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Ammoximation reaction in the gas and liquid phases with silica based catalysts: role of titanium

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Abstract

The catalytic behaviour in the liquid phase and in the gas phase ammoximation of cyclohexanone on amorphous silicas containing different amounts of titanium has been investigated. The silicas were prepared by impregnation and the sol-gel method. The behaviour of the silicas with and without titanium was different in the liquid and gas phases. The presence of titanium sites was found to be essential for the development of selectivity to oxime in the liquid phase. In the gas phase the paramount parameters are the textural and structural features of the silica and the introduction of titanium can only enhance the activity in both impregnated and sol-gel catalysts. It is proposed that the role of titanium in the gas phase is to favour the oxidation of imine, an intermediate in the vapour phase reaction, due to its ability to activate molecular oxygen.

Keywords: Ammoximation; Cyclohexanone oxime; Amorphous silica; Titanium

1. Introduction

In the ammoximation reaction, cyclohexanone is converted into the oxime by reaction with ammonia and different oxidants. Two different catalytic approaches have been studied: in the liquid phase and in the gas phase. In the liquid phase, ammoximation is carried out at 70–90°C with H_2O_2 and Ti-silicalite as the catalyst. A yield of over 98% (based on cyclohexanone) and 90% (based on H_2O_2) to cyclohexanone oxime is obtained [1,2]. A demonstrative unit (by EniChem) of 10,000 tons/year is presently in operation. In the vapour phase, the reaction is carried out at 200°C in air. High performances are obtained with an amorphous high surface area silica as the catalyst, such as Porasil A or AKZO F-7 [3–6]. A yield of over 30% is obtained. However, other commercial silica samples give extremely variable results. The low yields obtained and the fast deactivation, due to the formation of tars, prevent this process from being developed.

In previous works through experiments with various ketones, the reaction pathway for liquid phase ammoximation on Ti-silicalite has been determined [7]. The reaction proceeds via the hydroxylamine intermediate.

$$NH_3 + H_2O_2 \rightarrow NH_2OH + H_2O$$

$$\text{cyclohexanone} + NH_2OH \rightarrow \text{oxime} + H_2O.$$

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Through the action of Ti centres, NH_3 and H_2O_2 give initially the hydroxylamine, which then reacts with cyclohexanone to give cyclohexanone oxime.

In order to obtain a better understanding of the reaction network and the reaction mechanism of gas phase ammoximation, much work has been done by Trifirò et al. using a AKZO F-7 silica [8–11]. The reaction pattern hypothesized consists of the following main steps:

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

$$\text{imine} + O^* \rightarrow \text{cyclohexanoneoxime}.$$

It has been suggested that the first step occurs through the aid of surface silanol groups [9], while the second one, in which some activated oxygen species are involved, leads from imine to the by-products and to the oxime.

Nevertheless, the reaction pathways of the two processes might present some analogies. In particular, titanium could show a similar role and could also be fundamental in the activation of molecular oxygen. For these reasons it should be interesting to analyze the catalytic behaviour of silica samples with and without titanium in both the reactions.

In the present work we have prepared by impregnation and via a sol-gel method several amorphous silicas containing different amounts of titanium. The advantages of the sol-gel method are the compositional homogeneity and the high purity of the materials obtained. The role of titanium on amorphous silicas was studied and the reaction mechanisms in the liquid and gas phases were compared.

2. Experimental

2.1. Catalyst evaluation

In the liquid phase, the ammoximation tests were carried out by dispersing the catalyst in an ammonia-cyclohexanone aqueous–organic liquid phase and by feeding the hydrogen peroxide to the well-mixed slurry, using a metering pump. At the end, after cooling, the liquid was analysed by gas-chromatography. Nitrites and nitrates were determined by HPLC analysis. The conversion of cyclohexanone and of hydrogen peroxide and the yield of the products based on hydrogen peroxide were calculated as follows: cyclohexanone conversion = 100 − (moles of unreacted ketone/moles fed) × 100; H_2O_2 conversion = 100 − (moles of unreacted H_2O_2/moles fed) × 100; i-product yield = (moles of i-product/moles of H_2O_2 fed) × 100. Standard conditions for the catalytic tests were the following: H_2O_2/ketone = 1.0 mol/mol, NH_3/ketone = 2.1 mol/mol, temperature = 80°C. The apparatus has been described in detail in previous papers [2,12].

In the gas phase experiments, the apparatus for the catalytic tests consisted of a tubular fixed-bed glass micro-reactor with accumulation of the reaction products in a solvent and gas-chromatographic analysis using an internal standard method. A complete description of the reactor and of the analytical procedure has been reported elsewhere [8].

The conversion of cyclohexanone and the yield and selectivity of the products were calculated as follows: conversion = 100 − (moles of unreacted ketone/moles fed) × 100; oxime yield = (moles of oxime/moles of cyclohexanone fed) × 100; oxime selectivity = (oxime yield/conversion) × 100. 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: tars yield = ((tars weight/113)/total time-on-stream)/molar flow rate of cyclohexanone × 100, where 113 = molecular weight of the oxime.

Standard conditions for the catalytic tests were the following: reactant concentration in the reaction gas, cyclohexanone = 2.8% mol, NH_3 = 35% mol, O_2 = 10% mol, N_2 = balance; temperature = 220°C; molar flow rate (F) = 4.75×10^{-5} mol/min; total flow rate = 40 ml/min; W/F = 175 g h/mol, where W = catalyst weight.

2.2. Catalyst preparation

The sol-gel samples were prepared in acidic or in basic conditions, starting from tetraethyl orthosilicate (TEOS), titanium isopropoxide, water and nitric acid (65%) or ammonia (30%). The gels were all prepared by mixing, in the right molar ratios, the quantity of constituent in solution and stirring and heating until gelation occurred. Successively the gel was dried and calcined at 400°C.

The impregnated samples were prepared by impregnating commercial amorphous silicas with a solution of titanium isopropoxide in isopropyl alcohol and then drying and calcining. The Ti content is expressed in weight percent, based on the theoretical system TiO_2–SiO_2 (1.5 wt% $TiO_2 \Rightarrow$ 1.1 mol% Ti; 2.0 wt% $TiO_2 \Rightarrow$ 1.5 mol% Ti; 4.8 wt% $TiO_2 \Rightarrow$ 3.6 mol% Ti; 9.0 wt% $TiO_2 \Rightarrow$ 6.9 mol% Ti; 9.8 wt% $TiO_2 \Rightarrow$ 7.5 mol% Ti).

2.3. Physicochemical characterization

The surface areas of the sol-gel samples were measured with a Carlo Erba Sorpty 1700 using the B.E.T. method with N_2 adsorption. XRD powder patterns were obtained with Ni-filtered CuK_α radiation ($\lambda = 0.15418$ nm) using a Philips Goniometer equipped with a stepping motor. The IR spectra were recorded at room temperature using a Perkin Elmer 1750 Fourier Transform instrument. Both the KBr disk technique and a self-supporting disk technique were used. In the latter case the samples were activated in vacuum at different temperatures in the conventional IR cell (NaCl windows).

3. Results and discussion

3.1. Catalyst characterization

X-ray analysis of the sol-gel samples shows that all samples are X-ray amorphous and in the samples containing titanium they do not present the formation of anatase crystallites.

FT-IR spectra of titania–silica xerogels are characterized by the typical band assigned to framework titanium. This band is found at ca. 950 cm^{-1} and is an indication of the presence of Si–O–Ti linkages [13]. The band is rather well developed in both titania–silica prepared in acidic and basic conditions.

The OH stretching bands of the samples show an abundance of silanol nests. After evacuation at 450°C the samples prepared in basic conditions show a sharp band near 3745 cm^{-1}, due to the free surface silanol groups, while the samples prepared in acidic conditions also present a very broad shoulder centred between 3600 and 3700 cm^{-1}, assigned in the literature to H-bonded and/or ''internal'' hydroxy groups [14].

3.2. Catalytic activity

The results obtained in the gas phase ammoximation experiments with sol-gel silicas having different amounts of titanium are summarized in Table 1. The values of conversion and yields of the products are reported for the condition of maximum yield to the oxime. In view of the high purity of the materials obtained, the activity cannot be due to the presence of impurities in the samples. Two different behaviours are found depending on the preparation medium of the sample. The silicas prepared in acidic conditions are completely inactive; the formation of oxime and tars is negligible. The only products are volatile organic compounds, formed by homogeneous gas phase reactions, and traces of cyclohexanone imine. The addition of titanium does not modify the catalytic activity and the selectivity to oxime remains negligible.

The samples prepared in basic conditions are active in oxime formation. The pure silica shows a good conversion and the oxime yield and selectivity are interesting. Other reaction products are tars and volatile organic compounds. The introduction of a low content of titanium decreases the conversion but increases the selec-

Table 1
Ammoximation of cyclohexanone in the gas phase on sol-gel silicas

Catalyst	Ti/TEOS (mol/mol)	Surface area (m^2/g)	Cyclohexan. conversion (%)	Oxime sel. (%)	Oxime yield (%)	Tars yield (%)
SiO_2 A	0	500	20.3	0	0	0
SiO_2 B	0	240	54.7	30.7	16.8	19.2
Ti1-SiO_2 A	0.01	356	21.0	0	0	0
Ti3-SiO_2 A	0.03	320	20.5	0	0	0
Ti8-SiO_2 A	0.087	–	21.5	0	0	0
Ti1-SiO_2 B	0.01	220	44.0	46.9	20.6	11.2
Ti8-SiO_2 B	0.087	80	29.0	26.0	7.6	6.7
Ti-silicalite	–	–	25.0	4.0	1.0	5.0
Ti-silicalite [a]	–	–	40.9	32.8	13.3	5.3

SiO_2 A = silica prepared in an acidic medium; SiO_2 B = silica prepared in a basic medium.
[a] $W/F = 456$ g h/mol.

tivity and the yield to oxime. The introduction of a relatively high amount of titanium, Ti8–SiO_2 B, decreases the catalytic activity considerably. It must be pointed out that this effect may be related to physical factors, since the BET surface area is very low compared to that of the pure silica.

On the contrary, as reported in Table 2a and 2b, the sol-gel samples tested in the liquid phase show a completely different behaviour. For purposes of comparison the performances of Ti-silicalite are also reported. When amorphous silica alone is used, the ammoximation occurs only to a negligible extent, the same as without any catalyst. The introduction of titanium gives rise to the selectivity to oxime. In the samples prepared in the acidic medium an increase in titanium content up to 3 mol%, Ti_3–SiO_2 A, leads to an increase in selectivity (up to 50%) and in the yield to oxime. A further increase in the titanium content to 8 mol%, Ti8–SiO_2 A, leads to a decrease in selectivity to the oxime. The sample containing 8 mol% titanium prepared in basic conditions, Ti8–SiO_2 B, shows a

Table 2
Ammoximation of cyclohexanone in the liquid phase with sol-gel silica catalysts

(a) Catalyst	Cyclohexanone conversion (%)	Oxime selectivity (%)	Oxime yield (%)
Ti-silicalite	100	100.2	100.2
amorphous silica [a]	55.7	1.3	0.7
Ti1-SiO_2 A	46.4	4.8	2.2
Ti3-SiO_2 A	34.4	62.9	21.6
Ti8-SiO_2 A	39.8	31.8	12.7
Ti8-SiO_2 B	40.0	53.1	21.3

(b) Catalyst	H_2O_2			H_2O_2 yield to			
	conv. (%)	oxime (%)	NO_2 (%)	NO_3 (%)	N_2 (%)	O_2 (%)	N_2O (%)
Ti-silicalite	99.3	93.0	2.6	1.1	0	0	0
Ti1-SiO_2 A	76.9	2.0	0.6	0.9	3.7	14.2	0.3
Ti3-SiO_2 A	98.5	19.7	1.8	1.5	0.7	57.5	0.2
Ti8-SiO_2 A	96.6	12.8	–	–	1.5	49.7	0.4
Ti8-SiO_2 B	95.7	19.4	–	–	1.6	43.7	0.2

Reaction time 4 h; temperature 80°C.
[a] Silica prepared in acid conditions and silica prepared in basic conditions.

Table 3
Ammoximation of cyclohexanone in the gas phase with titanium supported on silica

Catalyst	Cyclohexanone conversion (%)	Oxime selectivity (%)	Oxime yield (%)	Tars yield (%)
Akzo F-7	72.1	41.4	29.8	21.6
Akzo + 2% Ti	77.7	39.3	30.5	26.0
Akzo + 4.8% Ti	83.5	42.0	35.0	33.2
Grace	55.4	23.5	13.2	25.9
Grace + 9% Ti	58.1	23.8	13.8	33.0

Reaction conditions: temperature 220°C.

catalytic behaviour like that of the 3 mol% titanium ''acidic'' silica. However, all samples prepared in both acidic and basic conditions show a high formation of byproducts, such as oxygen, nitrites and nitrates. These byproducts are formed by non-catalyzed (homogeneous) reactions and the high production means that the activity of the catalysts is low.

In order to analyze the effect of titanium in a completely different state of aggregation, titanium supported on silica was also studied. The catalytic activity of impregnated samples in the gas phase ammoximation is reported in Table 3. Two amorphous commercial silicas, Akzo F-7 and Grace, with high surface areas (470 m^2/g and 320 m^2/g, respectively) were used as supports. The Akzo silica presents good catalytic activity with high selectivity and yield to oxime and very high conversion. The Grace sample shows a low activity and low selectivity to oxime. On Akzo F-7 silica the addition of titanium in two different amounts (2 and 4.8 wt% as TiO_2) does not substantially modify the maximum selectivity to oxime, while it shows an effect on the cyclohexanone conversion and on the tar yield. In fact the increase in titanium increases both the conversion, from 72% to 83%, and the formation of tars. The increase in tar formation causes a fast deactivation of the catalyst, see Fig. 1.

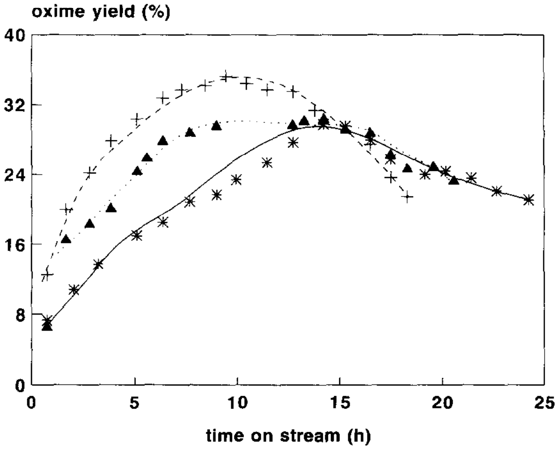

Fig. 1. Oxime yield of titanium impregnated Akzo F-7 in standard conditions. Akzo F-7 (*); Akzo+2% (▲); Akzo+4.8% Ti (+).

The evolution of the oxime yield as a function of time on stream for the three catalysts is reported in Fig. 1. The behaviour of the yield shows the typical evolution with time on stream for ammoximation in the gas phase [9]. With increasing titanium content, the maximum in oxime yield increases because of the increase in conversion. The life of the catalyst depends on the amount of titanium. The sample containing the highest amount shows rather fast deactivation and, as a consequence, the shortest life. As shown in a previous work, the deposition of tars is related to the deactivation, because the tars cover the sites responsible for O_2 activation [15].

On Grace silica the addition of 9% titanium (as TiO_2) shows the same effect on catalytic activity. In fact it increases slightly the cyclohexanone conversion and in a more relevant way the yield of the tars, while the oxime yield remains low.

For comparison, the catalytic activity of some impregnated silicas in liquid phase ammoximation are reported in Table 4 [12]. The prepara-

Table 4
Ammoximation of cyclohexanone in the liquid phase with titanium supported on silica

Catalyst	Cyclohexanone conversion (%)	Oxime selectivity (%)	Oxime yield (%)
amorp. silica	55.7	1.3	0.7
silica + 1.5% Ti	49.3	9.3	4.4
silica + 9.8% Ti	66.8	85.9	54.0

Reaction conditions: reaction time 1.5 h; temperature 80°C.

tion method was the same. The addition of titanium gives rise to the selectivity to oxime and with increasing titanium content the oxime selectivity increases up to a good catalytic activity. The effect is evident up to a 10 wt% titanium content.

3.3. Ammoximation mechanism

In the liquid phase ammoximation, the paramount role of titanium in silicalite has been clearly shown in previous works [2,7]. The results obtained on amorphous silica confirm the importance of titanium. Pure amorphous silicas prepared with different methods do not present selectivity to oxime formation. Only the introduction of titanium sites supplies catalytic properties in ammoximation, due to the ability of titanium to activate hydrogen peroxide. The differences in catalytic behaviour in the sol-gel and impregnated samples may be explained by a different state of aggregation and coordination.

In impregnated samples the titanium is deposited on the surface probably in the form of clusters of titanium dioxide and as the amount of titanium increases the surface coverage of silica increases. The method of supporting titanium most probably cannot fix isolated titanium firmly to the surface of the silica itself, but instead produces the formation of surface clusters of titanium dioxide in octahedral coordination even at low titanium concentration [2].

In the sol-gel sample, the titanium is rather dispersed in the amorphous structure of the silica with formation of Ti–O–Si bonds. However since the structure of the silica is amorphous and not crystalline, most of the titanium may not be accessible and the degree of dispersion can change during the sol-gel process in the different samples. These phenomena could explain the differences in catalytic activity among the sol-gel samples.

On the contrary in the gas phase ammoximation, the results demonstrate that the Ti-site is not fundamental for the formation of oxime. The silica itself can already be active in the reaction and its activity depends on the preparation conditions. The introduction of titanium does not modify the fundamental reactivity of the silicas neither in the sol-gel nor in the impregnated samples. Therefore, a paramount parameter of the ammoximation activity seems to be related to the textural and structural properties of the silica.

In a previous work [16] several amorphous silicas were prepared by the sol-gel method and two clearly different structural unit types were obtained depending on the preparation media. Under acidic conditions long siloxane particles are produced. The structure is characterized by a high bulk density and high surface area. The mean pore diameter is about 1.5 nm and no mesoporosity is present. Handy et al. [17] for titania–silica xerogels also have shown that acid catalysis leads to the build up of very tenuous wet-gel structures, which are highly susceptible to pore collapse during the drying process, resulting in considerable microporosity.

The base-catalyzed samples present features of a colloidal gel and the structure is characterized by low bulk density and relatively low surface areas. These silicas are mesoporous with a mean pore diameter between 10 and 20 nm. Both silicas, prepared in basic conditions and in acidic conditions, show an abundance of silanol nests. However the silicas prepared in acidic conditions present a higher concentration of H-bonded and/or "internal" hydroxy groups, when evacuated at relatively high temperature. These differences, in particular in the silanol distribution, may especially play a role in the activation of the cyclohexanone with the formation of imine, the first step of the ammoximation reaction [9].

In the sol-gel catalysts, the introduction of a low titanium content increases the selectivity to oxidation product, the oxime, while the introduction of a relatively high titanium content modifies the structure of the sample and as a consequence decreases the activity. The catalytic tests with impregnated samples also confirm that the presence of the Ti-site can only enhance the activity. However this improvement only slightly modifies the selectivity to oxime, while it strongly modifies the conversion and the formation of tars. These phenomena may be explained taking into account that in the gas phase the second step of the proposed reaction pathway is the oxidation of imine, the intermediate of reaction. We hypothesize that the role of titanium is to favour the oxidation of imine to oxime, due to its ability to activate molecular oxygen. Whereas in regard to the nature of the oxidant species on silica, our preferred hypothesis is that the oxime formation has to be attributed to the presence of tars and related to the textural features of the silicas themselves [15].

4. Conclusions

In the ammoximation reaction the role of titanium is completely different in the liquid and gas phases. In the liquid phase, the presence of titanium sites is essential to activate the hydrogen peroxide. Pure amorphous silicas prepared with different methods do not present activity in oxime formation; only the presence of titanium gives rise to the catalytic activity. The different activities of sol-gel and impregnated samples may be due to different states of aggregation and coordination of titanium.

In the gas phase, pure silica can be active in the ammoximation reaction and its activity depends on the preparation conditions. In the case of sol-gel samples, a paramount parameter of the ammoximation activity seems to be related to the textural and structural properties of the silica. The introduction of titanium can only enhance the activity in both impregnated and sol-gel catalysts. We hypothesize that the role of titanium is to favour the oxidation of imine, intermediate of the vapour phase reaction, due to its ability to activate molecular oxygen. Whereas the oxime formation on silica may be attributed to the presence of tars and related to the textural features of the silica itself.

The investigation of the activity of sol-gel silicas with low titanium contents in gas phase ammoximation and of the role of titanium in the formation of active oxygen species will be the topic of a future study.

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