

# A study of the organic by-products in the cyclohexanone ammoximation

A. Cesana<sup>\*</sup>, M.A. Mantegazza, M. Pastori

*EniChem Base Research Center, Via G. Fauser 4, 28100 Novara, Italy*

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## Abstract

The heterogeneous catalyzed ammoximation of cyclohexanone on titanium silicalite catalyst has been studied. Cyclohexanone oxime is formed by reaction of cyclohexanone with ammonia and hydrogen peroxide. The organic by-products formed in the reaction have been studied and the following products were identified: nitrocyclohexane, cyclohexenylcyclohexanone, cyclohexenone oxime and cyclohexanone azine. The effect of some reaction parameters on by-products formation have been investigated. Experiments have been performed to verify if these by-products are due to side or consecutive reactions and derive from non-catalyzed or catalyzed reactions.

*Keywords:* Heterogeneous catalytic oxidation; Ammoximation; Titanium silicalite; Hydrogen peroxide; Cyclohexanone oxime

## 1. Introduction

In the new ENICHEM process [1] cyclohexanone oxime is directly synthesized by ammoximation of cyclohexanone with ammonia and hydrogen peroxide on titanium silicalite, TiS, catalyst [2].

The conversion of cyclohexanone and hydrogen peroxide is over 99% and the cyclohexanone selectivity to cyclohexanone oxime is close to 100% [3]. It has been found that the ammoximation reaction proceeds via hydroxylamine intermediate [4] and the main ammoximation by-products, which are inorganic com-

pounds, such as nitrogen, nitrous oxide and ammonium nitrite and nitrate, are involved in hydroxylamine formation step.

In cyclohexanone ammoximation several organic by-products were found. The concentration of these by-products is negligible, but even in very small quantities they could affect the cyclohexanone oxime quality, so we investigated their formation in order to cut them down.

We have performed some experiments with and without TiS and silicalite, a zeolite non containing titanium, to verify:

(a) if these by-products derive from non-catalyzed or catalyzed reactions;

(b) if the catalytic activity is due to framework titanium atoms or to the zeolitic nature of the catalyst.

<sup>\*</sup> Corresponding author.

## 2. Experimental

Samples of silicalite and titanium silicalite were synthesized according to Refs. [2,5]. Ammoxidation runs were performed in a slurry continuous stirring tank reactor (0.35 l). Cyclohexanone was fed to reactor as a solution in *ter*-butylalcohol, hydrogen peroxide as an aqueous solution and gaseous ammonia was bubbled into the slurry.

The reaction mixture was collected getting a few samples for each run. They were diluted with water and extracted several times with diethyl ether. The organic phases were separated, dried and the solvent was evaporated. The products obtained were analyzed by a gas chromatograph (Carlo Erba model 2350) equipped with a FID detector and a 3 m × 6 mm o.d. glass column packed with 10% Carbowax 20 M on Chromosorb W 60 ÷ 80 mesh (Carlo Erba). Nitrogen was used as a carrier gas.

Cyclohexanone oxime and nitrocyclohexane oxidation tests were carried out in a batch jacketed reactor as described in Ref. [3].

The reaction between cyclohexanone oxime and hydrogen peroxide was carried out at 90°C. Hydrogen peroxide was fed to a mixture of cyclohexanone oxime (21 wt%) in aqueous am-

monia (15 wt%) and *ter*-butylalcohol solution (1:1 v/v). The catalyst concentration was 3 wt%.

The reaction between nitrocyclohexane and hydrogen peroxide was carried out by adding hydrogen peroxide to a solution of nitrocyclohexane (0.3 wt%) in aqueous ammonia (15 wt%) and *ter*-butylalcohol solution (1:1 v/v). The reaction mixtures were analyzed by gas chromatography with the procedure given above and the products characterized by gas chromatography-mass spectroscopy.

## 3. Results and discussion

### 3.1. Nitrocyclohexane formation

The main ammoxidation organic by-product is nitrocyclohexane. As shown in Fig. 1 in CSTR runs we have found that nitrocyclohexane concentration raises as the residence time increases. The direct dependence of nitrocyclohexane on residence time suggests that it could be a product of a consecutive reaction.

Fig. 2 reports the nitrocyclohexane concentration against cyclohexanone/hydrogen peroxide

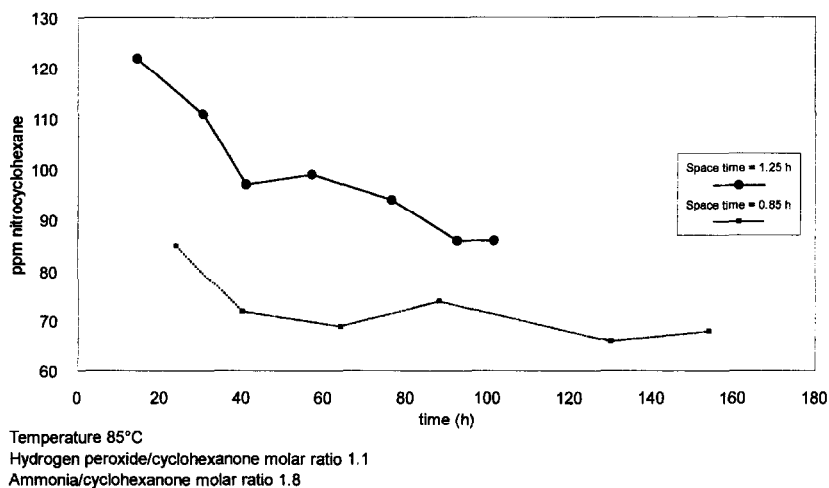


Fig. 1. Effect of space time on nitrocyclohexane formation.

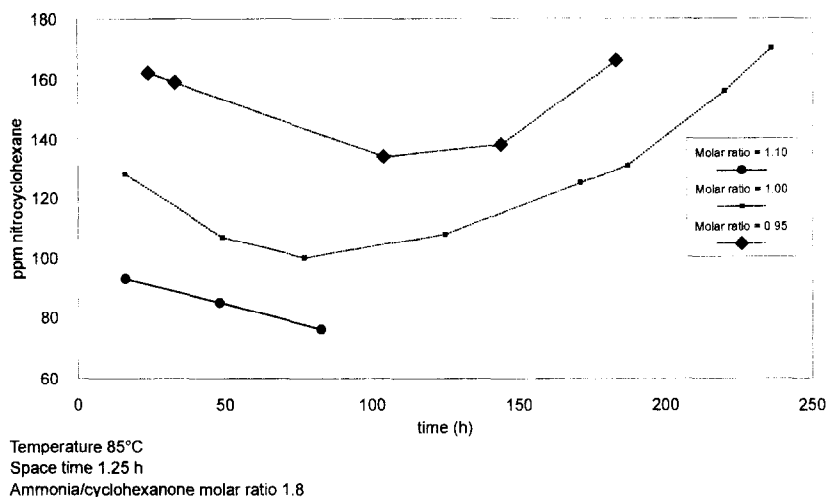


Fig. 2. Effect of cyclohexanone/hydrogen peroxide molar ratio on nitrocyclohexane formation.

molar ratio. The concentration of nitrocyclohexane decreases with the cyclohexanone/hydrogen peroxide molar ratio increase. This behaviour is not in agreement with the hypothesis that nitrocyclohexane is an oxidation product of the oxime.

In order to verify whether cyclohexanone oxime could be oxidized to nitrocyclohexane by hydrogen peroxide we performed a test in a

Table 1  
Nitrocyclohexane concentration (ppm) in cyclohexanone oxime reaction with hydrogen peroxide

Catalyst	Molar ratio hydrogen peroxide/cyclohexanone oxime	
	0.5	1.0
TiS	59	96
Silicalite	41	44
—	58	8

Table 2  
Nitrocyclohexane reactivity with hydrogen peroxide

Catalyst	Molar ratio $\text{H}_2\text{O}_2/\text{C}_6\text{H}_{10}\text{NO}_2$	Nitrocyclohexane conversion (%)	Cyclohexanone yield (%)	Cyclohexanone oxime yield (%)
TiS	10	51.2	—	50.0
Silicalite	6	24.5	5.1	12.0
—	10	99.1	62.2	—

batch reactor. The results are reported in Table 1.

We have found that nitrocyclohexane is formed in the reaction of cyclohexanone oxime with hydrogen peroxide whether in presence of TiS or silicalite or no catalyst.

Then in the ammoxidation conditions nitrocyclohexane is formed by non-catalyzed oxidation of cyclohexanone oxime. At hydrogen peroxide/cyclohexanone oxime molar ratio = 0.5 we have found the same concentration of nitrocyclohexane either we used TiS or silicalite or no catalyst.

Unexpectedly at hydrogen peroxide/cyclohexanone oxime molar ratio = 1 the quantity of nitrocyclohexane formed is considerably smaller without than with TiS and silicalite.

To explain this behaviour we have checked the nitrocyclohexane reactivity with hydrogen

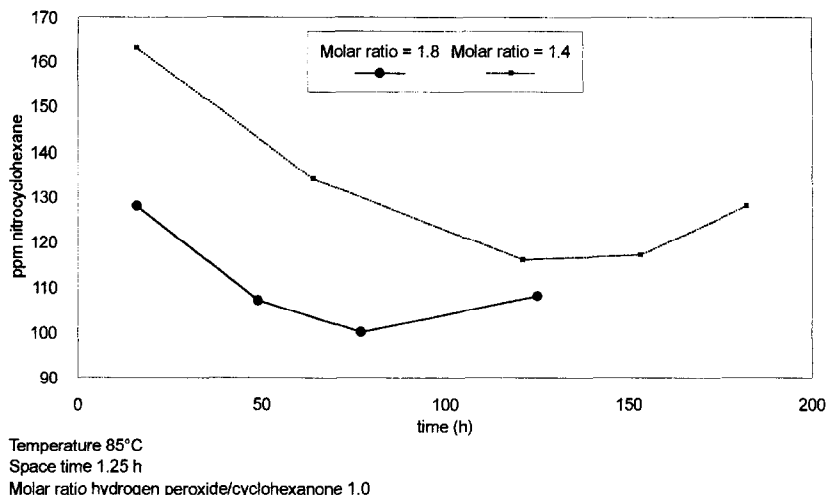


Fig. 3. Effect of ammonia/hydrogen peroxide molar ratio on nitrocyclohexane formation.

peroxide in the presence and absence of TiS and silicalite. The results are reported in Table 2.

In absence of both TiS and silicalite the nitrocyclohexane conversion is almost complete and the main product is cyclohexanone. With silicalite the nitrocyclohexane conversion is low, below 25%. In presence of TiS the conversion is about 50% with selective formation of cyclohexanone oxime. We can suppose that, due to the presence of TiS, the cyclohexanone formed is selectively ammoxidized.

Then the nitrocyclohexane with hydrogen peroxide is decomposed by homogeneous reaction. The presence of silicalite reduces the homogeneous decomposition reaction, probably because of the nitrocyclohexane adsorption into the zeolitic channels. With TiS the nitrocyclohexane decomposition is higher than with silicalite, because there is also a strong adsorption and activation of hydrogen peroxide on framework Ti atoms.

Fig. 3 shows the behaviour of nitrocyclohex-

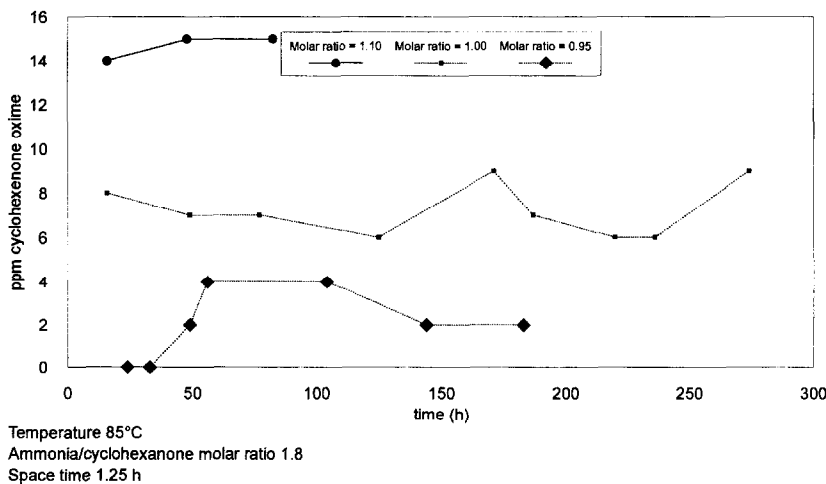


Fig. 4. Effect of cyclohexanone/hydrogen peroxide molar ratio on cyclohexenone oxime formation.

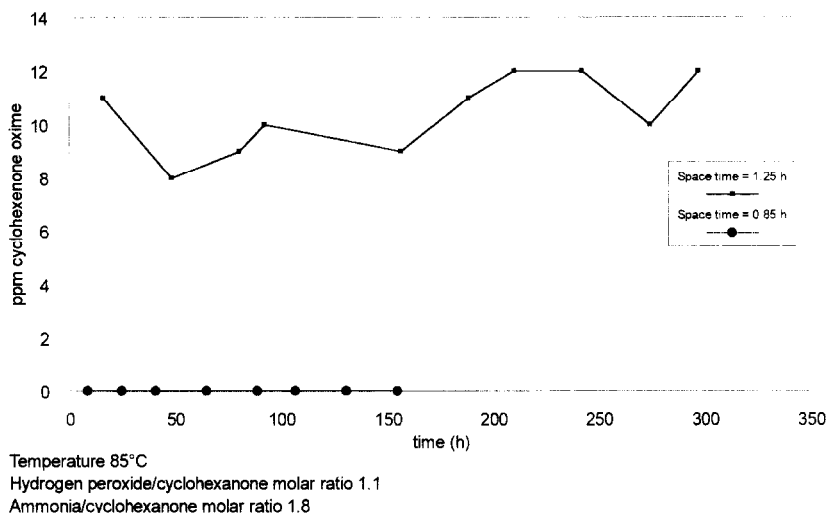


Fig. 5. Effect of residence time on cyclohexenone oxime formation.

ane concentration depending on ammonia/hydrogen peroxide molar ratio. The nitrocyclohexane selectivity decreases as a result of increasing of the ammonia/hydrogen peroxide molar ratio. It could depend on a competition between ammonia and cyclohexanone oxime in oxidation so that a higher concentration of ammonia favours hydroxylamine formation.

### 3.2. Cyclohexenone oxime formation

Figs. 4 and 5 show the influence of cyclohexanone/hydrogen peroxide molar ratio and resi-

dence time on cyclohexenone oxime selectivity. As already seen for nitrocyclohexane, cyclohexenone oxime selectivity becomes higher as the resident time increases. Selectivity also grows as cyclohexanone/hydrogen peroxide molar ratio increases indicating that cyclohexenone oxime is the product of cyclohexanone oxime oxidation by hydrogen peroxide. Cyclohexenone oxime was also found among the products of cyclohexanone oxime oxidation test. Moreover we tried to perform ammoximation of cyclohexenone in order to verify if the small quantity of cyclohexenone, always present

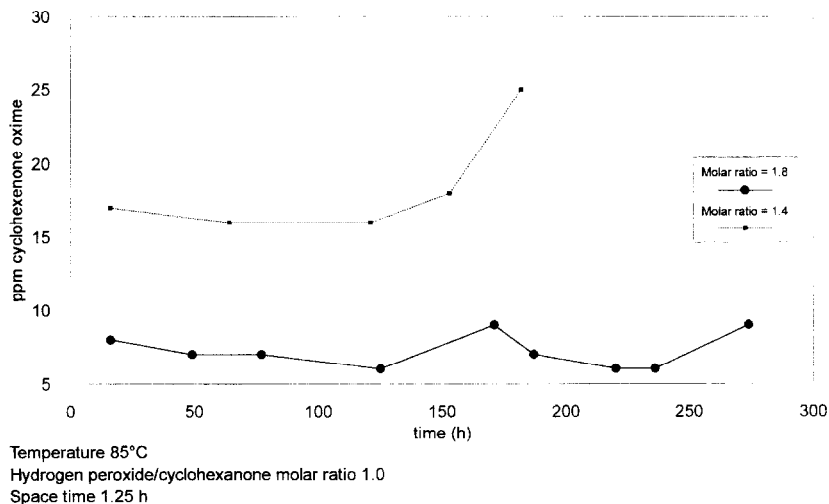


Fig. 6. Effect of ammonia/hydrogen peroxide molar ratio on cyclohexenone oxime formation.

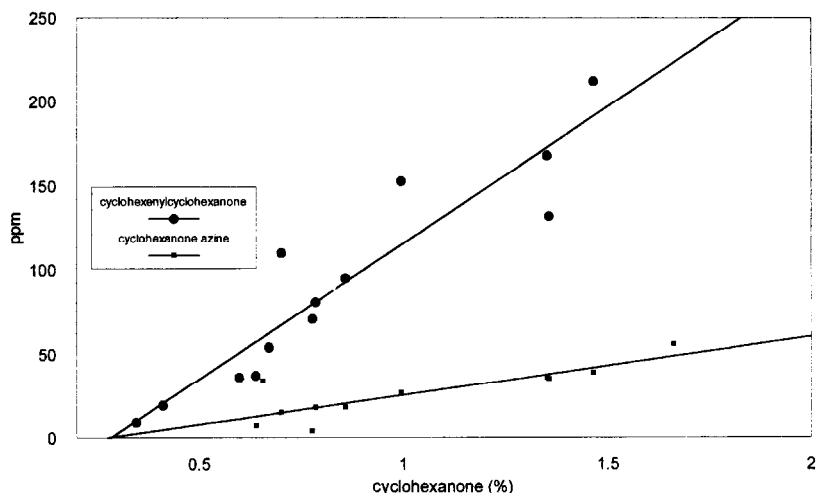


Fig. 7. Effect of cyclohexanone concentration in the output stream on cyclohexenylcyclohexanone and cyclohexanone azine formation.

as an impurity in cyclohexanone, would lead to cyclohexenone oxime but reaction was very difficult and proceeded with low yield giving a mixture of products. All this evidence support the fact that cyclohexenone oxime rises from cyclohexanone oxime oxidative degradation.

Fig. 6 shows that an ammonia/hydrogen peroxide molar ratio increase leads to a decrease in cyclohexenone oxime selectivity.

### 3.3. Cyclohexenylcyclohexanone and cyclohexanone azine formation

In Fig. 7 is reported cyclohexenylcyclohexanone concentration as a function of cyclohexanone concentration in the output stream. The different concentrations of cyclohexanone in the reactor were obtained varying both cyclohexanone/hydrogen peroxide molar ratio and catalyst concentration. It is well known that cyclohexenylcyclohexanone is the product of aldol condensation of cyclohexanone.

Fig. 7 shows cyclohexanone azine growth when cyclohexanone concentration increases. It is reported that azines can be obtained under mild conditions from ammonia and peroxy compounds derived from hydrogen peroxide in presence of a carbonyl compound [6]. It has been also reported that reaction proceeds through

imine and oxaziridine intermediate. Hydrogen peroxide alone has no action on ammonia but we cannot rule out azine formation in very little yield. We can say that both cyclohexenylcyclohexanone and cyclohexanone azine derive from homogeneous side reactions of cyclohexanone.

## 4. Conclusion

In ammoxidation reaction of cyclohexanone a series of by-products are formed. Besides inorganic products like nitrogen, nitrous oxide, ammonium nitrite and nitrate, which are the most important, several organic products are found. All the products investigated originated from homogeneous reactions and titanium active sites in titanium silicalite are not involved in their formation. Nitrocyclohexane and cyclohexenone oxime derive from homogeneous reactions of cyclohexanone oxime with hydrogen peroxide. Cyclohexenylcyclohexanone and cyclohexanone azine are formed by homogeneous side reactions of cyclohexanone.

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