FTIR spectroscopic investigation of the active sites on different types of silica catalysts for methane partial oxidation to formaldehyde

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Several commercial silica samples showing different catalytic activities in the partial oxidation of methane (MPO) to formaldehyde have been investigated using FTIR technique. Two IR absorption bands at 893 and 909 cm^{-1}, observed upon dehydroxylation of the silica catalysts and assigned to reactive siloxane sites on the surface ("strained siloxane bridges"), were found to disappear upon heating in methane at high temperature. The catalytic activity increases together with the intensity of the bands due to such "strained" sites in the different SiO_2 samples.

Keywords: methane activation; silica; selective oxidation; formaldehyde

1. Introduction

The silica surface possesses a unique catalytic behaviour driving the partial oxidation of methane (MPO) towards the formation of HCHO [1–3]. This issue has been largely underestimated although it is fundamental in controlling the reactivity of silica supported oxide catalysts in the MPO reaction [2]. A comparative study of the reactivity of several typical commercial SiO_2 samples in the MPO reaction has allowed one to conclude that the preparation method is fundamental in determining the reactivity of the SiO_2 surface [2]. In fact, the following reactivity scale, referring to the preparation method, has been stated: precipitation > sol–gel > pyrolysis. Such a different reactivity cannot be rationalised in terms of alkali and alkaline earth oxide impurities [4] and thus cannot be associated with the presence of strong basic sites on the surface. Several views on the catalytic role of silica are discussed in the literature [3,5].

Sun et al. [3] have attempted to explain the working mechanism of the MPO reaction over a SiO_2 surface by invoking the existence of surface siloxane defect sites generated during dehydroxylation of the SiO_2 surface at high temperature. It was inferred that the key step of the MPO is the methane activation on these sites, which gives rise to two kinds of intermediate complexes, surface methoxide and/or surface methyl groups, evolving towards the formation of HCHO or C_2H_6 [3]. Although without any experimental evidence, it was suggested [3] that different catalytic activity exhibited by various silicas could be associated with different concentration of such defects- "strained" siloxane bridges on the surface. Physico-chemical properties of these sites have been recently reviewed by Lygin [5].

Further insights into the reactivity of the SiO_2 in the MPO, as well as into the reaction mechanism, were provided by disclosing a strong correlation between the activity of silica and density of reduced sites under steady-state conditions [4]. On this account, it has been hypothesised that reduced sites on the silica surface are able to activate molecular oxygen [6]. Experimental results obtained by Pinelli et al. [7] for the gas phase ammoxidation of cyclohexanone and by Matsumura et al. [8] for CO oxidation suggested that the catalytic activity of silica was associated with paramagnetic oxygen species observed in the catalyst.

The purpose of this work was to obtain experimental evidences on the nature of active sites of silica responsible for its catalytic role in the MPO reaction. FTIR spectroscopy was applied to characterize silica samples upon dehydroxylation and reaction with methane at elevated temperatures.

2. Experimental

Four commercial silica samples were used in this study: Si4-5P (AKZO, 381 $m^2\ g^{-1}$), D11-11 (BASF, 137 $m^2\ g^{-1}$), 250 MP (GRACE, 180 $m^2\ g^{-1}$) and Cab-O-Sil M5 (CABOT, 200 $m^2\ g^{-1}$). Si4-5P and D11-11 were obtained by the precipitation method, while 250 MP and Cab-O-Sil M5 were obtained by sol–gel and pyrolysis

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processes, respectively. Physical and chemical properties of the samples were described previously [1,4].

Fine powders of the samples were pressed into pellets of about 0.02 g cm^{-2} and put into conventional quartz vacuum cell for IR spectroscopy with KBr windows. Progressive dehydroxylation of silicas was obtained by evacuation at increasing temperature at 300–850°C for 1 h at 1×10^{-4} Torr (1 Torr = 133.3 Pa) residual pressure.

After dehydroxylation at 650°C for 3 h the sample of Si4-5P silica was allowed to contact methane at 650°C for 1 h under static conditions. Finally the cell was cooled down to room temperature and the excess gas was evacuated.

All IR spectra were recorded with a Bruker-48 FTIR instrument using 4.0 cm^{-1} resolution and 256 accumulating scans.

EPR measurements (Varian E-109 spectrometer) did not reveal any paramagnetic species on the samples after the pretreatments, upon adsorption of oxygen and after heating in methane.

3. Results and discussion

FTIR spectra of Si4-5P silica, the most active catalyst [4], obtained after its dehydroxylation at 300, 500 and 850°C are presented in fig. 1 (spectra a, b and c, respectively). They show gradual disappearance of hydrogen bonded silanols (characterized by a broad absorption band at about 3700–3400 cm^{-1}) and formation of isolated hydroxyls (sharp band at 3750 cm^{-1}). While combination and overtone modes of silica frame showing up in the 1600–2100 cm^{-1} range are not sensitive to dehydroxylation treatments, significant though feeble variations are observed in the low frequency region (700–1000 cm^{-1}), which is dominated by the extremely intense absorptions due to Si–O vibrations of the silica frame. In fact, two absorption bands gradually developed in the so-called "silica window" at 909 and 893 cm^{-1} after evacuation at high temperature. These two bands disappeared when water was adsorbed at room temperature (spectrum d in fig. 1). Changes in other ranges showed absorption bands at 3500–3300 cm^{-1} (broad) due to OH stretching vibrations and at 1630 cm^{-1} due to the bending mode of adsorbed water [9]. The sharp band at 3750 cm^{-1} somewhat decreased in intensity as a consequence of partial rehydration of the surface.

The same sequence of experiments was performed with all samples but, for brevity, only the results obtained for "Cab-O-Sil" silica, the least active catalyst [4], are shown in fig. 2. The overall spectral features are very similar and only the overall intensity varies for the different catalysts. In particular, one can notice that the bands at 909 and 893 cm^{-1} appeared much less intense in fig. 2 as compared with those of the Si4-5P sample (fig. 1). In all cases water absorption at room temperature destroyed these two bands, which could be restored by repeating the dehydroxylation at the same temperature of the original pretreatment in vacuo.

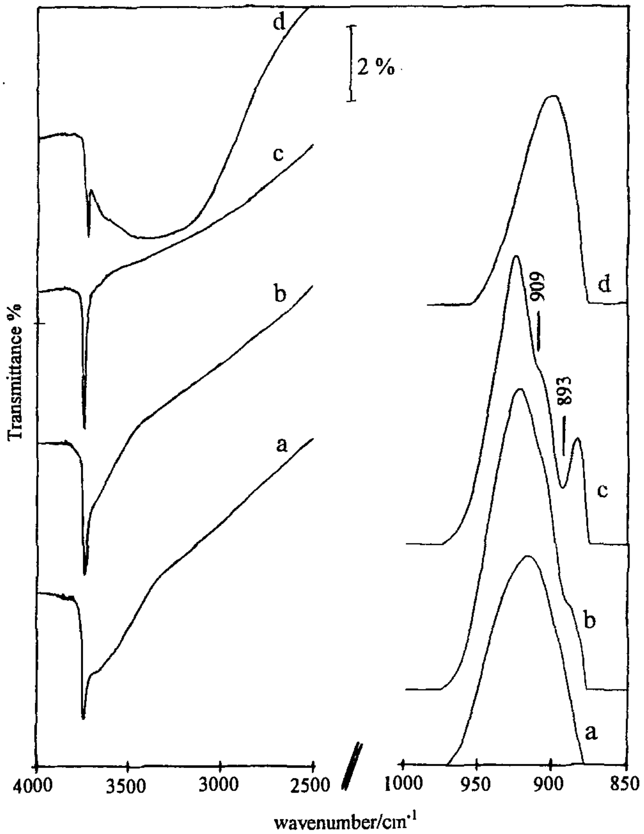


Fig. 1. FTIR spectra following Si4-5P silica dehydroxylation at (a) 300, (b) 500, (c) 850°C and (d) rehydration by exposing to water vapour at room temperature.

Literature data on the differences of "fumed" and "precipitated" silicas [10] reveal that the original population of hydroxyls in the former is considerably lower (within a factor of 2) after evacuation at 150°C. When the temperature of dehydroxylation increased up to 800°C the concentration of residual surface OH groups in both silicas decreased in parallel way, their population being still higher in the case of precipitated samples. Only after treatment at 1000°C IR spectroscopic observations showed approximately equal populations of residual silanols in both samples [11].

No comparison of different silicas has been done so far in respect to the absorption bands appearing after dehydroxylation at high temperature in 800–1000 cm^{-1} range. As for the assignment of the spectrum in this range, properties of species absorbing at 888 and 908 cm^{-1} were investigated thoroughly by Morrow et al. [12–16] and reviewed recently by Lygin [5]. The spectroscopic studies indicated that these bands appeared as a consequence of dehydroxylation at high temperature and were assumed to be due to "strained siloxane bridges" produced upon condensation of two hydroxyls:

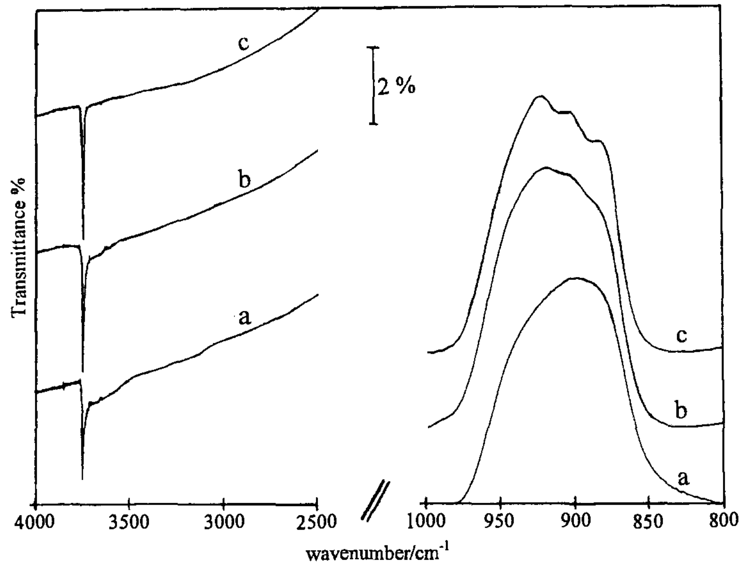
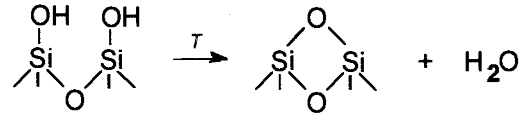
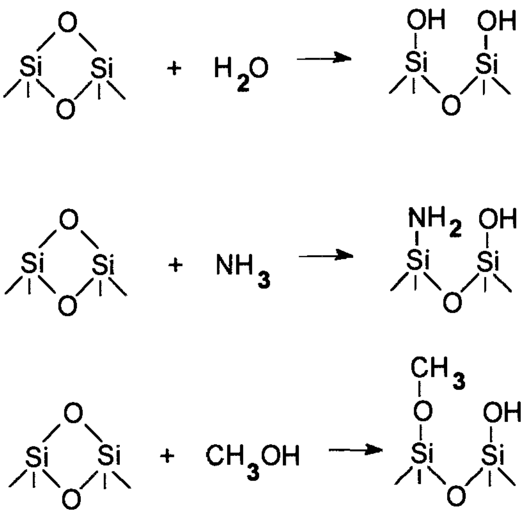


Fig. 2. FTIR spectra following Cab-O-Sil silica dehydroxylation at (a) 300, (b) 500, (c) 850°C.



Adsorption of H_2O, H_3COH, NH_3 and other molecules was found to eliminate these two bands even at room temperature [12–16]. It was shown that the reactions proceeded through dissociation of adsorbates on reactive siloxane sites according to the following paths:



Experiments with pyridine and trimethylamine adsorption on highly dehydroxylated Cab-O-Sil silica showed some Lewis acidity of the surface [14], likely associated with highly distorted silicon-oxygen tetrahedra. Finally, it was assumed that the absorption band at 908 cm^{-1} corresponded to the asymmetric (Si–O–Si) stretching of the bridge [15]. The other feature at 888 cm^{-1} did not find any definite explanation except for suggestion that it might be related to the motion of silicon atom with Lewis acidity [14].

Spectroscopic and theoretical investigations by Bunker et al. [17] showed that such "strained" species on silica exhibiting IR absorptions at 908 and 888 cm^{-1} were likely to be edge-shared silicate tetrahedral rings produced by condensation of two adjacent hydroxyls during dehydroxylation at temperatures above 500°C. However, the detailed structure of these sites is still matter of debate [5].

No evidence of methane interaction with strained siloxane bridges at room temperature has been reported [15], probably due to relatively high activation barrier of C–H bond cleavage in CH_4 as compared with that of O–H and N–H bonds in H_2O, H_3COH and NH_3 [12–16].

It is most significant that the bands at 893 and 909 cm^{-1} produced by dehydroxylation faded away upon heating at temperature higher than 500°C in 10 Torr of dry CH_4. Fig. 3 shows the results of this experiment (run at 650°C, the same as the reaction temperature [4]) in the case of Si4-5P silica. The inset is the difference (in absorbance) at low frequency of the spectrum before (curve a) and after (curve b) the treatment in CH_4 and evidences the destruction of the strained siloxane bridges. No absorption bands due to C–H stretching modes of Si-CH_3 or Si–O-CH_3 species at about 3000–2800 cm^{-1} and of Si–H at 2300–2000 cm^{-1} [18] have been observed in the spectrum of silica after such interaction with methane. The only difference was that the band of isolated hydroxyls at 3750 cm^{-1} became asymmetric on the low frequency side (fig. 3, curve b). Morrow et al. [15] estimated the number of potentially active siloxane bridges produced by dehydroxylation of silica at 1200°C to be in the order of 4.8×10^{19} g^{-1}. At lower

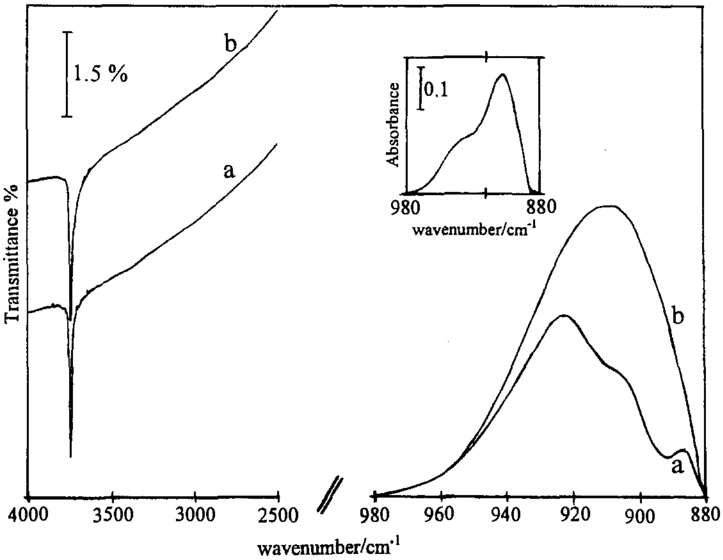
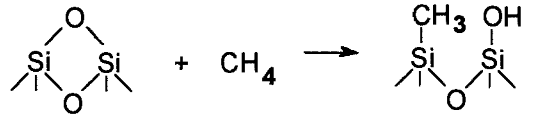


Fig. 3. FTIR spectra following methane interaction with Si4-5P silica: (a) background spectrum of the sample pretreated in vacuum at 650°C for 3 h; (b) after contact with 10 Torr of CH_4 at 650°C for 1 h. Inset: difference spectrum between (a) and (b) in absorbance.

temperature (650°C) the population is expected to be even lower [14] and consequently, IR spectroscopic detection of methane dissociation products might be impossible, also due to low extinction coefficients of the C–H stretching bands. However, the asymmetry of the sharp band at 3750 cm^{-1}, noticed above, suggests that reactions might well occur on the surface, producing new hydroxyl groups:



Admission of oxygen at room temperature did not modify spectrum b of fig. 3, but heating in oxygen at 500°C followed by outgassing at 650°C restored spectrum a and the cycle could be repeated.

As mentioned above, dehydroxylated Si4-5P and Cab-O-Sil samples showed different intensity of the IR bands associated with the "strained" siloxane sites (figs. 1 and 2). Significantly, these samples were also very different in catalytic activity, Si4-5P being a much more active catalyst [4]. To explore and confirm the evidence of a relation between the presence of "strained" sites and the activity in MPO reaction, the spectroscopic and catalytic [4] features of the various silica samples were compared.

For each type of silica the amount of reactive siloxane bridges was evaluated on the basis of the integrated intensities of the two bands at 893 and 909 cm^{-1} resulting from the difference between the spectrum of the sample dehydroxylated at 650°C and that obtained after rehydration at room temperature (and consequent depletion of strained bridges). The accuracy of the method was estimated to be ±20%. To relate with the catalytic data [4], the band intensities were normalized to the weight of the pellets, which all had the same dimensions.

Assuming the extinction coefficient of the bands at 893 and 909 cm^{-1} being equal for all silica samples, the data presented in table 1 suggest some, though not linear, relation between the concentration of siloxane defects and catalytic activity, expressed in terms of space time yields (STY) to HCHO ($g/(kg_{cat}\,h)$).

While the trend in the first three samples of table 1 is easily recognizable, it is much less between the last two. However, due to the very low values of both intensities and activities in these cases, the uncertainty is very high.

To better compare different silica samples a more significant normalizing factor might be adopted [19], taking into account the specific surface area of the samples. Also in this case concentration of the strained bridges and catalytic activity per surface area unit show to be related.

It might be stressed that since no evidence of ESR active species in silica samples was found after any dehydroxylation treatment, reduction with methane or oxygen chemisorption, these results support the idea of

Table 1
Catalytic activity of various silicas for methane partial oxidation to formaldehyde at 650°C (STY_{HCHO}: space time yield to formaldehyde) and integrated intensity (I/M, normalized to the weight of the pellet) of the IR absorption of "strained" siloxane bridges, produced after dehydroxylation at 650°C

Silica	I/M (cm^{-1}/g)	STY_{HCHO} ($g/(kg_{cat}\,h)$)
Si4-5P	537	304
D11-11	230	159
250 MP	151	60
M5	143	21

participation of "strained" bridges in methane oxidation to formaldehyde [3]. Those samples, which, due to the precipitation route, originally exhibited larger population of hydroxyls, are also the most active after appropriate pretreatment at high temperature. Indeed, surface OH groups are the precursors of the "strained bridges" proposed to play a role in the MPO reaction.

Specifically, the role of such defects would therefore be the activation and cleavage of C–H bond in CH_4 to produce species like surface CH_3 which can further react. In particular the surface methyl group might react with oxygen, when present in the mixture, to give oxygenated products [3,4].

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