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STUDY OF THE THERMAL BEHAVIOR OF SURFACE SPECIES FORMED BY DIRECT REACTION OF CYANOGEN WITH SILICA

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ABSTRACT

The pyrolysis of $\geqslant$SiNCO (the main species formed during the interaction at 420°C of cyanogen with silica outgassed at 1000°C) has been investigated by a slow thermal programmed desorption (TPD) method followed by isothermal pyrolysis (IP) at 1000°C. CO, CO_2 and N_2 are evolved but, whereas almost all the carbon can be restored to the gas phase, a large part of the nitrogen remains bound onto the surface as a silicon nitride. Treatment with oxygen at 1000°C allows restoration of all the nitrogen into the gas phase and regeneration of silica. CO_2 has been revealed as an important intermediary species able, at high temperatures, to react with silicon nitride and =SiNC (or $\geqslant$SiCN) species formed both during the pyrolysis of $\geqslant$SiNCO and the C_2N_2/SiO_2 interaction at 420°C. The slow restoration of the remaining small amount of carbon (as CO in the gas phase) during the final isothermal treatment is connected with the very difficult oxidation of the $\geqslant$SiCN (or =SiNC) species which occurs only above 900°C through the attack of siloxane bridges.

When C_2N_2 is allowed to react with a weakly dehydroxylated sample large quantities of CO_2 are formed during the TPD at rather low temperatures (600–700°C) whereas CO and N_2 are evolved at higher temperatures. In this case, CO_2 formation is thought to be the result of the decomposition of a surface species, namely, $\geqslant Si_2NCOOH$ which is produced by the reaction of a proximate silanol group with $\geqslant$SiNCO. The moderate quantities of hydrogen evolved during the ultimate high temperature treatment accounts for the pyrolysis of the very stable remaining $\geqslant$SiNHSi$\leqslant$ group.

INTRODUCTION

Within the framework of a study of heterogeneous phenomena which concerns some high temperature combustion reactions and pyrolysis, we have investigated the C_2N_2/SiO_2 interaction, firstly, because cyanogen has been extensively studied in the field of combustion [1–5] and especially in heterogeneous combustion [6] and, secondly, because silica is the material which is usually employed for the reaction vessel.

The use of a silica sample exhibiting a large specific surface area (300 m^2 g^{-1}) leads to an increase ($\times 10^5$) in the interface with respect to the vessel wall: this allows use of methods used in the field of catalysis, e.g. volumetry,

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calorimetry, thermal programmed desorption (TPD) and mass spectrometry, to study the three steps: adsorption of cyanogen, pyrolysis of surface species, and interaction of surface species with the constituents of the gaseous phase.

The first step has already been reported [7,8] and the present work deals with the second step: the stability of surface species formed during the C_2N_2/SiO_2 interaction and especially with the main species, $\geqslant$SiNCO. Isocyanates play an important role in the reaction of NO + CO mixtures on supported noble metal catalysts and it has been shown that their formation is first located on the catalyst [9] and that isocyanate groups are able, by "spillover", to move onto the support [10]. Except for a short study of $HNCO/SiO_2$ interaction by Solymosi and Bansagi [11], the thermal stability of isocyanate groups formed directly on the silica support (without the use of a catalyst) has received very little attention.

Therefore, we believe that the comparison of the stability of isocyanate species (formed by direct cyanogen chemisorption on silica) with that of isocyanate groups formed by NO + CO reaction on supported noble metal can provide useful information about the role played by the support in this reaction.

EXPERIMENTAL

The silica sample (Aerosil 300 Degussa 300 m^2 g^{-1}, 0.1–0.4 g.) was contained in a silica glass vessel, R (Fig. 1), located in a Tian-Calvet calorimeter (TC) which can operate for long periods at temperatures up to 1000°C. This device is connected to a micromanometer, 0–100 torr (M), and a Toeppler gauge, A, which allows all the gas contained in the reactor, R, to be sampled.

Mass spectrometric analysis (CEC 21-620 A) was used to detect the molecular species: H_2, CO, CO_2, N_2, HNCO, C_2N_2, HCN, O_2, N_2O, NO

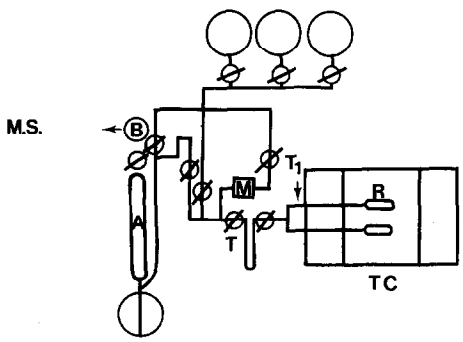


Fig. 1. Schematic diagram of the experimental facility. TC, Tian-Calvet calorimeter; M, micromanometer; A, Toeppler gauge; B, sample gas; R, reactor; T, nitrogen trap; M.S., mass spectrometry analysis.

and NO_2 and to measure their concentrations by taking into account their contribution in the a.m.u. range 2–52 with the aid of a P.E.T. Commodore computer.

Sample preparation and pretreatments

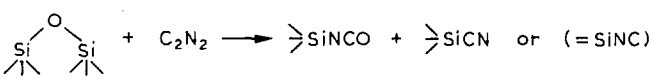
Silica samples were either outgassed for 15 h at 1000°C (X samples), 48 h at 470°C (Y sample), or 72 h at 360°C (Y′ sample). The results of Kiselev and Lygin [12] have shown that under these conditions the silanol group concentrations are expected to be 0.4, 2.0 and 2.6 OH groups per nm^2 for the X, Y and Y′ samples, respectively.

Cyanogen was obtained commercially (Matheson, 99%) and was purified before use by repeated freeze-pumping at −120 and 20°C in order to eliminate traces of CO_2.

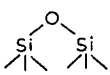
The cyanogen reaction was carried out at 420°C for the X and Y samples and at 360°C for the Y′ sample. The main reaction of cyanogen concerns the silanol groups for all the samples.

For highly dehydroxylated samples bearing only free isolated silanol groups (i.e. a low initial population), Ruttenberg and Low [13] and Morrow and Cody [14] have shown (by infra-red spectroscopy) the formation of isocyanate, cyanide and isocyanide species, according to the reactions

(1)



(2)

where 

represents a "strained siloxane bridge".

For Y and Y′ samples outgassed at low temperatures, which allows a high population of silanol groups to remain on the surface, reaction (2) was almost absent (only very few strained siloxane bridges were present) and a reaction involving several silanol groups occurred instead of reaction (1). This reaction will be specified further in the discussion which follows.

In short, use of X, Y and Y′ samples allowed the study of the pyrolysis of the mixed species, ≥SiNCO, ≥SiCN and =SiNC. In some cases, with the aim to operate the pyrolysis with the sole ≥SiNCO species, a conversion of ≥SiCN + =SiNC species was attempted by treatment with oxygen or N_2O at 420°C.

Thermal stability was studied by isothermal pyrolysis at different temperatures and TPD experiments from 360 or 420°C to 1000°C with a heating rate of 13.3°C h^{-1}. The sampling of the gas phase was accomplished at regular intervals of time (4 h). To obtain total restoration of carbon, TPD was followed by an isothermal pyrolysis at 1000°C. Finally, treatment with

oxygen at the same temperature allowed regeneration of the silica.

During TPD and isothermal pyrolysis (IP) the calorimeter was used as an ordinary oven, calorimetric sensors operating only for the study in isothermal conditions: adsorption of cyanogen, conversion of the adsorbed species (420°C) and regeneration of silica (1000°C).

RESULTS

Isothermal pyrolysis

When an X sample, after a cyanogen treatment but without subsequent conversion at 420°C, was subjected to temperatures of 540, 870 and 1000°C for 48 h, CO, CO_2 and N_2 formation was observed: their average rates of evolution are shown in Fig. 2. The apparent rate of evolution of CO_2 was quite independent of temperature, whereas the rates of evolution of CO and N_2 were linearly temperature dependent.

Extrapolation of the CO and N_2 curves of formation towards low temperatures supplied a limit for the ≥SiNCO stability since ≥SiCN is known to disappear only above 900°C as observed previously by Eley et al. [15]. This lower limit is close to 500°C, a rather high temperature when compared with the slow decomposition at 300°C and the almost complete disappearance observed at 400°C by Solymosi et al. [16] for isocyanate formed on Pt/SiO_2 by NO + CO reaction.

TPD experiments

When TPD 1 was carried out with a Y sample (after C_2N_2 adsorption but without subsequent conversion by oxygen at 420°C) bearing 240 μM of one surface species [assumed provisionally to be ≥SiNCO and measured from

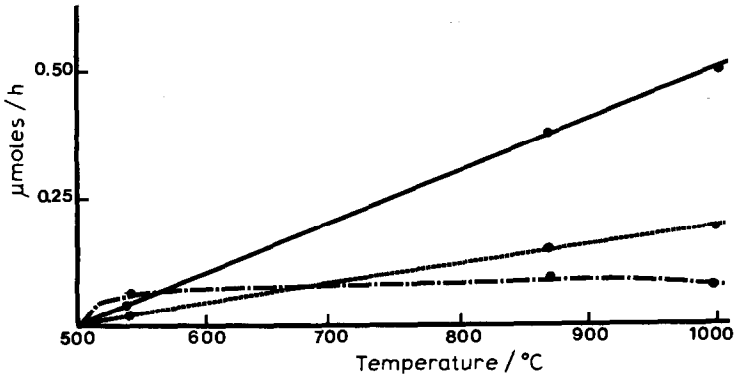


Fig. 2. Isothermal pyrolysis with an X sample. Average rate of ——, CO; ——, N_2; and —·—, CO_2 evolved at different temperatures.

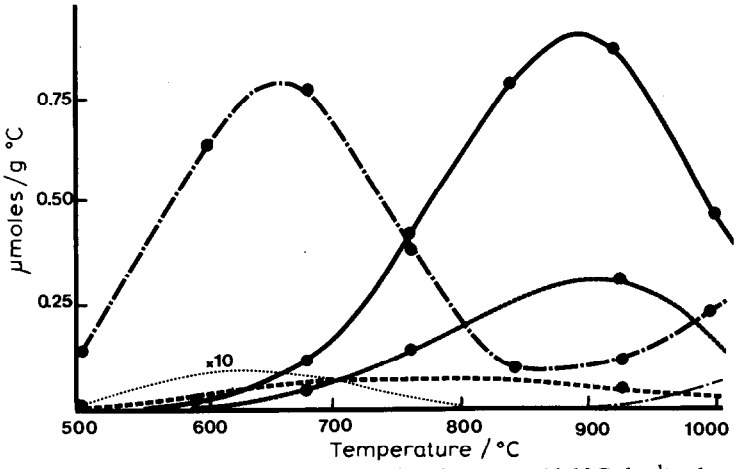


Fig. 3. TPD 1 with a Y sample (heating rate 13.3°C h^{-1}) showing the influence of temperature on the amount of gas evolved (in μmole g^{-1} of silica and °C). The curves have been standardized to allow for the somewhat variable interval of temperature used for the sampling of gases: ——, CO; —·—·, CO_2; ——, N_2; ------, HCN; ·····, HNCO; —·—, H_2.

C_2N_2 consumption and HCN formation with the ratios C_2N_2/HCN = 1 and ≥SiOH/HCN = 1 as depicted in reaction (1)]. CO_2, CO, N_2, HCN and traces of HNCO and hydrogen were observed (Fig. 3). CO_2 was mainly evolved at low temperatures with a maximum rate at about 650°C while CO and N_2 formation occurred at higher temperatures. Moreover, for these two species, simultaneous maxima were observed at about 900°C and their ratio CO/N_2 was close to three throughout the temperature range.

A mass balance showed that at the end of TPD 1 (see Table 1) 90.3% C, 29.7% N_2 and 134% O_2 (assuming 100% of oxygen was present initially as ≥SiNCO) were evolved as gases. After completion of the reaction by an isothermal pyrolysis (48 h at 1000°C) the total mass balance was 98.9% C, 38.3% N_2 and 142% O_2 restored in the gas phase. This showed that almost all the carbon and a large excess of oxygen (in regard to the ≥SiNCO assumed formed) are released in the gas phase (as CO + CO_2) and that about 60% of the initial nitrogen involved in the cyanogen adsorption remained bound onto the surface.

The three oxygen additions, 4.49, 9.5 and 18.2 torr, were carried out at 1000°C: these exhibited exothermic effects of 110–140 kcal per mole of O_2 (Fig. 4). Analysis of the resulting gaseous phase revealed an oxygen consumption with nitrogen release: O_2/N_2 ratios were close to 1.4. Note that for the first oxygen addition some H_2O formation was observed.

Qualitatively similar results were obtained for TPD 1 and isothermal pyrolysis on a Y′ sample. Nevertheless, a different figure was obtained for H_2 formation which was observed to be weak at the end of the TPD and became prominent during the ultimate isothermal pyrolysis at 1000°C, amounting to 50% of the gas phase composition.

Table 1

	μM	Gases evolved (μM)			CO_2/N_2	CO/N_2	N_s/N_g	O_2/N_2	% Restored		
		CO	CO_2	N_2					C	N_2	O_2
TPD 1 Y	240 ≥SiNCO	96.1	120	32.2	3	0.8	2.7		90.3	29.7	134
TPD 1 Y + IP 1000°C		116.7	121	42.6	2.7	1.0	1.8		98.9	38.3	142
TPD 1 Y + IP + O_2 1000°C		116.7	122.1	115.6				1.4	99.4	96.4	
TPD 2X	67.3 ≥SiNCO	29.7	16.3	10.8	2.8	1.8	2.7		68.4	32	92.6
TPD 2 + IP 2		46.7	18.3	16.6	2.8	2.6	1.0				
TPD 2 + IP 2 + O_2 1000°C		46.7	18.3	35.4				1.4			
TPD 3 X	75.3 ≥SiNCO + 35.4 ≥SiCN	44.6	15.9	10.17	4.4	2.8	4.2		56.9	18.6	114
TPD 3 + IP 3		79.2	20.4	23.4	3.4 3.9 [a]	3.9	1.35		91.7	43.9	158
TPD 3 + IP 3 + O_2 1000°C		79.2	20.4	52.8				1.6	91.7	96.2	

[a] Corrected for carbon bound on the surface. Carbon assumed to be evolved as CO with a ratio $CO/N_2 = 3$.

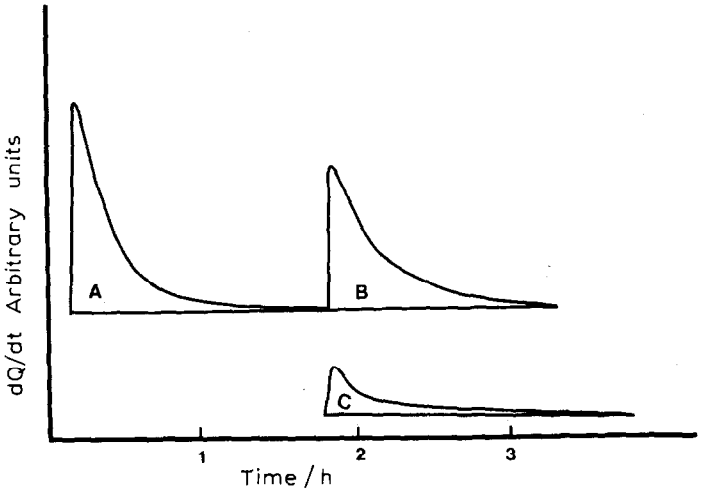


Fig. 4. Isothermal treatment with oxygen at 1000°C: heat flux evolution vs. time. A, First oxygen admission, 120 kcal mole^{-1}; B, second oxygen admission, 140 kcal mole^{-1}; C, third oxygen admission, 110 kcal mole^{-1}.

After the final oxygen treatment at 1000°C had been carried out on the Y sample, cyanogen was allowed to react at 420°C with the regenerated silica: owing to the previous destruction of silanol groups by C_2N_2, only 60 μM $\geqslant$SiNCO and 7 μM ($\geqslant$SiCN + =SiNC) were estimated to be bound with the surface. These conditions resembled an X sample condition owing to the high temperature treatment suffered by the Y sample.

After evacuation of the excess cyanogen, N_2O addition at 420°C was followed by a conversion of 8 μM ($\geqslant$SiCN + $\geqslant$SiNC) in $\geqslant$SiNCO in fairly good agreement with the previous 7 μM estimated before the conversion. Figure 5 shows a typical thermogram which shows not only the conversion,

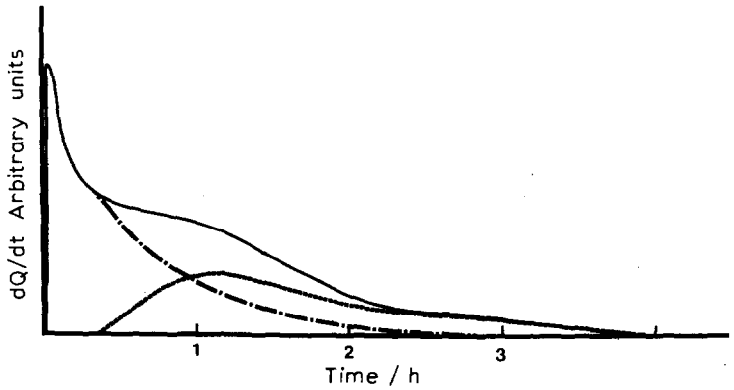


Fig. 5. Heat flux vs. time when oxygen is added to an X sample at 420°C. ——, Total heat flux; —·—·, heat flux from $\geqslant$Si–CN conversion; ——, heat flux from $\geqslant$SiNCO oxidation.

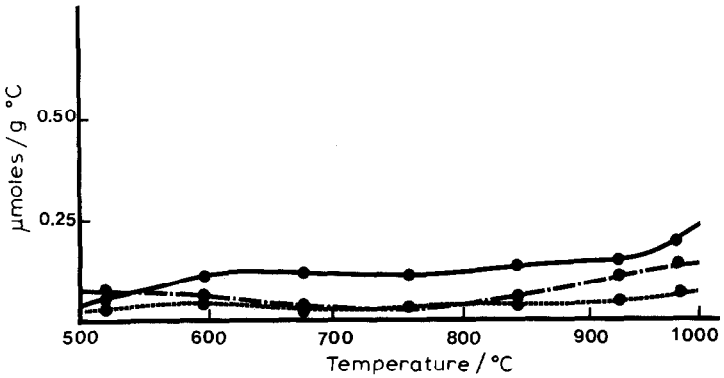


Fig. 6. TPD 2 with an X sample without ≻SiCN (heating rate 13.3°C h^{-1}) showing the influence of temperature on the amount of gas evolved (in μmole g^{-1} of silica and °C). The curves have been standardized to allow for the somewhat variable interval of temperature used for the sampling of gases: ———, CO; —·—·, CO_2; ——, N_2.

but also a slight side reaction attributed to the start of the ≻SiNCO oxidation. This interpretation is consistent with the findings of Ruttenberg and Low [13] who observed the increase in intensity of the 2310 cm^{-1} band (≻SiNCO) when O_2 is added (200–300°C) to a silica sample previously reacted with C_2N_2. Moreover, Morrow and Cody [14] noted a decrease in the intensity of the 2100 and 2218 cm^{-1} bands (assigned to ≻SiCN and =SiNC species). Extensive oxidation has also been claimed by these authors to occur above 500°C in the presence of oxygen.

Consequently, TPD 2 was only concerned with the ≻SiNCO species pyrolysis. The results show (Fig. 6) that the same main products are evolved (CO, N_2 and CO_2) as for TPD 1, except that traces of HCN were observed and HNCO and H_2 were no longer present. But large changes must be pointed out when TPD 2 is compared with TPD 1: the maxima for CO, CO_2 and N_2 have vanished and CO and N_2 were evolved from lower temperatures. Results from the mass balance show that 68.4% C, 32% N_2 and 96.6% O_2 are restored in the gas phase at the end of TPD 2 (Table 1).

After an additional isothermal pyrolysis at 1000°C (48 h) 96.6% C, 39% N_2 and 123% O_2 were released in the gas phase: the CO/N_2 ratios remained close to 3 for both TPD 2 and the ultimate isothermal pyrolysis.

At this point, water was no longer formed if further oxygen was added at 1000°C. Only a trace of CO_2 (1 μM) was evolved during the first oxygen admission and for subsequent additions the ratio N_2 evolved/O_2 consumed was close to 1.4.

For comparison, a silica X sample was treated with cyanogen at 420°C but the conversion treatment with oxygen at 420°C was omitted. Then TPD 3 was carried out with a mixture of ≻SiCN, =SiNC and ≻SiNCO species [75.3 μM ≻SiNCO + 35.4 μM (=SiNC + ≻SiCN)]. As with TPD 2, CO, CO_2 and N_2 were evolved (Fig. 7), again without maxima. The mass balance showed that only 57% C, 19% N_2 and 114% O_2 were restored as CO, CO_2

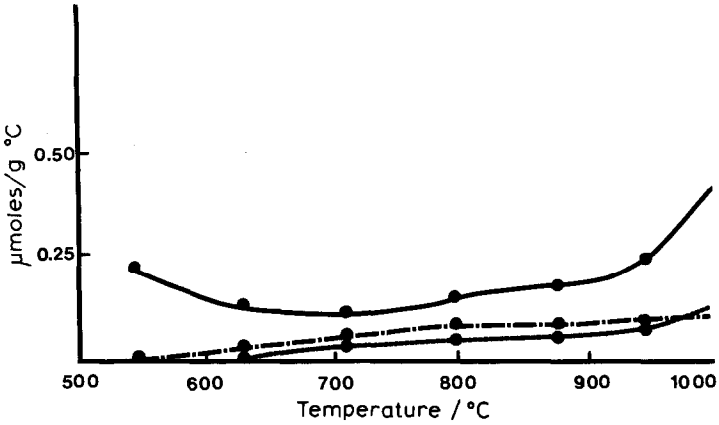


Fig. 7. TPD 3 with an X sample consisting of a mixture of ≻SiNCO + ≻SiCN (heating rate 13.3°C h^{-1}) showing the influence of temperature on the amount of gas evolved (in μmole g^{-1} of silica and °C). The curves have been standardized to allow for the somewhat variable interval of temperature used for the sampling of gases: ———, CO; —·—·, CO_2; ——, N_2.

and N_2 at the end of TPD 3. With an additional isothermal pyrolysis (1000°C, 120 h) 92% C, 40% N_2 and 150% O_2 were evolved. Ultimate oxygen treatment at 1000°C gave very little CO_2 formation and O_2/N_2 ratios were close to 1.6.

This was indeed a contrasting behavior showing that the slow carbon and nitrogen restorations must be attributed to the difficult ≻SiCN + =SiNC oxidation by oxygen of the siloxane bridges. In the same way, the excess of oxygen released is connected with the foregoing process.

Finally, a TPD experiment with an X sample was also carried out with a liquid nitrogen trap added at T_1 (Fig. 1), as close as possible to the exit of the reaction vessel. Analysis of the trapped gas plus gas phase collected in the range 420–1000°C (TPD 5) gave CO, 31%; CO_2, 65%; and N_2, 4%; compared with CO, 53%; CO_2, 29%; and N_2, 18% which was obtained in a similar experiment (TPD 6) without liquid nitrogen trapping.

These results showed that, in these conditions (X samples), a part of the nitrogen formation was connected with the destruction of nitrogeneous surface species by CO_2. Consequently, this compound must be recognized as an intermediate product at least at the highest temperatures.

DISCUSSION

Weakly dehydroxylated samples: Y samples

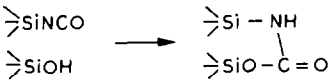
The TPD 1 experiment carried out with a Y sample exhibits an unusual CO_2 formation at a quite low and defined temperature. Moreover, the large excess of oxygen released in the gas phase as CO + CO_2 at the end of TPD involves the interaction of ≻SiNCO with an oxygen atom of the substrate.

As formation of CN· and NCO· radicals is unexpected at temperatures as low as 700°C, no attack of common siloxane bridges is expected and consequently, the large excess of oxygen evolved is mainly attributed to a species resulting from the interaction of cyanogen with several silanol groups.

When cyanogen stops reacting at 420°C the ratio C_2N_2 used/HCN = 1, as shown in reaction (1), is verified for both X and Y samples. But, whereas almost all the silanol groups are used with X samples (the ratio C_2N_2 used/$\geqslant$SiOH estimated initially present is close to 1), with a Y sample $C_2N_2/\geqslant SiOH_{e.} = 0.64$, showing that a large number of the silanol groups remain unavailable for reaction (1).

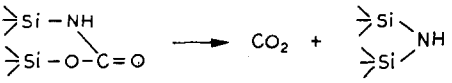
In agreement with these results, a previous investigation has evidenced (by calorimetric and kinetic methods) a different behavior for the reactions of cyanogen with X or Y samples [8]. It may be assumed that two silanol groups are involved in the reaction of cyanogen with Y samples, such that

(3)



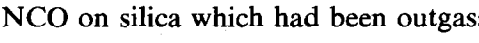
(4)

which, during TPD is followed by the decomposition



(5)

Reactions (4) and (5) can be compared with the urethane formation and decomposition observed by Eley et al. [15] during the adsorption of C_2H_5 NCO on silica which had been outgassed at low temperature.



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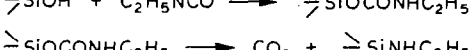
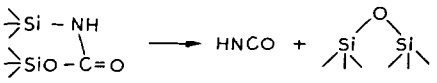


(7)

The simultaneous weak HNCO formation must be attributed to a side reaction of decomposition, i.e.



(8)

A similar reaction has been proposed by Lorimer and Bell [17] to explain isocyanate transport from the catalyst disk to the reference disk in their study of the NO + CO: Pt/SiO_2 system by infra-red spectroscopy.

In their infra-red work devoted to the reaction of ammonia with pyrogenic silica, Morterra and Low [18] assigned the 3450 cm^{-1} band adsorption to the formation, at low temperature, of a $\geqslant$SiNHSi$\leqslant$ species resulting from the interaction of strained siloxane bridges with ammonia. Yet, Bloomfield and

Little [19] assigned the 3450 cm^{-1} band to a ν(NH) mode of $-SiNH_2$. This assignment was later confirmed by Morrow et al. [20].

More recently, Fink and Plotzki [21] have assigned the 3390 cm^{-1} band (by comparison with the spectra of hexamethyldisilazane) observed when Aerosil is allowed to react in flow reactor with ammonia above 600°C to a ν(NH) mode of $\geqslant Si_2NH$. The growth of the 3390 cm^{-1} band is continued until 900°C (maximum working temperature) showing the extreme stability of that species. According to the same authors, the $\geqslant SiNHSi\leqslant$ formation is made at the expense of $-SiNH_2$ and $\geqslant SiOH$ groups.

$$2 \quad -SiNH_2 \longrightarrow NH_3 + \geqslant SiNHSi\leqslant \tag{9}$$

$$-SiNH_2 + SiOH \longrightarrow \geqslant SiNHSi\leqslant + H_2O \tag{10}$$

The question arises as to whether (in our Y sample conditions) $-SiNH_2$ formation is possible. Firstly, we note that 3 $\geqslant SiOH$ groups would be needed to build up $-SiNH_2$ from C_2N_2 (with HCN formation), and, secondly, there would not be enough $\geqslant SiOH$ groups on the silica Y sample to allow simultaneous formation of CO_2 (120 μM) and CO (96 μM) since the Y sample bears 385 μM of silanol groups before the reaction with C_2N_2. In consequence, we believe that only two silanol groups are involved in the formation of the surface species at the origin of the CO_2 formation and that the resulting species is $\geqslant SiNHSi\leqslant$.

At first sight, the question as to whether the silanol groups involved in reaction (3) are free or "bound" silanol groups seems fairly well resolved. Kiselev and Lygin [12] point out that most of the "bound" silanol groups of Aerosil are removed by degassing the sample at about 400°C and only free silanol groups remain attached to the surface. However, several works have confirmed the existence of closely located free silanol groups which are able to react in pairs with $SiCl_4$ [12] and $SiCl_2(CH_3)_2$ [22]. Also, the lack of reactivity of "bound" silanol groups has been evidenced. In contrast, $SiCH_3Cl_3$ [22], $TiCl_4$ [23] and $AlCl_3$ [24] are said to react with "bound" silanol groups.

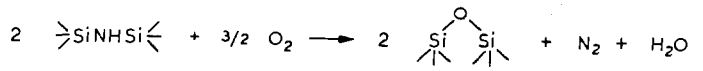
In consequence, we shall regard the large CO_2 formation at low temperatures (Y sample) as an estimation of the closely located free silanol groups.

The very small quantities of hydrogen observed during the TPD 1 for Y or Y′ samples and the larger quantities observed during the ultimate isothermal pyrolysis of the Y′ sample must be related to the high thermal stability of the $\geqslant SiHNSi\leqslant$ species. Thus, a part of $\geqslant SiNHSi\leqslant$ can be changed in the more heat resistant two-dimensional silicon nitride, Si_3N, (which is assumed to be the surface silicon nitride corresponding to the three-dimensional Si_3N_4 formed when C_2N_2 is allowed to react at 1000°C and where two monolayers of silicon atoms are concerned in the nitridation reaction [25]), according to the stoichiometry

$$3 \quad \geqslant SiNHSi\leqslant \longrightarrow Si_3N + N_2 + 3/2\ H_2 \tag{11}$$

Hydrogen formation can be concealed by reaction with siloxane bridges and regeneration of silanol groups.

Treatment with oxygen at 1000°C concerns both the destruction of the remaining ≥SiNHSi≤ species and the newly formed "surface silicon nitride" such that



(12)

(13)

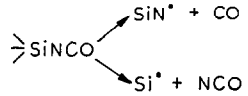
In both reactions the ratio $O_{2_{used}}/N_{2formed} = 1.5$ is in agreement with experimental results.

The calorimetric results (Fig. 4) corresponding to the destruction by the oxygen of the surface silicon nitride formed during TPD and IP of an X sample yield no information on the formula of the surface silicon nitride because the strength of the Si–N bond is expected to be different from the Si–N bond in Si_3N_4 (where it is 70 kcal [26]). This can be proved by a calculation using calorimetric data and B.D.E. (bond dissociation energy) values for the bonds Si–N, Si–O [27], O–O and N–N in which Si–N appears to be much higher than in Si_3N_4.

The pyrolysis of isocyanate species formed by the reaction of isolated silanol groups with C_2N_2 at 420°C will be discussed in the next section.

Highly dehydroxylated samples: X samples

When only ≥SiNCO is present (without ≥SiCN + =SiNC) at the beginning of the TPD, two paths of thermal decomposition can be inferred, i.e.



(14)

(15)

Consider the reactions

$$H{-}OH + C_2N_2 \rightarrow HNCO + HCN \qquad \Delta H_r = -9 \pm 3 \text{ kcal} \tag{16}$$

$$Si{-}OH + C_2N_2 \rightarrow SiNCO + HCN \qquad \Delta H_r = -12.2 \text{ kcal [7]} \tag{17}$$

where ΔH for reaction (16) is calculated from the heats of formation obtained by Okabe [28]: $\Delta H_f(H_2O) = -57.1$, $\Delta H_f(C_2N_2) = -73.4$, ΔH_f (HCN) = 32.4 and ΔH_f(HNCO) = −24 kcal. Use of the B.D.E. values of D(O–H) = 102 [29], D(NC–CN) = 128, D(H–CN) = 121 [30] and D(Si–OH) = 128 kcal [31] allows us to point out that almost the same values are obtained for the SiNCO and HNCO heats of atomization so that the Si–N and H–N bond strengths are comparable. As (H–NCO) = 113 kcal can be calculated from ΔH_f (HNCO), we may assume that D(Si–NCO) ≃ 113 kcal. This value is in quite good agreement with the value given by Walsh [31] in

Me_3Si–NHMe where D(Si–N) = 100 kcal. Since from ΔH_f(HNCO), D(HN–CO) = 78 kcal [30], it is obvious that cleavage of Si–N–CO is more likely to occur according to reaction path (14).

Then, SiN reorganization leading to Si_3N "surface silicon nitride" with N_2 formation agrees with the step

$$3\ SiN \rightarrow Si_3N + N_2 \tag{18}$$

This step is thought to be slow at low temperatures and operates to a certain extent only at high temperatures. Consequently, the weak N_2 release observed during TPD 2 at low temperatures must be assigned to another source.

In this connection, we note that the moderate CO formation observed during TPD 5 (trapping of CO_2) indicates that the presence of this compound is not dependent in any way on a reaction path involving CO_2. In consequence, reaction (14) exists but it is not the most important path.

Another pathway for the ≥SiNCO destruction may come from direct interaction between two nearest ≥SiNCO groups. By analogy with the well-known low temperature reaction of aryl isocyanates [32], i.e.

$$2\ ArNCO \rightarrow CO_2 + ArN{=}C{=}N\ Ar \tag{19}$$

we assume

$$2\ \geq SiNCO \longrightarrow CO_2 + \geq SiNCNSi\leq \tag{20}$$

$$\geq SiNCNSi\leq \longrightarrow -SiN + \geq SiCN \tag{21}$$

–SiN is converted by reaction (18), therefore the total apparent stoichiometry for the whole process is given by

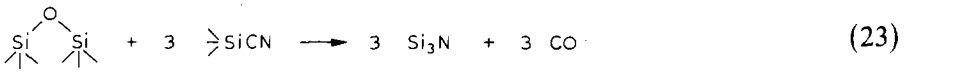
$$6\ \geq SiNCO \longrightarrow 3\ CO_2 + Si_3N + 3\ \geq SiCN + N_2 \tag{22}$$

The extent of CO_2 formation is clearly shown by TPD 5 where the gas phase composition at the end of TPD consists of 65% CO_2. Nevertheless, if it is likely that the neighboring ≥SiNCO groups are the source of CO_2 formation via reaction (20) at moderate temperature, it may be thought that this process, especially at higher temperatures, operates via the mobility of isocyanate groups. Reaction (22) emphasizes the connection between CO_2 and ≥SiCN formation. Besides, an analogous correlation has been observed previously between CO_2 formation and the non-restored carbon at the end of the TPD [33]. Moreover, the work of Eley et al. [15] substantiates this interpretation since during the pyrolysis of the species resulting from the interaction C_2H_5NCO/SiO_2, ≥SiCN formation was observed and ascribed it to the thermal decomposition of ≥SiNCO.

At this point of the discussion it may be interesting to examine numerical ratios from several theoretical borderline cases and compare them with our experimental data.

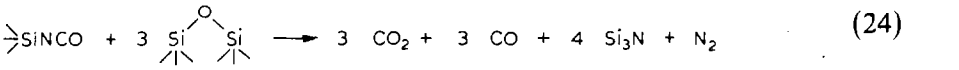
(a) If CO_2 is not allowed to undergo further reactions with the surface

species ($-Si_3N$, $\geqslant SiCN$ or their precursors, $-SiN$, $\geqslant SiNNCSi\leqslant$), $\geqslant SiCN$ will react necessarily with siloxane bridges (at the highest temperatures, i.e. above 900°C according the work of Eley et al. [15]).



(23)

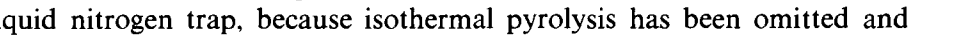
and reaction (22) becomes



(24)

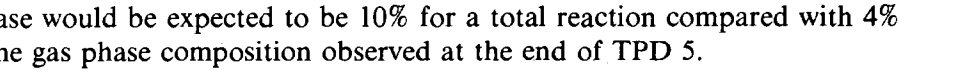
with the ratios $CO/N_2 = 3$ and $N_s/N_g = 2$ (N_s = nitride; N_g = gas). We note that these ratios are not in perfect harmony with the TPD 5 carried out with a liquid nitrogen trap, because isothermal pyrolysis has been omitted and reaction (18) has not completely taken place. From the CO formation, N_2 release would be expected to be 10% for a total reaction compared with 4% of the gas phase composition observed at the end of TPD 5.

(b) If CO_2 is allowed to react with the foregoing species, reaction (22) becomes



(25)

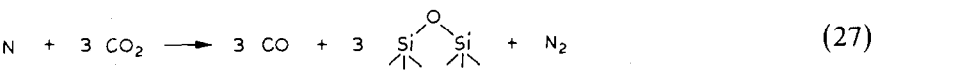
Including the reaction of the CO_2 intermediary produced with $\geqslant SiCN$



(26)

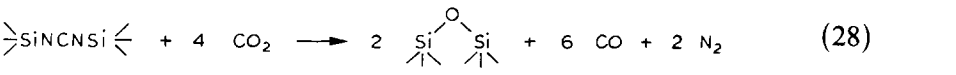
In this case, the ratios $CO/N_2 = 3$, $N_s/N_g = 1/2$ are obtained according to reaction (25), this reaction being equivalent to the sum of eqns. (22) and (26) where $\geqslant SiNCO$ is directly decomposed without CO_2 intermediary formation.

A CO_2 addition to a fully pyrolyzed sample (all the carbon being already restored in the gas phase) shows that the reaction involving CO_2 destruction is slow at 1000°C and practically non-existent at 700°C. In consequence, the slow reaction at 1000°C may be attributed to the reaction of the "surface silicon nitride" with CO_2, such that



(27)

whereas nitrogen evolved at lower temperatures (TPD 2, Fig. 6) is tentatively assigned to the reaction of $\geqslant SiCN$ and $\geqslant SiNCNSi\leqslant$ species with CO_2 according to eqn. (26) or



(28)

(c) In the case where the TPD concerns various mixtures of $\geqslant SiCN$ + $\geqslant SiNCO$, the borderline ratios CO/N_2 and N_s/N_g can be obtained for each composition from the sum of reactions (22) and (23) or (24) and (23) depending on whether the CO_2 is allowed to react or not. Figures 8 and 9

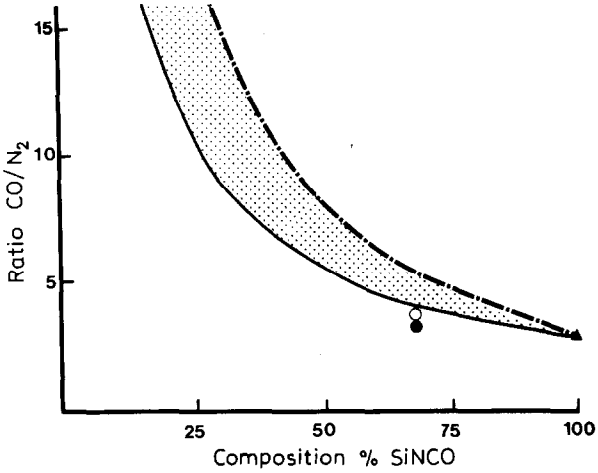


Fig. 8. Comparison of experimental ratios CO/N_2 for: ▲, TPD 2; ●, TPD 3 (uncorrected); and ○, TPD 3 (corrected for a complete pyrolysis assuming a ratio $CO/N_2 = 3$ for the slow carbon restoration) with theoretical ratios calculated assuming that CO_2 is reacting (———) or not (–·–·–) against the composition of the surface.

exhibit the evolution of the ratios vs. the SiNCO/SiCN composition. Figure 8 clearly shows that in the absence of initial ≥SiCN at the start of the pyrolysis the ratio $CO/N_2 = 3$ for both cases (CO_2 reacting or not) but as soon as ≥SiCN (or =SiNC) is increasingly present at the start of the pyrolysis, the ratio CO/N_2 increases and leads to the release of a lower part of the initial nitrogen in the gas phase. For a definite SiNCO/SiCN composition, CO/N_2 and N_s/N_g ratios are higher when CO_2 is not allowed to react.

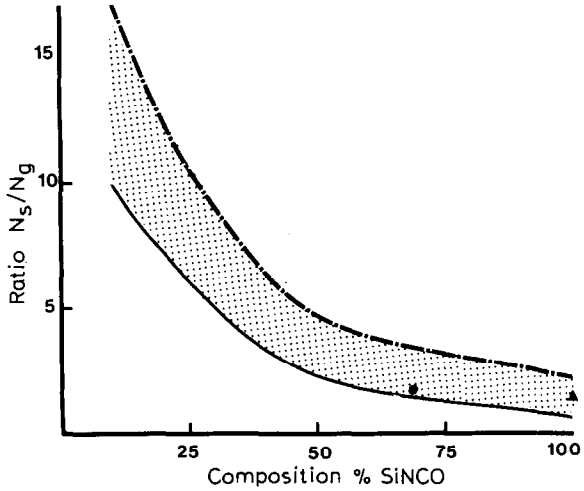


Fig. 9. Comparison of the experimental ratio N_s/N_g for: ▲, TPD 2; and ●, TPD 3 with theoretical ratios calculated assuming that CO_2 is reacting (———) or not (–·–·–) against the composition.

In the actual TPD and IP experiments, it is likely that only a part of the CO_2 is allowed to react with the different surface species according to the temperature and concentration of the species. In consequence, the experimental ratios, CO/N_2 and N_s/N_g, must be located inside the two curves corresponding with CO_2 reacting or not.

If, in the absence of initial ≥SiCN, experimental data (TPD 2 + IP 2) are consistent with the domain limited by the two border line ratios, not such a good agreement is obtained for TPD 3 + IP 3 (38% ≥SiCN) since the CO/N_2 ratio is slightly out of limit. But as can be seen from Table 1, the CO/N_2 ratio during TPD 3 is increased (in qualitative harmony with theoretical curves), whereas it remains close to 3 when ≥SiCN is absent at the beginning of the pyrolysis.

For the ratio N_s/N_g, a better agreement is also visible in the case where ≥SiCN is present at the beginning of the pyrolysis. The reason for the disagreement observed for the CO/N_2 ratio is not actually understood but it may have resulted from oversimplification of the real mechanism.

CONCLUSION

Although TPD has provided considerable information about the pyrolysis of surface species issued from the chemisorption of cyanogen on silica, no detailed mechanism can be devised, but an outline of the main probable behaviors of ≥SiNCO and ≥SiCN species has been evidenced. Many questions concerning the details of surface structure remain unanswered. Answers to most of these questions could not be obtained without supporting studies with other techniques, such as infrared spectroscopy.

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