Keggin-type polyoxotungstate as a catalyst in oxidative dehydrogenation of propane

S.M. Al-Zahrani*, B.Y. Jibril, A.E. Abasaeed

Chemical Engineering Department, College of Engineering, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia

Abstract

The Keggin, $K_3PW_{12}O_{40}$ compound was found to be active as a catalyst in oxidative dehydrogenation of propane. The reaction was conducted at 1 atm, 450–550°C, for a feed flow of 75 cm³/min (propane 20 cm³/min; oxygen 5 cm³/min; and the rest helium). At 450°C the activity was low (1.4% conversion and 52% olefins — propene and ethene — selectivity) while at 550°C the performance was improved (43% conversion and 71% olefins selectivity). The effects of partial pressures of both propane, P_P (0.06–0.53 atm) and oxygen, P_O (0.06–0.33 atm) on the performance of the catalyst were also investigated. A maximum olefins yield of 31% was obtained at 500°C, P_P of 0.53 atm and P_O of 0.13 atm. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Oxidative dehydrogenation; Propane; Propene; Ethene; Keggin-type polyoxotungstate

1. Introduction

There is a general tendency for the petrochemical industry to use more abundant alkanes as raw materials to produce both intermediate and end products. One approach is the conversion of the alkanes into alkenes that may in turn be further reacted. Pyrolysis, thermal and catalytic dehydrogenation of alkanes to alkenes that are currently employed take place at temperatures above 600°C, resulting in high-energy requirements. The high temperature often leads to cracking of the alkanes to coke, thus deactivating the catalyst. These difficulties are minimized in oxidative dehydrogenation reactions. The alkanes are activated at lower temperatures, but still difficult to obtain high yield since both the alkanes and alkenes have tendencies towards further oxidation.

In attempts to improve the reaction, several promising catalytic systems have emerged. The most studied catalysts for the propane conversion are based on vanadium [1–9], vanadium–antimony [10], metal molybdates [11–13] and phosphates [14,15]. So far, all of these catalysts need further studies to understand their structure and improve their performances. Even though vanadium-based catalysts are studied extensively, there is no common conclusion with respect to the selective site. The site was attributed to *ortho*-vanadate [7–9,16], *pyro*-vanadate [3,4] and isolated VO_4 tetrahedra [6,17] by different researchers. Previous attempts to improve V-Mg-O catalyst had not been successful [18]. In a recent report, metals tungstates are believed to be as promising as vanadium-based system [19].

On some of these promising catalysts, a selectivity of 63% was obtained at propane conversion of 7% [20] and high propene yield (23.9%) was obtained at the expense of selectivity (38%) [21]. The reaction tested on other catalytic systems such as metal phosphates [15]

* Corresponding author. Tel.: +966-1-4676-873;
fax: +966-1-4678-770.
E-mail address: szahrani@ksu.edu.sa (S.M. Al-Zahrani).

and molybdates [13] gave maximum propene yield of 15%. This was improved to 16–18% on B-Al-O catalyst [22]. Design of catalysts to give high propene yields at propene selectivities higher than 70%, for instance, is still a challenging task in this area of research [23–25]. Both redox and acidity/basicity properties of the catalyst [26] are among the important factors that are believed to determine the products selectivity in the reaction.

In this study, we focus on a Keggin-type heteropolycompound as a catalyst for oxidative dehydrogenation of propane (POD). The heteropolyacids and their corresponding salts are polycompounds that consist of a unit formed by an anions cage known as Keggin unit [27]. The importance of this unit as a catalyst lies in the concept of site isolation, according to which the catalyst is prepared in such a way as to isolate an element of group 'f' elements that constitute the active center within a matrix of different compositions. This makes it possible to alter the reactivity of the structure. Elements P and Si are usually used as central atom in the unit. The atom is in tetrahedral coordination surrounded by twelve atoms of (in most cases) Mo or W and sometimes other transition metals [27]. Unit cell of Keggin-type catalyst is given elsewhere [28]. The proton of the acid can be replaced by alkaline metals to form salts. The reactivity of Keggin unit could be tailored by introducing different metals (both central and cationic) without altering the crystal structure.

This class of catalysts has a great potential in oxidative dehydrogenation (OXD) reactions because of their unique tunable redox properties. They have high thermal stability under reaction conditions, ease of preparation and modification and available literature about their structure [29]. Previously, they have been tested in both liquid- and gas-phase oxidation reactions of olefins and parafins [30] and in a one-step transformation of isobutane to mixtures of methacrolein and methacrylic acid [31,32]. The catalysts have been highly selective (85%) in hetero-oxidation of methacrolein to methacrylic acid [33] and oxidative dehydrogenation of isobutyric acid to methacrylic acid [34].

Despite its attractive properties there are few examples in the literature of Keggin-type catalysts tested in the oxidative dehydrogenation of lower alkanes [28,35]. This paper reports a preliminary study on the oxidative dehydrogenation of propane tested on a Keggin-type heteropolysalt, $K_3PW_{12}O_{40}$.

2. Experimental

2.1. Catalyst preparation

The Keggin-type polyoxotungstate catalyst was prepared similar to the procedure given elsewhere [29]. The Keggin salt was obtained by precipitation from H_3PO_4 and aqueous solution of Na_2WO_4. A solution of 0.7 pH was achieved by addition of HNO_3, thereafter, KNO_3 was added to obtain a $K_3PW_{12}O_{40}$ (Keggin salt) as a precipitate. The salt was dried and calcined at 450°C in air for 3 h. The catalyst was pressed, crushed and sieved to a particle size of 20–40 mesh before use. A portion (1.4 g) of the sample was used for pore and surface area measurements on Quantachrome Autosorb Automated Gas Adsorption System. The multi-point BET was found to be $0.80 \, m^2/g$, the pore area $0.27 \, m^2/g$ while the micro pore volume was $1.302 \times 10^{-4} \, cm^3/g$.

2.2. Catalysts testing

The catalysts were tested in a fixed-bed, quartz laboratory reactor, operated at atmospheric pressure, temperature range of 450–550°C and a feed flowrate of $75 \, cm^3/min$ (propane $20 \, cm^3/min$; oxygen $5 \, cm^3/min$; and the rest is helium). The gases were high purity, used as obtained from Linde. They were sourced from cylinders at laboratory temperature, passed through micro-filters for additional purification and delivered to the reactor preheat zone by metering through Omega electronic mass flow controllers.

The experimental setup is shown elsewhere [36]. The reactor was 70 mm long quartz tube of 7 mm internal diameter (i.d.) tapered to a 2 mm i.d. to remove the reaction gases from the reaction zone as fast as possible. Thus minimizing possible gas phase reactions. One grams of the 20–40 mesh size particles of the catalyst was placed in the reaction zone of the reactor and supported on quartz wool directly above the junction of the reaction zone with the bottom of the reactor. The temperature of the catalyst bed was monitored by a thermocouple placed on the reactor wall from outside. A temperature controller (Omega) was

used to monitor the temperature. The actual temperature of the catalyst bed was calibrated in a separate experiment using a second thermocouple positioned in the center of the catalyst bed. This is the reaction temperature reported in this work. In each case, the catalyst was pretreated in a stream of a mixture of oxygen and helium for 30 min, at 450°C. Then helium alone was passed for about the same time. Thereafter, the reactant gases (a 75 cm³/min mixture of C_3H_8, O_2 and He) were passed through the reactor at desired reaction temperatures. The same catalyst was tested for 10 h on stream and showed no activity loss.

A gas chromatograph (HP6890) was used for an on line analysis of both the feed and product streams. The products flowed directly through a heat-traced line to the GC sampling valve. The hydrocarbons; CH_4, C_2H_6, C_2H_4, C_3H_8 and C_3H_6 were separated by HP-plot column and analyzed with FID detector, while O_2, CO and CO_2 were separated by MS and Hayesep column and analyzed with a TCD detector. Carbon balances were typically better than 95%.

3. Results and discussion

In all experiments, the major products were propene, ethene and carbon oxides. Conversion (X) and selectivity (S_i) are as defined below. The yield is a mathematical product of conversion and selectivity. The background reactivity of the propane with oxygen was found to be insignificant when measured in a reactor filled with quartz granules of the same amount and mesh size as the actual catalyst at the reaction conditions.

$$X = \frac{n_{Pi} - n_{Po}}{n_{Pi}} \quad \text{and} \quad S_i = \frac{n_i}{n_{Pi} - n_{Po}}$$

where n_{Pi} is the number of moles carbon in inlet propane, n_{Po} is the number of moles of carbon in outlet propane and n_i is the number of moles of carbon in any product i in the exit stream.

The catalytic performance of Keggin, $K_3PW_{12}O_{40}$ compound has been tested for propane oxidative dehydrogenation. The reaction was conducted at 1 atm, 450–550°C, for a feed flow of 75 cm³/min (propane 20 cm³/min; oxygen 5 cm³/min; and the rest helium). The effects of partial pressures of both propane (0.06–0.53 atm) and oxygen (0.06–0.33 atm) on the

performance of the catalysts at 450 and 500°C were also investigated. The main reaction products were C_3H_6, C_2H_4 and CO_x. Fig. 1 shows the effect of temperature on the reaction (for 20 cm³/min propane; and 5 cm³/min oxygen). The catalyst showed increase in activity with temperature. The conversion of both propane and oxygen increased with temperature, with total consumption of oxygen at about 525°C. The decrease in selectivity of C_3H_6 with increase in temperature is accompanied by an increase in C_2H_4 selectivity.

This decrease in propene selectivity could be attributed to a number of factors. One of these factors could be the cleavage of the carbon–carbon bond of the adsorbed propene or propyl species at higher temperatures. Another factor could be the structural modifications of the catalyst at higher temperatures. In addition to these, the number and activity of the active and selective centers might not be constant with temperature changes [37]. The structural modifications might not be expected since the structure of this catalyst was shown to be unaltered even at higher temperatures up to 900°C [29]. Another important possibility is related to the different modes of surface interactions between the catalyst and the gas mixture at higher reaction temperatures which might alter the acid–base character of the catalyst.

The catalyst acid–base character is an important feature that determines the activity and products distribution in the reaction [2,23,26,27]. The decrease in C_3H_6 selectivity was probably due to a decrease in surface acidity with increase in the reaction temperature. If the decrease in the C_3H_6 selectivity was a result of a decrease in acidity, then a similar effect might be caused by introducing a more basic (reducing) environment (i.e. higher propane-to-oxygen ratio). In order to study the effect of surface acidity alone, the experiments were conducted at fixed temperatures of 450 and 500°C. Fig. 2 shows the effect of increase in the propane partial pressure (P_P) in the feed at 450°C and a fixed oxygen partial pressure (P_O) of 0.13 atm. The low activity of the catalyst at 450°C was not enhanced by the increase in P_P. The C_3H_6 selectivity appeared to show a minimum and then increase with P_P. Selectivity of C_2H_4 has shown a little decrease from 22% at 0.13 atm to 15% at 0.53 atm.

In Fig. 3, the effect of P_O is shown. Unlike the case of P_P, increase in P_O showed a slight increase in the C_3H_6 selectivity while the C_2H_4 selectivity exhibited
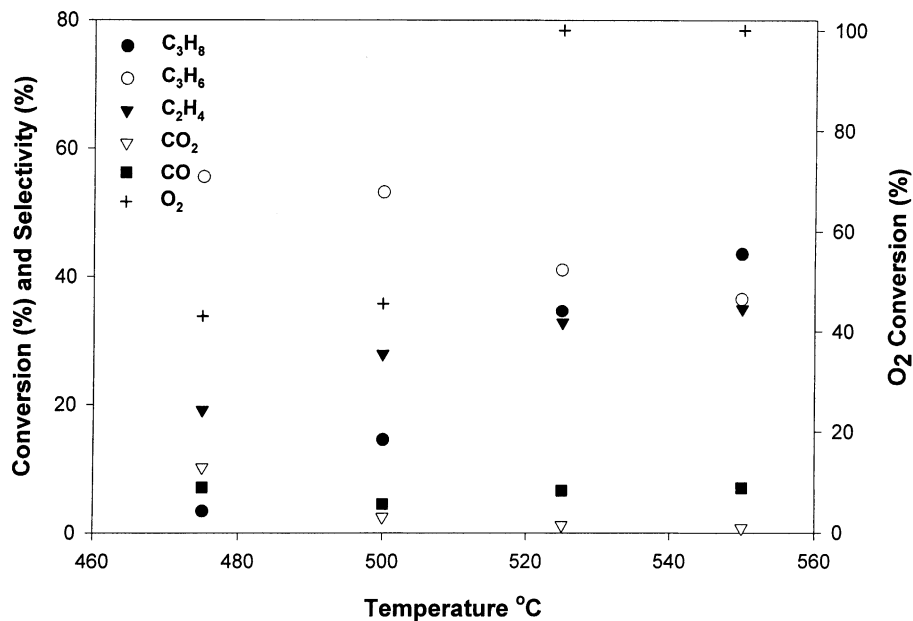
Fig. 1. Propane conversion and products distributions as functions of temperature from 450–550°C at $P_P/P_O = 4$.
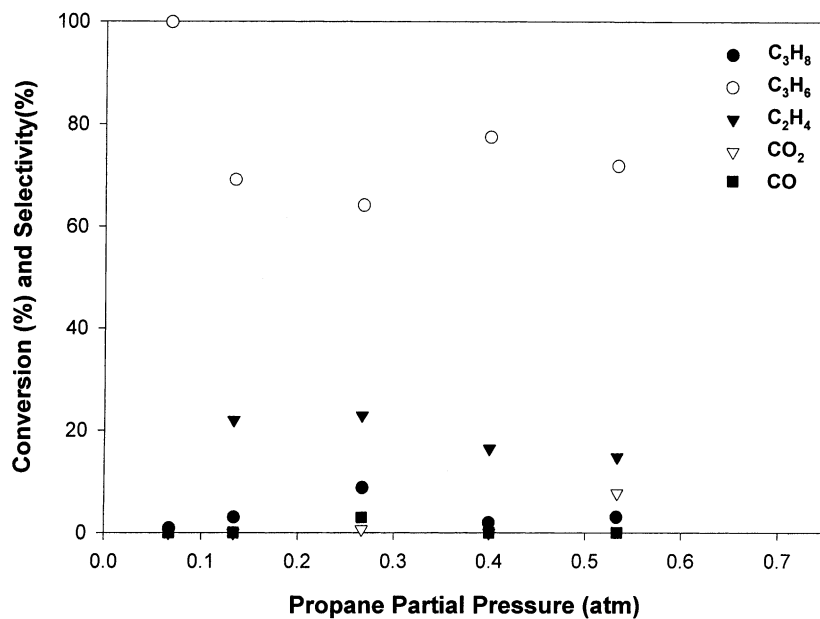

Fig. 2. Propane conversion and products distributions as functions of propane partial pressure at 450°C and oxygen partial pressure of 0.13 atm.
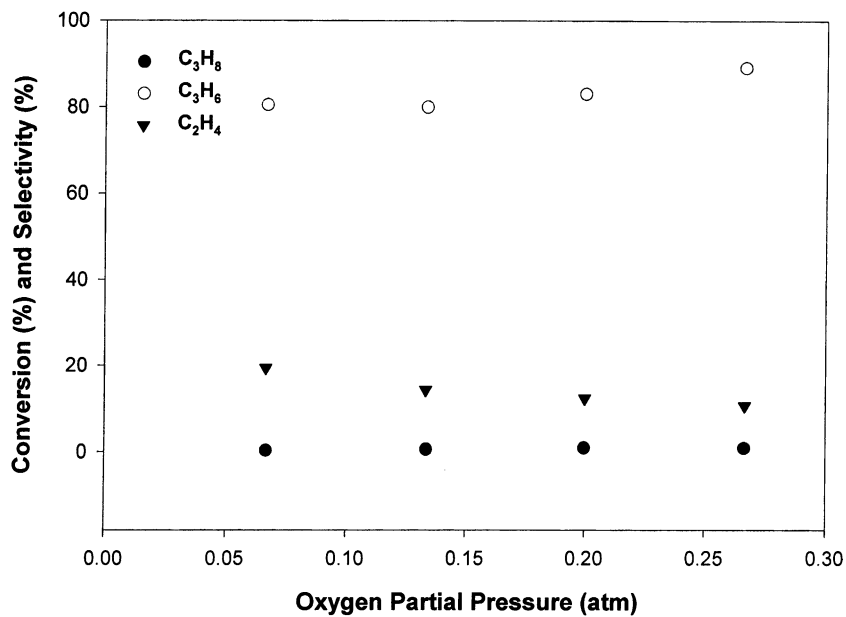
Fig. 3. Propane conversion and products distributions as functions of oxygen partial pressure at 450°C and propane partial pressure of 0.27 atm.
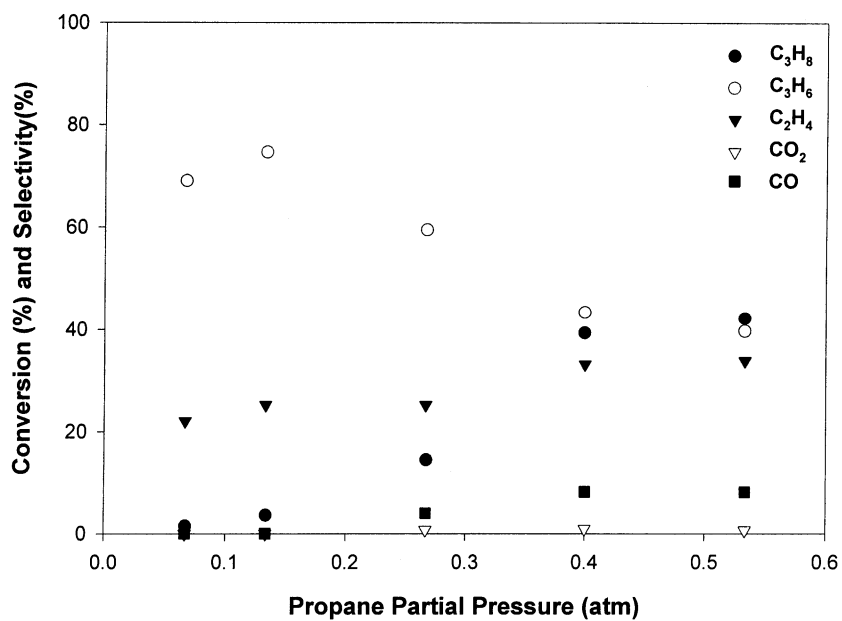

Fig. 4. Propane conversion and products distributions as functions of propane partial pressure at 500°C and oxygen partial pressure of 0.13 atm.
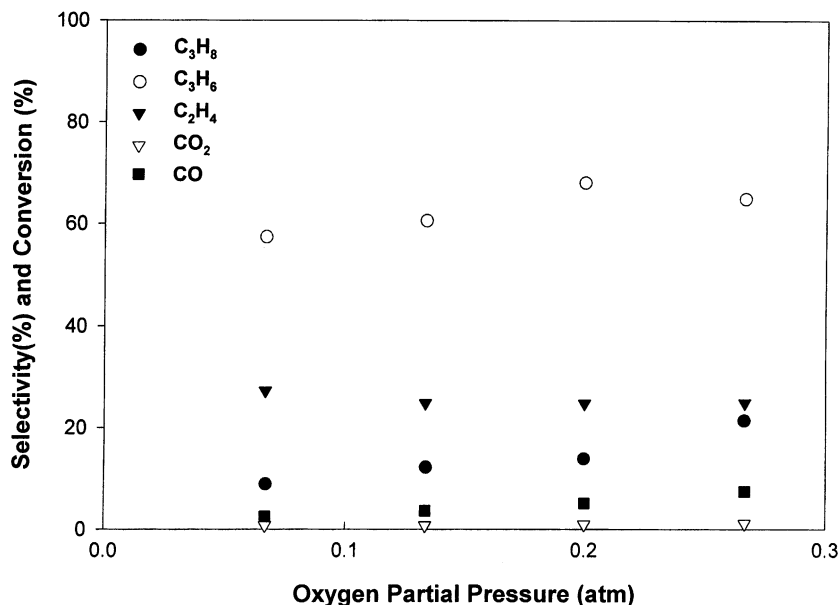
Fig. 5. Propane conversion and products distributions as functions of oxygen partial pressure at 500°C and propane partial pressure of 0.27 atm.

a slight decrease. The orders of rate of production for both C_3H_6 and C_2H_4 are approximately equal to zero with respect to both propane and oxygen at 450°C. It is evident from the figures that higher reaction temperatures are required to elucidate the effect of surface acidity.

As the temperature is increased to 500°C, the effect of P_P was different from the observation in Fig. 2. The C_3H_6 selectivity decreased sharply with increase in P_P, while the C_3H_8 conversion increased as shown in Fig. 4. This shows the interactive effects of temperature and feed compositions. This observation is in line with the discussion in Fig. 1. It suggests that introducing a more reducing (basic) environment (higher propane-to-oxygen ratio) enhanced the activity of the catalyst and selectivity to C_2H_4 and decreased selectivity to C_3H_6. Fig. 5 shows the effect of P_O at 500°C. Along the lines of the above argument, increase in P_O (increase of acidity) showed a slight but observable increase in C_3H_6 selectivity. It increased from 57% at P_O of 0.06 atm to 65% at P_O of 0.26 atm. It appeared that both temperature and/or acid–base character of the catalyst's environment affect the reactivity of its active centers. The effect of surface acidity becomes more pronounced at higher reaction temperatures. It

is interesting to observe that in this study C_2H_4 is favored at low acidity than C_3H_6. Further studies are being conducted to shed more light on the nature of the active centers in the Keggin-type polyoxotungstate in the reaction.

4. Conclusion

The Keggin-type polyoxotungstate, $K_3PW_{12}O_{40}$ compound was found to be active as a catalyst in oxidative dehydrogenation of propane. There was low reactivity (1.4% conversion and 52% olefins selectivity) at 450°C, while at 550°C the performance was improved (43% conversion and 71% olefins selectivity). There was total oxygen consumption at 525°C. The propene selectivity decreases with increase in temperature and/or the acid–base character of the catalyst. The same effect in acid–base character of the catalyst at the surface was induced by varying the feed composition. Increase in propane-to-oxygen ratio (more basic environment) at a fixed reaction temperature showed similar decrease in the C_3H_8 selectivity. The tunable characteristics of Keggin-type catalysts make it particularly interesting for further study.

References

[1] A. Corma, J.M. Lopez Neito, N.J. Paredes, J. Catal. 144 (1993) 425.

[2] H.H. Kung, M.C. Kung, Appl. Catal. A 157 (1997) 105.

[3] D. Siew Hew Sam, V. Soenen, J.C. Volta, J. Catal. 123 (1990) 417.

[4] A. Gurrero-Ruiz, I. Rodriguez-Ramos, J.L.G. Fierro, V. Soenen, J.M. Herrmann, J.V. Volta, New developments in selective oxidation in heterogeneous catalysis, in: P. Ruiz, B. Delmon (Eds.), Studies in Surface Science and Catalysis, Vol. 72, Elsevier, Amsterdam, 1992, p. 203.

[5] L. Owen, H.H. Kung, J. Catal. 148 (1994) 587.

[6] A. Corma, J.M. Lopez, N. Paredes, A. Dejoz, I. Vazquez, New development in selective oxidation, in: V. Cortes Corberan, S. Vic Bellon (Eds.), Proceedings of the 2nd World Congress and 4th European Workshop Meeting, Paper B.4, Malaga, 1993.

[7] A. Corma, J.M. Lopez, N. Paredes, Y. Shen, H. Cao, S.I. Suib, New developments in selective oxidation in heterogeneous catalysis, in: P. Ruiz, B. Delmon (Eds.), Studies in Surface Science and Catalysis, Vol. 72, Elsevier, Amsterdam, 1992, p. 213.

[8] A. Corma, J.M. Lopez, N. Paredes, M. Perez, Appl. Catal. A. 97 (1993) 159.

[9] M.A. Chaar, D. Patel, H.H. Kung, J. Catal. 109 (1988) 463.

[10] F. Cavani, G. Centi, F. Trifiro, R.K. Grasselli, Catal. Today 3 (1988) 185.

[11] Y.C. Kim, W. Ueda, Y. Moro-oka, Catal. Today 13 (1992) 673.

[12] D.L. Stern, R.K. Grasselli, J. Catal. 167 (1997) 550.

[13] C. Mazzocchia, C. Aboumrad, C. Diagne, E. Tempesti, J.M. Herrmann, G. Thomas, Catal. Lett. 10 (1991) 181.

[14] M. Ai, Catal. Today 12 (1992) 679.

[15] Y. Takita, H. Yamashita, K. Moritaka, Chem. Lett. (1989) 1903.

[16] P.M. Michalakos, M.C. Kung, I. Jahan, H.H. Kung, J. Catal. 140 (1993) 226.

[17] P. Concepcion, J.M. Lopez Nieto, J. Perez-Pariente, Catal. Lett. 19 (1993) 333.

[18] R.H.H. Smits, K. Seshan, J.R.H. Ross, Catalytic selective oxidation, in: S.T. Oyama, J.W. Hightower (Eds.), ACS Symp. Ser. 523 (1993).

[19] D.L. Stern, R.K. Grasselli, J. Catal. 167 (1997) 570.

[20] M.C. Kung, H.H. Kung, J. Catal. 134 (1992) 668.

[21] T. Miyazaki, T. Doi, T. Miyamea, I. Matsuura, Stud. Surf. Sci. Catal. 110 (1997) 245.

[22] O.V. Buyevskaya, M. Kubik, M. Bearns, ACS Symp. Ser. 638 (1996) 155.

[23] E.A. Mamemov, V. Cortes Corberan, Appl. Catal. A: Gen. 127 (1995) 1.

[24] T. Blasco, J.M. Lopez Nieto, Appl. Catal. A: Gen. 157 (1997) 117.

[25] M. Bearns, O. Buyevskaya, Catal. Today 45 (1998) 13.

[26] E.A. Mamedov, V. Cortes Corberan, Appl. Catal. A: Gen. 127 (1995) 1.

[27] F. Cavani, F. Trifiro, Appl. Catal. A: Gen. 88 (1992) 115.

[28] B.B. Bardin, R.J. Davis, Appl. Catal. A 185 (1999) 283.

[29] F. Cavani, C. Comuzzi, G. Dolcetti, E. Etienne, R.G. Finke, F. Trifiro, A. Trovarelli, in: Proceedings of the Symposium on Heterogeneous Hydrocarbon Oxidation, Presented Before the Division of Petroleum Chemistry Inc., 211th National Meeting, American Chemical Society, New Orleans, LA, 1996.

[30] M. Misono, Catal. Rev. Sci. Eng. 29 (1987) 269.

[31] F. Cavani, E. Etienne, E. Favaro, M. Galli, F. Trifiro, G. Hecquet, Catal. Lett. 32 (1995) 215.

[32] F. Cavani, F. Trifiro, in: R.K. Grasselli, S.T. Oyama, A.M. Gaffney, J.E. Lyons (Eds.), Proceedings of the 3rd World Congress on Oxidation Catalysis, San Diego, CA, USA, 21–26 September 1998, p. 19.

[33] M. Misono, Catal. Rev. Sci. Eng. 29 (1987) 269.

[34] M.J. Bartoli, L.Monceaux, E. Bordes, G. Hecguet, P. Curtine, New developments in selective oxidation in heterogeneous catalysis, in: P. Ruiz, B. Delmon (Eds.), Studies in Surface Science and Catalysis, Vol 72, Elsevier, Amsterdam, 1992, p. 81.

[35] B.Y. Jibril, S.M. Al-Zahrani, in: Proceedings of the 16th Canadian Symposium on Catalysis, Book of Abstracts, Banff, Alberta, Canada, 23–26 May 2000, p. 82.

[36] S.M. Al-Zahrani, B.Y. Jibril, A.E. Abasaeed, Ind. Eng. Chem. Res. 39 (2000) 4070.

[37] C.N. Satterfield, Heterogeneous Catalysis in Industrial Practice, 2nd Edition, McGraw-Hill, New York, 1991, p. 65.