Ti-silicalite as catalyst for gas-phase ammoximation of cyclohexanone with molecular oxygen

D.P. Dreoni, D. Pinelli, F. Trifirò *

Department of Industrial Chemistry and Materials, V.le del Risorgimento, 4-40136 Bologna, Italy

and

Z. Tvaruzkova, H. Habersberger and P. Jiru

Heyrovsky Institute of Physical Chemistry and Electrochemistry Dolejskova,
3-18223 Praha (Czechoslovakia)

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The catalyst behaviour of titanium silicalite, which was found the most active and selective catalyst for liquid-phase ammoximation of cyclohexanone to the corresponding oxime with hydrogen peroxide, was investigated in the gas-phase ammoximation with molecular oxygen in and compared with those of pure silicalite and samples of vanadium and chromium silicalites. The results showed that Ti-silicalite is a selective catalyst not only in the reaction with hydrogen peroxide but also in the reaction with molecular oxygen. However, a big limitation was found in the poor activity of the silicalites which do not allow to reach high oxime yields.

Keywords: Ammoximation of cyclohexanone; Ti-silicalite oxidation catalyst

1. Introduction

Cyclohexanone oxime is an important intermediate for the industrial production of caprolactam [1]. Two new processes have been patented in the last decade for the direct synthesis of cyclohexanone oxime from cyclohexanone by ammoximation reaction. This new type of reaction involves the interaction of the ketone with ammonia and an oxidizing agent. The first process has been studied by Armor et al. [2–6] and patented by Allied Chem. Corporation [7]. It uses molecular oxygen as the oxidizing agent and is a heterogeneously catalyzed gas phase process, the catalyst being an amorphous silica. The second process was patented by Montedipe [8–10]; it employs hydrogen peroxide as the oxidizing agent and is heterogeneously catalyzed in the liquid phase by titanium silicalite.

Although the Allied process is the most attractive one because of the lower cost of O_2 as compared with H_2O_2, its development was not continued because deposition of tars deactivates the catalyst and worsens its performance. On the contrary, the Montedipe process seems to be near to industrial application, thanks to the high activity and selectivity of the catalyst.

Much work has been done by some of us [12–15] in order to obtain a better understanding of the nature of the reactions involved in the ammoximation in gas-phase with molecular oxygen and to investigate the origin of the oxidizing capability shown by silica. Previous work [12–14] gave useful information about the reaction network. In particular, the reaction pathway might present some analogy with that suggested by Roffia et al. (Montedipe) for ammoximation in the liquid phase with hydrogen peroxide and titanium silicalite [16]. We also showed [15] that, in the case of gas-phase ammoximation with O_2, the introduction of Ti in an amorphous silica results in an increase in both conversion and oxime yield, without affecting the rate of deposition of tars (no apparent changes in the structure and acidity occur in the catalyst). On the basis of this evidence, it was tentatively hypothized that, like that which occurs in the proposed mechanism for the ammoximation with hydrogen peroxide, the Ti ions might interact with and stabilize some activated species such as superoxide radicals ($O_2^{-\cdot}$), involved with the selective pathway. Because of the analogy existing between the mechanisms of ammoximation reactions with O_2 and H_2O_2 and the positive effect of Ti on the oxime selectivity, it is interesting to compare the catalytic behaviours of Ti-silicalite and AKZO F-7 silica, which was found to be the most active and selective catalysts among the amorphous silica tested [13,15]. In this work, therefore, we investigated the catalytic behaviour of titanium silicalite in the gas-phase ammoximation using O_2 as the oxidizing agent and compared it not only with that of the amorphous silica used in previous work but also with those of the some samples of silicalites, pure and doped with transition metals known to be active in oxidation reactions. The work was carried out in order to verify if Ti-silicalite may be a good catalyst also for gas-phase ammoximation with O_2, to confirm the effect of the presence of Ti in the catalyst and to verify the possible positive effect of the insertion of the ions of transition metals in a crystalline structure. As in the previous work [14], also in the present work, I.R. spectroscopy techniques using self-supported catalyst pellets were employed to characterize and compare the acidities of the samples.

2. Experimental

CATALYST PREPARATION

The Ti-silicalite sample was prepared according to the patent by G. Bellussi et al. [16]. The template was decomposed in flowing air at 580 °C for 4 h. The pure silicalite sample was prepared following the same method used to prepare

Table 1
Main characteristics of the catalysts

Catalyst Id.	Surf area (m^2/g)	Pore vol. (cm^3/g)	App. density (g/ml)	Al_2O_3 (% wt)	Other (% wt)	Particle size (mm)
Silica AKZO F-7	472	2.0	0.246	0.07	0.01	0.10–0.15
Pure silicalite	–	0.16 *	0.519	< 0.01	–	0.3 -0.6
Ti-silicalite	–	0.14 *	0.486	< 0.01	0.12% Ti	0.3 -0.6
Cr-silicalite	–	0.16 *	0.293	< 0.01	0.40% Cr	0.3 -0.6
V-silicalite	–	0.14 *	0.479	< 0.01	0.43% V	0.3 -0.6
Grace Nr.2	320	1.20	0.351	–	–	0.3 -0.6
Ti-Grace Nr.3	328	1.91	0.301	–	0.28% Ti	0.3 -0.6

The pore volumes of the samples marked with an asterisk * were determined by Ar sorption at −195 ° C and 80 mm thus includes only the volume of micropores.

the Ti-silicalite but without adding titanium. The chromium and vanadium silicalites were prepared according to patents by Marosi et al. [18,19] and freed from the organic template by calcination in a flow of N_2 at 580 ° C for 4 h. The AKZO F-7, Grace Nr.2 and Titania Grace Nr.3 amorphous silicas are commercial samples by AKZO and GRACE. The main characteristics of all the samples are summarized in table 1.

CATALYTIC TESTS

The catalytic tests were carried out in a tubular glass fixed-bed plug-flow micro-reactor (maximum capacity 4.0 ml, 1.0 g of catalyst). The flow-rate of the ammonia and the oxygen were regulated by conventional flow-meters and micrometric valves. The cyclohexanone was added to the carrier gas by an infusion pump directly into the reactor and vaporized just over the catalytic bed. Further detail on the laboratory equipment and apparatus used in this work is given elsewhere [13].

The products were collected in a solvent (n-hexane) and analyzed by gas-chromatography. A Carlo Erba gas-chromatograph mod. MEGA HRGC 5300 was used with a methyl-silicon capillary column and a F.I.D. detector. The conversion of cyclohexanone, the yield and the selectivity of the products were calculated as reported in ref. [13]. The reactor was weighed before and after the catalytic tests to determine the increase in weight of the catalyst and quantify the tars deposited on its surface. The yield of tars that deposit on the catalyst was calculated assuming that they consist of a polymer of a monomer with the same molecular weight as the oxime [13].

The following symbols will be used hereinafter: CH = cyclohexanone, CHN = cyclohexanone imine, CHO = cyclohexanone oxime. The typical reaction conditions were: $NH_3 = 34\%$ mol, $O_2 = 10\%$ mol, cyclohexanone CH = 2.8% mol and the remainder nitrogen, $T = 170–250$ ° C, catalyst weight $W = 0.5–1.3$ g loaded as powder (0.125–0.150 mm) or grains (0.3–0.6 mm), contact time = 3.0–5.0 s (GHSV = 720–1200 h^{-1}).

F.T.-I.R. MEASUREMENTS

The IR spectra were recorded at r.t. by a F.T.-I.R. Nicolet MX-1E spectrometer. The catalyst was pressed into self-supporting pellets (thickness 10–12 mg/cm^2) and activated in vacuum in the conventional IR cell (KBr windows) connected to a greaseless gas-manipulation/evacuation Pyrex glass ramp. D_3-acetonitrile, a hyperpure product from FLUKA, was vaporized in vacuum after multiple purification by freeze-pump-thaw cycles. The acidity measurements were carried out according to the following procedure: after previous evacuation at 350 °C over night, d_3-acetonitrile was adsorbed at room temperature and equilibrium pressure $p = 1$ mm for 15 min. The I.R. spectra in the regions where the vibrations of the OH groups and the CN vibrations are found were recorded after evacuation, after adsorption of d_3-acetonitrile and after its desorption.

3. Results

CATALYTIC TESTS

A first catalytic test was carried out with a sample of Ti-silicalite in the conditions in which the best performances were obtained in previous work [13] with the commercial amorphous silica AKZO F-7 (0.5 g of catalyst, $T = 220$ °C, $W/F = 175$ g h/mol., standard reactant concentrations). The catalytic behaviour was followed for 6 h. The very poor conversion (25%) and oxime yield (1.0% mol.) obtained suggested that the amount of the catalyst should be increased and the contact time prolonged. A new catalytic test was carried out with 1.30 g of titanium silicalite instead of 0.50 g. The catalytic behaviour was followed until deactivation of the catalyst. The data obtained are reported in fig. 1 and table 2. For comparison, the best performance obtained with the AKZO F-7 silica after a 13 h catalytic test in the standard conditions is also reported in table 2.

In order to understand the role of the titanium in the Ti-silicalite, a catalytic test was carried out with pure silicalite in the same conditions as in fig. 1. The corresponding catalytic data are reported in fig. 2 and table 2. The same phenomenology is observed for both the sample containing Ti and the sample without Ti. The rate of tar deposition is about the same and the cyclohexanone conversion is only a little lower, while the oxime yield is sensibly lower.

Another two catalytic tests were carried out with silicalite and Ti-silicalite samples in which the cyclohexanone concentration was halved and the temperature increased to 230 °C. These new conditions allowed the catalytic perfor-

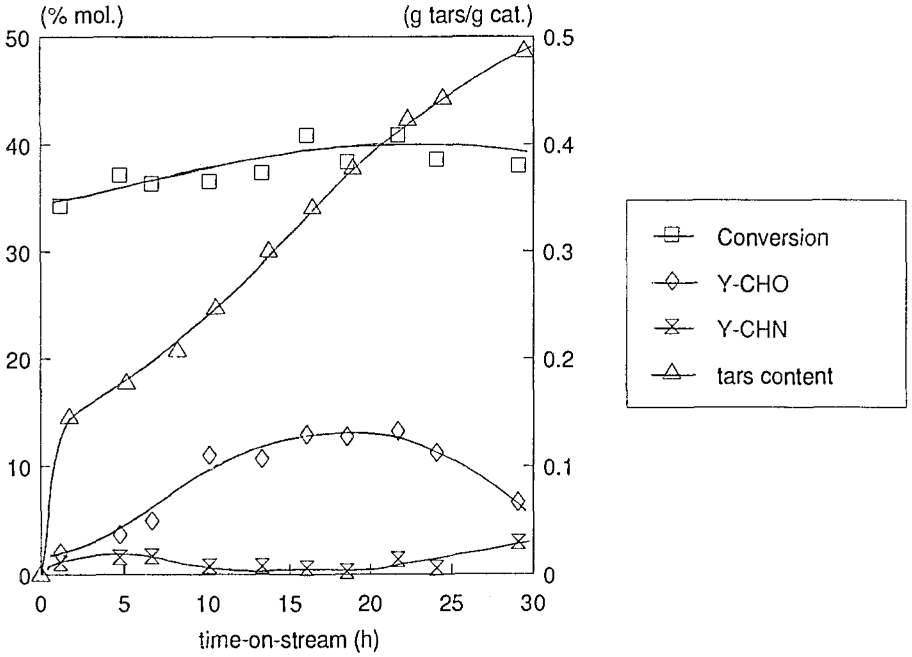

Fig. 1. Behaviour of the Ti-silicalite catalyst with increasing time-on-stream. Reaction conditions: $T = 220\,^\circ C$, catalyst weight = 1.3 g, contact time = 4.67 s ($W/F = 456$ g h/mol). Reactant mixture composition: CH = 2.8%, $NH_3 = 35\%$, $O_2 = 10\%$, He = 52.2%.

mance to be measured at higher conversion. The results of these tests are reported in table 2. The increase in the conversion results in an increase in the oxime selectivity for both catalysts, and, in particular, in the case of Ti-silicalite

Table 2
Performances of the catalysts tested in the present study and in previous works

Catalyst	T (°C)	W (g)	CH (%mol.)	W/F (g/h.mol)	Conversion (%mol.)	Y-CHO (%mol.)	Y-tars (%mol.)
AKZO F-7 *	220	0.5	2.8	175	72.1	32.2	18.9
Ti-Grace Nr.3 #	220	0.5	2.8	175	75.8	25.4	26.9
Grace Nr.2#	220	0.5	2.8	175	55.4	13.2	25.9
Ti-silicalite	220	1.3	2.8	456	40.9	13.3	5.3
Silicalite	220	1.3	2.8	456	35.7	2.4	6.6
Cr-silicatite	220	1.3	2.8	456	32.2	2.0	4.6
V-silicalite	220	1.3	2.8	456	33.1	0.2	3.0
Ti-silicalite	230	1.3	1.4	912	55.5	24.0	9.4
Silicalite	230	1.3	1.4	912	46.8	5.2	6.8

* Complete catalytic data in ref. [13], # complete catalytic data in ref. [14], W = weight of fresh catalyst, CH = concentration of cyclohexanone gas phase, F = molar flow rate of cyclohexanone in the test.

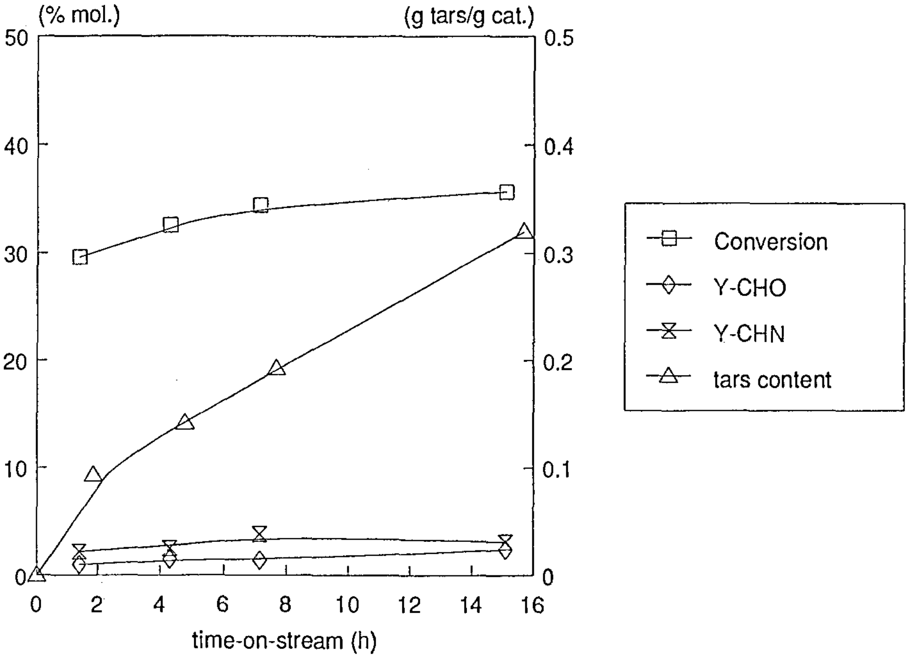

Fig. 2. Behaviour of the silicalite catalyst with increasing time-on-stream. Reaction conditions: $T = 220\,^{\circ}\mathrm{C}$, catalyst weight = 1.3 g, contact time = 4.67 s ($W/F = 456$ g h/mol). Reactant mixture composition: CH = 2.8%, $NH_3 = 35\%$, $O_2 = 10\%$, He = 52.2%.

about the same selectivity is obtained as in the case of AKZO F-7 amorphous silica.

Samples of vanadium and chromium silicalites were also tested. The results are summarized in table 2. The V-silicalite produced only traces of oxime while Cr-silicalite exhibited very poor yields. With the exception of the very low production of tars, the catalytic behaviours of both the samples are very similar to that of the test without the catalyst [12,13].

I.R. CHARACTERIZATION

The I.R. results for the AKZO F-7 sample are reported in fig. 3. As usual for silicas, a sharp band was observed near 3745 cm^{-1} due to free surface silanol groups. Other broad absorption bands are also evident at the lower frequency side of this band, assigned in the literature to H-bonded and/or "internal" hydroxy groups. The adsorption of d_3-acetonitrile on the AKZO sample is followed by the interaction of proton-donor centers (free silanol Brønsted sites), represented by the sharp band at 3740 or 3750 cm^{-1}, with the d_3-acetonitrile, which in turn influences the CN bond with the appearance of a band at 2274 cm^{-1}. In the range of the OH group vibrations, a H^+-bridge is formed, causing a shift of the band at 3740 cm^{-1} by $d\upsilon = 310$ cm^{-1}. The possibly different acid

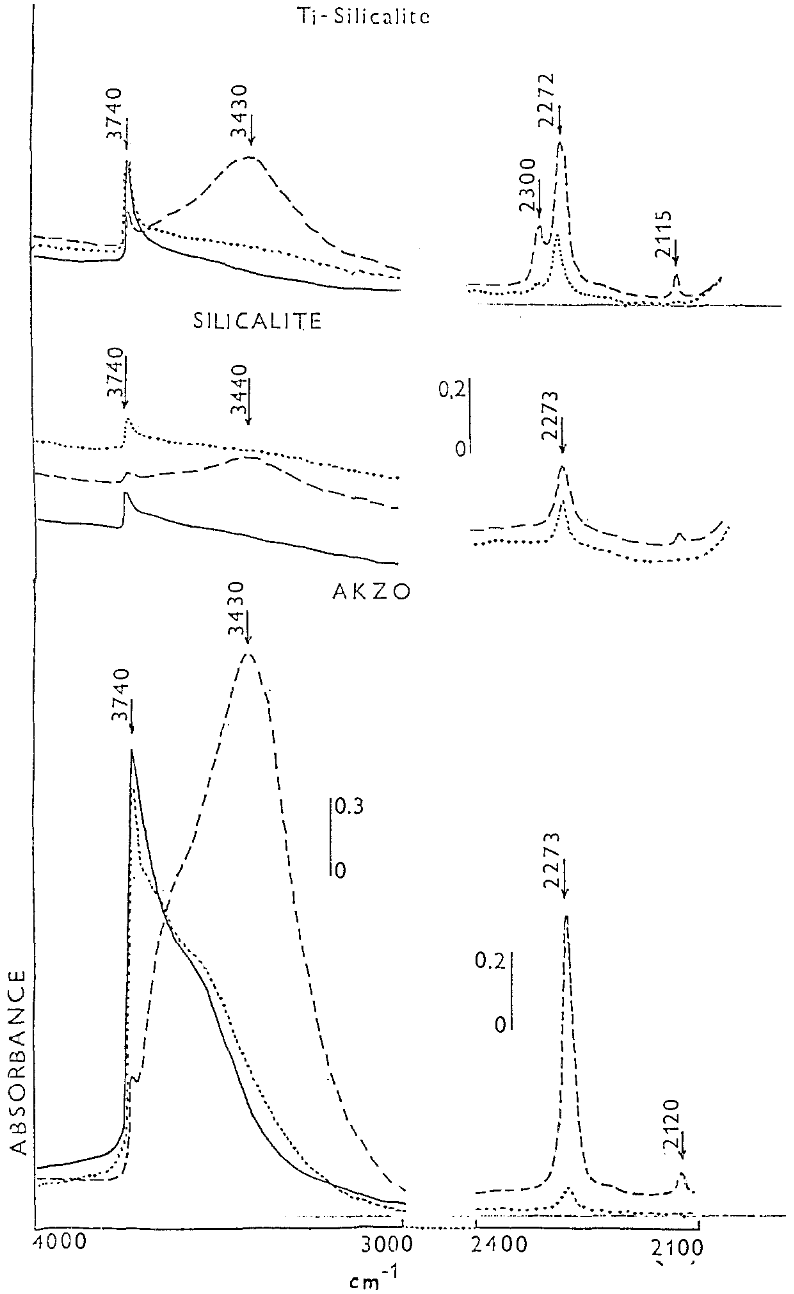

Fig. 3. F.T.-I.R. spectra of AKZO F-7, Ti-silicalite and pure silicalite after evacuation at 623 K (a, ———), after adsorption of CD$_3$CN (b, - - - - - -) and after desorption of CD$_3$CN at room temperature (c, · · · · · ·).

properties of the perturbed and/or hydrogen bonded hydroxy groups could not be discerned by d$_3$-acetonitrile adsorption since in the υ/CN vibration range there is only a single symmetrical band at 2273 cm^{-1}. The concentration of proton-donor centres is much higher than usually found in silica, especially for the component due to the perturbed and/or hydrogen bonded hydroxy groups, their strength being normal, as follows from the position of the band at 2273 cm^{-1} and from its thermal stability. These data indicate the presence of Brønsted acidity on the catalyst stronger than that usually found on pure silica surfaces and probably related to the presence of small amounts of Al^{+3} (0.07% wt). A similar characterization was carried out for the other catalysts used tested. The I.R. spectra of Ti-silicalite and pure silicalite are reported in fig. 3. As compared with the AKZO sample, the Ti-silicalite has a much lower concentration of free OH groups (3740 cm^{-1} band) and this band does not present the broad shoulder at lower wave-numbers. On the other hand, the positions of the bands for the OH groups and those generated by their interaction with d_3-acetonitrile are the same as those of the AKZO sample. Therefore, it may be concluded that the Ti-silicalite contains only free silanol proton-donor centres, whose strength, but not concentration, is comparable with that of the AKZO catalyst. In addition, an additional band at 2300 cm^{-1} appears after d_3-acetonitrile adsorption which could be ascribed to electron-acceptor centres. Taking into account the absence of aluminum in the silicalite, these Lewis acidity sites could be ascribed to titanium in the form of Ti^{4+}, possibly inserted into the zeolite network. However, the thermal stability of this surface complex is surprisingly low. Finally, the comparison of the spectra of Ti-silicalite and pure silicalite indicates that the former is surely more acidic than the latter as demonstrated by the very weak band at 3740 cm^{-1} and the lower wave-number value (2265 cm^{-1}) for the band generated by the interaction of the d_3-acetonitrile with the proton-donor centres of the catalyst. The vanadium and chromium silicalites exhibited about the same characteristics of Brønsted acidity as the pure silicalite.

4. Discussion

The comparison between the catalytic behaviours of the Ti-silicalite and the pure silicalite showed that the presence of Ti in the sample is fundamental to obtain a high oxime selectivity. In particular, the yields of tars are comparable, evidence that the side reaction of tar production is not influenced by the presence of Ti. In a previous work [15], an analogous comparison has been made between a commercial amorphous silica by Grace without Ti (Grace Nr.2) and another commercial silica sample, also produced by Grace, with very similar characteristics of surface area, pore volume, purity grade and surface acidity and 0.28% wt of Ti localized on the catalyst surface. The catalytic performances of the amorphous silica samples are summarized in table 2. Also in that case, the same positive effects on conversion and oxime yield without any change in the rate of deposition of tars were observed. The comparison between the performances of the amorphous silicas by Grace and the silicalites shows that the increase in oxime selectivity seems to be considerably higher in the case of silicalite samples and this suggests that the effects observed are present when Ti ions are dispersed on the catalyst surface, but are much stronger if the metal ions are inserted in the crystalline lattice of the silicalite just as in the case of liquid phase ammoximation with hydrogen peroxide. In that case, in fact, amorphous silica samples proved to be mediocre catalysts because of the lower selectivity exhibited and, above all, because of the much lower activity and greater hydrogen peroxide decomposition [16].

The I.R. spectroscopy measurements showed that Ti-silicalite has less Brønsted acidity than AKZO silica. This evidence accounts for the lower activity, since the first step in the process is the production of Si-bonded imine on the catalyst silanol groups [14]. Previous works [13,14], in fact, showed that the imine is formed on the Brønsted sites of the catalyst. The results presented in the present work confirmed this evidence. The comparison between the acidity and the activity of AKZO silica and silicalites showed that the concentration and strength of Brønsted sites on the catalyst surface determine the ability of the catalyst to supply the adsorbed imine species for oxidation and aldol condensation reactions. Furthermore, the comparison between the catalytic performances of the catalyst with and without Ti showed that the real key step in the process is the ability to activate molecular oxygen. In fact, a fast transformation of the imine into the oxime prevents its transformation into the aldol condensation products, and this accounts for the observation that the increase in yield of oxime is generally higher than the increase in conversion. On the other hand, when Ti is added to the catalytic system, the enhancement of the oxime selectivity produces only an increase in conversion and a reduction in the importance of the aldol condensation reactions and does not influence at all the rate of tar formation. This evidence suggests that the Ti is not involved in the process of formation of the tars and that, therefore, it is not possible to suppress this side pathway but only to reduce its importance by making the selective one faster. In this regard, it should be kept in mind that tar formation reactions occur only in the presence of oxygen and are affected by the catalyst deactivation in the same way as oxime formation, i.e. by the destruction of the catalyst site responsible for oxygen activation. The tests with vanadium and chromium silicalites showed that the type of metal added to the silicalite is fundamental to obtain an increase in oxime selectivity and that elements with typical redox mechanisms in catalytic oxidation are not suitable for cyclohexanone ammoximation, confirming the peculiarity of this reaction as compared to the other well-known oxidation reaction (i.e. o-xylene or n-butane oxidation).

In conclusion, the catalytic data presented in the present paper showed that the Ti-silicalite can be a selective catalyst for ammoximation of cyclohexanone not only in the liquid phase reaction with hydrogen peroxide but also in gas phase reaction with molecular oxygen. However, a big limitation is constituted by the poor activity of the silicalite which does not allow to reach high oxime yields. Consequently, using Ti-silicalite as the catalyst, about the same selectivity can be achieved as in the case of AKZO silica, but it is not possible, at present, to obtain a paragonable oxime yield.

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