

Copper(II) Oxide Supported on Alumina: Interaction of Copper Ions with Hydroxyl Groups of Alumina

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The state of CuO deposited on alumina depends on the copper loading: at low loadings (CuO content smaller than 6 wt%), copper is present in the form of Cu^{2+} ions formed by exchange with the hydrogen atoms of the alumina hydroxyl groups, whereas at high loadings, the formation of bulk copper oxide is observed and the hydroxyl groups of alumina are recovered.

Copper(II) oxide is one of the most efficient catalysts which can be used as a noble metal substitute for the combustion of hydrocarbons.¹ The use of a thermally stable support such as alumina allows the CuO active phase to be dispersed. However the catalytic properties of the $\text{CuO}/\text{Al}_2\text{O}_3$ solids towards methane oxidation are strongly dependent on the CuO loadings and the conditions of preparation.^{2,3}

Alumina, whatever its structure, is known to possess surface hydroxyl groups, their concentration being dependent upon the type of alumina.⁴ It is well known that the OH groups of a support may act as anchoring sites depending upon the pH of the solution and nature of catalyst precursor, *i.e.*, charge of the metallic complexes, pH of the solution and acid–basic properties of the OH groups.⁵ Thus in some well known cases highly dispersed metallic catalysts are obtained after reduction of the precursor.⁶ The same might also be true for supported oxides, and it seems possible to obtain well dispersed oxide phases provided the number of the precursor ions does not exceed the amount of OH groups.

In the present study, the changes in the density of the OH groups of alumina were followed as a function of the amount of copper phase deposited.

The support was an alumina (Rhône-Poulenc, SCM 129) consisting of a mixture of the γ and δ forms, having a Brunauer–Emmett–Teller (BET) area of $106 \text{ m}^2 \text{ g}^{-1}$ and a pore volume of $0.6 \text{ cm}^3 \text{ g}^{-1}$. Known amounts of aqueous solutions of copper nitrate were added to a suspension of alumina in water. The solids were dried overnight at 120°C after the removal of water under reduced pressure. Finally the samples were calcined under flowing oxygen at 500°C for 14 h in order to achieve the decomposition of the copper salt. Three catalysts containing 2.1, 4.8 and 9.2 wt% CuO have been prepared.

FTIR Spectrometry was used to follow the changes in the hydroxyl group coverage of alumina. The catalysts were compressed in a self-supported wafer calcined at 500°C under oxygen and finally treated *in vacuo* for two hours at 550°C . The spectra of pure Al_2O_3 and of the $\text{CuO}/\text{Al}_2\text{O}_3$ samples show four ν_{OH} bands at 3790, 3750, 3730 and 3690 cm^{-1} . The most intense band at 3730 cm^{-1} was used as an indicator of the concentration of alumina hydroxyl groups. Whatever the copper loading, the four ν_{OH} bands were observed with similar relative intensities (Fig. 1). Taking into account the weight of the wafers, the optical density (OD) of the 3730 cm^{-1} band was measured and expressed per gram of sample. The evolution of the OD of the 3730 cm^{-1} band as a function of the copper loading is shown in Fig. 2. The integrated absorbance of the ν_{OH} bands was also measured in the $4000\text{--}3500 \text{ cm}^{-1}$ range and normalized to one gram of catalyst. Its variation with the copper content is also given in Fig. 2. Both curves follow the same changes with the copper loading suggesting that the interaction of copper species with the alumina surface is not specific to one type of hydroxyl group.

For the first three samples, *i.e.*, for pure alumina and for the two less loaded $\text{CuO}/\text{Al}_2\text{O}_3$ catalysts, the concentration of surface OH groups decreases continuously with the copper content. Extrapolation of this part of both curves leads to a value of 6–7 wt% CuO for the complete disappearance of the hydroxy groups. Previous UV–VIS measurements³ performed

on the same samples have shown that copper ions are essentially in an octahedral coordination state and surrounded by six oxygen ions; the shape and the position of the absorption band observed at 750 nm by reflectance spectroscopy correspond to the CuO_6 chromophore suggesting that copper ions are isolated at the surface of the alumina. In contrast, for the sample containing 9.2 wt% CuO, the UV band at 750 nm is not observed and is replaced by a band at 620 nm which is characteristic of bulk copper oxide.³ At the same time, the density of alumina hydroxyl groups reverts to the value observed for pure alumina.

The following explanation may be advanced for this behaviour. During the impregnation step, aqua complexes of Cu^{2+} ions interact with the alumina hydroxyl groups probably by hydrogen bonding. During the calcination step the water removal leads to isolated copper(II) ions in strong interaction with the support. A substitution of OH groups may be postulated with the formation of Cu^{2+} ions bridged between two Al–O surface groups. Because of the density of surface hydroxyl groups the number of isolated copper ions so bonded

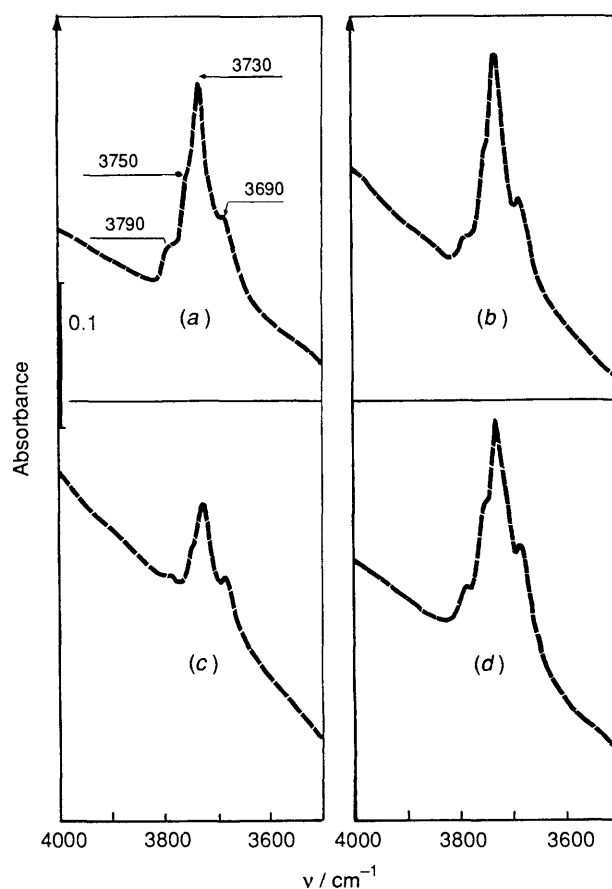


Fig. 1 Infrared spectra in the ν_{OH} range of alumina and $\text{CuO}/\text{Al}_2\text{O}_3$ samples after evacuation at 550°C : (a) pure alumina (32 mg), (b) 2.1 wt% $\text{CuO}/\text{Al}_2\text{O}_3$ (37 mg), (c) 4.8 wt% $\text{CuO}/\text{Al}_2\text{O}_3$ (31 mg), (d) 9.2 wt% $\text{CuO}/\text{Al}_2\text{O}_3$ (38 mg)

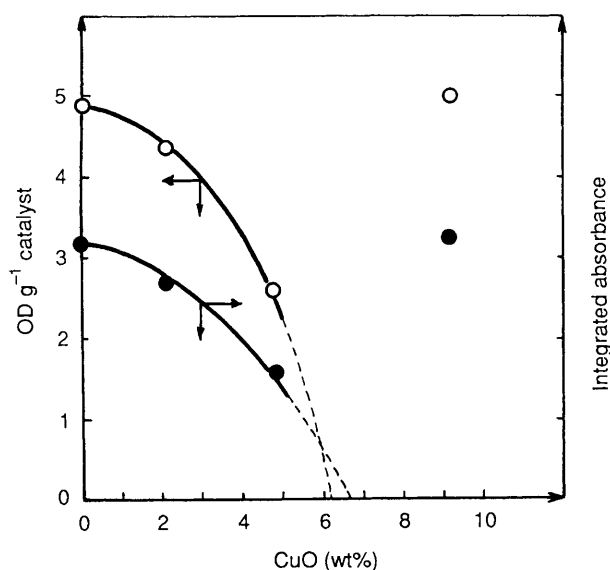


Fig. 2 Variation of the hydroxyl group density with the CuO loading. Open circles (○): optical density (OD) of the 3730 cm^{-1} band expressed per gram of sample. Closed circles (●): integrated absorbance in the $4000\text{--}3500\text{ cm}^{-1}$ range normalized to one gram of catalyst.

is limited. As soon as the number of introduced copper species exceeds the exchange capacity of the support, copper ions sinter into particles of bulk copper oxide. For the highest copper loading (9.2 wt% CuO), the initial OH coverage of pure alumina is recovered, the UV spectrum of isolated Cu^{2+} ions completely disappears and the UV spectrum of bulk CuO is observed. These observations suggest that isolated copper ions agglomerate as soon as particles of bulk CuO are formed. It seems that during the calcination step, there is a kind of a superficial tension forcing the copper ions to agglomerate around the particles of bulk CuO. The ability for copper ions to sinter into bigger particles is related to the crystal field stabilization energy. This extra stabilization is proportional to the crystal field. For isolated ions the crystal field is weaker owing to longer and weaker $\text{Cu}^{2+}\text{--O}^{2-}$ bonds, as revealed by the Cu^{2+} ion absorption band. When the concentration of ions becomes too high there is a tendency for copper ions to gather into copper oxide particles: for such an oxide the crystal field is higher, the copper–oxygen bond is shorter and the stability of copper ions in such species is higher.

The CuO concentration limit for the observation of isolated Cu^{2+} ions is found to be between 6 and 7 wt%. Taking into account the specific area of the alumina support a density of ca. 5 Cu^{2+} ions per nm^2 can be determined. With the hypothesis of the substitution of two hydroxyl groups by one copper ion, it appears that around 10 OH groups per nm^2 are

involved in this exchange process. This value is close to the maximum coverage of the alumina surface by hydroxyl groups.⁴ For higher copper loadings there are no more hydroxyl groups available for exchange; copper introduced in excess is in the form of bulk CuO causing the sintering of the isolated copper ions previously formed. Similar results concerning the influence of copper loading for $\text{CuO}/\text{Al}_2\text{O}_3$ samples have been already reported: most of them concern the appearance of copper oxide particles after a threshold of copper loading as observed by X-ray diffraction.⁷ Particles of CuO appeared. The present study confirms these findings showing that, at least for alumina, there is a concentration limit of precursor which leads to the formation of isolated ions which occurs at the expense of the hydroxyl group content. Above this limit, a bulk oxide form is observed. Isolated ions previously obtained disappear probably because of a nucleation process around the particles of bulk oxide.

Finally and concerning the state of isolated copper ions, no UV band attributable to a tetrahedral coordination of Cu^{2+} ions was observed whatever the loading. Thus the alumina–copper phase is not related to the copper alumina spinel, over which there is still some controversy.⁸ The isolated ions observed in the present study are probably located on the surface with an octahedral or pseudo-octahedral environment of alumina oxygen atoms. In that sense, the cations seem to be 'guest' in some surface hosts. If one copper ion substitutes two OH groups, both belonging to vicinal surface tetrahedral AlO_3OH species, then the Cu^{2+} ion is between two surface AlO_4 tetrahedra and becomes pseudo-octahedrally coordinated, or at least pentacoordinated. These so coordinated ions are still accessible for reactants, for example in catalytic combustion.

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