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CHARACTERIZATION OF COPPER-SILICA CATALYSTS BY MEANS OF *IN SITU* DIFFUSE REFLECTANCE INFRARED FOURIER TRANSFORM SPECTROSCOPY

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Copper silica catalyst precursors have been characterized by diffuse reflectance infrared Fourier transform spectroscopy. The measurements were performed both under atmospheric conditions and under controlled gasatmospheres at elevated temperatures. Two reflection bands at 3615 and 690 cm^{-1} have been attributed to hydroxyl vibrations associated with the presence of copper ions highly dispersed over the silica surface. Calcination of a catalyst precursor at 800 K led to the disappearance of the copper-related surface hydroxyl groups.

1. Introduction

The properties of a supported metal catalyst are determined by its detailed preparation and thermal activation procedure. Many different preparation procedures can be applied either to deposite a metal precursor onto a separately produced solid support or to co-precipitate precursors of both the metal and the support. The temperature (gradient) and the (dynamic) gasatmosphere (composition, flow-rate) during the thermal activation have appeared to additionally determine the properties of the final catalyst.

Extensive characterization of catalysts may facilitate the establishment of the relation between the catalytic properties and the procedures used with the preparation and the thermal activation. In this paper we concentrate on the infrared spectra of the solid catalyst precursors, and especially on the hydroxyl vibrations at the surface. Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy was performed either at atmospheric conditions or during calcination or reduction in an environmental chamber. The spectra are presented both in reflectance and in Kubelka Munk units. The DRIFTS-results have been corroborated with data on temperature-programmed reduction and X-ray diffraction of the catalysts. To identify the structure of the copper-silica catalysts precursors, the infrared spectra were compared with spectra of three mineral copper hydrosilicates, viz. *chrysocolla, dioptase, and plancheite.*

2. Experimental

The silica-supported copper catalysts were prepared by injection of copper ions into a silica suspension (Aerosil 200V, Degussa, F.R.G., 230 m^2/g) kept at a constant pH-level and temperature (catalyst CI 20 pH5.5 T303, 20 wt% Cu), by co-precipitation of copper and silica ($SiCuO_x$, 2.5 wt% Cu) [1], and by homogeneous deposition precipitation using the decomposition of urea at either 363 or 523 K (catalysts CuU30, 30 wt% Cu, and Xhy3, 40 wt% Cu) [2]. The dried catalyst samples were powdered within an agate mortar. The samples were diluted to approximately 20% by either potassium bromide or chloride. These halides were dried at 400 K before use.

The atmospheric measurements were performed with a diffuse reflectance accessory ('collector 1800', Barnes Analytical/Spectra Tech.) in a Perkin Elmer 1710 FT-IR equiped with a DTGS-detector. One hundred scans were co-added, after which the resultant interferogram was Fourier transformed to obtain a resolution of 4 cm^{-1} over the spectral range. The spectra were ratioed to a pure potassium bromide reference sample. The results are shown as reflectance spectra.

A 'Praying Mantis' type diffuse reflectance accessory with a HVC-DR2CN reaction chamber (Harrick Scientific Corp.) was used for the *in-situ* measurements. The infrared spectra were obtained with a Nicolet 7199 FT-IR spectrometer equipped with a medium bandpass MCT detector cooled by liquid nitrogen. The powdered catalyst samples diluted with potassium chloride were exposed to either oxygen (purity 99.8%) or hydrogen (purity 99.98%). The temperature of the sample cup, indicated in the figures, was increased step-wise to 820 K. With hydrogen this maximum temperature could not be reached due to the high thermal conductivity of hydrogen. Furthermore, the actual temperature of the catalyst may have been 100–200 K below the temperature of the heating element due to the poor thermal conductivity of the samples. One thousand interferograms were coadded and Fourier transformed to obtain a resolution of 4 cm^{-1}. The spectra were ratioed against a pure potassium chloride sample at the same temperature to correct for the reflectance of the background.

3. Results

3.1. ATMOSPHERIC MEASUREMENTS

The spectra of the catalysts prepared by different methods are shown in fig. 1. For comparison the spectrum of a bare silica support has been included in this

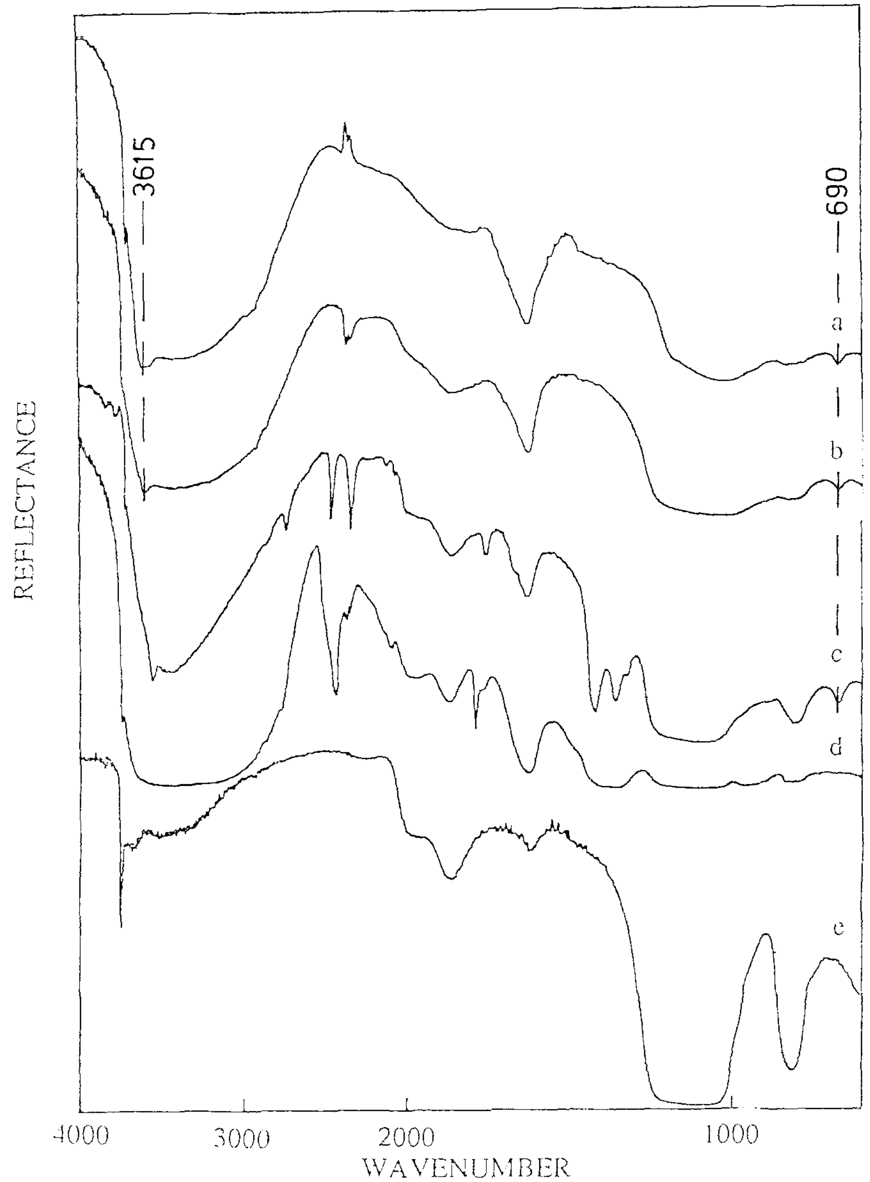

Fig. 1. DRIFT-spectra of copper-silica compounds, a) silica supported copper (CuU30), b) chrysocolla, c) $Cu_2(OH)_3NO_3$ besides silica, d) coprecipitate $SiCuO_x$, e) bare silica (Aerosil).

figure. It appears that the spectrum reflects the dispersion of copper over the support. The main differences are observed in the hydroxyl stretching region (3800–3200 cm^{-1}). With atmospheric measurements a large amount of adsorbed water usually gives rise to the presence of a broad absorption (reflection) band in the hydroxyl region. The sharp bands as observed in some of the spectra of fig. 1, however, are due to isolated hydroxyl groups with a characteristic absorption frequency [3].

The hydroxyl band at 3615 cm^{-1} is indicative of a high dispersion of copper over the surface of the silica support (fig. 1a). This high dispersion is established by homogeneous deposition-precipitation with urea decomposition. The preparation conditions during urea decomposition give rise to the deposition of copper ions onto a reactive (slightly soluble) silica support. Years ago, it has been supposed that the interaction between the copper ions and the silica support results in the formation of some copper hydrosilicate [4]. It is thus interesting to note that we also observed the 3615 cm^{-1} OH vibration in the naturally occurring mineral *chrysocolla*, $CuSiO_3 \cdot 2H_2O$ (fig. 1b). A detailed description of this copper hydrosilicate, which has recently been applied as a catalyst support [5], is given by Pohlmann and Alson [6]. The microcrystalline mineral chrysocolla has been investigated by means of X-ray diffraction. The structure proposed by Van Oosterwijck-Gastuche clearly shows an atomic dispersion of OH-covered copper ions over the silica support [7]. We thus associate the OH-stretch at 3615 cm^{-1} with isolated hydroxyl groups attached to these highly dispersed copper ions. The copper ions in chrysocolla exhibit an octahedral coordination and are associated to either two or four hydroxyl groups. Other copper hydrosilicates described in the literature contain copper ions in either tetrahedral or octahedral coordination [8,9]. The infrared spectra of *dioptase* and *plancheite* exhibit isolated hydroxyl vibrations at wavenumbers between 3400 and 3000 cm^{-1}. Thus infrared measurements on minerals of a well-established structure facilitate to unravel the complex arrangement of copper ions in the catalyst precursor.

As evidenced by X-ray diffraction, injection of a copper nitrate solution at a pH-level of 5.5 at a temperature of 303 K results in precipitation of basic copper nitrate (*gerhardite*) $Cu_2(OH)_3NO_3$ beside the suspended silica support [1]. Since there is no interaction between the nuclei of this basic copper salt and the silica surface, large crystallites are formed. Due to the low dispersion of copper in gerhardite and the absence of any copper-silica compound in this sample, the 3615 cm^{-1} vibration is not found (fig. 1c). Instead reflection bands are observed at 3549 cm^{-1} due to a hydroxyl vibration, and at 2741, 2468 and 1760 cm^{-1} for the NO_3-species in $Cu_2(OH)_3NO_3$ [10].

Figure 1d shows the spectrum of the catalyst $SiCuO_x$ prepared by addition of silicic acid to an acidic copper nitrate solution (co-precipitation) [1]. There are no vibrations around 3600 cm^{-1} due to isolated hydroxyls present in the DRIFT spectrum of this sample. Remarkable vibrations are, however, detected at 2429 and 1788 cm^{-1}. A definite assignment of these bands has not been accomplished as yet. The presence of some NO_3 in the catalyst can, however, not be excluded. Apparently, there are no highly dispersed copper ions present at the surface of the catalyst prepared by co-precipitation. A more extensive characterization has shown that the copper ions are completely incorporated into the silica support with this catalyst.

The spectrum of the silica support, prepared by flame hydrolysis (Aerosil 200 V, Degussa, F.R.G.), shows the free silanol vibration at 3748 cm^{-1}, which is also observed in the other samples (fig. 1e). The peak at 3748 cm^{-1} arises from free OH groups at the silica surface, either single or geminal silanol groups ([11] and references cited therein). Since theoretical calculations predict very closely spaced frequencies for these two structures, a distinction cannot be made based on infrared spectroscopy [12].

After reduction at 1000 K in 10% H_2/Ar and passivation in 10% O_2/Ar, samples CuU30 and $SiCuO_x$ were characterized again by atmospheric measurements. The vibration at 3615 cm^{-1} ascribed to hydroxyl groups associated to highly dispersed copper ions on silica has now disappeared, whereas the isolated hydroxyl on silica remained present. The spectrum of the $SiCuO_x$ catalyst has changed dramatically upon reduction, since no hydroxyl vibrations are observed at all. Closer examination of this sample by X-ray diffraction during temperature-programmed reduction showed the formation of crystobalite at approximately 900 K [1]. The reduced copper is covered completely by this silica modification and thus not accessible anymore. The reduced and evacuated catalyst could not be re-oxidized at temperatures up to 1000 K. The effect of heat treatments on the spectrum of the catalysts will be dealt with in more detail with the *in-situ* measurements.

The presence of hydroxyl groups at the surface of the solid catalyst precursors CuU30 and Xhy3 during both calcination and reduction was investigated by means of in situ DRIFT spectroscopy, using an environmental chamber.

3.2. CALCINATION

The reflection spectra obtained during calcination of sample Xhy3 at increasingly higher temperatures are shown in fig. 2. Upon calcination, the broad band in the hydroxyl-stretch region (3800–3000 cm^{-1}) due to physisorbed water and hydrogen bonded hydroxyl groups strongly decreased already after treatments at 300 K. As a consequence the isolated hydroxyl vibrations due to silanol and the highly dispersed copper species can be observed more clearly than with the atmospheric measurements. It can be seen that the band at 3615 cm^{-1} disappears only after calcination at 823 K. The intensity of the isolated silanol group also decreases during calcination. Since the reflectance may not be a correct (proportional) measure for the intensity, the results are also presented in a Kubelka-Munk plot (fig. 3). Apart from changes in the frequency range 4000–3000 cm^{-1}, a band at 690 cm^{-1} disappears from the spectrum as well (*vide supra*).

3.3. REDUCTION

After calcination the Xhy3 sample was cooled to room-temperature in oxygen, evacuated, and subsequently exposed to a flow of hydrogen. The spectra obtained

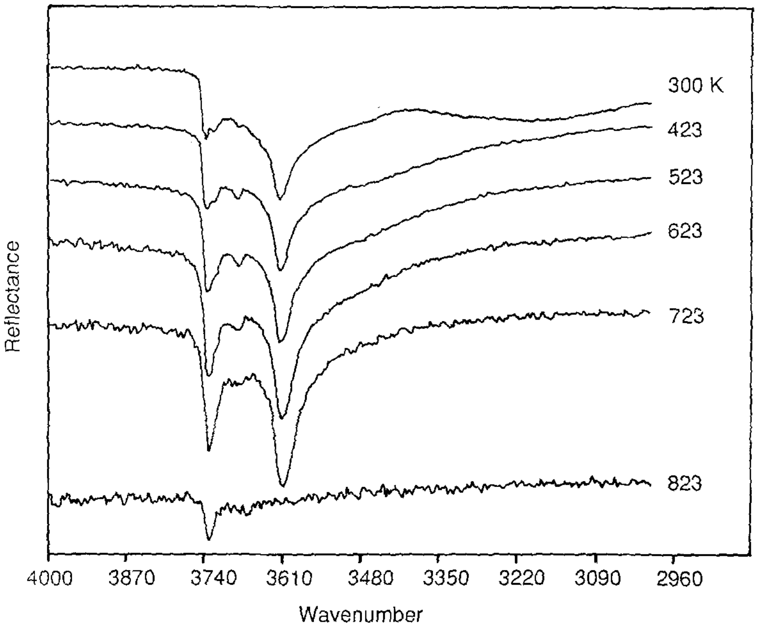

Fig. 2. Diffuse reflectance of Xhy3 during calcination at indicated temperature.

during the subsequent temperature ramp are shown in Kubelka-Munk units (fig. 4). By increasing the temperature the reduction process is initiated; the reduction is completed at higher temperatures. The spectrum obtained at low temperatures

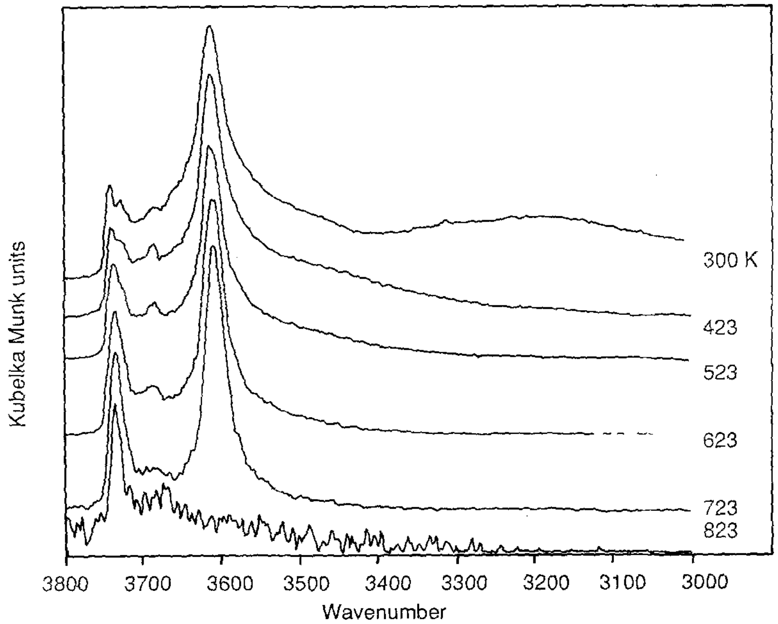

Fig. 3. Kubelka-Munk plot of Xhy3 during calcination at indicated temperature.

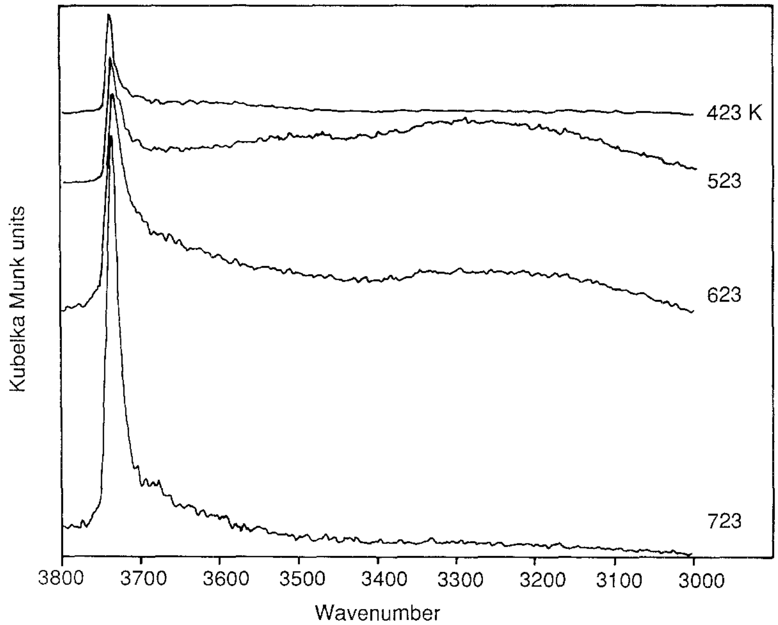

Fig. 4. Kubelka-Munk plot of a pre-calcined Xhy3 catalyst during reduction at indicated temperature.

essentially shows only the isolated silanol group at 3748 cm^{-1}. Upon raising the temperature the intensity of this band increases and a broad band shows up in the region 3700–3000 cm^{-1} at temperatures where the catalyst precursor is known to be reduced, viz. 520 K. At higher temperatures the broad band due to water set free by the reduction of copper ions disappears and the intensity of the silanol groups increases even more. This can be explained by agglomeration of copper in metal particles, upon which a larger hydroxyl-covered silica surface is created.

A Xhy3 sample was also reduced without prior calcination (fig. 5). When we compare the spectra obtained during heating of this catalyst in hydrogen instead of in oxygen, it is clear that in a hydrogen atmosphere the 3615 cm^{-1} band disappears at lower temperature, viz. the temperature at which the reduction to metallic copper starts. These results support the hypothesis that the 3615 cm^{-1} hydroxyl band is associated to the presence of highly dispersed silica-supported copper ions. These hydroxyl vibrations are only observed in the catalyst precursor if the copper ions are homogeneously distributed over the silica support. Upon dehydration in oxygen, the OH-bands disappear from the spectrum and the reducibility of the copper ions is improved by this treatment. During reduction of a fresh catalyst the characteristic OH-bands also disappear from the spectrum due to the agglomeration of the produced copper atoms into small metal particles (7–10 nm in diameter) on the silica support. Once the dispersion of the copper

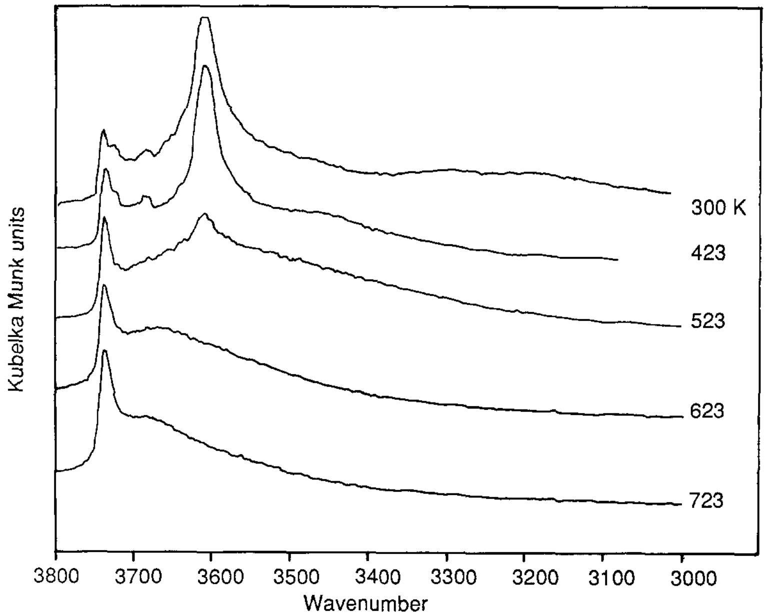

Fig. 5. Kubelka-Munk plot of Xhy3 (fresh) during reduction at indicated temperature.

has been decreased by the formation of metal particles, the OH bands at 3615 and 690 cm^{-1} could not be re-established by any heat treatment in hydrogen and/or oxygen.

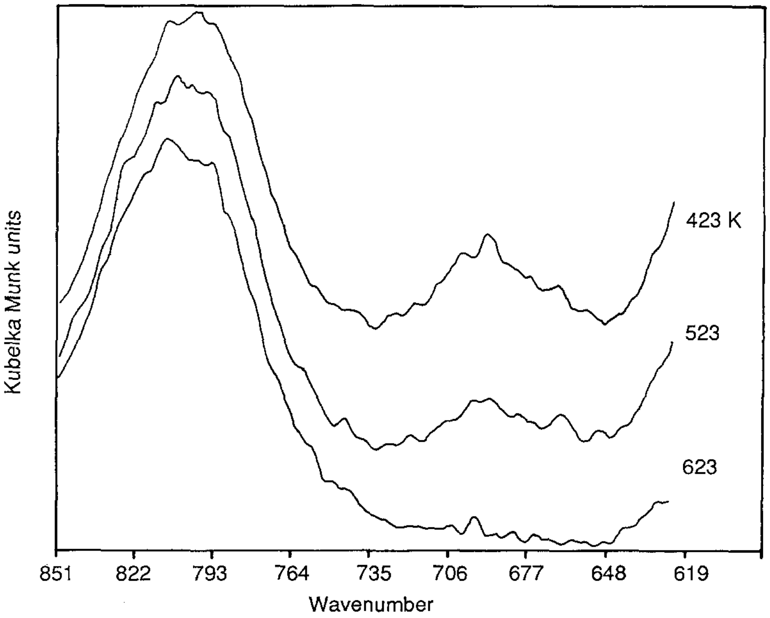

Fig. 6. Kubelka-Munk plot of Xhy3 (fresh) during reduction at indicated temperature.

In addition to the spectral changes in the hydroxyl stretching region, a band at 690 cm^{-1}, which was also observed during the atmospheric measurements, disappeared upon calcination at 827 K as well as upon reduction (fig. 6). After re-oxidation of a reduced catalyst, this band did not show up again. Studying the infrared spectrum of basic copper nitrate, Secco and Worth reported a Cu-O-H deformation vibration at 675 cm^{-1} [10]. Tarte investigated the frequency of OH vibrations of a variety of copper hydroxysalts in more detail. Based on frequency-shifts upon OH-OD exchange, the band at 677–684 cm^{-1} was unequivocally assigned to the planar deformation OH-vibration (δ Cu-O-H) [13]. The analogous behavior of the bands at 3615 and 690 cm^{-1}, during different treatments, indeed suggests that both peaks are due to the same copper associated surface hydroxyl group.

4. Discussion

The results of our atmospheric and environmental DRIFT measurements show interesting differences with the samples prepared and pretreated under various conditions. The differences in the spectra of the solids can be related to the reducibility of the copper-silica compound. The 3615 cm^{-1} reflection band in both *chrysocolla* and the catalysts prepared by urea decomposition strongly suggests the presence of this copper hydrosilicate in our catalysts. With the atmospheric experiments we found that only catalysts having a high copper dispersion exhibit bands at 3615 and 690 cm^{-1}. The behavior of the bands at 3615 and 690 cm^{-1} during calcination and/or reduction can be explained by highly dispersed copper ions giving rise to special OH vibrations.

During calcination (dehydration) the octahedrally surrounded copper ions in the chrysocolla structure are converted into two-dimensional CuO-on-silica, explaining the loss of the OH-absorption bands. Upon reduction, the formation of copper metal particles causes the disappearance of Cu-O-H absorption bands and the increase of the isolated silanol peak at 3748 cm^{-1}.

5. Conclusions

DRIFT spectroscopy is a valuable technique for the characterization of solid catalyst surfaces. Especially, *in-situ* measurements during thermal treatment of a catalyst provides useful information on the processes occurring at the surface. However, at present there is still a lack of reference data. It is therefore important, to investigate different thermal treatments on well-characterized samples as well as on naturally occurring and synthetic minerals. *In-situ* infrared measurements can be performed under any condition (gas pressure, temperature) imposed during characterization in other equipment, so that comparison of data need not be hindered by different experimental conditions. Thus DRIFT spectroscopy can always be applied to provide additional information on changes occurring at the surface of the catalyst. Monitoring these changes directly by means of IR spectroscopy is highly relevant in understanding what is going on at the catalyst surface during any treatment.

As an illustration of the potentialities of DRIFT spectroscopy, the characterization of differently prepared and pre-treated copper-on-silica catalysts has been described in this paper. In the catalyst precursors prepared by homogeneous deposition precipitation, the two bands at 3615 and 690 cm^{-1} could unequivocally be attributed to hydroxyl vibrations associated with the presence of highly dispersed silica-supported copper ions. Upon calcination the bands are lost suggesting the decomposition of surface copper hydrosilicate to copper oxide. Reduction of a fresh catalyst precursor is also accompanied by the disappearance of the 3615 and 690 cm^{-1} bands from the spectrum. Reduction of a catalyst previously calcined *in-situ*, shows the intermediate formation of hydroxyl groups as a pre-stage of water formation. The infrared results are in line with earlier characterization data and provide additional insight into the processes occurring during the preparation and thermal activation of the catalyst.

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