ELSEVIER

Catalysis Today 74 (2002) 15–21

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Study on process integration of the production of propylene oxide and hydrogen peroxide

Chunyan Wang, Baoguo Wang*, Xiangkun Meng, Zhentao Mi

School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China

---

Abstract

Titanium silicalite (TS-1) is an effective catalyst for selective oxidation of hydrocarbons and their derivatives with hydrogen peroxide under mild conditions. The industrialization of these processes is at present penalized by the high cost of hydrogen peroxide. The process integration of the production of propylene oxide (PO) with the production of hydrogen peroxide (H_2O_2) by the anthraquinone route is presented in this paper. Two integrated processes are discussed: in the first process, the solvent for the epoxidation step is recycled to extract H_2O_2 from the anthraquinone working solution; while in the second process, two oxidation processes, the epoxidation of propylene and the oxidation of anthrahydroquinone, are carried out in one circulating reactor. The influences of various reagents on the performance of TS-1 and the compatibility of the two oxidation processes were investigated. The results show that it is better to integrate the production of PO with the production of H_2O_2 when TS-1 is used as catalyst. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Process integration; Propylene oxide; Titanium silicalite

---

1. Introduction

It is well known that titanium silicalite (TS-1) is an efficient catalyst for the epoxidation of various olefins with hydrogen peroxide under mild conditions [1–3]. As a typical environmentally benign process, the epoxidation of propylene with hydrogen peroxide is of commercial interest in order to replace the traditional production method. It is well documented that propylene oxide (PO) can be produced with high yield and nearly complete conversion for H_2O_2 in the presence of TS-1 in a methanol based solvent system. However, the high cost of H_2O_2 has prevented the commercialization of this reaction system. Process integration is often used as an alternative method for optimization. Now nearly all manufacturing facilities for H_2O_2 are based on the autoxidation of anthrahydroquinone (AO process) [4]. Another process is alcohol autoxidation, especially isopropanol autoxidation. But the competing oxidation of isopropanol to acetone is harmful to the epoxidation of propylene. The direct reaction of H_2 and O_2 to form H_2O_2 can be achieved in a number of ways but none is industrially important because of poor economics or processing problems. Only the AO process is of commercial importance for integration. Two recent patents [5,6] disclose integration of propylene epoxidation and hydrogen peroxide production. In one integrated process [5], the solvent for epoxidation of propylene is used as the extracting agent for H_2O_2 from the anthraquinone working solution (Process I), as shown in Fig. 1. In the other [6], both the epoxidation of propylene and the oxidation of anthrahydroquinone are carried out in the same reactor (Process II), as shown in Fig. 2.

---

* Corresponding author.
E-mail address: bgwang@public.tpt.tj.cn (B. Wang).

PII: S0920-5861(01)00526-0

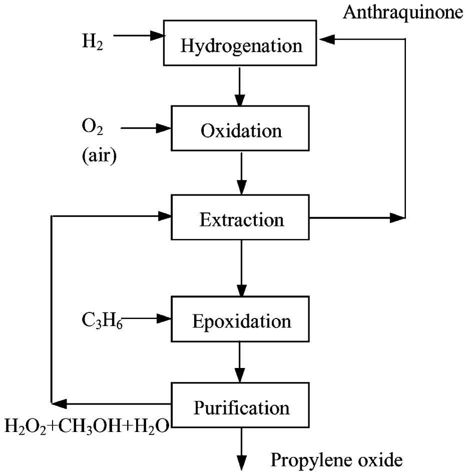


Fig. 1. Integrated process for the production of propylene oxide by extracting H_2O_2 from anthraquinone working solution using methanol–water (Process I).

In Process I, unwanted components will be brought to the epoxidation process along with H_2O_2, while some TS-1 and PO will enter into the H_2O_2 production process. In Process II, it is obvious that there are more problems associated with the integrated reaction process [7]. Firstly, the two oxidation reactions are both sensitive to the composition of the solvent [4,9]. Therefore, a complex solvent system has to be used which must be favorable not only to the epoxidation of propylene but also to the oxidation of anthrahydroquinone. Secondly, TS-1 is absolutely necessary to propylene epoxidation, while oxidation of anthrahydroquinone can be carried out without any catalyst. Thirdly, the temperature, pressure and composition of feed suitable for both reactions need to be decided. The last problem is about the separation and purification of PO from the effluent of the reactor. In this paper, an improved integration process is proposed and the influences of different process variables on the performance of the integrated processes are presented.

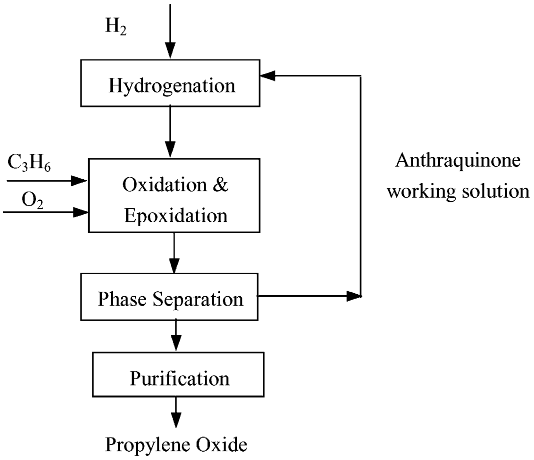


Fig. 2. Integrated process for production of PO by the oxidation of anthrahydroquinone and the epoxidation of propylene in one reactor (Process II).

2. Experimental

The semi-continuous stirred-tank reactor used in this study is shown in Fig. 3. It consisted of a 300 ml of stainless steel tank, an electromagnetic stirrer and a heating jacket. Anthrahydroquinone reduced solution, methanol, and TS-1 catalyst were charged into the reactor before reaction, while the gaseous components including propylene and/or air were fed into the reactor by a control valve at the same rate as it was consumed. Thus, the pressure was maintained constant. Concentrations of H_2O_2 and PO were determined by iodimetry and gas chromatography, respectively. For comparison, a circulating flow reactor was also used, as shown in Fig. 4. This stainless-steel reactor consisted of a riser and a downcomer with the same

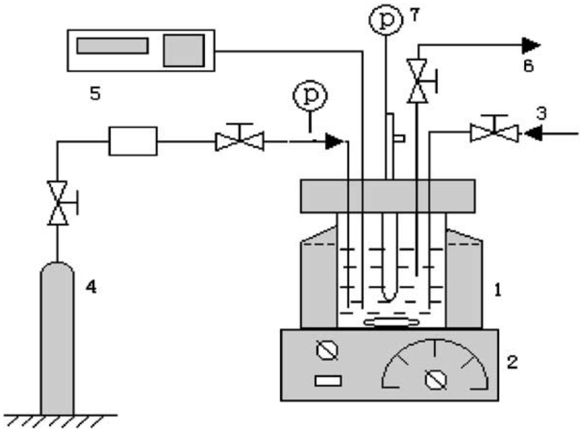


Fig. 3. Semi-continuous experimental apparatus: (1) autoclave with heating/cooling jacket; (2) electromagnetic stirrer; (3) inlet for slurry of TS-1, methanol and H_2O_2; (4) propylene; (5) temperature indicator-controler; (6) outlet for sampling; (7) pressure gauge.

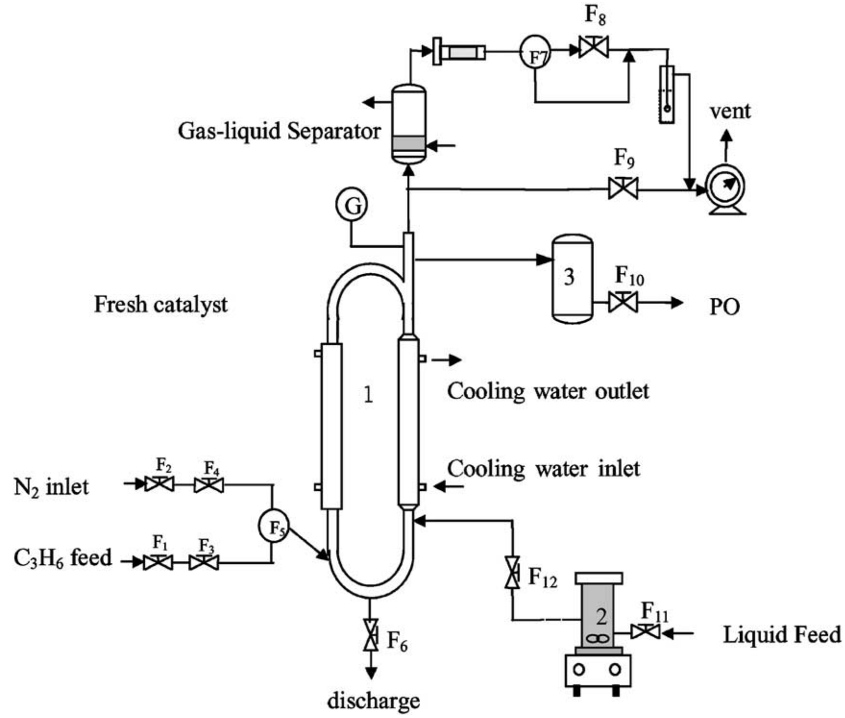


Fig. 4. Schematic diagram of the gas-lift loop reactor: (1) gas-lift loop reactor; (2) peristaltic pump; (3) product tank.

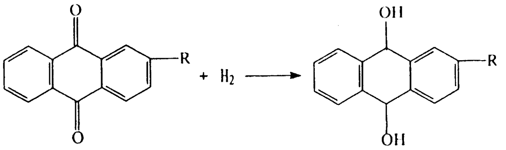
diameter of 10 mm. The volume of the reactor was 120 ml. The slurry, which included the TS-1 catalyst, water, H_2O_2, anthraquinone working solution and other reagents, can circulate in reactor driven by the flow of the gas mixture. This type of reactor is one of the most promising methods for two or three phase reactions with large heat effects [8]. It can be handled continuously and it is easier for on-line catalyst regeneration.

The TS-1 catalyst with size of 0.1–0.3 μm was prepared in the Research Institute of Petroleum Processing of Sino-Petrochemical Corporation. The anthraquinone working solution and hydrogen peroxide (27 wt.%) were provided by the Dongfang Chemical Factory in Tianjin.

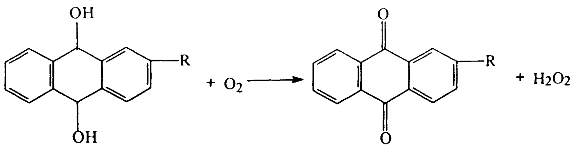
3. Results and discussion

H_2O_2 was produced by hydrogenation of anthraquinone followed by oxidation of anthrahydroquinone (Eqs. (1) and (2)), then propylene was epoxidized by H_2O_2, as shown in Eq. (3). However, several side reactions might take place simultaneously to deteriorate the process. These mainly include the hydrolysis of PO and non-selective ring opening reactions of the PO (Eqs. (4) and (5)). In addition, decomposition of H_2O_2 and the deep oxidation and decomposition of anthraquinone derivatives might also take place.

Many factors can affect the selectivity and yield of propylene oxide. Extensive investigation was conducted and part of results is shown in Figs. 5–8.



(1)



(2)

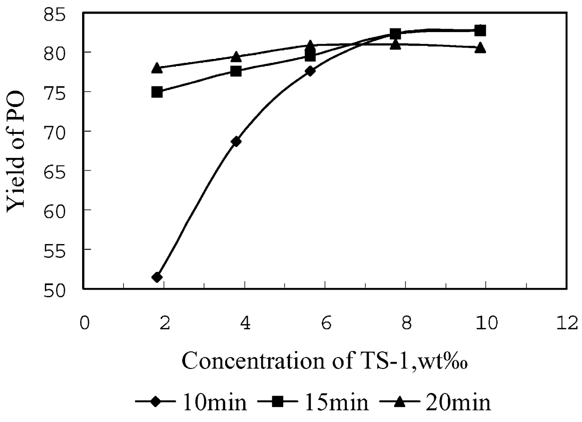


Fig. 5. The influence of concentration of TS-1 on the yield of PO.

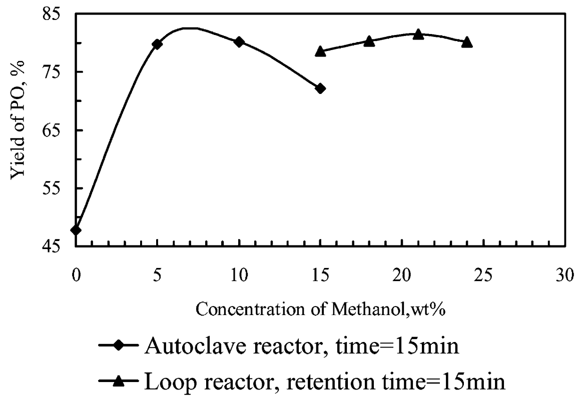


Fig. 6. The influence of methanol in solvents on the yield of PO.

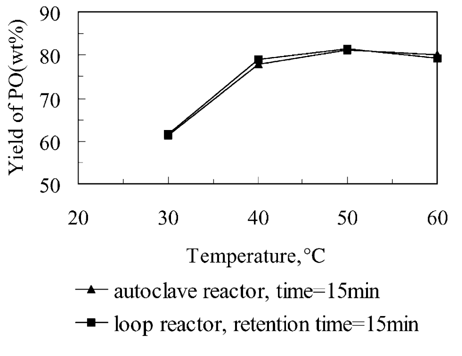


Fig. 7. The influence of temperature on the yield of PO.

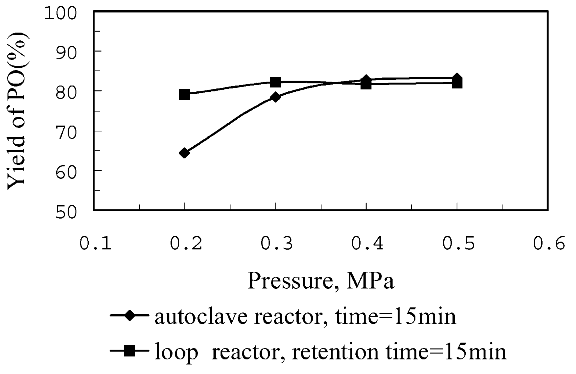
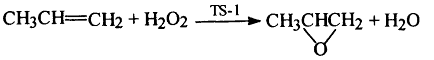
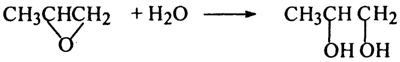


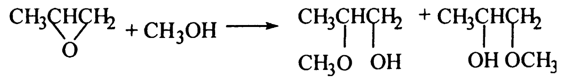
Fig. 8. The influence of pressure on the yield of PO.



$$CH_3CH{=}CH_2 + H_2O_2 \xrightarrow{TS\text{-}1} CH_3\underset{O}{CHCH_2} + H_2O \tag{3}$$



$$CH_3\underset{O}{CHCH_2} + H_2O \longrightarrow CH_3\underset{OH}{CH}\,\underset{OH}{CH_2} \tag{4}$$



$$CH_3\underset{O}{CHCH_2} + CH_3OH \longrightarrow CH_3\underset{CH_3O}{CH}\,\underset{OH}{CH_2} + CH_3\underset{OH}{CH}\,\underset{OCH_3}{CH_2} \tag{5}$$

3.1. *Composition of the extractant*

In integrated Process I, with methanol–water mixture as extractant, anthraquinone derivatives and their solvents and some reagents including stabilizers and corrosion inhibitors in working solution will be brought to the epoxidation installation together with H_2O_2. The experimental results showed that most of the components have no obvious influence on the epoxidation of propylene and the deactivation of TS-1. But when H_3PO_4 or NH_4NO_3 was used as the stabilizer and corrosion inhibitor of hydrogen peroxide, the yield of PO decreased considerably because these substances seem to deactivate the TS-1. Alkaline components, such as K_2CO_3 and trimethylamine, increase the state of side reactions. Small quantities of products and impurities in the propylene epoxidation process might also be carried over to the H_2O_2 production unit, but they did not affect the hydrogenation and oxidation of the anthraquinone working solution. Therefore, it is important to avoid reagents such as H_3PO_4, NH_4NO_3, K_2CO_3 and trimethylamine in integrated Process I.

3.2. Catalyst

Anthrahydroquinone can be automatically oxidized by air or oxygen without catalyst, while TS-1 is absolutely necessary for epoxidation of propylene to achieve high selectivity and yield of PO. As described above, the components in the anthraquinone working solution have no obvious negative effect on the performance of TS-1 and the oxidation of anthrahydroquinone was not influenced by TS-1. This is because the catalyst used is highly shape-selective and its pore size is as small as about 0.55 nm. In integrated process II, propylene and oxygen or air were fed into the reactor simultaneously, then reactions 2 and 3 were carried out in the same reactor. Our experimental results show that the amount of TS-1 had significant influence on the yield of PO. With the increase of concentration of TS-1, the yield of PO increased and then maintained constant or slightly decreased. The data shown in Fig. 5 were obtained in the semi-continuous autoclave. When the concentration of catalyst was larger than 5 g/l, it became very difficult or even impossible to form a homogeneous dispersion. So the yield of PO was limited in this case. However, the yield of PO became non-sensitive with change of concentration of catalyst after 15 min because reaction rate was very fast. Side reactions were enhanced when the reaction time was too long. Fig. 5 shows that the yield of PO at 20 min was lower than that at 15 min when the concentration of TS-1 was higher than 6 wt.‰.

The TS-1 catalyst was effective for epoxidation in methanol–water medium, but it was difficult to disperse the complex system including large quantity of anthraquinone and its solvents in a stirred tank reactor. So the performance of TS-1 was not only influenced by its concentration in the complex medium but also by the concentration of the solvent.

3.3. Composition of solvent mixture

A complex solvent was used in this reaction system. The solvent included methanol, different reagents in the anthraquinone working solution (including trimethylbenzene, trioctylphosphate and some stabilizers and corrosion inhibitors of hydrogen peroxide). Methanol functioned not only as a solvent for propylene and PO but also as a co-catalyst [9]. With the increase of methanol concentration, the epoxidation of propylene was enhanced and the yield of PO should be increased. The increase of methanol led to the decrease of the quantity of solvent for anthrahydroquinone and the concentration of anthrahydroquinone in the complex medium, thus the oxidation of anthrahydroquinone was restrained. Therefore, the overall yield for PO decreased slightly when the content of methanol was too high. The high yield of PO could be maintained when the content of methanol was in the range of 5–10% in the autoclave reactor as shown in Fig. 6.

The performance of both integrated systems was affected by the concentration of methanol because the system tends to form two liquid phases and TS-1 was difficult to disperse in such a system. In a gas-lift loop reactor, gaseous and liquid reactants, methanol and solvent for anthraquinone, and the solid catalyst are well mixed by the high speed of circulating. Therefore, the two reactions can be carried out in two different but intensely contacted liquid phases, a methanol–water phase and an anthraquinone working solution phase. Anthrahydroquinone was oxidized in the working solution phase and H_2O_2 was produced, which was easier to move to the methanol–water phase, favoring the reaction of anthrahydroquinone. The epoxidation of propylene took place in the methanol–water phase and PO was produced and part of PO could move to the working solution phase. In this way, the two main reactions were enhanced and side reactions were suppressed. In addition, the content of methanol could be increased to some extent without affecting the oxidation of anthrahydroquinone. Thus, the process was improved a lot by using a circulating reactor with a suitable composition of solvent system. It was indicated from Fig. 6 that a high yield of PO was achieved using the circulating reactor with a higher concentration of methanol, which could favor the phase separation of the effluent.

3.4. Temperature and pressure

With the high catalytic performance of TS-1 molecular sieve, the optimal reaction temperatures for the coupled oxidation reactions were very close to each other. It was shown from Fig. 7 that, with the increase of temperature, the yield of PO reached a maximum value and then decreased slightly. Pressure played a role in reaction by affecting the solubility of gaseous reactants, propylene and oxygen, in the liquid. Gas solubility increased with the increase of pressure. Considering these effects as well as the operating cost, the optimal temperature was in the range of 40–50 °C and the optimal pressure was about 0.4 MPa in the semi-continuous autoclave reactor. The circulating reactor is less sensitive to pressure changes because the mass transfer between gas and liquid phases is driven by mixing through circulation rather than by increasing the pressure. Therefore, the reaction can be run at lower pressure in the loop reactor than in the stirred tank reactor. Experiments showed that the same results could be obtained at 0.2 MPa in the loop reactor as at 0.4 MPa in the autoclave reactor.

3.5. *Composition of the feed*

There are two streams of feed into the reactor, including a gas feed and a slurry feed. The required amount of oxygen and propylene was dependent on the explosion limit of propylene, concentration in liquid and the oxidation and decomposition of anthrahydroquinone derivatives. Too much oxygen might cause deep oxidation and decomposition of anthrahydroquinone and its derivatives. Excess propylene has to be discharged or recycled, which leads to the increase of operating cost as well as environmental and safety problems. Experimental results show that the yield of PO could be maintained at a high value when oxygen was in the range of 20–30% in volume. The ratio of the overall gas components to the liquid mixture in the feed can affect the flow pattern of the three-phase flow and then affect mass and heat transfer.

3.6. *An improved integrated process*

From the experiments described above, we propose an improved integration process flowsheet shown in Fig. 9. It includes the oxidation reactor, in which the two oxidation processes carried out, and the unites for splitting and phase separating the effluent, recovering methanol, purifying PO, and regenerating the oxidized working solution. It was shown that mass transfer was important to carry out the two reactions in one reactor, because there were two liquid phases as well as a gas and a solid phase. In the production of H_2O_2 by the anthraquinone route, a process intensification reactor was used to strengthen mass transfer. Here, a gas-lift three-phase circulating loop reactor, shown in Fig. 4, was used and the solvent system was adjusted with addition of methanol–water mixture. By using the loop reactor and increasing the methanol concentration, the mass and heat transfer were improved, and this again could enhance the main reactions and suppress the side reactions. In addition, it became easier to regenerate the catalyst on-line and it favored the phase separation of the effluent from the integrated reactor. Experimental and simulation results showed that this integrated process was an effective and economic one for the production of propylene oxide. It was not only energy-saving by avoiding the separation and purification of H_2O_2 and simplifying the separation of the effluent from the reactor, but also it used one reactor

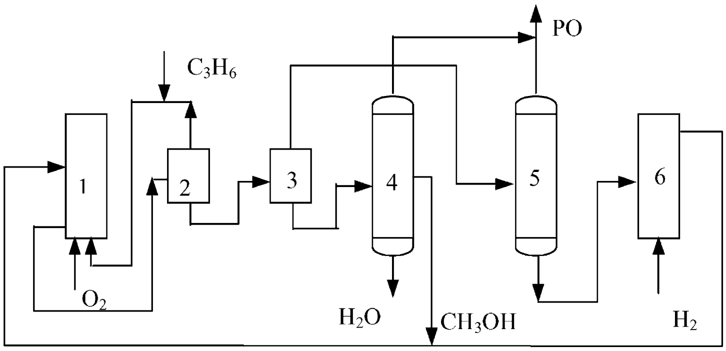


Fig. 9. Improved integrated process flow sheet for PO production: (1) integrated reactor; (2) splitter; (3) phase separator; (4) distillation; (5) distillation; (6) hydrogenation for working solution.

instead of two different ones for the epoxidation of propylene and the oxidation of anthrahydroquinone. The integrated process was effective to obtain PO with high selectivity and yield under optimized reaction conditions with a yield as high as 82%, and a selectivity as high as 85% based on anthrahydroquinone.

4. Conclusions

Through the investigation of the influences of different process variables on the process performance, the operation conditions were optimized and an improved integrated process was proposed with a maximum yield of PO of 82% based on anthrahydroquinone. The separation and the purification of the product were simplified and the capital and operating costs of the whole process could be reduced to a large degree.

It is possible to commercialize Process I in the near future if TS-1 of good performance can be prepared at a large scale. For Process II, it has been proved through this research that the gas-lift loop reactor is suitable for this integrated process. However, it has to deal with a gas–liquid–liquid–solid system and 0.1–0.3 μm TS-1 catalyst. The dispersion of TS-1 catalyst in the complex solvent could be overcome by using a loop reactor. Further research is to investigate the scale up of the loop reactor and to develop a reliable model for such a process.

Acknowledgements

The financial support from The National Natural Science Foundation of China and Sino-Petrochemical Corporation is greatly appreciated (Project No. 29792070). We are grateful to the late Prof. Xien Xu for his special caring for this project.

References

[1] M.G. Clerici, G. Bellussi, EP315248 (1988).
[2] C. Neri, F. Buonomo, EP102097 (1986).
[3] L. Neri, US4833260 (1989).
[4] Kirk-Othmer, Encyclopedia of Chemical Technology, Vol. 13, 3rd Edition, Wiley, New York, 1978, p. 12.
[5] M.G. Clerici, G. Bellussi, EP 526945A1 (1993).
[6] M.G. Clerici, P. Ingallina, EP 549013A1 (1993).
[7] X.K. Meng, PhD Dissertation, Tianjin University, PR China, 1998.
[8] L.S. Fan, Gas–Liquid–Solid Fluidization Engineering, Butterworths, London, 1989.
[9] M.G. Clerici, G. Bellussi, U. Romano, J. Catal. 129 (1991) 159–167.