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Oxidation with no-redox oxides: ammoximation of cyclohexanone on amorphous silicas

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Abstract

The ammoximation in gas phase of cyclohexanone is a reaction with an oxidation step performed on an insulator oxide such as amorphous silica. Conventional mechanisms for such a kind of reaction are not useful. This paper reviews the efforts carried out to understand the catalytic behavior of the silica and highlights the particular catalytic features of the tars, the carbonaceous products formed during the ammoximation, in the oxidation step of the reaction. The catalytic behavior and the role of the acid sites, of the tars and of the activated forms of molecular oxygen were investigated on several commercial amorphous silicas and on pure and doped silicas prepared by sol-gel method. The silica catalyst shows a bifunctional behavior: acid sites are necessary for the formation of imine, the intermediate of the reaction, and oxidizing sites for the formation of oxime. For the first step the presence of silanols of the right acidity results is essential. For the oxidative step the carbonaceous products formed during the reaction seem to play an essential role. It has been suggested that the tars are formed by a polymerization reaction which occurs at the silica surface and involves, in the initiation stage, activated oxygen species generated by the silica surface. The reaction progression with time involves increasing amounts of the carbonaceous products, with a corresponding decline in access to the active sites by pore blockage and, as a consequence, with a corresponding decline in the catalytic activity. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Amorphous silica; Carbonaceous products; Ammoximation; Cyclohexanone oxime

1. Introduction

For the oxidation reactions the most used catalysts are reducible oxides. However, a few number of reactions which involves the activation of oxygen uses irreducible oxides as catalysts. As an example in the oxidative coupling of methane very active catalysts are oxides of the rare earth elements and of the alkaline earth metal elements promoted by alkaline additives [1]. These catalysts in general are characterized by the structural imperfection caused by oxygen defects, so showing semiconducting properties. The catalyst performances are determined by the ability of the oxide to activate molecular dioxygen [2–4].

In other cases insulators with acid–base properties, such as alumina, phosphates, zeolites, that do not contain a multiple valency metal are catalysts for oxidation and ammoxidation reactions such as the oxydehydrogenation of alkylbenzenes, in particular of ethylbenzene [5–9]. Extensive studies have shown that these insulating acid–base materials catalyze the formation of carbonaceous products which are catalytically active in oxydehydrogenation [10,11]. In

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these processes the accumulation of carbonaceous products does not cause deactivation of the catalysts, at least in the first hours of reaction, but causes promotion of activity as a result of the catalytic properties of the carbonaceous product itself [12]. The original catalyst fulfils the roles of a catalyst for the formation of the carbonaceous product and a support for that deposit.

Another reaction involving oxidation and forming carbonaceous products using an insulator oxide, amorphous silica, as catalyst is the ammoximation in gas phase of cyclohexanone to the corresponding oxime [13–16].

Cyclohexanone oxime is the reactant for the production of ε-caprolactam, the monomer for nylon 6. Ammoximation is an alternative heterogeneous catalytic process to the conventional ones. The reaction is carried out at 200°C with air and ammonia and relatively high performances are obtained with amorphous high surface silicas, such as Porasil A or Akzo F-7 [17–22]. A yield of over 30% can be obtained, however other commercial silicas give extremely variable results [23].

In order to obtain a better understanding of the reaction network and of the reaction mechanism of gas phase ammoximation, much work has been done [24–28]. A reaction pattern has been proposed and consists of the following main steps:

$$\text{cyclohexanone} + NH_3 \Leftrightarrow \text{imine} + H_2O$$

$$\text{imine} + O^* \Leftrightarrow \text{cyclohexanone oxime}$$

Particular efforts have been made to understand the nature of the active sites and in particular of the oxidizing sites. At this aim samples of amorphous silicas were prepared by sol-gel method in order to obtain an high purity oxide [29]. A careful characterization was carried out and also the effect of doping elements was studied [30,31].

The aim of this paper is to review the efforts carried out to understand the catalytic behavior of the silica and to highlight the particular catalytic features of the tars, the carbonaceous products formed during the ammoximation, in the oxidation step of the reaction.

2. Catalytic activity in the ammoximation

Up to now in the gas phase ammoximation the most active catalysts are amorphous silicas. However, the maximum activity of different commercial samples is very different, see Table 1, while the catalytic behavior with time on stream is very similar [16,24,32]. As an example Fig. 1 illustrates the changes of activity for one of the best catalysts Akzo F-7. The catalytic tests were carried out in a tubular glass fixed-bed micro-reactor, which has been described in detail elsewhere [25]. The typical reaction conditions were: NH_3=34% mol, O_2=10% mol, cyclohexanone =2.8% mol and N_2=balance; GHSV=1200 h^{-1} (W/F=175 g.h/mol).

During all the life of the catalyst, four main types of products are found. Together with the oxime and the tars, the cyclohexanone imine and other condensation products are produced. The evolution with time on stream is very complex. The rate of formation of tars, the heavy products irreversibly deposited on the catalyst, is constant for some hours of time-on-stream and then decreases to zero. In the first hours the cyclohexanone conversion and the oxime yield increase considerably indicating a process of activation of the catalyst. Then the catalytic behaviour is approximately constant for some hours. After that the activity

Table 1
Maximum performances of commercial silicas in ammoximation of cyclohexanone

Catalyst	Surface area (m^2/g)	Cyclohexanone conversion (%)	Oxime selectivity (%)	Oxime yield (%)	Tars yield (%)
Akzo F-7	472	72	45	32	19
Grace n. 2	320	55	24	13	26
Cabosil	140	42	3	1	14
Ti-Grace n. 3	328	76	33	25	27
Aerosil 200	130	75	12	9.9	35
Porasil A	–	63	46	29	26

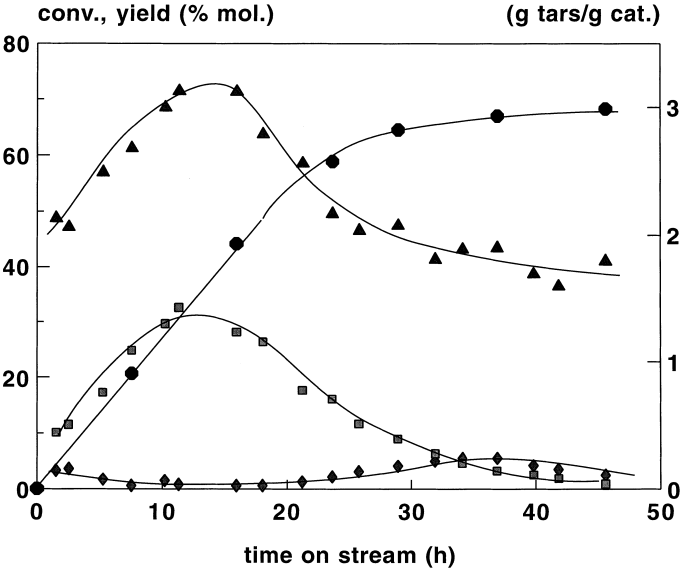

Fig. 1. Time evolution of the catalytic behavior of Akzo F-7 amorphous silica. Cyclohexanone conversion (▲); cyclohexanone oxime yield (■); cyclohexanone imine yield (◆); tars content (●).

decreases due to a deactivation phenomenon. The other volatile organic products (dimers and trimers of the ketone or of the imine) consist mainly in condensation products, aldol condensation and other kind of condensations, and their yield changes only slightly with the time of stream. A certain amount of imine is continuously present. Tests carried out at different temperatures and contact times showed that imine is a primary product [25]. When the oxime is produced in high yields, the yield of imine decreases. The catalytic reactions in presence of only O_2, without NH_3, are almost negligible.

In order to evaluate the importance of the homogeneous gas phase reaction, some tests in absence of the catalysts showed that the cyclohexanone reacts with ammonia in the gas phase producing the corresponding imine and the aldol condensation products. No tars deposition was evidenced. Furthermore the molecular oxygen does not interact with the organic compounds present in the gas phase and no oxime was observed.

The comparison with the data obtained with and without catalyst showed that the imine is also produced by a catalytic reaction on the acid sites of the silica [25]. The tars are formed by the interaction of the imine with oxygen. The tars can also partly be formed by other secondary reaction products such as the aldol condensation products.

CO_x are formed only at temperatures higher than 220°C or for long contact times. They seem to be produced by the unselective oxidation of the oxime and other products. However, the amount of CO_x is negligible in the usual reaction conditions.

3. Role of tars

3.1. Nature of tars

During the reaction on active catalysts a huge amount of tars are formed, which remains irreversibly adsorbed on the catalyst. In general in oxidation reaction the presence of oxygen prevents or reduces the coke deposition, although in a few cases the presence of carbonaceous deposits has been noted. In the case of ammoximation on silica, the presence of oxygen shows an opposite effect: it promotes the formation of the heavy organic compounds. In fact the rate of tars formation increases with the increase of the partial pressure of oxygen in the reaction mixture and with the increase of the cyclohexanone partial pressure [26]. The amount of tars deposited at a given time on stream increases with increasing the reaction temperature up to a maximum [25].

The elemental composition shows that the tars contain N and O and the average composition is the following: $C_6H_7N_1O_{0.5}$. The C:H ratio is higher than that of the starting reactant.

Electronic paramagnetic resonance (EPR) spectra of carbonaceous deposit show signals corresponding to organic radicals. The EPR spectrum consists of a single broad line, with a peak to peak width of 0.56 mT, characterized by a *g* value of 2.0035 [33]. In order to investigate the changes occurring at the silica surface due to the tars deposition, six samples of discharged catalysts, containing different amounts of tars deposited on the catalyst surfaces, were prepared by running the reaction on Akzo F-7 in the standard conditions and then stopping the reaction at different reaction times (0.5, 2.0, 4.0, 8.0, 16.0, 32.0 h). All samples gave rise to the same EPR spectrum with different intensities. The intensity increased with time-on-stream with the same trend as the yield of oxime during the activation process, see Fig. 2. However, the signal intensity can not simply be correlated to the tar content, it seems to be more related to the activation process of the catalyst, which takes place during the first 10–15 h of reaction.

Summarizing these results, the carbonaceous products formed during the ammoximation reaction over silica are nitrogen and oxygen-containing unsaturated compounds rich of organic radicals. The presence of conjugated bonds and oxygen-containing functional groups increases the concentration of the paramagnetic centers.

3.2. *Catalytic properties*

The tars, as previously mentioned, show a high concentration of paramagnetic centers, however, they can actually play a role in the oxime formation or are only byproducts that reduce the oxime selectivity. If the catalytic data, obtained with amorphous silicas, are analyzed as a function of the time on stream the extrapolated rate of formation of the oxime at t=0 h is about zero (as an example see Fig. 1). These observations suggest that the tars can effectively play a role in the activation process and in the selective oxidation pathway. In order to confirm this hypothesis, other catalytic studies were carried out and the first hour of reaction was studied in more detail, as reported in Fig. 3. The rate of formation of the oxime in the first minutes of reaction is really null.

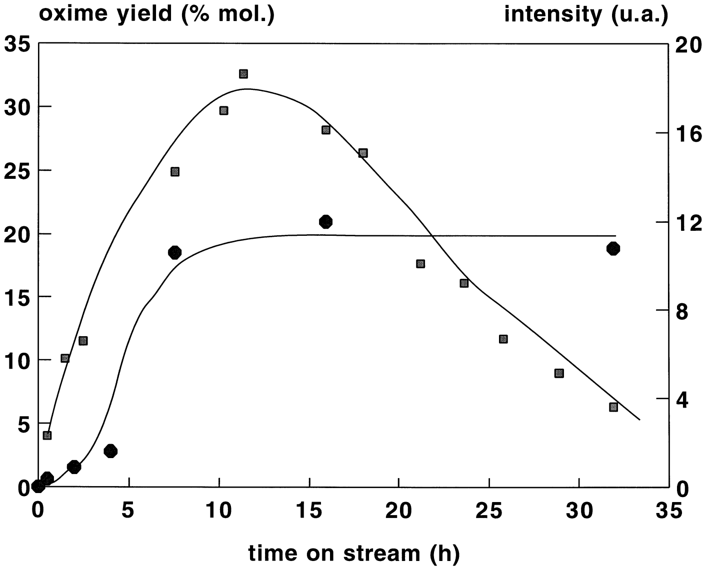

Fig. 2. Time evolution of the intensity of E.P.R. signal of tars organic radical and comparison with the oxime yield for Akzo F-7. Signal intensity (●); cyclohexanone oxime yield (■).

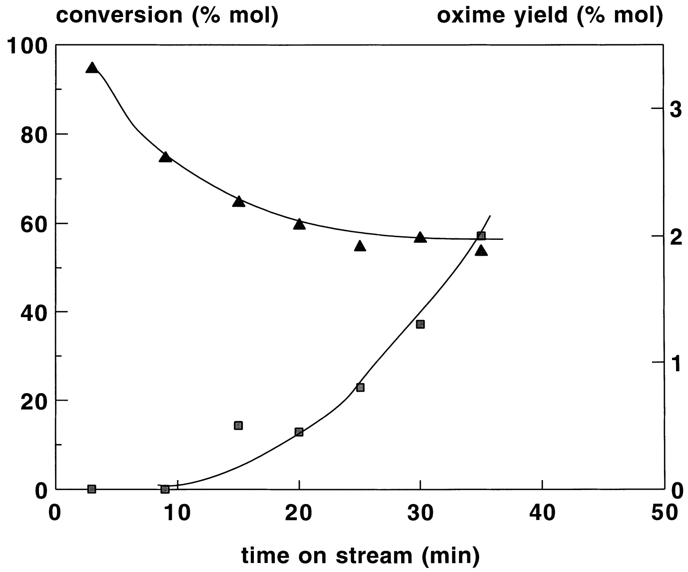

Fig. 3. Catalytic behavior of Akzo F-7 in the first minutes of reaction. Cyclohexanone conversion (▲); cyclohexanone oxime yield (■).

On the other hand if the amorphous silica is activated in the reactor with a reactant mixture without oxygen a small amount of tars is produced. The catalytic tests with this pre-activated catalyst show that at the beginning of reaction the rate of formation of oxime is higher than that of a clean catalyst, even if the maximum yield of oxime is slightly lower. The rate of formation of oxime results related to the total tar content. Furthermore, when a discharged catalyst is regenerated, burned off the carbonaceous product by air, the catalyst becomes clean and if it is tested in the ammoximation the catalytic activity

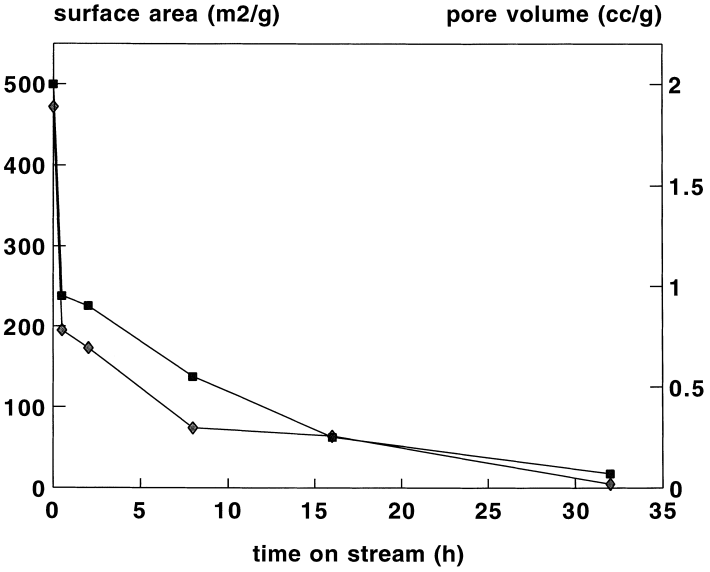

Fig. 4. Behavior of surface area (◆) and pore volume (■) as a function of time on stream of ammoximation for Akzo F-7 silica.

and its behavior are similar to those of an unused sample.

All these results lead to the assumption that a catalytically active surface is formed during the ammoximation over amorphous silica.

3.3. Effect on the catalytic deactivation

All the catalysts show a strong deactivation after some hours on stream and the values of surface area of spent catalysts are very low. In the case of Akzo F-7 silica the behavior of surface area and of pore volume as a function of time on stream were studied and the results are reported in Fig. 4. In the first minutes, the surface area strongly decreases as the micropores are filled. From the beginning of reaction to the time, at which the oxime yield is maximum (and also conversion is maximum), the surface area decreases from 470 to 80 m^2/g and the mean radius of pores is about 10–15 nm. When no more oxime is formed, the surface area falls to 4.5 m^2/g and that suggests almost all the pores are covered by tars.

Therefore, the decrease of activity in oxime formation may be attributed to the filling or to the non-accessibility of the mesopores because of covering of the surface, external surface of grains, by tars.

4. The effect of impurities

In order to verify whether the presence of impurities in the amorphous silica (for instance traces of titanium or aluminum) shows an influence on the catalytic activity, some samples were prepared by sol-gel method in different preparation media. The starting materials were: tetraethyl orthosilicate, water and nitric acid (65%) or ammonia (30%) [29]. In this way high purity silicas were obtained with two clearly different structural unit types on the base of the preparation media.

The silicas prepared under basic conditions are mesoporous amorphous materials with a medium surface area and result active in the ammoximation reaction, as reported in Fig. 5(a). The conversion of cyclohexanone is rather high and the oxime yield and selectivity rather good, but not as high as the performance of the commercial amorphous silicas, such as Akzo F-7 and Porasil A. The rate of tars deposition is slightly higher, however, the deposited total amount is lower. The volatile organic compounds are also formed.

On the contrary the silicas prepared in acidic conditions are microporous materials with a high surface area and result inactive in the oxime formation. They show the cyclohexanone imine formation only other than the volatile organic compounds formation (see Fig. 5(b)). The oxime is absent in all the tests.

These results indicate that pure silica is able to form the oxime and the presence of impurities of other elements is not necessary. Furthermore an intrinsic property of the silica, related to its textural and structural features, seems to be a paramount parameter, determining the catalytic activity.

On the other hand the introduction of other elements in low amounts can show an influence on the catalytic activity, however, it does not modify the fundamental behavior of the sample.

As an example, the introduction of titanium via sol-gel method on a silica prepared in acidic conditions does not modify its fundamental reactivity and oxime or tars are not formed [31]. On the contrary the introduction of titanium on a silica prepared in basic conditions strongly increases its activity. However, with increasing the titanium content the activity decreases, as reported in Table 2.

Also on the evolution with time on stream significant modifications occur, see Fig. 6. For the low titanium content catalysts the conversion and the oxime yield increase very rapidly up to a maximum. After that the conversion shows a fast decrease, while the selectivity does not change very much for some hours. With increasing the titanium, the maximum of conversion and yield decreases and as a consequence so does the selectivity, while the catalyst life strongly increases. With the titanium-rich catalysts the behavior no longer shows an activation and deactivation but an almost flat behavior with a slow deactivation and a long catalyst life.

At low value titanium content the volatile organic compounds formation is drastically reduced, while the tars formation is almost constant. With the increasing the titanium content a second effect is seen other than the decrease of oxime yield. The tars yield decreases and as a consequence the rate of deposition on the catalyst surface decreases, as reported in Fig. 7. The pure silica and the sample at low titanium content

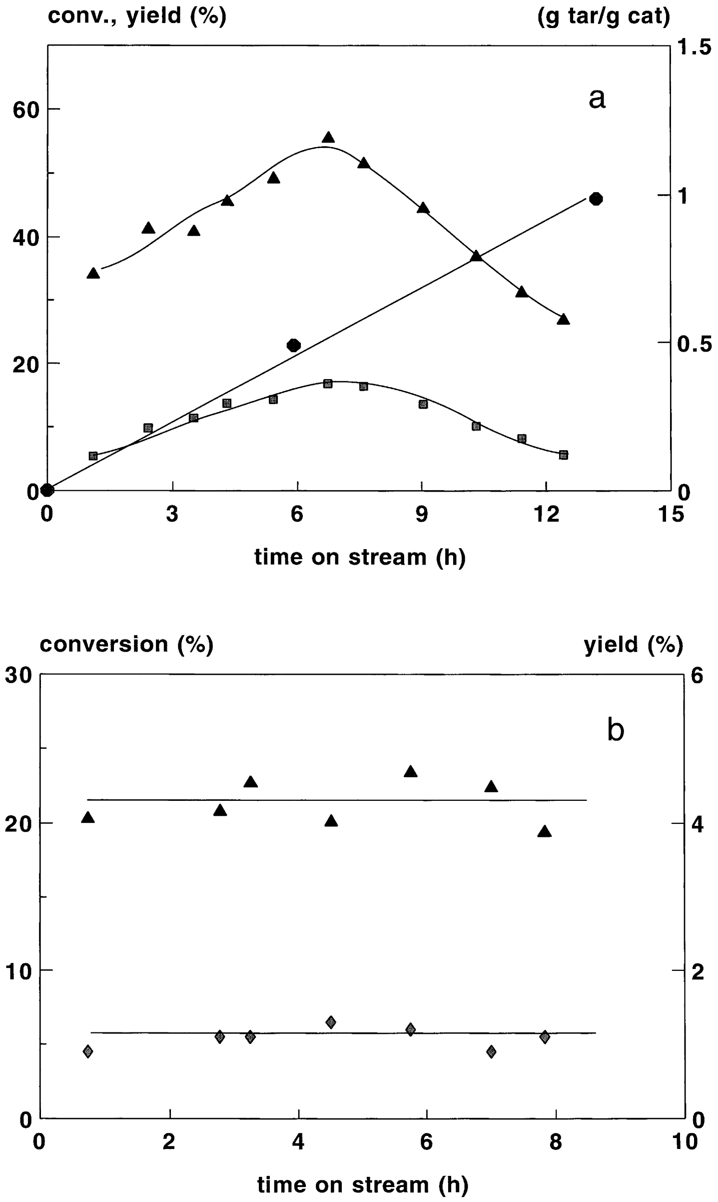

Fig. 5. Time evolution of the catalytic behavior of silica prepared: (a) in basic conditions; (b) in acidic conditions. Cyclohexanone conversion (▲); cyclohexanone oxime yield (■); cyclohexanone imine yield (◆); tars content (●).

show the same rate of formation of tars and the maximum of activity is at the same time on stream notwithstanding the strong differences in the oxime formation. The higher stability of the samples with increasing the titanium content can be related to less tars production.

In order to explain the activation effect due to the presence of titanium E.P.R. analysis were carried out. In the case of titanium promoted samples a strong signal is shown, whose intensity increases with the amount of titanium [30]. The signal has been attributed to the presence of O_2^- species anchored on

Table 2
Maximum performances of silicas pure and modified with titanium in ammoximation of cyclohexanone

Catalyst	Titanium content (mol %)	Surface area (m^2/g)	Cyclohex. conversion (%)	Oxime selectivity (%)	Oxime yield (%)	Tars yield (%)
Acid-sil.	0	800	20	0	0	0
Basic-sil.	0	240	54	31	17	19
Ti-025	0.25	218	62	63	39	18
Ti-05	0.5	240	62	56	35	15
Ti-1	1.0	220	40	42	17	11
Ti-3	3.0	80	32	38	12	9

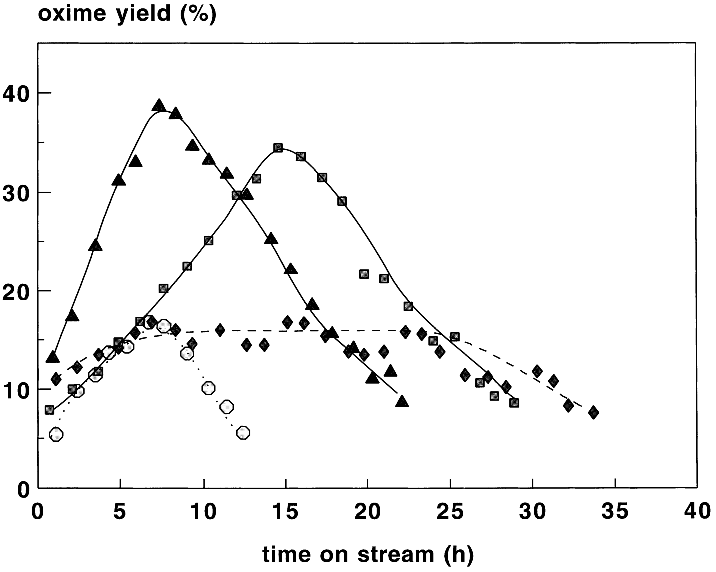

Fig. 6. Time evolution of the cyclohexanone oxime yield of silicas modified with titanium. Pure silica (●); Ti-025 (▲); Ti-050 (■); Ti-1 (◆).

titanium ions [30,34], the same signal even if of very low intensity was previously seen also on Akzo F-7 [33]. This phenomenon confirms the ability of titanium to activate molecular oxygen and may be related to the oxidation step, assumed under these reaction conditions as the lowest step of the reaction [26]. However, a straight correlation between the signal intensity and oxime yield or cyclohexanone conversion does not exist.

Therefore, on the titanium promoted samples the presence of Ti-sites can actually enhance the oxime selectivity and yield and make the selective oxidation faster, however, the fundamental role seems to be played by the tars formed inside the pores. The oxime formation may be attributed to a combined effect of the tars and of the oxygen species activated on titanium ions.

5. Role of the oxygen adsorbed species on silica

In order to find if any kind of oxygen species is in equilibrium with gaseous oxygen at the surface of the amorphous silicas at the temperature of ammoximation reaction, different types of commercial silica with different activities were investigated by means of surface potential measurements [32], as reported in Table 3. The adsorption of gaseous oxygen on silica catalysts creates O_2^- species in the same range of temperature at which ammoximation reaction is per-

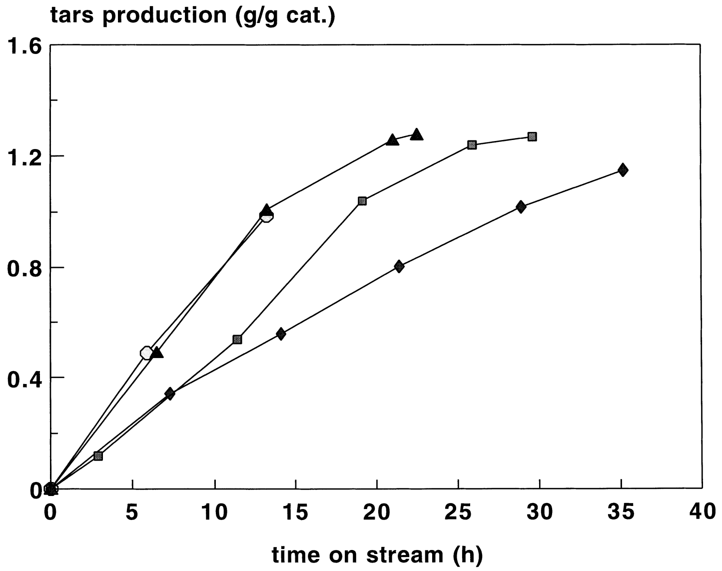

Fig. 7. Time evolution of the tars content of silicas modified with titanium. Pure silica (●); Ti-025 (▲); Ti-050 (■); Ti-1 (◆).

Table 3
Oxygen species adsorbed on the surface of different silicas

Catalyst	Temperature (°C)	Oxygen species
Akzo F-7	200	O_2^-
	220	O_2^-
	240	O_2^-
Aerosil 200	160	O_2^-
	220	O_2^-
	280	O^-
Cabosil	200	O_2^-
	225	O_2^-

formed. There seems not to exist any correlation between the activity in the synthesis of oxime and the presence of this oxygen species on the basis of the following considerations:

- silicas with very different selectivity in oxime formation presents the same oxygen species;
- the maximum of activity of the silicas is reached when the surface is covered by relevant amounts of tars.

On the other hand the formation of oxime is not a property strictly related with the initial fresh surface (object of potential measurements), however, the O_2^- species seems to be related to the formation of tars. Our hypothesis is that activated oxygen species formed on the surface may be involved in determining the initiation stage of a radical polymerization mechanism and the chain propagation occurs on unsaturated compounds, such as the adsorbed imine.

6. Role of the acidic sites

In order to verify the importance of the surface acidity in the production of the intermediate imine, a complete investigation was carried out by adsorption of base with different basicity and FT–IR measurements [30,35]. The FT–IR studies evidence the absorptions in the OH stretching vibrations region. Free silanols (SiOH) are present and vibrate at 3745 cm^{-1}. The spectra also exhibit the presence of silanol nests. These nests are indicated by broad bands in the region between 3750 and 3000 cm^{-1}. The position and shapes of these bands reflect the occurrence of H-bonding which weakens the OH bond. The silanol nests are particularly abundant in pure silicas and Akzo F-7. The strength and surface concentrations of free and H-bonded silanols were measured by comparison of the absorptions in the OH stretching region and by adsorption of a weak base as deuterated acetonitrile [35]. By comparison of different silicas the acid strengths result almost comparable while the concentrations of these centers are very different.

In order to investigate the mechanism of the formation of the imine and of the oxime from the ketone, FT–IR studies were carried out adsorbing the ketone or ammonia on different silicas at the reaction temperature and studying the nature of the adsorbed species.

The tests showed that, when cyclohexanone is put into contact with the catalyst at 200°C for increasing times, the IR band corresponding to free silanols (3745 cm^{-1}) and the higher-frequency components of the broad stretching OH band almost disappear, while other bands appear, together with those relative to cyclohexanone hydrogen bonded to surface silanol groups, indicating the formation of at least one new species. Bands were observed which were associated with C=C stretching (1598 cm^{-1}) and unsaturated =CH– bond stretchings (3075 and 3045 cm^{-1}) [36]. It was hypothesized that an enolic form of cyclohexanone is formed under these conditions. Successive evacuation shows that these new species are more strongly bonded to the surface than cyclohexanone.

If the ammonia is added to the samples active in oxime formation, for instance Akzo F-7 or pure silica prepared in basic conditions, containing cyclohexanone interaction complexes, then the remaining OH groups from silanol nests form H–bonded and $\mathrm{NH_4^+} \dots {}^{-}\mathrm{O(sil)}$ ion-pair complexes with $\mathrm{NH_3}$. This is indicated by the appearance of νNH bands between 3400 and 3260 and a broad band at 1485 cm^{-1}. Adsorption of ammonia also completely eliminates the original cyclohexanone interaction complexes and stimulates the formation of new species characterized by the new band at 1655 cm^{-1}. The evacuation removes ammonia, ammonium ions and cyclohexanone from the surface while new species remain. However, two bands at 1650 and 1665 are seen instead of the previous one at 1655 cm^{-1}. All these spectral changes, together with positions of new bands near 1650 cm^{-1}, point to the surface reaction of cyclohexanone with ammonia to cyclohexanone imine. The absorption band at 1655 cm^{-1} is attributed to a C=N stretching mode. Splitting of the band at 1655 cm^{-1} into two components after the ammonia desorption can be explained, according to the known chemistry of silica with amines, by the formation of two imine interaction complexes, as it was observed similarly for cyclohexanone, probably the surface ketimine and enamine species bonded to the surface via Si–N bonds.

The above experiments was repeated adsorbing cyclohexanone in the presence of small amounts of co-adsorbed ammonia. The results were the same than in the previous case and the new absorption bands were evidenced.

On the inactive silicas, such as Cabosil or sol-gel silica prepared in acid conditions, the adsorption bands at 1650 cm^{-1} is not seen. Furthermore these silicas are able to protonize less adsorbed ammonia molecules than the active samples.

To compare the activity of silica catalysts active or inactive in the ammoximation a small amount of cyclohexanone was added over the ammonia covered surface. On the active silicas the band at 1655 cm^{-1} consequently appeared and slowly grew after prolonged adsorption while no band at 1655 cm^{-1} was recognized on the background of the band of adsorbed

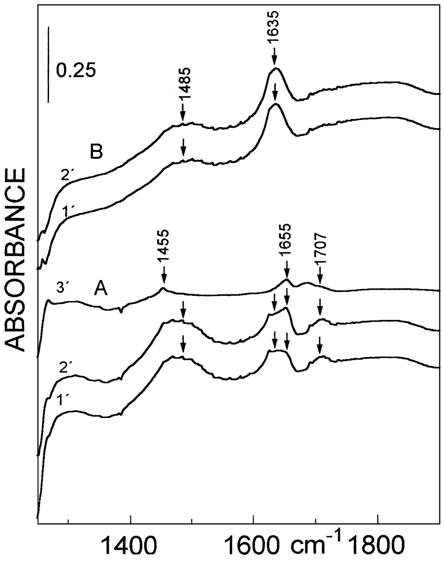

Fig. 8. FT–IR spectra, obtained by the subtraction of the spectrum of sample before the adsorption, of silica prepared in basic conditions pretreated at 200°C (A) after adsorption of ammonia at 15.8 mbar and addition of about 3 mmol cyclohexanone per gram of catalyst, interaction for 15 min (1′), 45 min (2′) and after evacuation for 5 min (3′); FT–IR spectra of silica prepared in acid conditions pretreated at 200°C (B) after the adsorption of ammonia and addition of cyclohexanone after 15 min (1′) and 45 min (2′).

ammonia at 1635 cm^{-1} of the inactive silicas, as reported in Fig. 8.

Therefore, cyclohexanone alone can react with the surface silanols of the catalyst giving an enol species bonded to the catalyst surface by a covalent Si–O–C bond. In the presence of ammonia on active silicas two types of adsorbed species are formed, identified as an enamine and a ketimine form of the cyclohexanone imine bonded to the silica surface by a Si–N bond. Adsorbed cyclohexanone imine can undergo oxygen insertion by reaction with some activated oxygen species, giving rise to an adsorbed form of the oxime having a Si–O–N bond. This reactivity can be related to the partial double bond character of Si–N bonds, due to the interaction between the full *p*-type nonbonding orbital of nitrogen and the empty *d*-type orbitals of silicon, as well as to the known ability of silicon to enlarge its coordination number from 4 to 6, due again to the availability of its *d*-orbitals [37].

7. Reaction mechanism

The changes in the nature of the catalyst that take place in the course of the process owing to the accumulation of the catalytically active tars lead to a reaction mechanism that varies with the time. The mechanism on the fresh catalyst differs from the mechanism on the used catalyst.

Fig. 9 depicts the complex mechanism suggested for the ammoximation the reaction intermediate is the imine and in particular an activated form of imine adsorbed on the catalyst surface. The adsorbed species can be oxidated to oxime by some oxygen species activated on the tars, that contain a high concentration of organic radicals. In the usual reaction conditions the rate limiting step of the reaction is assumed to be the oxidation of the adsorbed imine.

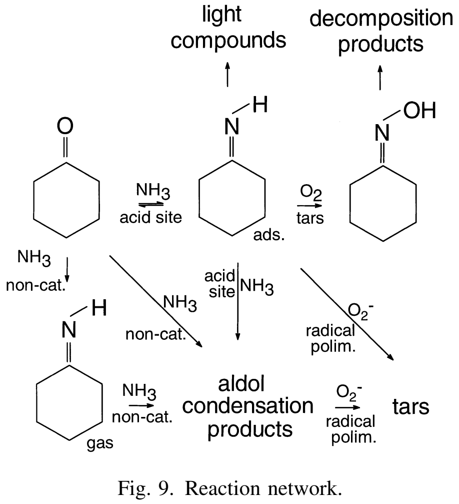

Fig. 9. Reaction network.

EPR results show that on silica itself a slight presence of radical species can be observed [30] and the surface potential measurements reveal the presence of O_2^- species on the clean surface of the silica samples. These superoxide radicals generated by the silica surface are supposed to be involved in the initiation stage of a radical polymerization mechanism. The tars are formed by this polymerization reaction which occurs at the silica surface and involves N containing compounds (imine and condensation compounds adsorbed on the surface). In absence of oxygen only a slight formation of tars can occur on acid sites.

The imine can be formed by homogeneous gas phase reaction or can be formed on the acidic sites of the silica. The FT–IR results show that probably only the ‘activated’ imine adsorbed on the surface is able to be oxidized by the oxygen species activated by the tars to form the oxime. The acid sites are constituted by the silica silanols. These sites show a weak acidity even if of a slight different strength. It is difficult to decide if the responsible of the activity are the free silanols or the silanols nests.

The volatile products are a mixture of different compounds, their formation occurs at least partly in the gas phase by condensation reactions, such as aldol condensation, and also by a catalytic reaction on the acid sites.

The complex behavior of the catalytic activity as a function of time on stream may be explained by means of tar formation. The formation of tars gives rise to two effects:

1. an activation effect, expressed as oxidizing effect;
2. a deactivation effect due to the deposition of tars on the surface and the consequently coverage of active sites.

In the first hours of reaction the radical polymerization, that produces the tars, starts. In the first period the catalyst is activated and the increase of the tars amount increases its oxidation activity and as a consequence the production of oxime due to the oxidation of the adsorbed imine, formed on the acid sites of the silica. The kinetics of the process are now regulated by the fast transformation of the adsorbed imine into the oxime and the conversion exhibits the same trend. However the amount of the paramagnetic species of the tars reaches a constant value over that it does not increase and the oxime formation levels off.

The continuously formation of tars causes the coverage of the surface, at first the filling of micropores then the mesopores, and the tar content reaches such a value as to decline in access to the active carbonaceous centres by pore blockage. The conversion and the formation of oxime start to decrease and then even the acid sites responsible to the adsorbed imine are blocked and also the tars formation decreases. At last all the pores are covered by tars and the surface area is decreased at values near to zero. A low level of residual activity may be attributed to the remaining tars-covered external surface of the silica and to the homogeneous gas phase reactions.

8. Conclusions

The ammoximation of cyclohexanone is a reaction with an oxidation step performed on an insulator oxide such as amorphous silica. Also very high purity silicas prepared by sol-gel method result active in the reaction, producing the oxime. Conventional mechanisms for such a kind of reaction are not useful.

The reaction pathway assumes the imine as the intermediate of the formation of oxime. The catalyst shows a bifunctional behavior: acid sites are necessary for the formation of imine and oxidizing sites for the formation of oxime. For the first step the presence of silanols of the right acidity is essential. For the oxidative step the fresh or the regenerated catalyst is not able to produce oxime while the carbonaceous products formed during the reaction play an essential role. In fact the tars show a promoting effect on the oxidation compounds. Up to now in the literature only a few cases in which the carbonaceous products have a positive effect are reported, for instance the oxydehydrogenation of alkylbenzenes.

The tars are probably formed by a polymerization reaction which occurs at the silica surface and involves N containing compounds (imine and condensation compounds adsorbed on the surface). In the initiation stage activated oxygen species, superoxide radicals, generated by the silica surface are supposed to be involved. The tars are nitrogen- and oxygen-containing unsaturated compounds and show a large amounts of paramagnetic centers, such as organic radicals.

The reaction progression with time involves increasing amounts of the carbonaceous products, with a corresponding decline in access to the active sites by pore blockage. Therefore, the formation of tars gives rise to two effects:

1. an activation effect, expressed as oxidizing effect;
2. a deactivation effect, expressed as coverage of active sites.

In the ammoximation notwithstanding the presence of oxygen the tars are not partly burned off and as a consequence their amount is continuously increasing, so showing the strong deactivating effect, which is the main drawback of the reaction.

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