Oxidation of Anhydrides Over MgO Promoted Cobalt and Vanadium Oxide Catalysts

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Phthalic anhydride and maleic anhydride could be completely oxidised to CO_2 and H_2O over Co-Mg-O/Al_2O_3 and V-Mg-O/TiO_2 catalysts. Experimental results showed that the cobalt and vanadium oxide catalysts promoted with MgO had superior combustion activity than the unpromoted catalysts.

In the production of phthalic anhydride and maleic anhydride, the anhydride product is recovered by passing the reactor effluent gas to a condenser. The key parameter that controlling the condenser temperature is the water vapour content in the gas. If water is allowed to condense, the anhydride product will change to acid form, thus, equipment corrosion will occur. Usually, at the temperature the water vapour begins to condense, part of the anhydride product still remains in the gaseous phase. The anhydride residue has to be removed before venting the effluent gas to the atmosphere.

Conventional methods such as using scrubber or burning have been used to eliminate the anhydride residue. Both methods, however, do not completely eliminate the problems concerned. Catalytic combustion is another alternative. The type of catalyst depends on the ratio between organic and oxygen. Pt-based catalysts work well at around stoichiometric ratio while metal oxide catalysts work well in oxygen rich atmosphere. In this research, therefore, the metal oxide catalyst is chosen.

Metal oxides known to have capability to oxidise organic compounds are usually acidic or amphoteric, e.g. oxides of V, Co, Cr. These oxides are less likely to adsorb acidic organic compounds. It is interesting if a basic oxide is added to an acidic/amphoteric metal oxide catalyst in order to enhance the adsorption of the acidic compound and make the promoted oxide catalyst suitable for the oxidation of anhydrides.

To test the idea, the oxides of cobalt and vanadium promoted with MgO were investigated. MgO was selected because its basicity is not too low or too high since too high basicity can cause carbonate formation.[1] Cobalt oxide was selected because it was a known hydrocarbon combustion catalyst.[2] Vanadium oxide was selected because it is a well known base catalyst for the production of phthalic and maleic anhydrides.[3] Naturally, the vanadium oxide catalyst does not prefer the further oxidation of the anhydrides to CO_2.

The oxide catalysts studied Co/Al_2O_3 (8.9 wt% Co, surface area 178 m^2g^{-1}), MgO/Al_2O_3 (1.1 wt% Mg, surface area 244 m^2g^{-1}), CoMgO/Al_2O_3 (8.1 wt% Co, 0.68 wt% Mg, surface area, 124 m^2g^{-1}), V_2O_5/TiO_2 (9.1 wt% V (as V_2O_5), surface area 45.2 m^2g^{-1}), MgO/TiO_2 (5.2 wt% Mg, surface area 40.5 m^2g^{-1}) and VMgO/TiO_2 (9.1 wt% V (as V_2O_5), 5.2 wt% Mg, surface area 6.67 m^2g^{-1}) were prepared by wet impregnation method. For the cobalt oxide system, Al_2O_3 (JRC-ALO2, surface area 251 m^2g^{-1}) was added to an aqueous solution of cobalt nitrate and/or magnesium nitrate. For the vanadium oxide system, TiO_2 (JRC-TIO1, surface area 55.2 m^2g^{-1}) was added to an aqueous solution of ammonium metavanadate and/or magnesium nitrate. The solution was dried at 353 K until achieving a thick paste. The obtained paste was calcined in air at 823 K for 6 h to convert the paste into the oxide form.

The structure of CoMgO/Al_2O_3 catalysts prepared from different methods was studied in a separate study[4] by means of X-ray diffraction and electron spin resonance. All the catalysts showed no sign of the high spin Co^{2+} species, suggesting that the cobalt species of the cobalt catalysts studied here must have been in the 3+ state. The study[4] also indicated that cobalt and magnesium likely formed separate oxide compounds.

The structure of vanadium oxide species on the catalyst surface was tested by varying vanadium content. Without MgO, the X-ray diffractometer could detect the presence of V_2O_5 species down to about 4.8 wt%. Since the VMgO/TiO_2 studied here, which contained higher amount of vanadium, did not show any diffraction line of V_2O_5 crystal, we concluded that some vanadium and magnesium formed some binary oxide species on the TiO_2 surface. Because vanadium can easily form binary oxides (ortho-, meta-, or pyro-vanadate) with magnesium oxide and the valance of vanadium cation in these oxides is 5+. It is likely that the vanadium cation is in the form of V^{5+}.

The catalytic performance test was performed in a 3/8″ OD SS-304 stainless steel fixed-bed reactor packed with 0.1 gram of catalyst (100–150 mesh). The anhydrides (phthalic and maleic) were fed via a vaporiser. Pure dry air was used as oxygen source. The feed contained 0.016–0.05 mol% anhydride in air, total flow rate 100 ml min^{-1}. The reaction was studied in the temperature range 473–823 K. CO, CO_2, and H_2O were analyzed using a gas chromatograph Shimadzu GC 8A equipped with a TCD and a MS-5A Porapak-Q column. The anhydrides were analyzed using a gas chromatograph Shimadzu GC 9A equipped with a FID and a chromosorb W column. Total carbon balance in the reactor effluent gas was with in the range 100 ± 5%.

The catalytic activity of the cobalt oxide system is shown in Figures 1 and 2. For both reactions, the main carbon containing product found was only CO_2. Figure 1 shows that Co/Al_2O_3 exhibited slightly higher activity towards phthalic anhydride

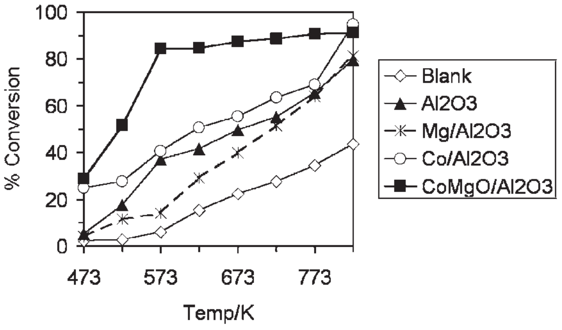

Figure 1. Phthalic anhydride oxidation (0.05 mol% PA in air).

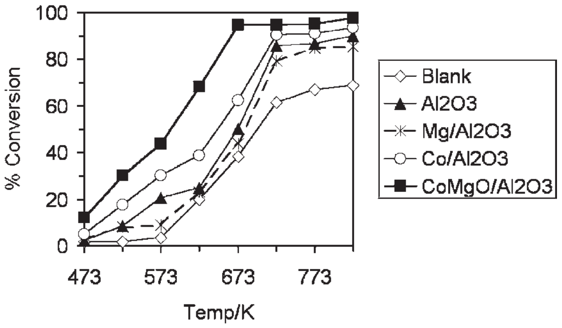

Figure 2. Maleic anhydride oxidation (0.05 mol% MA in air).

combustion than that of pure Al_2O_3. On the contrary, Al_2O_3 doped with MgO (MgO/Al_2O_3) exhibited lower combustion activity. This result indicated that MgO itself was not an oxidation catalyst for the combustion of phthalic anhydride.

When cobalt and magnesium were combined together, however, the combustion activity significantly increased. The phthalic anhydride combustion activity of $CoMgO/Al_2O_3$ significantly higher than that of Co/Al_2O_3. The addition of MgO promoted the catalytic combustion activity of the cobalt possibly by enhancing the adsorption of phthalic anhydride on the catalyst surface. Thus, allowing phthalic anhydride to stay on the catalyst surface long enough to be oxidised by the adjacent cobalt active sites. The conversion of phthalic anhydride over $CoMgO/Al_2O_3$ could achieve 80% at 573 K. Due to the catalyst bed was rather thin, part of the reactant gas could channel through the bed without contacting with the catalyst. This limited the maximum conversion to be a little bit lower than 100%.

Maleic anhydride conversion is shown in Figure 2. Co/Al_2O_3 showed slightly higher activity towards maleic anhydride combustion than that of pure Al_2O_3. On the contrary, Al_2O_3 doped with MgO (MgO/Al_2O_3) showed lower activity. The result indicated that MgO itself did not promote the combustion of maleic anhydride. However, when cobalt and magnesium were combined together, the activity significantly increased. The reason how MgO increased the maleic anhydride combustion activity of cobalt oxide is the same as the case of phthalic anhydride combustion. The oxidation results showed that magnesium acted as a promoter for cobalt oxide in the oxidation of both anhydrides.

The catalytic activity of the vanadium oxide system is shown in Figures 3 and 4. For both reactions, the main carbon containing product observed was also CO_2. Figure 3 shows the results obtained from phthalic anhydride oxidation. V/TiO_2 possessed slightly lower activity towards phthalic anhydride combustion than that of TiO_2. TiO_2 doped with MgO exhibited much lower activity. When cobalt and magnesium were combined together, the combustion activity significantly increased. The role of MgO in the vanadium oxide system is believed to be same as the role of MgO in the cobalt oxide system. The conversion of phthalic anhydride over $VMgO/TiO_2$ could achieve 80% at 723 K.

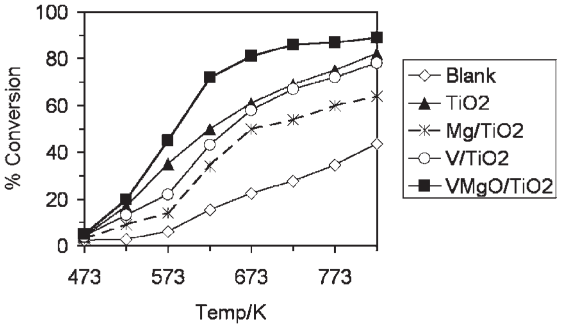

Figure 3. Phthalic anhydride oxidation (0.016 mol% PA in air).

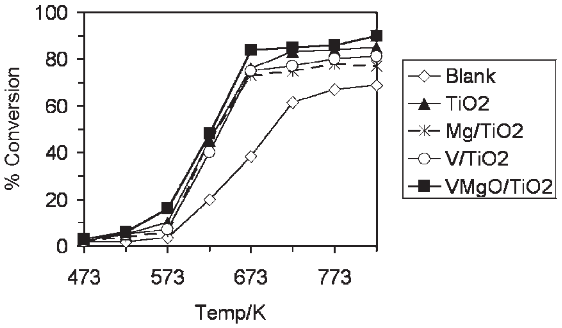

Figure 4. Meleic anhydride oxidation (0.05 mol% PA in air).

Figure 4 illustrates the conversion of maleic anhydride. V/TiO_2 showed slightly lower activity towards maleic anhydride combustion than that of TiO_2. TiO_2 doped with MgO (MgO/TiO_2), showed further lower activity than that of V/TiO_2. When vanadium and magnesium were combined together ($VMgO/TiO_2$), however, the combustion activity significantly enhanced. The oxidation of phthalic anhydride and maleic anhydride showed that MgO acted as a promoter for vanadium oxide in the oxidation of both anhydrides.

For the vanadium oxide catalyst, the promoting effect of MgO for the combustion of maleic anhydride was not so pronounced as in the case of the combustion of phthalic anhydride. This is possibly because the structure of maleic anhydride was easier to decompose than the structure of phthalic anhydride. Maleic anhydride has two active structure, the C=C bond and the anhydride functional group. The phthalic anhydride has the active position to initiate the reaction only at the anhydride ring while the benzene ring is hardly to decompose.

The combustion of phthalic anhydride and maleic anhydride indicated that magnesium oxide showed the role of promoter for both cobalt and vanadium oxide systems. Magnesium oxide promoted the adsorption of the anhydrides on the catalyst surface, providing more opportunity for the anhydrides to react with the adjacent cobalt or vanadium active sites.

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