 1 clearly show the selectivity is directly related to the metal concentration in the catalyst. Obviously, catalysts with loadings of approximately 2.3 ppm Pt are preferred, giving 100% oxidation of the CO and only 3% of the butane present in the stream at 410°C.

One of the primary causes of deactivation of supported metal catalysts is the decrease in metal dispersion and hence surface area due to sintering (12). Prolonged exposure to elevated temperatures and/or certain atmospheres such as hydrogen can cause such changes in metal crystallite size. It is also known that for some metal supported catalysts thermal treatments in oxygen at certain temperatures result in increases in the metal dispersion. As shown in Table 2, pretreatment of the platinum-containing zeolite A with hydrogen at 400°C generally leads to significant initial improvements in selectivity resulting from the probable decrease in metal surface area on treatment in hydrogen and/or the decrease in numbers of metal sites on the external surface of the zeolite; however, the improve-

TABLE 2

Effect of H_2 Pretreatment on Oxidation Selectivity of Pt-A Zeolites at 410°C

Pt loading (~ppm)	CO to CO_2 (%)		C_4H_{10} to CO_2 (%)		
	Untreated	Treated	Untreated	Treated	After 12 h
230[a]	100	100	55	20	—
120[b]	100	100	40	4	—
12[b]	100	100	36	17	37
2.3[b]	100	100	3	8	—

[a] ICP analysis.
[b] Estimated based upon above.

ments were transient. After 12 h on-line (in the oxidizing atmosphere), the selectivity values for PtA with an approximate Pt loading of 12 ppm returned to those observed for the untreated catalyst. This indicates a probable redispersion of the metal resulting from heating in the oxidizing atmosphere.

The Pt-containing zeolite A catalysts have been shown to be selective for the oxidation of CO in the presence of butane and a potential candidate for use in Scheme 1 above. For Scheme 2, the other major product–reactant in the stream is maleic anhydride. It is important that the catalyst be inert toward this product. To test this, a 10% aqueous solution of maleic anhydride was passed over the Pt-containing zeolite A catalyst under reaction conditions. The effluent from the reaction contained acrylic acid (~50%), acetic acid (~13%), acetaldehyde (~27%), CO_2, coke, and no maleic anhydride. It was postulated that the platinum-containing zeolite A may be acting as a bifunctional catalyst due to its acidity which may be leading to the decomposition of the maleic anhydride. Since the acid strength of the zeolite is dependent upon the aluminum content of the zeolite (13), other supports were examined. The results of this study are given in Table 3. The data

TABLE 3

Effect of Catalyst Composition on Decomposition of Maleic Anhydride

Catalyst	Metal (~ppm)	Approximate Al/(Si + Al)	CO to CO_2 (%)	C_4H_{10} to CO_2 (%)	% Maleic anhydride reacted
Pt-A	2.3	0.5	100	3	100
H,Pt-silicalite	600	0.0035	100	60	100
Na,Pd-silicalite	500	0.0035	100	2	100
Silicalite	0	0	0	18	21
Silica gel	0	0	0	6	8
Pd/SiO$_2$	3.6	0	100	3	7
Empty reactor	0	—	0	5	5

TABLE 4

Effect of Pd Loading on Oxidation Selectivity for Pd/SiO$_2$

Pt loading (~ppm)	CO to CO$_2$ (%)	C$_4$H$_{10}$ to CO$_2$ (%)	% Maleic anhydride reacted
0.16	25	0	—
1.8	100	1	6
3.6	100	3	6
110	100	40	—
1100	100	60	50

generally indicate that the lower the alumina content the less decomposition of maleic anhydride occurs; however, this does not exclude contribution of the metal loading to this decomposition. Silica gel showed essentially no decomposition of the maleic anhydride. Although the silica gel does not possess the uniform microporosity of zeolites thought necessary to impart kinetic control over this reaction (i.e., shape/size selectivity), samples of palladium-exchanged silica gel were examined as catalysts for the selective oxidation of CO in the presence of butane and maleic anhydride.

The Pd/SiO$_2$ catalysts were prepared by contacting the silica gel with dilute solutions of (NH$_3$)$_4$Pd^{2+} salts. This procedure is known to give highly dispersed metal particles (6). The results for the oxidation of CO in a CO/butane stream over a series of Pd/SiO$_2$ catalysts with varying metal concentrations are given in Table 4. The data indicate that in the estimated Pd concentration range 2–4 ppm excellent selectivity is observed with all the CO oxidized to CO$_2$ and negligible butane loss. Pd/SiO$_2$ catalysts with comparable Pd loadings were tested and were also found to be inactive to maleic anhydride decomposition. In addition, a Pd/SiO$_2$ catalyst with an approximate Pd loading of 1.8 ppm was evaluated for lifetime in the presence of CO, O$_2$, and butane. After 346 h, the catalyst showed no observable change in activity or selectivity.

One preferred catalyst for the oxidation of butane to maleic anhydride is a silica-containing vanadium-phosphate catalyst (14). This material was treated with a (NH$_3$)$_4$Pd^{2+} salt to give a catalyst with comparable loadings of Pd as above. The resulting catalyst was tested for

CO oxidation, butane oxidation, and maleic anhydride reactivity under process conditions. The catalyst showed 100% oxidation of CO to CO$_2$, conversion of butane to maleic anhydride (comparable to a control), and essentially no observable decomposition of maleic anhydride.

The results of this study show that although in many cases a zeolite support is needed to exert a kinetic control for improved selectivity, in this example of the selective oxidation of CO in the presence of butane and maleic anhydride, thermodynamic control is sufficient to give the desired selectivities. Care must also be taken in metal loading and choice of support materials to limit side reactions resulting from high activity and bifunctionality.

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