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**CATALYTIC REACTIVITY OF Cr/SiO₂ IN THE LIQUID
PHASE OXIDATION OF CYCLOHEXANOL
BY *tert*-BUTYL HYDROPEROXIDE**

Monica L. Parentis, Norberto A. Bonini and Elio E. Gonzo

INIQUI – UNSa
Buenos Aires 177 – 4400 Salta - Argentina

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Abstract

Silica supported chromium is a heterogeneous, active and selective catalyst for the liquid phase oxidation of cyclohexanol by *tert*-butyl hydroperoxide (TBHP) in the presence or absence of oxygen. It is also active for the decomposition of TBHP. The reactivity at 70°C and atmospheric pressure is higher than over other catalysts and the cyclohexanone selectivity is 100%.

Keywords: Chromium catalysts, cyclohexanol oxidation, alkyl hydroperoxide

INTRODUCTION

It has been stated numerous times that oxidation, both in vapor and liquid phases, is one of the most important areas of the production of final and intermediate petrochemical products. In recent years, however, the development of liquid phase processes has been accelerated because of certain process economic advantages, associated especially with liquid phase oxidation. Such advantages are higher yield, improved selectivity and milder reaction conditions. Furthermore, one of the advantages in heterogeneous catalysts that is the economical separation of products from catalyst, also can be achieved.

Recently, Sheldon and co-workers [1-3] reported that chromium substituted aluminophosphates (CrAPO-5) and (CrAPO-11), hydrothermally synthesized, are both active and fairly selective catalysts for the oxidation of secondary alcohols and hydrocarbons using either molecular oxygen or TBHP as the oxidant. Chromium supported on a surface, functionalized silica gel showed excellent selectivity for the epoxidation of cyclohexene to cyclohexene oxide and for the oxidation of ethylbenzene to acetophenone, using air as the oxidant at 130°C [4]. Also, it was shown that a chromium containing mesoporous molecular sieve (a chromium silicate) efficiently catalyzes the oxidation of aliphatic and aromatic primary amines into the corresponding nitro derivatives using TBHP [5] or H₂O₂ [6] as oxidants.

We have prepared and characterized a silica supported chromium catalyst [7], which is very active and selective for the gas phase oxydehydrogenation and dehydrogenation of primary and secondary alcohols [8].

Now we wish to report here the catalytic activity and selectivity of our chromium catalysts in the liquid phase oxidation of cyclohexanol to cyclohexanone using TBHP as the oxidant in the presence or absence of oxygen.

EXPERIMENTAL

The catalysts were prepared by the ion-exchange method. A catalyst with chromium content of 1.57% was used in all the experiments. Details of preparation and characterization of Cr/SiO₂ have been published previously [7, 8].

tert-Butyl hydroperoxide was a Merck Reagent (70% of hydroperoxide by volume). A 1.3 M anhydrous solution of TBHP in chlorobenzene was prepared following a published procedure [9].

Catalytic activity and selectivity tests

The oxidation of cyclohexanol was carried out in a 125 mL thermostated flask equipped with a condenser and a magnetic stirrer. In a typical run, 32.4 mmol of substrate, 217.5 mmol of chlorobenzene (solvent) and 500 mg of Cr/SiO₂ containing 0.151 mmol of chromium were added to this flask. In the experimental run in absence of O₂, the charged flask was bubbled with N₂ at a rate of 15 mL min⁻¹. For the oxidation in the presence of O₂, oxygen was bubbled at a rate of 15 mL min⁻¹ through the reaction mixture. In both cases, the charged flask was heated to 70°C. Finally, 16.2 mmol of TBHP in 106.5 mmol of chlorobenzene was added into the reaction mixture. The reaction, in both cases, was continued for 8 h.

For the quantitative analysis we used a Shimadzu gas chromatograph with a stainless steel column (2 m x 3 mm), filled with Carbowax 20 M on Cromosorb W. The concentration of TBHP was determined by iodometric titration.

RESULTS AND DISCUSSION

In Fig. 1 the percentage yield of cyclohexanol *versus* reaction time are reported for the oxidation with both procedures (with molecular oxygen or in a N₂ atmosphere). After an induction time of about 12.5 min, constant rates for cyclohexanone production were observed. In this zone, the turnover number (assuming the Cr is atomically dispersed on silica) is 39.5 h⁻¹, three times higher than that observed over CrAPO-5 at 110°C [3].

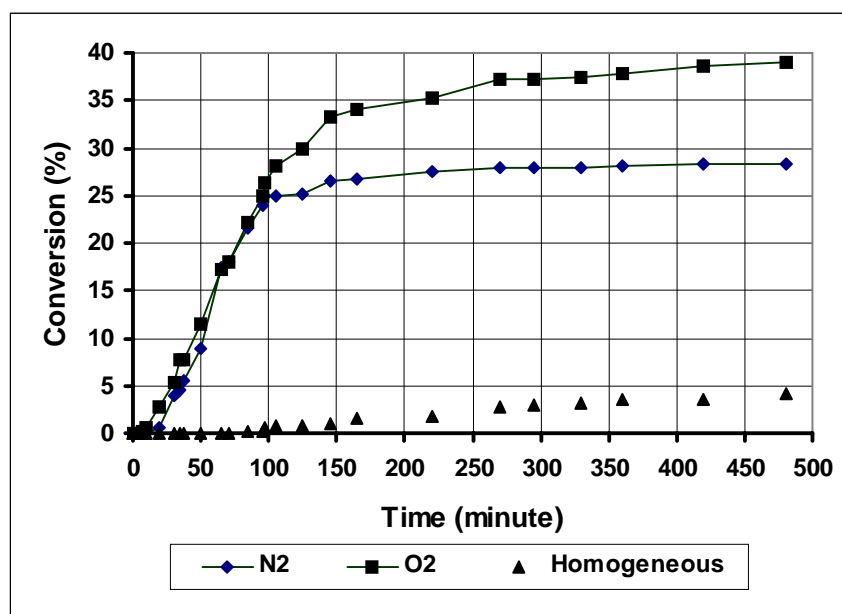


Fig. 1. Percentage conversion of cyclohexanol to cyclohexanone in different reaction atmospheres

At almost total conversion of the hydroperoxide (>94%), cyclohexanone was obtained with 100% selectivity on cyclohexanol conversion base.

When the experiments were carried out with TBHP as oxidant (without molecular oxygen) a maximum conversion of 27.5% was reached after 5 h of

reaction. Meanwhile in the presence of oxygen the conversion was 37.5%, increasing slowly until $\approx 39.1\%$ over 8 hours. The mmoles of TBHP present in the reaction mixture as a function of time is presented in Fig.2. It shows that 95% of the hydroperoxide is consumed in the first 5 h of reaction. Nevertheless, in the presence of oxygen the consumption of TBHP is a little lower and the conversion of cyclohexanol 30% higher than in N_2 atmosphere. These results clearly indicate that O_2 is also acting as an oxidant.

No leaching of chromium from Cr/SiO_2 was found after the reaction, which agrees with previous findings [7].

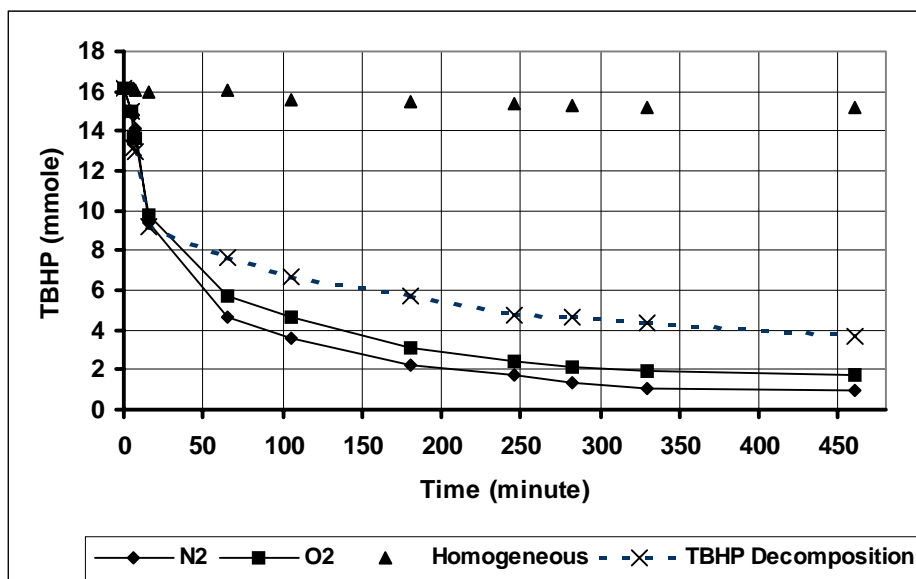


Fig. 2. TBHP conversion as a function of time for different cases

Remarks

With the aim to evaluate the homogeneous reaction contribution, an experiment was carried out without catalyst, but with O_2 . The results are presented in Figs 1 and 2. The homogeneous reaction in the presence of oxygen, in contrast with the heterogeneous one, under the same conditions gave virtually no oxidation (conversion of 4.3% after 8 h of reaction). Meanwhile the consumption of TBHP was negligible (Fig. 2).

Table 1
Catalytic liquid phase oxidation of cyclohexanol with TBHP

Catalyst	Cr/SiO ₂	Cr/SiO ₂	CrAPO-5 ^b [3]
Solv./Subst. ^a	10	10	2.5
TBHP/Subst. ^a	1/2	1/2	1/10
Subst./Cr ^a	214	214	68
Temperature (°C)	70	70	110
Gas / P (KPa)	N ₂ - 87	O ₂ - 87	O ₂ - 912
Time (h)	5	5	5
Conversion (%)	27.4	37.5	30
Selectivity (%)	≈ 100	≈ 100	97

^aMolar relation ^bcarried out in an autoclave

The decomposition of TBHP was carried out with the same setup described for the oxidation of cyclohexanol in the presence of oxygen. In this case the substrate was not added to the reaction system. The results (Fig. 2) show that Cr/SiO₂ is very active. The decomposition rate is as high, in the initial period, as during the alcohol oxidation (turnover number of 167.2 h⁻¹), without induction period. Figure 2 also shows that after the first 15 min the decomposition rate is second order in TBHP.

Another fundamental result was found when the catalytic oxidation was carried out in O₂ atmosphere but without TBHP. After an 8 h run, no alcohol conversion was detected.

The catalyst has a pale green color before reaction, after the induction period it turns orange (pale yellow when dried) and changes again to pale green after 5 h of reaction, a time which is coincident with the total consumption of TBHP (Fig. 2). This strongly suggests that during the induction period Cr(III) is oxidized to Cr(VI) which in turn oxidizes the alcohol *via* a redox mechanism [10] (Fig. 3), in agreement with previous findings [3, 7]. These results indicate that TBHP acts as both an oxidant and an initiator [11].

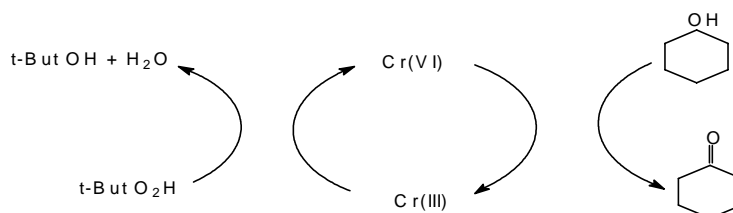


Fig. 3. Mechanism of alcohol oxidation

CONCLUSION

The Cr/SiO₂ catalysts are very active for the liquid phase oxidation of cyclohexanol by TBHP in O₂ atmosphere. Activities higher than over other catalysts under more severe conditions were obtained. Selectivity of 100% to cyclohexanone for conversion up to 40% of cyclohexanol and total consumption of TBHP was found.

In the process presented here catalyst activation by the TBHP molecule is of paramount importance. TBHP acts as oxidant and initiator. When the reaction is carried out with oxygen flowing through the reacting mixture, O₂ also participates as oxidant.

The homogeneous reaction between cyclohexanol and TBHP proceed to an extent no significant, compare with that obtained in the catalytic process.

No alcohol conversion was detected when the heterogeneous reaction was carried out without TBHP and in the presence of O₂.

After the first 15 minutes the decomposition rate of the hydroperoxide is second order in TBHP.

Further research on the kinetics of this reaction, the role and recyclability of the Cr/SiO₂ and the effective use of TBHP for this and other liquid phase oxidations is in progress.

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REFERENCES

1. J.D. Chen, J. Dakka, E. Neeleman, R.A. Sheldon: *J. Chem. Soc., Chem. Commun.*, 1379 (1993).
2. J.D. Chen, R.A. Sheldon: *J. Catal.*, **153**, 1 (1995).
3. J.D. Chen, H.E.B. Lempers, R.A. Sheldon: *J. Chem. Soc., Faraday Trans.*, **92**, 1807 (1996).
4. J. Chisen, I.C. Chisen, J.S. Rafelt, D.J. Macquarie, J.H. Clark: *J. Chem. Soc., Chem. Commun.*, 2203 (1997).
5. B. Jayachandran, M. Sasidharan, A. Sudalai, T. Ravindranathan: *J. Chem. Soc., Chem. Commun.*, 1523 (1995).
6. N. Ulagappan, C.N.R. Rao: *J. Chem. Soc., Chem. Commun.*, 1047 (1996).
7. M.L. Parentis, N.A. Bonini, E.E. Gonzo: *Lat. Am. Appl. Res.*, **30**, 41 (2000).
8. M.L. Parentis, N.A. Bonini, E.E. Gonzo: *React. Kinet. Catal. Lett.*, **72**, 303 (2001).
9. J.G. Hill, B.E. Rossiter, K.B. Sharpless: *J. Org. Chem.*, **48**, 3607 (1983).
10. C. Doornkamp, V. Ponec: *J. Mol. Catal.*, **162**, 19 (2000).
11. Á. Zsigmond, A. Horváth, F. Notheisz: *J. Mol. Catal. A-Chemical*, **171**, 95 (2001).