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Process development for low temperature CO oxidation in the presence of water and halogen compounds

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Abstract

A new process has been developed to oxidize CO at low temperatures (<423 K) in vent streams that also contain halogenated compounds and water. A $PdCl_2$–$CuCl_2$ catalyst supported on carbon was successfully implemented to treat the oxidation reactor vent stream of a terephthalic acid plant that contained water, CH_3Br and other organic compounds in addition to CO. The CH_3Br remained intact during the treatment and did not deactivate the catalyst. In this catalyst system, palladium remained as a molecular Pd(II) species while solid $Cu_2Cl(OH)_3$ was the active copper phase. The formation of stable $Cu_2Cl(OH)_3$ was essential for activity and stability of the catalyst. After obtaining a stable catalytic activity for six months in a pilot plant test with a side stream of real vent gases, the first installation and operation of the process were made successfully to handle 50,000 Nm^3/h of vent stream in a terephthalic acid plant. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: CO oxidation; Low temperatures; Water; Halogens; $PdCl_2$–$CuCl_2$/carbon

1. Introduction

Carbon monoxide is a common air pollutant present in many industrial emissions. These streams also contain moisture usually at its saturation level and other contaminants such as halogens. Current industrial catalysts based on heterogeneous noble metals are poisoned by these contaminants and thus require higher temperatures than 573 K although the oxidation of pure CO is a fairly easy reaction. In the reactor vent of terephthalic acid (TA) plants containing CO, CH_3Br and other hydrocarbons, CO_2, N_2 and saturated water vapor, a commercial supported Pt–Pd catalyst must be operated at 593 K to completely oxidize CO. This catalytic system needs a large furnace to reach this high reaction temperature and thus higher capital investment, and fuel costs are required than for an ideal low temperature catalytic system as depicted schematically in Fig. 1. Furthermore, the catalyst also oxidizes CH_3Br at such a high temperature to form HBr and Br_2 which cause corrosion problems downstream if their scrubbing is not complete. Therefore, a new catalytic process which can selectively oxidize CO at low temperatures in the presence of water and halogens is in order. There have been a number of reported low temperature CO oxidation catalysts; metal oxide catalysts such as hopcalite [1] and SnO_2–CuO [2] need temperatures much lower than 473 K, but they are easily poisoned by water vapor contained in the most industrial vent gas stream. Recently, advanced mixed metal oxide catalysts such as Ag–Co oxides and Ag–Mn–Co oxides have been reported to be more

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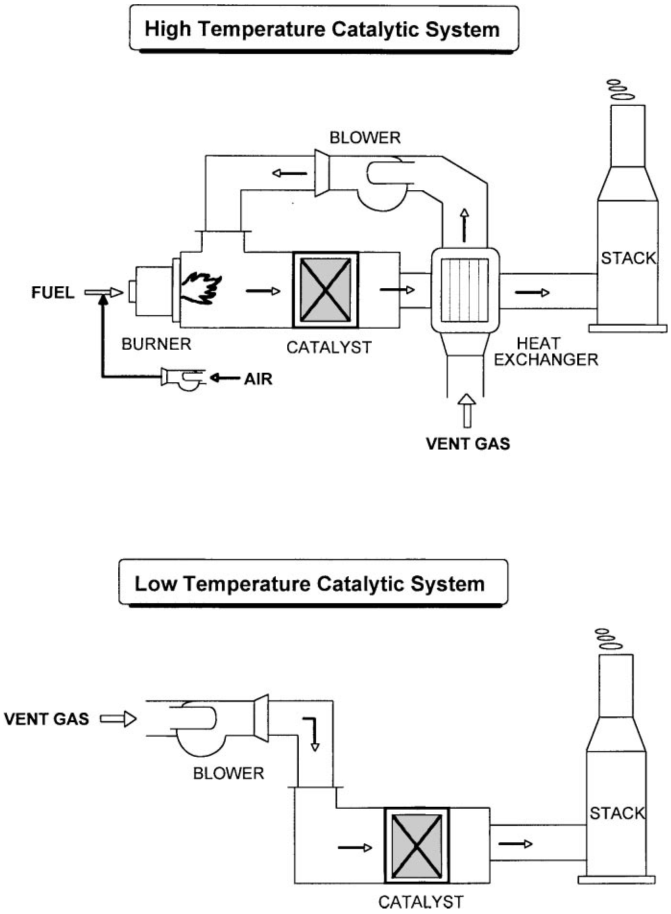

Fig. 1. Schematic diagram of low and high temperature catalytic oxidation systems.

active than other previously known metal oxide catalysts [3]. Other new catalytic systems such as Au/metal oxide [4] and Pt/SnO_2 [5] have also been reported to be highly effective for low temperature CO oxidation even in the presence of water. Compared with these heterogeneous catalysts, supported Wacker-type catalysts are conceptually closer to a heterogenized homogeneous catalytic system. The catalyst, in which an aqueous solution of $PdCl_2$–$CuCl_2$ is loaded into the pores of high surface area supports, is known to accelerate the oxidation of carbon monoxide at low temperatures [6–13]. It exhibits high CO conversions near room temperature and is stable in the presence of water in the feed. These catalysts known for low temperature CO oxidation were screened in the presence of CH_3Br and supported $PdCl_2$–$CuCl_2$ catalyst system was selected as a promising candidate. Through a pilot plant test program, a new process has been developed that selectively converts CO in the presence of CH_3Br and water at low temperatures so that low quality steam could be used as the sole heat source instead of a high temperature furnace.

2. Experimental

2.1. Catalyst preparation

Ag–Mn–Co oxides were prepared by a coprecipitation method according to the procedure described by Haruta et al. [3]. The selected mole ratio of Ag,

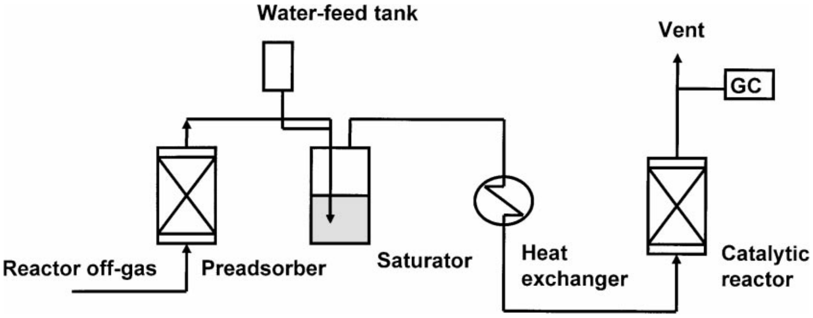

Fig. 2. Schematic diagram of the pilot plant.

Mn and Co was 1 : 4 : 20, which was within the reported optimum range for these three component metal oxides. The catalysts were calcined in air at 673 K for 5 h before reaction. Mn–Cu oxide (KCG-1) and Au/Fe_2O_3/Al_2O_3 catalyst (AUS) was purchased from Catalysts & Chemicals of Japan and used without any pretreatment. The Wacker-type catalyst was prepared by a wet impregnation method to impregnate supports with an aqueous solution of palladium and copper. Activated carbon (Aldrich, BET surface area: 1127 m^2/g) was dried at 383 K for 12 h in an oven before impregnation. The metal precursors were $PdCl_2$ (Sigma, 99.9%), $CuCl_2 \cdot 2H_2O$ (Aldrich, 99.9%) and $Cu(NO_3)_2 \cdot 3H_2O$ (Aldrich, 99.9%). $PdCl_2$–$CuCl_2$/activated carbon contains 1.7 wt% Pd and 6 wt% Cu. The catalyst used for the pilot test contains 2 wt% Pd and 8 wt% Cu (mole ratio of $CuCl_2$ to $Cu(NO_3)_2$ was 1 : 2) and was denoted as low temperature catalytic removal of carbon monoxide (LTCRC) catalyst. This catalyst was dried at ambient temperature and used for the reaction without any further pretreatment.

2.2. CO oxidation

In bench scale experiments, the catalytic oxidation of carbon monoxide was examined in a fixed-bed flow reaction system under atmospheric pressure. The reactor was a 3/8-in. Pyrex tube with a sintered glass disc to hold the catalyst in the reactor. Reaction temperature was monitored by a thermocouple inserted into the center of the catalytic bed. A pre-mixed $CO/O_2/N_2$ stream was supplied to the reactor through a mass flow controller. The feed stream was saturated with water through a saturator enclosed in a constant temperature bath and fed to the reactor. When CH_3Br was fed with reactants, this gas bypassed the water saturator and was supplied into the reactor directly to avoid its dissolution in water. The constant reaction temperature of the reactor was achieved by controlling the temperature of an electric furnace surrounding the reactor. Reactants and products were analyzed by an on-line gas chromatography (HP5890A, molecular sieve 13X column for TCD and HP-FFAP capillary column for FID) and CO infrared analyzer (Thermo Environmental Instrument).

A pilot plant was installed in a side stream (3000 ∼ 10,000 cm^3 (STP)/h) of an oxidation reactor vent of a TA plant. It was composed of a preadsorber, a saturator, a preheating unit, a catalytic reactor, and an on-line gas chromatography as shown in Fig. 2. The preadsorber was filled with activated carbon to remove solid particulates and heavy organics. The saturator and the pre-heater was installed to test the effects of water contents and reaction temperature on the catalytic activity. The pre-heater was designed to be able to increase the reaction temperature above 473 K and the pressure was maintained at 9.5 bar by a back pressure regulator. The feed stream was directly supplied from the reactor vent of a TA plant and its composition is given in Table 1. Although there were some fluctuations in vent gas composition depending on the process conditions, its variance was not so severe as to induce instability for the pilot test.

2.3. Characterization of catalysts

X-Ray powder diffraction patterns were obtained at room temperature using a M18XHF(MAC Science) with Ni-filtered Cu K_α radiation (1.54056 Å). The

Table 1
Typical composition of TA Vent Gas[a]

Component	Concentration
Methyl acetate	408 ppm
Toluene	2 ppm
Benzene	2 ppm
p-xylene	7 ppm
Methanol	90 ppm
Methyl bromide	35 ppm
CO	3500 ppm
H_2O	4300 ppm
O_2	2.5 ~ 5%

[a] Off-gas is balanced with N_2 and CO_2.

X-ray tube was operated at 40 kV and 200 mA. Samples were finely ground and packed into a glass holder having a 18 × 18 × 2-mm opening. No adhesive or binder was necessary. The 2θ angles were scanned at a rate of $4^\circ min^{-1}$.

The palladium and the copper contents in the catalyst were determined by Perkin–Elmer AAS 5100PC and the chlorine content was measured by a UV–VIS spectrophotometer (Perkin–Elmer Lambda 5).

3. Results and discussion

3.1. Catalyst screening

Effects of CH_3Br in the feed on CO oxidation were examined over various low temperature CO oxidation catalysts. As shown in Fig. 3(A), Ag–Mn–Co oxides reported to be superior to commercial Hopcalite in CO oxidation by Haruta et al [3] showed a decreasing catalytic activity in the presence of CH_3Br while a stable activity was maintained in the absence of CH_3Br. This decreasing activity in CO conversion was also observed over Mn–Cu oxides (Fig. 3(B)). CH_3Br was also oxidized to Br_2 and HBr over both catalysts and its conversion was higher over Ag–Mn–Co oxides than over Mn–Cu oxide. Therefore, metal oxides were not suitable for our purpose. Supported gold catalysts have been reported to oxidize CO even below 273 K and to show a higher CO conversion in the presence of water as long as gold is well-dispersed [4,14]. Commercial $Au/Fe_2O_3/Al_2O_3$ catalysts showed a stable activity even in the presence of water at 333 K but the activity decreased in the presence of CH_3Br both at 333 and 423 K as shown in Fig. 4. CH_3Br conversion was negligible at 333 K, but at 423 K, the oxidation of CH_3Br was the main reaction catalyzed by $Au/Fe_2O_3/Al_2O_3$. The strong adsorption and dissociation of the halogen compound on metal seems to cause a decreased activity [15]. Carbon-supported $PdCl_2$–$CuCl_2$ catalysts showed no detectable change in activity in the presence and absence of CH_3Br (Fig. 5), and CH_3Br merely adsorbed on the catalysts (probably physically on carbon) without being converted to inorganic Br compounds. The physical adsorption of CH_3Br was confirmed by observing a ready desorption of CH_3Br when temperature was raised. The results of screening tests are summarized in Table 2. Metal oxides including Co_3O_4, MnO_2, CuO, NiO and mixed metal oxides showed a stable activity only in the absence of water vapor at low temperatures and the supported noble metal catalysts such as Pt and/or Pd supported on alumina and titania possesses an oxidizing ability in the presence of water and halogens only at high temperatures [16]. Although metal oxide-supported gold catalysts such

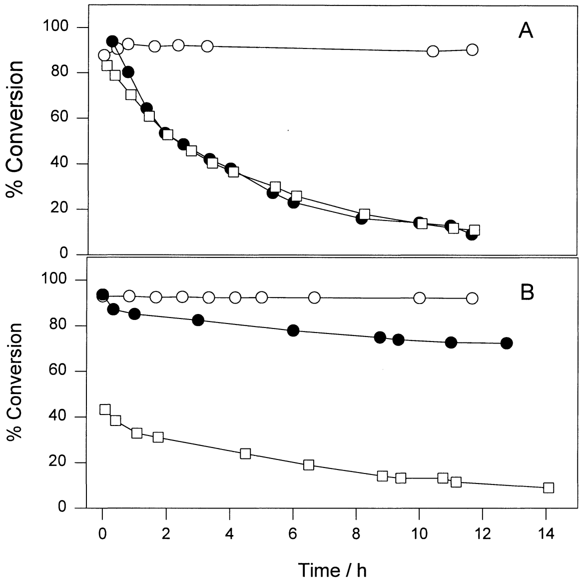

Fig. 3. Effects of CH_3Br on CO oxidation over Ag–Mn–Co oxides (A) and Mn–Cu oxide (B) at 393 K. The reactants, CO, O_2 and H_2O were fed to the catalyst at a rate of 45,000 cm^3 feed/g-cat/h and at a concentration of 1, 10 and 1.5 vol% each in nitrogen; CO conversion in the absence of CH_3Br (○) and in the presence of 35 ppm CH_3Br (●), and CH_3Br conversion (□).

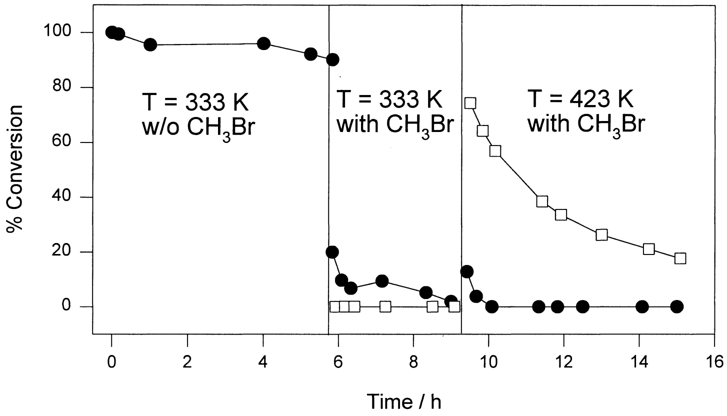

Fig. 4. Effects of CH_3Br on CO oxidation over $Au/Fe_2O_3/Al_2O_3$ at 333 and 423 K. The reactants, CO, O_2 and H_2O were fed to the catalyst at a rate of 45,000 cm^3 feed/g-cat/h and at a concentration of 1, 10 and 1.5 vol% each in nitrogen; CO conversion (●), and CH_3Br conversion (□).

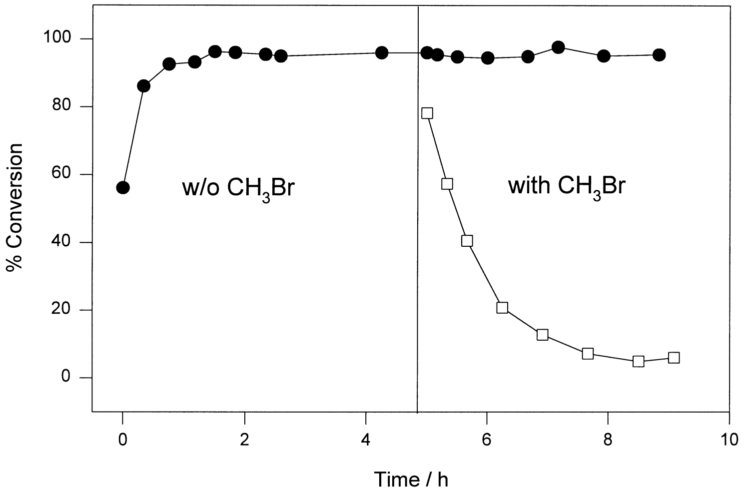

Fig. 5. Effects of CH_3Br on CO oxidation over $PdCl_2$–$CuCl_2$/activated carbon at 313 K. The reactants, CO, O_2 and H_2O were fed to the catalyst at a rate of 6000 cm^3 feed/g-cat/h and at a concentration of 0.35, 10 and 1.5 vol% each in nitrogen; CO conversion (●), and CH_3Br conversion (□).

as Au/Fe_2O_3 and Au/Co_3O_4 showed a higher activity in the presence of water than without water, CH_3Br deactivated these catalysts [16]. However, supported Wacker catalysts showed a stable activity in the presence of water and even CH_3Br at reaction temperatures suitable for a low-temperature CO oxidation process. The final catalyst chosen for the pilot plant test contained both $CuCl_2$ and $Cu(NO_3)_2$ as copper precursors. Lloyd and Rowe [7] has claimed that $Cu(NO_3)_2$ serves as a promoter for this type of catalyst when supported on alumina and used for CO oxidation. A similar promotional effect was found on active carbon-supported catalysts as well. As reported elsewhere [13], addition of $Cu(NO_3)_2$ promoted the formation of the active solid phase of copper, $Cu_2Cl(OH)_3$, which facilitated the reoxidation of reduced Pd species in the Wacker chemistry. In this catalyst system, it was demonstrated by X-ray absorption fine structure (XAFS) that palladium remained as a molecular Pd(II) species containing Cl and possibly CO ligands [17–18].

Table 2
Summary of the screening test for CO oxidation[a]

Catalytic system	Reaction temperature	In dry condition	In wet condition[b]	In the presence of CH_3Br[c]
Metal oxides (Ag–Mn–Co oxide, Mn–Cu oxide)	<100°C	active	inactive	inactive
	100–150°C	active	active	inactive
	>300°C	active	active	not determined
Supported noble metal (Pt/TiO_2, Pd–Pt/TiO_2)	<100°C	inactive	inactive	inactive
	100–150°C	active	inactive	inactive
	>300°C	active	active	active
Au/metal oxides (Au/Fe_2O_3/Al_2O_3 Au/Co_3O_4)	<100°C	active	active	inactive
	100–150°C	active	active	inactive
	>300°C	active	active	not determined
$PdCl_2$–$CuCl_2$–$Cu(NO_3)_2$/carbon	<100°C	inactive	active	active
	100–150°C	inactive	active	active
	>300°C	not determined	not determined	not determined

[a] Typical reaction conditions were same as shown in Fig. 3.
[b] 1–3 vol% H_2O was fed.
[c] 35–50 ppm CH_3Br was fed.

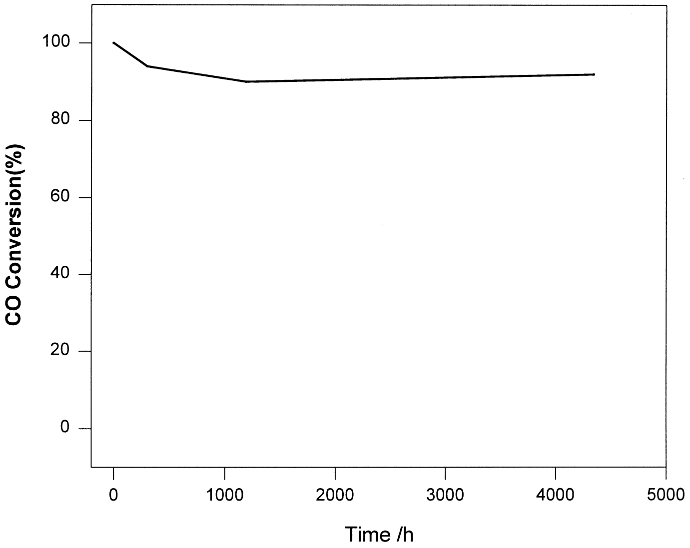

Fig. 6. CO conversion in a pilot test at 393 K and 9.5 bar at a space velocity of 20,000 cm^3 feed/g-cat./h; the feed stream passed through a saturator at 363 K.

3.2. Pilot plant test

The LTCRC catalyst was tested in a pilot plant with a side stream (3000–10,000 cm^3(STP)/h) of an oxidation reactor vent gases of a TA plant. At 393 K and 9.5 bar, the catalyst maintained a stable CO conversion of ca. 90% in treating 20,000 cm^3 feed/g-cat/h containing ca. 3500 ppm of CO in a continuous operation of six months as shown in Fig. 6. The catalytic activity decreased initially but a steady-state activity was reached. To understand the initial decline in activity, the catalyst tested for 500 h in the pilot plant were characterized. Fig. 7 shows the X-ray diffractogram of the LTCRC catalyst before and after reaction for 500 h. Only a $Cu_2Cl(OH)_3$ phase was observed in both catalysts, but the peak intensity decreased after the

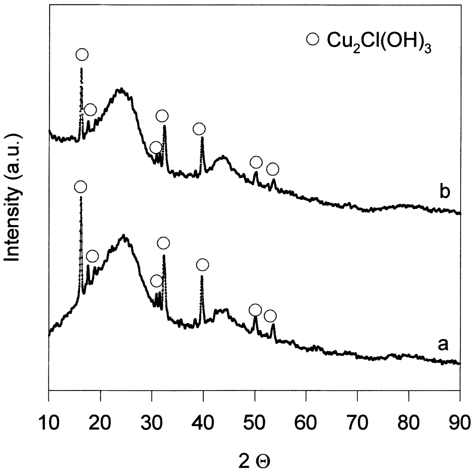

Fig. 7. X-ray diffractogram of a carbon-supported Wacker-type catalyst before the reaction (a), after 500 h of the reaction in the pilot plant.

reaction. As has been reported elsewhere [13], the XRD line intensity of $Cu_2Cl(OH)_3$ from a catalyst was proportional to its catalytic activity and that the change in catalytic activity in CO oxidation with respect to different reaction and preparation conditions was directly related to the change in the XRD line intensity of the active copper phase with respect to those variables. Therefore, the initial decreasing activity seems to be related to a change in amount of active copper phase. The chemical analysis was also performed. No change in Pd content was observed but the amount of Cu and Cl decreased from 8.06 and 2.23 wt% to 5.58 and 0.89 wt%, respectively, after 500 h of operation. This loss of copper and chlorine is believed to be responsible for the decreased peak intensity of $Cu_2Cl(OH)_3$. A slight decrease of BET surface area from 643 to 621 m^2/g was also observed. A temperature higher than 373 K was required to prevent the condensation of aromatic hydrocarbons that were present in a trace amount in the vent stream of the TA plant in the catalyst pores.

3.3. Process description of the commercial CO removal plant

The schematic diagram of the process installed in a TA plant for low temperature CO oxidation is shown in Fig. 8. This process can remove CO in the off-gas from the high pressure scrubber of TA processes down to the level allowed legally (<350 ppm) and bring the purified gas to the downstream process. This process consists of a preadsorber which removes the high molecular weight organic compounds, a saturation unit which provides the off-gas with water vapor, a heating unit, a catalytic oxidation unit, and a scrubbing unit. A part of CO-removed off-gas is dried in order to be used in pneumatic conveying of TA product powders and the rest is brought to the off-gas expander for power recovery.

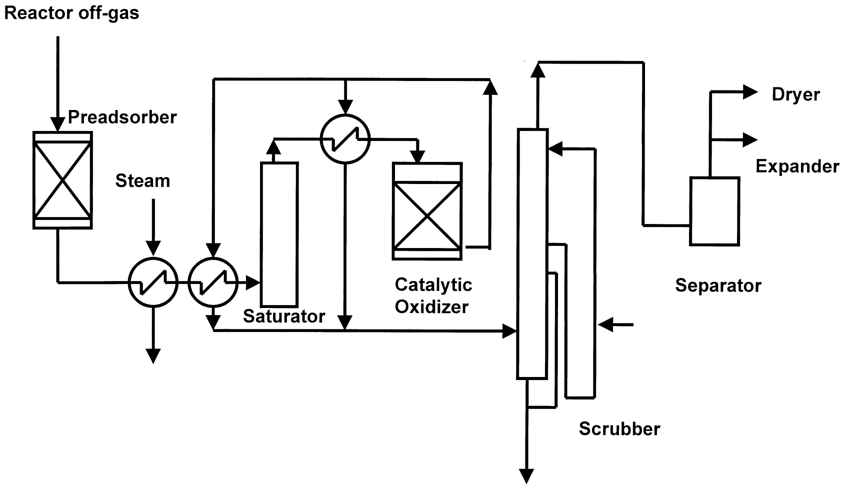

Fig. 8. Schematic diagram of a process developed for the low temperature oxidation of CO generated from a terephthalic acid plant.

The LTCRC catalyst can maintain its activity in the presence of water vapor. Therefore, the saturation unit provides the off-gas with the saturation amount of water at 363 K and the subsequent heating unit increase the gas temperature to 393 K. The saturation unit is also designed to be able to remove solid particulates. Extra heat generated in exothermic CO oxidation is carried by the treated off-gas from the catalytic oxidizer and utilized to heat the inlet gas stream. In the catalytic oxidizer, the LTCRC catalyst in the form of granules (4–14 mesh) is packed to oxidize CO into CO_2. Compared with the high temperature oxidation process, the decomposition of Br compounds does not occur to cause the corrosion problem in the downstream. A vent scrubber is installed for the purpose of decreasing the off-gas temperature. The off-gas is vented from the scrubber at 313 K and the excess water is removed in a separator for the stability of downstream process. The part of vent gas is brought to the vent gas dryer and the rest to the off-gas expander. The first application of the process has been made successfully to handle 50,000 Nm^3/h of vent stream.

4. Conclusion

Supported Wacker-type catalyst was stable in the presence of water and CH_3Br at low temperatures. Other catalysts known for low temperature CO oxidation such as metal oxides and supported gold catalysts were deactivated by CH_3Br. In this catalyst system, palladium remains as a molecular Pd(II) species while solid $Cu_2Cl(OH)_3$ is the active copper phase. The formation of stable $Cu_2Cl(OH)_3$ is essential for activity and stability of the catalyst. A new process was developed to oxidize CO at low temperatures (<423 K) in vent streams that also contained halogen compounds. An unreduced Pd and Cu supported on activated carbon was successfully implemented to treat the vent stream of a terephthalic acid plant that contained CH_3Br and water. The CH_3Br remained intact during the reaction and did not deactivate the catalyst. This process can be a promising candidate for solving CO emission problems economically for other vent streams containing organic halogen compounds.

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