ELSEVIER

Catalysis Today 45 (1998) 65–71

CATALYSIS TODAY

Investigations on the oxidative dehydrogenation of *n*-butane over VMgO-type catalysts

A.A. Lemonidou*, G.J. Tjatjopoulos, I.A. Vasalos

Department of Chemical Engineering, Aristotle University of Thessaloniki and Chemical Process Engineering Research Institute, PO Box 1517, 54006 Thessaloniki, Greece

Abstract

The oxidative dehydrogenation of *n*-butane was investigated over VMgO mixed oxide and pure magnesium ortho- and pyrovanadate catalysts. The formulation containing 30 wt% V_2O_5 and consisting of the $Mg_3(VO_4)_2$ and MgO crystal phases is more selective than the pure $Mg_3(VO_4)_2$, while the $Mg_2V_2O_7$ phase is the least selective. The selectivity to butenes and butadiene increases with the reaction temperature and the feed molar ratio of butane/oxygen. Addition of water tends to decrease the conversion of butane and enhances the oxydehydrogenation product selectivity. The relative importance of the primary and secondary paths of the reaction network was analyzed by the method of addition of intermediate products. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Oxidative dehydrogenation; N-butane; Vanadium-magnesium oxide catalysts

1. Introduction

Oxidative dehydrogenation of light saturated hydrocarbons is an attractive alternative for the production of more valuable unsaturated hydrocarbons. Considerable research efforts have been made towards the development of catalysts active at low temperature and selective in the formation of alkenes. Most catalysts described in the literature are based on vanadium oxide as the main component as recently reviewed by Mamedov and Cortes Corberan [1]. In particular, much attention has been given by various research groups to VMgO mixed oxide catalysts that exhibit high activity and selectivity for the oxidative dehydrogenation of *n*-butane to butenes and butadiene as well as of propane to propene [2–12]. The nature and function of the active phases in VMgO-type catalysts has been investigated extensively. Chaar et al. [2] claimed that the active phase is $Mg_3(VO_4)_2$ while Siew Hew Sam et al. [4] and Gao et al. [6] proposed that $Mg_2V_2O_7$ was the most selective phase in propane oxydehydrogenation. Recently other researchers stated that biphasic VMgO catalysts exhibited quite different catalytic performances than the pure phases and a cooperation between the phases may exist [5,13]. Pantazidis and Mirodatos [11] claimed that selectivity is little dependent on V content or certain crystal phases while a high dependency of the intrinsic activity on surface composition and structure was observed.

The role of water in the oxidative dehydrogenation of light alkanes has not been elucidated yet. Most researchers agree that the addition of steam to the reacting mixture has a negative effect on the conver-

---

*Corresponding author. E-mail: lemonido@eng.auth.gr

0920-5861/98/$ – see front matter © 1998 Elsevier Science B.V. All rights reserved.
PII: S0920-5861(98)00250-8

sion while, concerning the selectivity, the beneficial or not effect of steam depends on the catalyst and process variables [14–16].

The present work aims at the following three objectives: (1) to study the influence of the various phases of VMgO catalysts (orthovanadate, pyrovanadate and mixed orthovanadate and magnesium oxide) on the *n*-butane oxydehydrogenation, (2) to investigate the effect of various process variables on product selectivities, and (3) to determine the rates of primary and secondary steps with the method of addition of intermediate products.

2. Experimental

The preparation of mixed oxide catalyst comprising 30 wt% V_2O_5 and 70 wt% MgO (30VMgO) has been described before [12]. Pure $Mg_3(VO_4)_2$ was prepared by wet impregnation of MgO (Ganstflot F381) with the appropriate amount of NH_4VO_3 (Merck). After agitation, the suspension was filtered and dried overnight at 120°C. The resulting solid was crushed and calcined in air at 600°C for 40 h. Pure $Mg_2V_2O_7$ was similarly prepared. The chemical composition of the samples was determined by inductively coupled plasma (ICP) technique. Surface areas were measured in a Micromeritics Accusorb 2100 system by nitrogen adsorption according to the BET method. X-ray diffraction was performed on a Siemens D500 diffractometer with Cu K_a radiation.

The experiments were conducted at atmospheric pressure in a conventional microfixed bed apparatus consisting of a flow measurement and control system, a mixing chamber, a quartz reactor and an on line gas chromatographer. The internal diameter of the reactor tube in the catalytic zone was 9 mm. The axial temperature profile was measured using a chromel–alumel thermocouple placed in a thermowell centered in the catalyst bed. The products were analyzed on line by a Varian 3400 chromatographer equipped with a TC detector. Three columns in a series-bypass configuration were used in the analysis: a 20% BEEA-20% DC 200/500, a Porapak N-Chromosorb 106, and a MS 5A. The atomic balances were satisfied with a maximum absolute deviation of less than 2%.

Catalyst evaluation experiments were performed at 500–560°C using 0.1–2 g of catalyst and a constant *n*-butane to oxygen ratio (1/2) unless otherwise stated. The reactant mixture was highly diluted with He (up to 85%) while in the runs conducted in the presence of steam part of He was substituted by steam (20%). In the series of kinetic experiments where the addition of the products (C_4H_8-2, C_4H_6 and CO) to the reactants feed was studied, the temperature was 520°C the catalyst weight 0.1 g and the partial pressures of the butane and oxygen were kept constant at 0.047 and 0.094 atm, respectively. The partial pressures of the added compounds were varied between 0.003–0.012 atm.

3. Results and discussion

The chemical composition, the specific surface areas and the crystal phases of the prepared catalysts are presented in Table 1. The large differences in the surface areas obtained between the mixed oxide catalyst 30VMgO (54 m^2/g) and the two pure magnesium ortho- and pyrovanadates (2 and 3.45 m^2/g, respectively) are attributed to the severe calcination conditions (600°C, 40 h) applied to ensure the formation of certain crystal phases compared to those applied for the mixed oxide sample (600°C, 5 h). X-ray diffraction showed that for mixed 30VMgO catalyst the crystal phases are $Mg_3(VO_4)_2$ and MgO. For the other pure phases with stoichiometric V/Mg proportions the diffractograms obtained, confirm that the ortho- and pyromagnesium vanadates were formed with purities better than 95%.

The catalytic properties of VMgO catalysts during oxidative dehydrogenation of butane are presented in Table 2. As it is clearly shown at 540°C and with $C_4H_{10}/O_2=1/2$, the 30VMgO catalyst is very active with 42% butane conversion and selectivity to dehydrogenating products (C_4H_8 and C_4H_6) up to 55%. These results agree quite well with the data presented

Table 1
Characteristics of the prepared samples

Catalyst	V_2O_5 (wt%)	Crystal phases	Surface area (m^2/g)
30VMgO	30	$Mg_3(VO_4)_2$–MgO	54
$Mg_3(VO_4)_2$	60	$Mg_3(VO_4)_2$	2
$Mg_2V_2O_7$	70	$Mg_2V_2O_7$	3.45

Table 2
Conversion and product selectivity in *n*-butane oxidative dehydrogenation over VMgO catalysts (T_R=540°C, C_4H_{10}/O_2=1/2)

Catalyst	*W* (g)	Conversion (%)		Selectivity (%)			
		C_4H_{10}	O_2	C_4H_8	C_4H_6	C_2+C_3	CO_x
30VMgO	0.02	5.4	7.1	52.6	12.8	1.8	32.8
	0.15	42.0	63.2	23.5	30.9	3.0	42.6
$Mg_3(VO_4)_2$	0.5	4.0	6.5	47.3	6.8	0.5	45.4
	2	10.5	16.2	42.7	11.6	2.9	43.8
$Mg_2V_2O_7$	0.5	4.5	8.5	46.2	5.1	–	48.7
	2	14.9	3.5	32.8	7.8	4.8	54.4

by Chaar et al. [2]. For the $Mg_3(VO_4)_2$ catalyst, at low conversion, the initial selectivity to butenes is slightly lower than that of the catalyst 30VMgO (47.3% versus 52.6%, respectively). Almost the same results are also obtained with the magnesium pyrovanadate catalyst. However, the two pure phases have much lower selectivity to butadiene compared to that of the mixed oxide catalyst. As shown in Table 2 using higher *W*/*F* ratios (increasing the catalyst weight) the activity of the ortho and pyro phases increases, but not significantly, probably due to the very low surface area of the samples. Comparing the selectivities of the two phases, it is clear that there are significant differences in the product distribution. Actually the $Mg_2V_2O_7$ catalyst is less selective than $Mg_3(VO_4)_2$ in dehydrogenation products (selectivity of 40.6% compared to 54.3%).

In order to investigate in more detail the observed differences in selectivity, runs were conducted at 540°C using variable *W*/*F* ratios to get butane conversion in the range up to 20%. The influence of the conversion on the product distribution is depicted in Fig. 1. The two isomers of butenes (butene-1 and butene-2) were plotted in separate graphs. From Fig. 1 it is seen that the initial selectivities of C_4H_8-1, C_4H_8-2 and C_4H_6 are almost the same for the mixed oxide 30VMgO, $Mg_3(VO_4)_2$ and $Mg_2V_2O_7$ catalysts. The differences between the samples are mainly on the rates of further reactions of the primary olefinic products. While the selectivity to C_4H_8-1 decreases with the conversion in the same way for the three catalysts, significant differences are observed in the C_4H_8-2 and C_4H_6 selectivity.

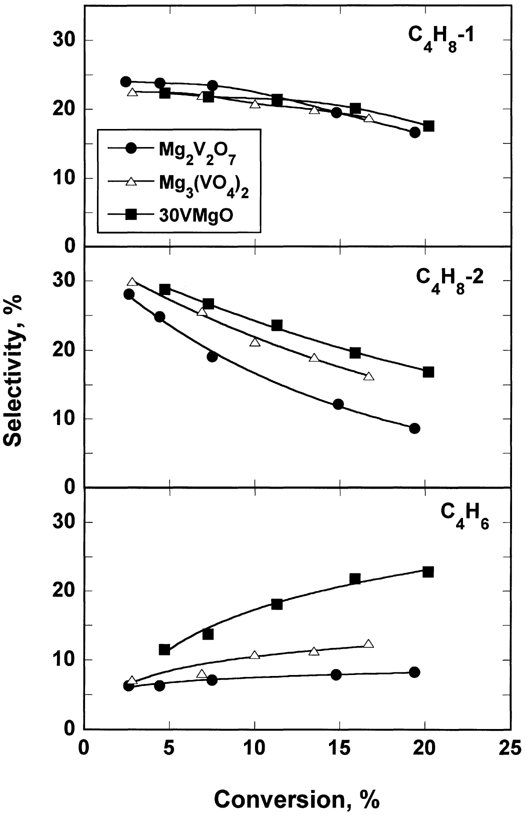

Fig. 1. Selectivity of C_4H_8-1, C_4H_8-2 and C_4H_6 as a function of butane conversion in the presence of mixed oxide 30VMgO, $Mg_3(VO_4)_2$ and $Mg_2V_2O_7$ catalysts (T=540°C, C_4H_{10}/O_2=1/2).

The C_4H_8-2 selectivity decreases more rapidly with the conversion in the presence of $Mg_2V_2O_7$ compared with that of the $Mg_3(VO_4)_2$ and 30VMgO catalysts. The differences in selectivity are much higher in butadiene selectivity. While C_4H_6 selectivity is 23% at 20% butane conversion in the presence of the mixed VMgO, it is only 13% and 6%, respectively, when pure ortho- and pyromagnesium vanadate phases are used. From these results it is clear that the pure ortho and pyro phases are quite selective in the initial formation of alkenes with a small superiority of $Mg_3(VO_4)_2$. As the reaction proceeds it seems that the rates of secondary decomposition of C_4H_8-2 and C_4H_6 are higher resulting in lower selectivities especially over $Mg_2V_2O_7$. The increased rates of decomposition may be attributed to stronger adsorption of these species on acid sites on the surface of $Mg_2V_2O_7$.

Because of the strong adsorption, the consecutive reactions of further oxidation are promoted, leading to a decrease in the selectivity to olefins. Besides, as reported in [1], the acidity of the pyro phase is higher than that of the ortho phase.

Superior catalytic performance with a much higher activity and selectivity is obtained with the catalyst 30VMgO comprising $Mg_3(VO_4)_2$ and MgO phases as presented in Table 2 and Fig. 1. The selectivity to C_4H_8-2 decreases at a lower rate than in the case of $Mg_2V_2O_7$ and $Mg_3(VO_4)_2$ while the C_4H_6 selectivity increases at a higher rate, resulting in a 58% overall alkenes selectivity at 20% conversion. It seems that desorption of intermediates (C_4H_8 and C_4H_6) is faster in the presence of mixed phases than in the presence of pure phases. There may exist a cooperation between the two phases $Mg(VO_4)_2$ and MgO present on the catalyst surface [17]. The higher basicity induced by the presence of MgO on the surface of 30VMgO catalyst facilitates the desorption of alkenes thus prohibiting side reactions. The significance of the role of the acid–base character of catalysts in hydrocarbon partial oxidation reactions has been pointed out in [18]. It is confirmed by this study that coexistence of MgO and $Mg_3(VO_4)_2$ is beneficial for the increased production of butenes and butadiene.

Besides the chemical nature of the catalyst, other process variables such as temperature, feed butane/oxygen ratio and the presence of steam also affect the selectivity of products. In order to determine the conditions where the selectivity to olefins is maximized, experiments were conducted with the 30VMgO catalyst at various temperatures, C_4H_{10}/O_2 ratios and feed steam contents. At a constant butane conversion of 7.5% and C_4H_{10}/O_2 of 1/2 it is evident from Fig. 2(a) that the selectivity to C_4H_8 and C_4H_6 increases with the reaction temperature. The increased selectivity is due to the higher activation energy of formation of alkenes compared to that of carbon oxides [19]. The influence of the C_4H_{10}/O_2 ratio on the product distribution was investigated at 520°C at a constant butane conversion of 5.5%. As it is shown in Fig. 2(b), as the reactant mixture is enriched in oxygen the initial selectivity to C_4H_8 decreases significantly while the selectivity to combustion products increases. The butadiene is much less affected by the oxygen variation. The product selectivities are strongly influenced by increasing levels of oxygen in the feed stream probably because of promotion of nonselective reactions of butenes, further dehydrogenation to butadiene and deep oxidation to CO_x thus leading to C_4H_8 selectivity losses. Therefore, higher reaction temperatures and higher C_4H_{10}/O_2 ratios promote the formation of selective dehydrogenation products.

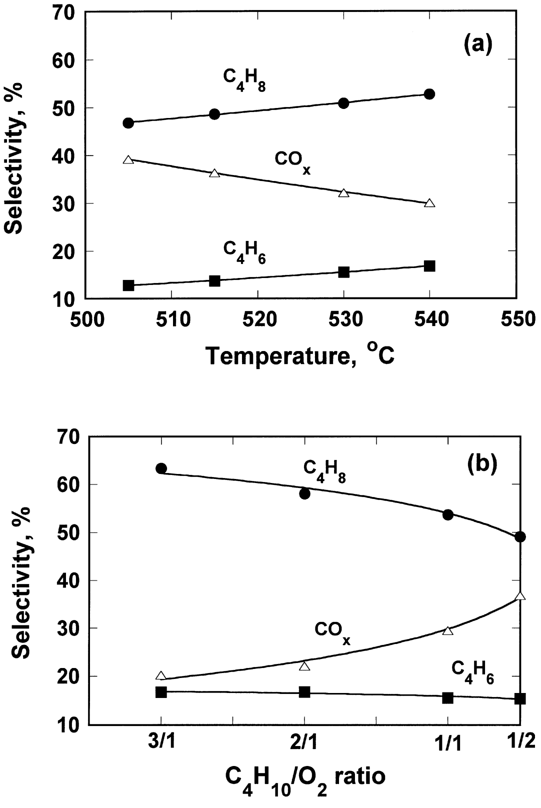

Fig. 2. Effect of reaction temperature (a) and of molar ratio C_4H_{10}/O_2 (b) to the products distribution at constant butane conversion over 30VMgO catalyst: (a) C_4H_{10} conversion 7.5%, $C_4H_{10}/O_2=1/2$; (b) C_4H_{10} conversion 5.5%, $T_R=520°C$.

The effect of water addition to the feed stream was also investigated. The role of water is not yet fully understood. Erdohelyi and Solymosi [14] observed that in partial oxidation of ethane over V_2O_5/SiO_2, the rate of C_2H_6 disappearance decreases by the introduction of water vapor into the reacting mixture. The influence of steam to the oxydehydrogenation of C_2H_6 over various types of ion exchanged zeolite catalysts was found to be strongly dependent on the type of cation and the temperature used in the experiments as reported by Chang et al. [15]. Savary et al. [16] found

Table 3
Oxidative dehydrogenation of *n*-butane over 30VMgO catalyst in the presence and in the absence of steam ($C_4H_{10}/O_2=1/2$, steam 20% on total feed flow)

T_R (°C)	Steam	Conversion (%)		Selectivity (%)			
		C_4H_{10}	O_2	C_4H_8	C_4H_6	C_2+C_3	CO_x
520	N	11.3	20.4	39.0	17.4	2.4	41.2
	Y	8.1	13.2	47.4	10.8	2.8	39.0
540	N	18.6	26.5	34.2	20.1	3.5	42.2
	Y	12.6	21.1	40.1	15.0	4.4	40.5
560	N	35.7	55.8	22.7	23.4	4.5	49.4
	Y	18.1	35.9	34.5	18.7	6.6	40.2

that the addition of water in the feed gas (C_3H_8, O_2) over VPO/TiO_2 catalyst results in lower activity with higher propene selectivity. The higher propene selectivity was attributed to the lower conversion and/or to the increase of Brønsted sites that are linked with propene formation.

The effect of steam addition to the oxydehydrogenation of butane was studied in the temperature range of 500–560°C. Steam was added to the reacting mixture at relative proportion of 20%. The experimental results of steam addition are presented in Table 3 together with results obtained without steam at the same conditions. It is clearly seen that in the presence of steam, the conversion of *n*-butane decreases significantly. This loss of activity is probably due to significant decrease of active sites on the catalyst surface because of adsorption of water molecules. The selectivity to the desired products seems to be affected positively by the presence of steam since it is higher compared to the selectivity of the C_4H_8 and C_4H_6 when no steam is added. The higher olefins selectivity in the presence of steam may be due to the lower conversion level and also to the high degree of hydroxylation of the surface as discussed in [18]. It is also inferred from Table 3 that steam promotes selectively the cracking reactions leading to slightly increased selectivities in C_2H_4 and C_3H_6, especially at higher temperature 560°C. It is worthy to mention that qualitatively similar results were obtained when a lower proportion of steam (10%) was added to the reactants and that the activity of the catalyst was fully restored when the flow of steam was discontinued.

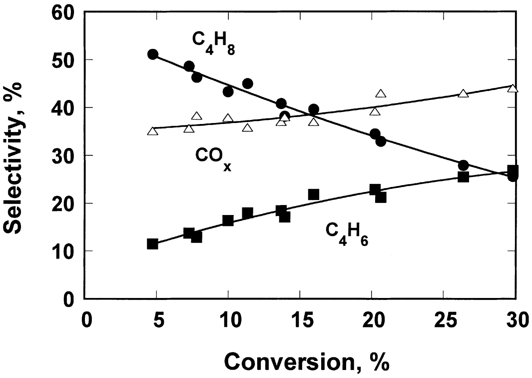

Fig. 3. Product distribution as a function of butane conversion in the presence of 30VMgO catalyst (T=520°C, $C_4H_{10}/O_2=1/2$).

The parameter that mainly affects the distribution of the products is the conversion level. It is well known that conversion and selectivity in oxidation reactions are inversely correlated and as the conversion increases, the selectivity to the desired products decreases. This relation is shown for the 30VMgO catalyst in Fig. 3. At constant temperature of 520°C and $C_4H_{10}/O_2=1/2$ the selectivity to butenes decreases with increasing conversion while the selectivity for butadiene increases. The total dehydrogenation selectivity decreases with the conversion of butane but at a much lower rate. The decline observed in the butenes selectivity is common to all hydrocarbon partial oxidation reactions and results from further dehydrogenation and deep oxidation of the primary dehydrogenation products. It should be pointed out, however, that butadiene and carbon oxides are formed simultaneously with butenes as inferred from Fig. 3. Furthermore, the increase in butadiene and CO_x selectivity with conversion, suggests that these components are also produced via consecutive nonselective paths.

In order to extract more detailed information on the relative importance of the primary and secondary paths of the reaction network, a number of experiments were conducted with the method of addition of products [20] at 520°C under differential conditions. According to the method, small amounts of each of the intermediate products of the reaction, i.e. butenes, butadiene and carbon monoxide, were separately added to the feed mixture and the resulting perturbed product distributions were recorded under steady state conditions. The feed molar flow rates of the added components were sufficiently small so as not to disturb the structure and the intrinsic kinetics of the reaction network (typically, the added molar flow rate was less than 10% of the feed molar flow rates of *n*-butane and oxygen). Moreover, the total pressure, total molar flow rate and the partial pressures of *n*-butane and oxygen were kept constant in all experiments. The experimental data were then analyzed under the assumption that all reaction steps are first-order with respect to the partial pressures of the carbon-containing reactants.

The experiments of CO addition demonstrated the fact that there exists a separate reaction path leading to the formation of CO_2 via deep oxidation of carbon monoxide. It was found that the specific reaction rate of CO oxidation amounts to about 0.13 μmol/g s. The experiments of butadiene addition showed that both CO and CO_2 are simultaneously formed via oxidation of C_4H_6 with intrinsic specific rates of 0.44 and 0.84 μmol/g s, respectively, thus leading to a CO_2/CO ratio of about 2/1. On the other hand, addition of C_4H_8-1 and C_4H_8-2 resulted in the simultaneous formation of butadiene and carbon oxides. In this case the intrinsic specific rates of carbon monoxide and carbon dioxide formation were 0.32 and 0.92 μmol/g s, indicating a molar ratio of $CO_2/CO=3/1$ for this branch of the network. The rate of butenes consumption to butadiene is found to be comparable to the rates of carbon oxides production (about 1 μmol/g s), whereas the relative distribution of C_4H_8-1 and C_4H_8-2 is close to the one predicted on the assumption of thermodynamic equilibrium (ca. 6% relative conversion). Moreover, overall balance calculations indicate that only a small amount of butadiene is formed by direct dehydrogenation of *n*-butane, whereas the rates of CO and CO_2 formation via oxidation of *n*-butane amount to ca. 0.37 and 0.93 μmol/g s, respectively. These results agree very well with the conclusions reached previously [12] on the basis of integral kinetic data over the 30VMgO catalyst, which suggested that, under similar operating conditions, the molar ratio of carbon dioxide-to-carbon monoxide attains values in the narrow range 2.5–3.

The information presented above provides direct evidence that the oxidative dehydrogenation of *n*-butane can be represented by a lumped network of six reactions [12] comprising (1) three parallel primary steps describing the production of butenes, carbon oxides and butadiene from *n*-butane, and (2) three parallel secondary steps describing the formation of butadiene and carbon oxides from butenes, and also the deep oxidation of butadiene to carbon oxides. These conclusions on the structure of the reaction network agree with the work of Patel et al. [3] and Dejoz et al. [19]. In view of the observed narrow range of the CO_2/CO molar ratio, the carbon oxides can be lumped into a single species.

4. Conclusions

The mixed oxide VMgO (30 wt% V_2O_5) formulation exhibits superior catalytic performance as compared to the magnesium ortho- and pyrovanadate pure phases. Although the initial selectivities of the products are almost the same for the mixed oxide and pure phases, it appears that the rates of the nonselective reactions leading to deep oxidation of hydrocarbon species are much higher when pure phases are present, especially with $Mg_2V_2O_7$. A plausible explanation of this behavior is that the coexistence of the basic MgO and $Mg_3(VO_4)_2$ phases favors the desorption of intermediates, thus leading to enhanced selectivities to the desired products in the case of the mixed oxide VMgO catalyst. Higher reaction temperatures and higher butane-to-oxygen feed ratios favor the formation of dehydrogenated compounds. It was also shown that the presence of steam in the feed mixture decreases the conversion of butane probably because of adsorption of water on selective active sites. Experiments with addition of intermediate products revealed useful information on the structure of the reaction network. More specifically, it was shown that carbon oxides are formed through both the primary and secondary reaction paths, i.e. from *n*-butane as well as butenes and butadiene. The latter is mainly formed through dehydrogenation of butenes, and to a lesser extent from *n*-butane.

Acknowledgements

Dr. Lemonidou acknowledges the General Secretariat of Research and Technology, Greece for the financial support. Mrs. A. Stambouli and G. Pazarski are gratefully acknowledged for their assistance in experimental work.

References

[1] E.A. Mamedov, V. Cortes Corberan, Appl. Catal. A 127 (1995) 1.
[2] M.A. Chaar, D. Patel, M.C. Kung, H.H. Kung, J. Catal. 105 (1987) 483.
[3] D. Patel, P.J. Andersen, H.H. Kung, J. Catal. 125 (1990) 132.
[4] D. Siew Hew Sam, V. Soenen, J.C. Volta, J. Catal. 123 (1990) 417.
[5] A. Corma, J.M. Lopez Nieto, N. Paredes, J. Catal. 144 (1993) 425.
[6] X. Gao, P. Ruiz, Q. Xin, X. Guo, B. Delmon, Catal. Lett. 23 (1994) 321.
[7] D. Bhattacharyya, S.K. Bei, M.S. Rao, Appl. Catal. A 87 (1992) 29.
[8] R. Burch, E.M. Crabb, Appl. Catal. A 100 (1993) 111.
[9] R.X. Valenzuela, E.A. Mamedov, V. Cortes Corberan, React. Kinet. Catal. Lett. 55(1) (1995) 213.
[10] D.L. Stern, J.N. Michaels, L. De Caul, R.K. Grassellli, Appl. Catal. A 153 (1997) 21.
[11] A. Pantazidis, C. Mirodatos, ACS Symposium Series 638 (1996) 207.
[12] A.A. Lemonidou, A.E. Stambouli, G.J. Tjatjopoulos, I.A. Vasalos, Proceedings of the First European Congress Chemical Engineering, Florence, Italy, 1997, p. 2997.
[13] X. Gao, P. Ruiz, Q. Xin, X. Guo, B. Delmon, J. Catal. 148 (1994) 56.
[14] A. Erdohelyi, F. Solymosi, J. Catal. 123 (1990) 31.
[15] Y.F. Chang, G.A. Somorjai, H. Heinemann, Appl. Catal. A 96 (1993) 305.
[16] L. Savary, J. Saussey, G. Costentin, M.M. Bettahar, M. Gubelman-Bonneau, J.C. Lavalley, Catal. Today 32 (1996) 57.
[17] A.A. Lemonidou, S. Korili, unpublished results.
[18] H.H. Kung, Ind. Eng. Chem. Prod. Des. Dev. 25 (1986) 171.
[19] A. Dejoz, J.M. Lopez Nieto, F. Malo, J. Vazquez, Ind. Eng. Chem. Res. 36 (1997) 2588.
[20] M. Forissier, D. Foujols, C. Lesselbaum, J.L. Portefaix, Bull. Soc. Chim. France 6 (1985) 1195.