Effects of Cl Ions upon Combustion of Particulate on TiO_2-supported CuO Catalysts

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Combustion of diesel particulate on titania-supported copper oxide was enhanced when it was prepared from copper chloride. This was ascribed to chlorine ions still remaining in the catalyst, since the catalyst prepared from copper nitrate showed a poor activity for combustion. It was also found that the high activity was elongated by an addition of KCl into the catalyst prepared from copper chloride.

Combustion of particulate matter in exhausts from a diesel engine is one of the problems to be solved for better environments. Yoshida et al. are the first who developed techniques for simultaneous abatement of both NOx and particulate in diesel exhausts using CuO-based catalysts.[1] Kagawa et al. have studied reactions between NO, O_2 and particulate on various perovskite and spinel type oxides, and has concluded that K doped $CuFe_2O_4$ was quite effective for the simultaneous abatement of both NOx and particulate around 573 K.[2] It is obvious that the particulate reacted with O_2, as well as with NOx, during reaction to yield CO_2 in the presence of catalyst, though noncatalytic combustion of soot particulate has been reported to take place at 873 K.[3]

In this work combustion of soot particulate was carried out on CuO/TiO_2 catalysts prepared from different precursors;copper nitrate and chloride. Catalysts were prepared by a conventional impregnation using TiO_2 powder, obtained through hydrolysis of titanium iso-propoxide, and aqueous solution of $Cu(NO_3)_2 3H_2O$ or $CuCl_2 2H_2O$. Impregnated catalysts were dried at 383 K for 24 h, followed by calcination at various temperatures for 4 h. CuO loading was settled to be 10 wt % of the catalysts. The catalyst powder was mechanically mixed with particulate, derived from a diesel and light-gas engine, and the weight ratio of catalyst to particulate was 10. Catalyst/particulate mixture (0.5 g) was held in a reactor, connected to a flow system. The reactor was heated up to 973 K, with a temperature rising rate of 5 K min^{-1}, in flowing 10 % O_2/He with a flow rate of 10 ml min^{-1}. Water vapor and CO_2 yielded by the combustion were eliminated using molecular sieve trap in order to estimate the amounts of O_2 consumed by a TCD detector; so called TPO measurements.

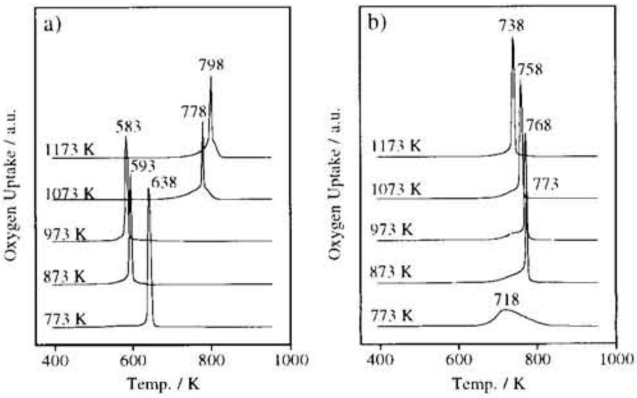

Figure 1. TPO spectra of the catalyst/particulate mixtures. ((a):catalyst from copper chloride, and (b):from copper nitrate)

Figure 1-a shows the results obtained for catalysts prepared from $CuCl_2$ and calcined at various temperatures before mixed with the particulate. Oxygen consumption was measured around 600 K for catalysts calcined at 973 K or lower, while for the catalysts calcined at temperatures higher than 973 K oxygen consumption took place around 790 K. Since catalyst activity is evaluated by an ignition temperature where combustion of particulate starts, the catalysts calcined at temperatures lower than 973 K are concluded to be more active than those calcined at higher temperatures. Figure 1-b shows TPO spectra of catalyst/particulate mixtures; the catalyst was prepared from $Cu(NO_3)_2$. O_2 consumption was always observed around 758 K, regardless of the catalyst calcination temperature.

In order to reveal the reason why the catalysts prepared from $CuCl_2$ and calcined at lower temperatures were active for the combustion of particulate, XRD of the catalysts were measured. Figure 2-a shows changes in the XRD patterns of catalysts from $CuCl_2$ with calcination temperature. It was found that chlorine ions still remained in the catalysts, calcined at 973 K or lower, in the crystallographic structure of $Cu_2Cl(OH)_3$ and/or CuCl(OH).

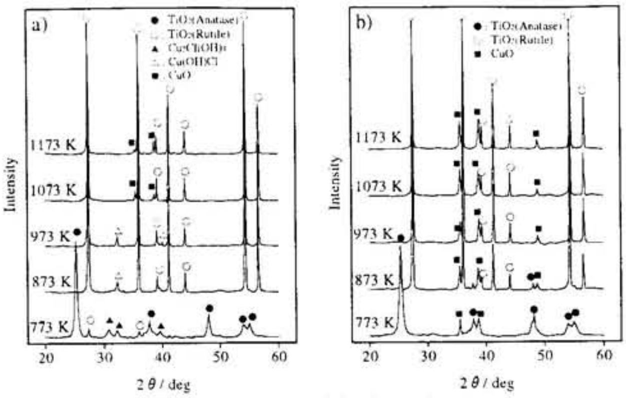

Figure 2. XRD of the catalysts calcined at various temperatures. ((a):catalyst from copper chloride, and (b):from copper nitrate)

It must be noted that the hydroxy chlorides were never detected in the catalyst after particulate combustion, suggesting evolution of HCl from the catalyst during combustion. Less activity was observed when the catalysts were iteratively used. No chlorine ions were detected in the catalysts calcined at the temperatures higher than 973 K, and only the diffraction peaks assigned to TiO_2 or CuO were detected. Figure 2-b shows XRD patterns of the catalysts prepared from $Cu(NO_3)_2$ calcined at various tem-

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peratures, merely indicating the crystallographic transformation from anatase to rutile and crystal growth of CuO as calcination temperature increased. These observations likely lead us to the conclusion that chlorine ions remaining in the catalyst are responsible for the combustion of particulate as low as around 600 K. One of the possible elucidation of the role of chlorine ions for particulate combustion is the formation of active oxygen ions, caused by evolution of HCl from hydroxy chlorides as follows; $CuCl(OH) \rightarrow CuO^{*} + HCl$ or $Cu_2Cl(OH)_3 \rightarrow 2CuO^{*} + HCl + H_2O$, where O* in CuO* means the active oxygen ions. According to the paper by Kagawa et al.,[2] combustion of particulate passes through oxygen containing active species, $C^{*}[O]$, as a reaction intermediate. Thus, the active oxygen ions in CuO^{*} enhance the rate of $C^{*}[O]$ formation at temperature as low as 600 K. Moulijn and coworkers[4] have proposed that the particulate combustion takes place on the active oxygen ions generated from Cu_2OCl_2, formed by the reaction between CuO and KCl additives.

In order to distinguish the reactivity of the active oxygen in CuO^{*} and of the lattice oxygen in CuO, TPR measurements were carried out using 10 % H_2/He in the same way as mentioned in TPO measurements. Figure 3 depicts the results obtained for the catalysts from $CuCl_2$. No distinct peaks were observed for the catalyst calcined at the temperatures higher than 973 K, which means that the lattice oxygen ions in CuO are less active toward hydrogen. In the TPR spectra for the catalysts calcined at 973 K or lower, two small peaks were detected. The first peak observed at the temperatures lower than 573 K is due to the evolution of HCl, caused by the reaction of chlorine ions in the catalysts and gaseous, or adsorbed, hydrogen, and the second peak is due to the reaction of active oxygen in CuO^{*}, generated by the HCl evolution, and gaseous or adsorbed hydrogen. Now, we conclude that active oxygen ions are generated by the evolution of HCl from CuCl(OH) remaining in the catalysts, and that the oxygen ions in CuO lattice are less active toward hydrogen as well as soot particulate.

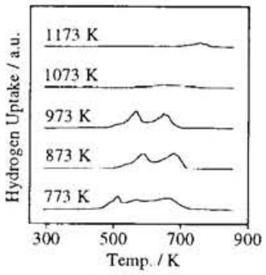

Figure 3. TPR spectra of the catalysts prepared from $CuCl_2$.

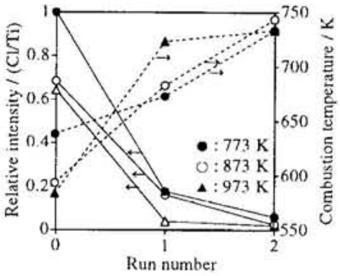

Figure 4. XPS peak intensity ratio of Cu/Ti and combustion temperatures.

Concentration of chlorine ions on the catalyst surfaces was estimated by means of XPS measurements, where chlorine concentration was given in terms of the peak intensity ratio of Cl/Ti in the XPS spectra. Figure 4 shows changes in the relative concentration of Cl ions on fresh and iteratively used catalysts, prepared from copper chloride and calcined at 773~973 K. The ignition temperature of the particulate combustion on respective catalyst is also given in Figure 4, indicating the decrease in Cl ion concentration on the catalyst surface with the number of iterative use for particulate combustion, hence the elevation of ignition temperature. This result also supports the conclusion that chlorine ions remaining on the catalysts, which generate the active oxygen ions by the evolution of HCl, are responsible for enhanced combustion of the soot particulate.

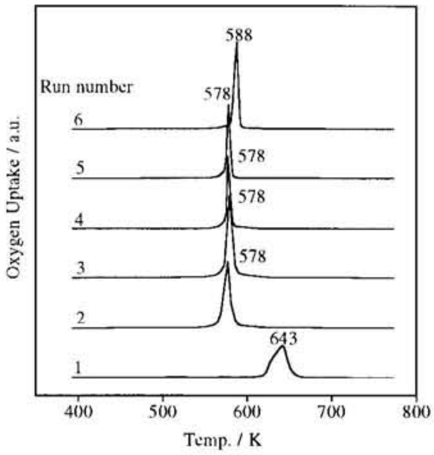

Figure 5. TPO spectra of KCl-doped catalyst/particulate mixtures.

Since the catalyst activity was found to depend upon the amount of chlorine ions remaining in the catalyst, a significant amount of KCl (10 wt% of the catalyst) was dispersed in the catalyst by coimpregnation using a mixed aqueous solution of $CuCl_2 2H_2O$ and KCl, followed by calcination at 773 K for 4 h. Then, the catalyst was mixed with the particulate, in the same manner as noted above, to be submitted to iterative combustion experiments. Results obtained are given in Figure 5, showing no increase in the ignition temperature during 6 times of iterative combustion. The role of doped KCl will be to supply an enough amount of chlorine ions to the catalyst so as to generate active oxygen ions on the catalyst surface by the solid state reaction as follows; $CuO + KCl + H_2O \rightarrow CuCl(OH) + KOH$, and $CuCl(OH) \rightarrow CuO^{*} + HCl$. A catalyst exhausting HCl should not be applied to automobiles, but the generation of active oxygen ions will be designed on catalyst surfaces by other chemical reactions.

References

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