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Wacker oxidation of cyclohexene in the presence of $\text{Pd}(\text{NO}_3)_2/\text{CuSO}_4/\text{H}_3\text{PMo}_{12}\text{O}_{40}$

Marisa S. Melgo, Alexandra Lindner, Ulf Schuchardt*

Instituto de Química, Universidade Estadual de Campinas, P.O. Box 6154, 13084-971 Campinas, SP, Brazil

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Abstract

The Wacker oxidation of cyclohexene to cyclohexanone, using the chloride ion-free catalytic system $\text{Pd}(\text{NO}_3)_2/\text{CuSO}_4/\text{H}_3\text{PMo}_{12}\text{O}_{40}$, was investigated at different air pressures, temperatures, and catalyst concentrations. The results show that this system is very efficient and highly selective. After 1 h of reaction at 80 °C and an air pressure of 50 bar, a conversion of 80%, with a turnover frequency of 260 h^{-1} , and a selectivity of more than 99% for cyclohexanone was obtained. Using aqueous hydrogen peroxide and no external pressure, the oxidation was more rapid, giving 80% conversion already after 30 min and 95% conversion after 60 min without the formation of any byproducts.

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1. Introduction

Cyclohexanone has its main industrial application in the synthesis of ϵ -caprolactam, which is used for the production of nylon-6. Usually, cyclohexanone is obtained through cyclohexane oxidation, carried out at 160 °C with an air pressure of 15 bar and in the presence of a homogeneous cobalt catalyst. After 40 min, the reaction gives a conversion of 4%, with 80% selectivity for a cyclohexanone/cyclohexanol mixture (1:2 ratio) [1]. At higher cyclohexane conversions, the selectivity decreases considerably. Cyclohexanone can also be produced by the phenol hydrogenation in the presence of a nickel catalyst [2,3]. Nevertheless, this process is less used due to low conversions (10%), severe conditions of pressure and temperature, and high cost of phenol. Another cyclohexanone synthesis involves cyclohexene hydration to cyclohexanol under acidic conditions followed by its dehydrogenation to cyclohexanone in the presence of a basic copper catalyst [3].

An interesting alternative is the Wacker oxidation of cyclohexene in the absence of chloride. However, the classic

Wacker system, $\text{PdCl}_2/\text{CuCl}_2$, is only efficient in the industrial production of acetaldehyde and acetone from ethylene and propene, respectively. In the oxidation of cyclic and internal olefins, this system shows low activity and selectivity, producing large quantities of organic chlorides [4]. This limitation can be overcome by using heteropolyacids in the presence of chloride-free palladium compounds. Ogawa et al. [5], using the system $\text{PdSO}_4/\text{H}_3\text{PMo}_6\text{W}_6\text{O}_{40}$, obtained a cyclohexene conversion of 85% after 24 h, however, the turnover frequency was low (6 h^{-1}). Yokota et al. [6], using $\text{Pd}(\text{OAc})_2/\text{hydroquinone}/\text{Na}_n\text{PMo}_x\text{V}_{12-x}\text{O}_{40}$, obtained cyclohexanone with a conversion of 58% after 20 h, which corresponds to a turnover frequency of only 0.6 h^{-1} . Miller and Wayner [7], using $\text{Pd}(\text{OAc})_2/\text{hydroquinone}$, obtained 100% conversion in 1 h (turnover frequency 100 h^{-1}); however, the amount of hydroquinone employed was similar to the amount of cyclohexanone produced. The best results for the chloride ion-free Wacker oxidation of cyclohexene were reported by Kim et al. [8], who used $\text{Pd}(\text{NO}_3)_2/\text{CuSO}_4/\text{H}_3\text{PMo}_{12}\text{O}_{40}$ as catalyst in an aqueous solution of acetonitrile at 80 °C and 10 bar of oxygen. They obtained a conversion of 49%, with 97% selectivity for cyclohexanone (turnover frequency 173 h^{-1}). Here we wish to report our results on the Wacker oxidation of cyclohexene using dif-

* Corresponding author. Tel.: +55 19 3788 3071; fax: +55 19 3788 3023.
E-mail address: ulf@iqm.unicamp.br (U. Schuchardt).

ferent pressures of synthetic air, temperatures, and catalyst concentrations. Furthermore, we performed some oxidation reactions using the same catalytic system but hydrogen peroxide instead of air as oxidant.

2. Experimental

The reagents $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (Strem Chemicals, 99.9%), cyclohexene (Merck, >99%), and acetonitrile (EM Science, 99.98%) were used as purchased. The aqueous 70 wt.% hydrogen peroxide was obtained from Peróxidos do Brasil. The heteropolyacid $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 5\text{H}_2\text{O}$ was prepared according to the method described by Polotebnova et al. [9] and characterized by X-ray diffraction (Shimadzu XRD6000), ICP-OES (Perkin Elmer 3000DV) and by thermogravimetric analyses (TA Instruments, 2050 model). The heteropolyacids containing vanadium were prepared in the same way, however, a 20% excess of vanadium was used in order to guarantee the introduction of vanadium into the structure.

All oxidation reactions were carried out in a Parr autoclave, 4565 model, equipped with a 100 mL PTFE[®] vessel, mechanic stirring, manometer, and a temperature control system. Typically, 37.3 mg of $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (0.1 mmol), 139.8 mg of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.56 mol), and 1.07 g of $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 5\text{H}_2\text{O}$ (0.56 mmol) were dissolved in 15 mL of a 3% H_2SO_4 aqueous solution and 7.5 mL of acetonitrile, which were introduced together with 3.7 g of cyclohexene (45 mmol) into the reactor. The stirring was then adjusted to 600 rpm and the system pressurized with 50 bar of synthetic air. After a heating-up period of 15–20 min, the reaction was started at 80 °C for the indicated reaction time. No experiments were carried out at constant air pressure, which

typically dropped 5 bar during the reactions, indicating that approximately half of the oxygen was consumed. The reaction mixture was then extracted with cyclohexane (5×15 mL) and ethyl ether (1×20 mL). The ether phase was distilled for purification. The distilled ether phase was added to the cyclohexane solution, diluted with ethyl acetate and analyzed by gas chromatography using an HP 5890 gas chromatograph equipped with an HP-5 column ($25 \text{ m} \times 0.20 \text{ mm} \times 0.33 \mu\text{m}$) and a FID detector. In some reactions 3.28 g of aqueous 70 wt.% hydrogen peroxide (67.5 mmol) were added to the reaction mixture and the reactor just closed without pressurization with synthetic air.

3. Results and discussion

In order to turn the conversion independent on the stirring rate, 600 rpm were used in all experiments. The influence of the initial synthetic air pressure on the cyclohexene conversion after 1 h of reaction time is given in Fig. 1, which shows a linear growth up to a pressure of 50 bar, when the stoichiometric amount of molecular oxygen is present and a conversion of 80% is reached. Increasing the synthetic air pressure to 60 bar results only in a slightly higher conversion of 83%. The turnover frequency increases linearly with the pressure up to 50 bar and then stabilizes. The selectivity for cyclohexanone is always better than 99%.

Comparing our results obtained after 60 min at 50 bar of synthetic air (80% conversion, turnover frequency 260 h^{-1} , 99% selectivity) with those of Kim et al. [8], using 10 bar of oxygen (49% conversion, turnover frequency 173 h^{-1} , 97% selectivity), we first erroneously thought that the higher total pressure used in our experiments provided a better saturation of oxygen in the liquid phase. However, after looking more

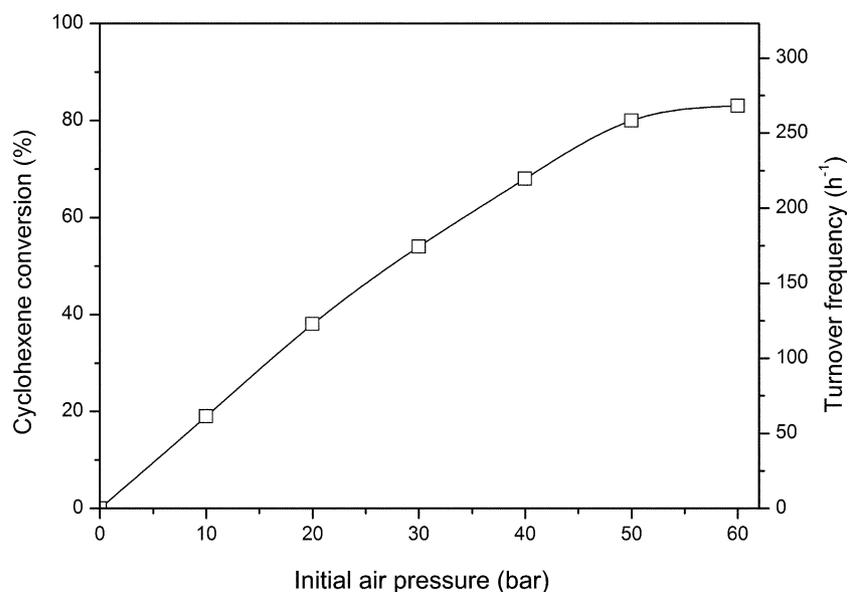


Fig. 1. Dependence of cyclohexene conversion and turnover frequency on the initial pressure of synthetic air. Conditions: 0.14 mmol of $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, 0.56 mmol of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 0.56 mmol of $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 5\text{H}_2\text{O}$, 45 mmol of cyclohexene, 1 h at 80 °C.

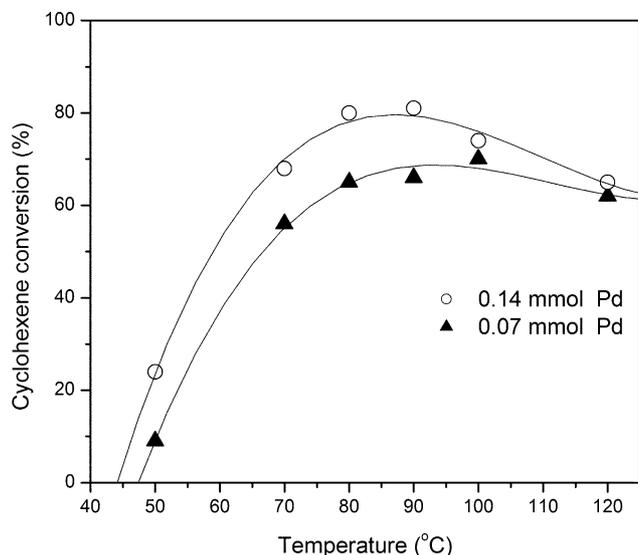


Fig. 2. Temperature dependence of cyclohexene conversion. Conditions: 0.14 or 0.07 mmol of $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, 0.56 mmol of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 0.56 mmol of $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 5\text{H}_2\text{O}$, 45 mmol of cyclohexene, 50 bar of air, 1 h.

carefully into this we realized that the supply of molecular oxygen in the experiments of Kim et al. [8] was insufficient for a higher conversion of cyclohexene. We, therefore, repeated the experiment of Kim et al. with the amount of reagents and solvent used in our experiments (which is half of the amounts Kim et al. used) and 10 bar of oxygen pressure in a 100 ml reactor. We obtained a very similar conversion (78%) to that observed in our experiments with 50 bar of synthetic air. This shows that our better results are only due to a higher supply of molecular oxygen during the reactions.

Fig. 2 shows the temperature dependence of the cyclohexene conversion for reactions carried out at 50 bar of synthetic air using the catalytic system $\text{Pd}(\text{NO}_3)_2/\text{CuSO}_4/\text{H}_3\text{PMo}_{12}\text{O}_{40}$ in the ratios 0.14:0.56:0.56 and 0.07:0.56:0.56.

Both catalytic reactions show a similar reaction profile up to 90 °C, when the highest conversion is obtained. At higher temperatures the activity of the palladium catalyst is reduced due to some decomposition of the catalytically active species. This is principally observed for the more concentrated catalyst solution and is probably due to enhanced formation of palladium black. The selectivity for cyclohexanone is at all temperatures better than 99%.

The oxidation reaction was accompanied during 3 h analyzing the cyclohexene consumption and cyclohexanone

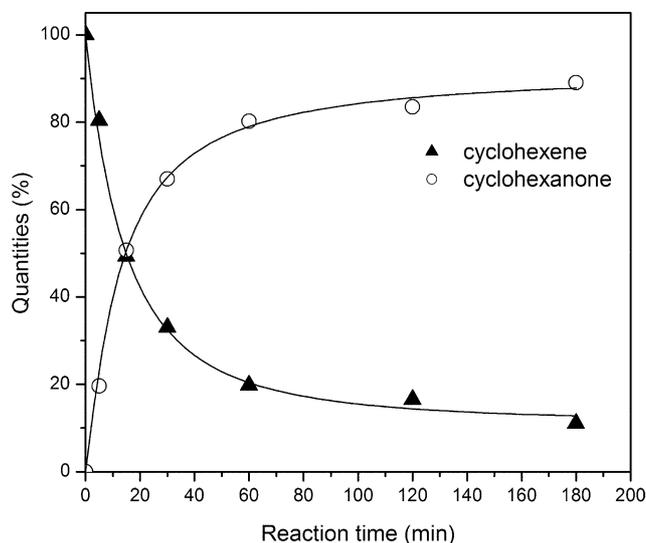


Fig. 3. Cyclohexene conversion and cyclohexanone production at different reaction times. Conditions: 0.14 mmol of $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, 0.56 mmol of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 0.56 mmol of $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 5\text{H}_2\text{O}$, 45 mmol of cyclohexene, 50 bar of air, 80 °C.

production. According to Fig. 3 and Table 1, 22.8 mmol of cyclohexanone are produced in the first 15 min of reaction, which means that the cyclohexene conversion is already 50% (average turnover frequency 652 h^{-1}). After 1 h, the reaction is almost complete, reaching a conversion of 80% and an average turnover frequency of 260 h^{-1} . After 3 h the conversion is about 89% (average turnover frequency 97 h^{-1}). For all reaction times studied, the selectivity is always better than 99%.

The turnover frequency, which is initially very high reduces rapidly during the course of the reaction, showing that the catalytic system is not stable. This is confirmed by the formation of inactive palladium black, which is already observed in a minor extent for the reaction of 15 min and increases for longer reaction times. Due to the instability of the catalytic system we do not believe that a detailed kinetic study of the system would be very meaningful, however, estimate from the angular coefficient an initial oxidation rate of $0.05 \text{ mol L}^{-1} \text{ min}^{-1}$.

In order to reduce the catalyst quantity and to distinguish between the key components of the catalytic system, reactions with different catalyst composition were performed for 1 h each (Table 2). Reaction 1 allows a conversion of 80% with a turnover frequency of 260 h^{-1} . On reducing the copper

Table 1
Cyclohexene conversion and turnover frequency after different reaction times at 80 °C

Time (min)	Cyclohexene (mmol)	Cyclohexanone (mmol)	Conversion (%)	Total turnover	Turnover frequency (h^{-1})
5	36.0	9.0	20	64	771
15	22.2	22.8	51	163	652
30	14.9	30.0	67	214	428
60	8.9	36.4	80	260	260
120	7.1	38.2	84	273	137
180	5.0	40.2	89	290	97

Table 2
Influence of the catalyst composition on the turnover frequency and cyclohexene conversion^a

Reaction	Pd:Cu:PMo ₁₂ (mmol)	Cyclohexene (mmol)	Cyclohexanone (mmol)	Turnover frequency (h ⁻¹)	Conversion (S ^b) (%)	Conversion (S ^b) (%) [8]
1	0.14:0.56:0.56	9.0	36.5	260	80 (>99)	49 (97)
2	0.14:0.28:0.28	11.0	34.0	242	76 (98)	47 (94)
3	0.14:0.14:0.14	24.2	17.0	121	42 (97)	–
4	0.14:0.28:0	34.6	7.8	56	18 (98)	13 (50)
5	0.14:0:0.28	34.5	7.5	54	18 (98)	6 (96)
6	0.07:0.56:0.56	15.5	28.0	400	65 (97)	–
7	0.07:0.28:0.28	16.5	25.7	367	61 (96)	–
8	0.07 ^c :0.56:0.56	20.8	21.0	300	50 (95)	–

^a 1 h at 80 °C.

^b Selectivity for cyclohexanone.

^c Pd(OAc)₂.

and heteropolyacid quantities by 50% (reaction 2), the conversion is slightly reduced to 76% and the selectivity to 98%. With further reduction of the copper and heteropolyacid quantities (reaction 3), cyclohexene conversion decreases strongly to 42%. The use of only copper or only HPA as palladium reoxidant (reactions 4 and 5) results in a very strong reduction of cyclohexene conversion. However, reducing the palladium quantity to 0.07 mmol (reactions 6 and 7) still gives a good conversion of cyclohexene and an only slightly reduced selectivity (98%). Under these conditions the turnover frequency is as high as 400 h⁻¹. The use of palladium acetate is not advantageous compared to palladium nitrate (reaction 8), probably because the palladium acetate does not dissociate as completely as palladium nitrate.

From these results we may conclude that the presence of both copper(II) ions and heteropolyacid is important for a good conversion and a high turnover frequency. This agrees with earlier results [8] which show that the interaction between copper(II) and the heteropolyacid (HPA) is essential for the Pd(0) to Pd(II) reoxidation. However, our results prove that a higher oxygen amount is necessary to guarantee a better conversion of cyclohexene and a higher selectivity for cyclohexanone.

In an attempt to further increase the amount of oxygen available for the catalytic system, we substituted the synthetic air by aqueous 70 wt.% hydrogen peroxide. In these reactions the same reactor and the same amount of solvent and reagents were used, however instead of pressurizing the reactor with synthetic air, we simply added the hydrogen peroxide and closed the reactor. The reaction with hydrogen peroxide is more rapid giving already 65% conversion after 15 min (average turnover frequency 836 h⁻¹) and 80% conversion after 30 min (average turnover frequency 517 h⁻¹). After 60 min the reaction is practically finished and cyclohexanone is obtained as the only product with 95% conversion (average turnover frequency 308 h⁻¹). All three components of the catalytic system are still necessary for the reaction with hydrogen peroxide and an additional pressure of synthetic air does not improve the results. The reactions with hydrogen peroxide were not optimized and we believe that even higher turnover frequencies would be possible.

In the last series of experiments we used different heteropolyacids for the systems employing synthetic air and hydrogen peroxide as oxidant. The conversions are shown in Fig. 4. The heteropolyacid H₃PMo₁₂O₄₀ shows the best performance for both systems, however, H₃PW₆Mo₆O₄₀ gives also good results. The heteropolyacids, which contain vanadium give intermediate results with synthetic air, however, are not appropriate for the oxidation with hydrogen peroxide as they decompose the oxidant without formation of significant amounts of cyclohexanone. Neumann and de la Vega [10] also observed significant decomposition of hydrogen peroxide when using H₅PV₂Mo₁₀O₄₀ as oxidation catalyst and we observed a strong decomposition of hydrogen peroxide when using H₇PV₄Mo₈O₄₀ as catalyst for the bleaching of commercial pulps [11]. Again, the only product observed in all reactions with the different heteropolyacids was cyclohexanone. Such high conversions and selectivities for cyclohexanone have never been described before for the Wacker oxidation of cyclohexene.

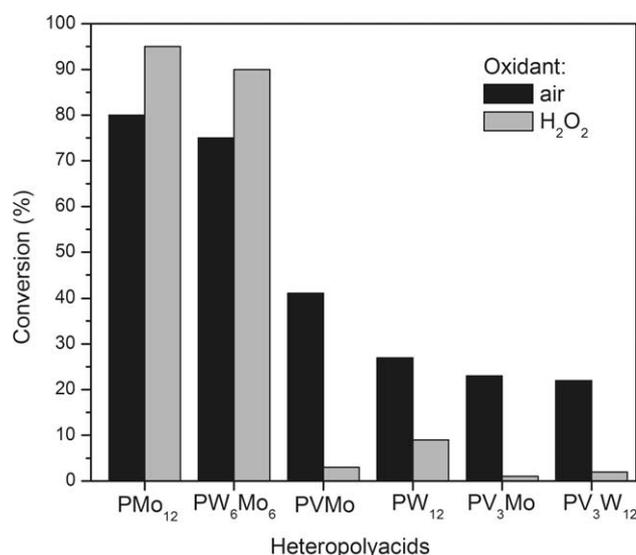


Fig. 4. Dependence of cyclohexene conversion on the heteropolyacid used. Conditions: 0.14 mmol of Pd(NO₃)₂·2H₂O, 0.56 mmol of CuSO₄·5H₂O, 0.56 mmol of heteropolyacid, 45 mmol of cyclohexene, 50 bar of air or 67.5 mmol of hydrogen peroxide, 1 h at 80 °C.

4. Conclusions

Cyclohexene conversions of 80% and selectivities of over 99% to cyclohexanone are interesting for substitution of the cyclohexane oxidation process used in industry. As in the alternative Asahi process two stages are required (cyclohexene hydration to cyclohexanol followed by its dehydrogenation to cyclohexanone) [12], direct oxidation of cyclohexene to cyclohexanone would simplify this process. The even better result with aqueous hydrogen peroxide would only be of industrial interest if the higher conversion compensates for the cost of the oxidant. Catalyst reuse and costs of the process should be further studied in order to investigate its economical feasibility.

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