MoO$_3$/MgO as a catalyst in the oxidative dehydrogenation of n-butane in a two-zone fluidized bed reactor

M.L. Pacheco[a], J. Soler[a], A. Dejoz[b], J.M. López Nieto[b],
J. Herguido[a], M. Menéndez[a], J. Santamaría[a,*]

[a] *Departamento de Ingeniería Química y TMA, Universidad de Zaragoza, 50.009 Zaragoza, Spain*
[b] *Instituto de Tecnología Química, UPV-CSIC, Avda los Naranjos s/n, 46.022 Valencia, Spain*

Abstract

Butadiene has been produced from butane by oxidative dehydrogenation on a MoO$_3$/MgO catalyst using a two-zone fluidized bed reactor (TZFBR). The effect of the main TZFBR operating variables was studied, and its performance was compared with that of conventional fluidized beds and fixed bed reactors loaded with the same catalyst. These results have been compared with those obtained on a selective V$_2$O$_5$/MgO catalyst. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Oxidative dehydrogenation; Fluidized bed reactor; n-Butane

1. Introduction

In addition to the development of more selective catalysts, the type of reactor and the mode of contact employed play a key role in selective oxidation processes. In oxidative dehydrogenation (OXDH) of alkanes, it is often found that the reaction takes place using oxygen from the catalyst lattice, and the contribution of gas phase oxygen is generally considered detrimental to selectivity. This has led to reactor designs that attempt (a) to reduce the concentration of gas phase oxygen in the reaction atmosphere (such as porous membrane reactors, see for instance the review in [1]), or (b) to avoid completely the simultaneous presence of hydrocarbons and oxygen over the catalyst. The last concept has been used in circulating bed systems with transfer of reducible catalyst between the reactor and the regenerator, such as those commercially employed for the oxidation of butane to maleic anhydride [2], and

in two-zone fluidized bed reactors previously used in laboratory studies of OXDH processes [3–5].

The two-zone fluidized bed reactor (TZFBR) uses segregated feeds for the oxidant and the hydrocarbon in a single reactor vessel. This allows hydrocarbon oxidation to take place with lattice oxygen in the reduction zone of the bed (above the hydrocarbon inlet) in the absence of gas phase oxygen. The oxygen-depleted (reduced) catalyst is then regenerated (reoxidized) by internal recirculation to the oxidation zone at the bottom part of the reactor where oxygen is fed. This system has proved itself very efficient in the oxidative dehydrogenation of butane [4,5] if a selective catalyst of sufficient redox capacity is employed (V$_2$O$_5$/MgO) and a full segregation of oxidation and reduction zones can be achieved. In other words, the oxygen fed to the reactor must be consumed before reaching the catalyst reduction zone. Under these conditions, butadiene yields up to 200% higher than those obtained in a conventional fluidized bed reactor have been reported [5].

---

* Corresponding author.

The aim of this work is to apply the TZFBR for the production of butadiene in catalytic systems different from V_2O_5/MgO. Vrieland and Murchison [6] reported that a MoO_3 catalyst dispersed on MgO provided 40–50% conversion of *n*-butane at 80% selectivity to butadiene and butenes when exposed to 5–10 s pulses of *n*-butane followed by air regeneration. This makes it an obvious candidate for operation in the TZFBR.

2. Experimental

2.1. Catalyst preparation

The MoO_3/MgO catalyst was prepared by impregnation of MgO with an aqueous ammonium heptamolybdate solution, following the method described by Vrieland and Murchison [6]. The sample was stirred at 80°C for 3 h, dried at 150°C overnight and then calcined at 600°C for 4 h. Chemical analysis of Mo and Mg showed a Mo content of 17.8 wt.% of MoO_3. The powder was pelletized, ground and sieved to the desired size range (100–250 μm).

2.2. Catalyst characterization

The elementary analysis of catalyst samples was carried out in a Perkin-Elmer P-40 apparatus by plasma analysis (ICP). BET surface areas were determined using N_2/He mixtures in a Micromeritics Pulse Chemisorb 2700 apparatus. X-ray diffraction (XRD) patterns were collected in a Philips 1060 diffractometer equipped with graphite monochromator operating at 40 kV and 40 mA and using nickel-filtered Cu Kα radiation ($\lambda=0.1542$ nm). Temperature-programmed reduction (TPR) results were obtained in a Micromeritics apparatus. To this end, 10 mg samples were contacted with a H_2/Ar mixture (50 ml min^{-1}) and heated at a rate of 10°C min^{-1} to a final temperature of 850°C.

The kinetic tests for catalyst reoxidation were carried out in a fixed bed differential reactor (75 mg of catalyst) using samples previously reduced at different temperatures under 50 ml min^{-1} of a mixture containing 10% H_2 in N_2. Reoxidation was then carried out by shifting the feed to a O_2/N_2 gas stream with the same flow rate using a 4-way valve. Different oxygen concentrations were used, and the oxygen signal at the reactor exit was continuously monitored using an on-line HIDEN HAL 2/201 quadrupole mass spectrometer until a constant oxygen concentration was reached.

The kinetic tests for catalyst reduction were carried out on 150 mg samples using a CI Electronics thermobalance. The procedure was similar: The sample was oxidized for 15 min using a gas stream (11.7 Nml s^{-1}) containing 15% O_2 in N_2 followed by reduction under a H_2/N_2 stream with different partial pressures of hydrogen.

2.3. Catalytic tests

The TZFBR used for oxidative dehydrogenation of propane has been described previously [5]. The reactor was of 30 mm i.d., 25 cm long quartz tube equipped with a quartz distributor plate (for the He/O_2 mixture) and a movable axial quartz probe (butane inlet). A second movable quartz probe also located approximately along the reactor axis was used to take samples at different bed heights. The main operating variables studied were the bed temperature (T), the relative velocity ($u_r=u/u_{mf}$), the percentage of butane in the reactor feed (P_h), the oxygen/butane ratio (R_{oh}), the total height of catalyst in the bed (H), and the height at which the hydrocarbon was introduced (h_h). Table 1 shows the reference values used in the study. The size fraction between 100 and 250 mm had a minimum fluidization velocity (He, 550°C) of 0.63 cm s^{-1} (0.61 cm s^{-1} with air at 25°C). During the catalytic run (84 h), about 20% of the original catalyst weight was discarded as out-of-range fines due to catalyst attrition in the fluidized bed.

The performance of the TZFBR has also been compared with that of a conventional fluidized bed reactor

Table 1
Reference conditions for the experimental study

Variable	Reference value	Range studied
T	600°C	525–600°C
u_r	1.5 (112 N cm^3 min^{-1})	1.2–2.5
P_h	4%	–
R_{oh}	2	0.5–4.0
H	11 cm (34 g catalyst)	–
h_h	7 cm	–

(CFBR) and a fixed bed reactor. In CFBR operation the same reactor was used, but different gases (butane, oxygen, helium) were premixed and fed through the quartz distributor. For the experiments in the fixed bed, a continuous flow, stainless steel tubular reactor (i.d. 20 mm, length 520 mm) was used. The feed consisted of a mixture of *n*-butane, oxygen and helium with a molar ratio of 4:8:88. The total flow rate of reactants was varied in order to achieve different contact times.

3. Results and discussion

Fig. 1 shows the XRD patterns for both fresh and used catalysts. $MgMoO_4$ ($2\theta=23$ and 26) and MgO ($2\theta=43$ and 37) are the main crystalline phases in both cases, although $MgMoO_4$ is barely discernible in the fresh catalyst. The crystallinity of the used catalyst is higher, indicating an increase of crystal size. This is in agreement with the loss of surface area observed in used catalyst. Thus, while the fresh catalyst had a BET surface area of $42.5\,m^2\,g^{-1}$, the area of the catalyst used for 84 h decreased to $31.9\,m^2\,g^{-1}$.

The TPR results for the fresh and used catalysts are shown in Fig. 2, where the TPR diagram of the V_2O_5/MgO catalyst [4,5] is also shown for comparison. The MoO_3/MgO catalyst displays reduction temperatures between 110 and 140°C higher than V_2O_5/MgO. Although similar patterns were observed on both fresh and used MoO_3/MgO samples, a slight displacement of the main reduction peak towards higher temperatures was observed in used catalyst.
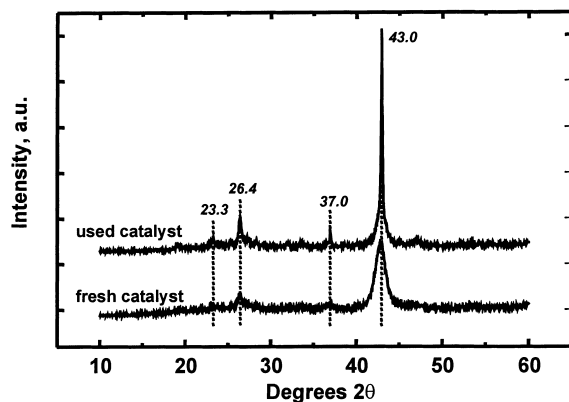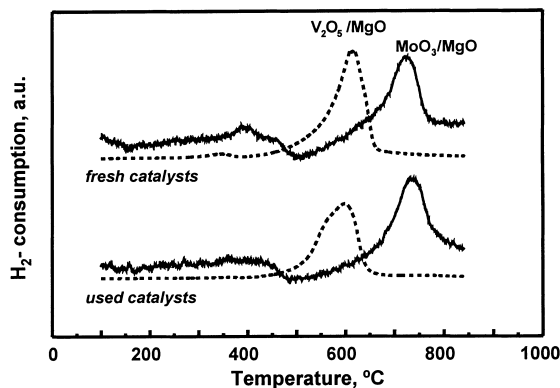

Fig. 2. TPR diagrams of fresh and used MoO_3/MgO and V_2O_5/MgO catalysts.

This is probably due to some sintering of the $MgMoO_4$ (as observed by XRD and BET area) since due to diffusional resistance, larger crystals need more time for reduction, this is interpreted as a higher reduction temperature in TPR diagrams.

Fig. 3 shows the evolution of the oxidation or reduction degree with the time on stream during the reduction or reoxidation at 550°C with several reactant (H_2 or O_2, respectively) partial pressures. The time required to attain a certain degree of reduction is about two orders of magnitude higher than the time required attaining the same degree of reoxidation. Thus, the kinetic tests for oxidation and reduction of MoO_3/MgO indicate that the reduction stage is slower, and therefore kinetically controlling in the
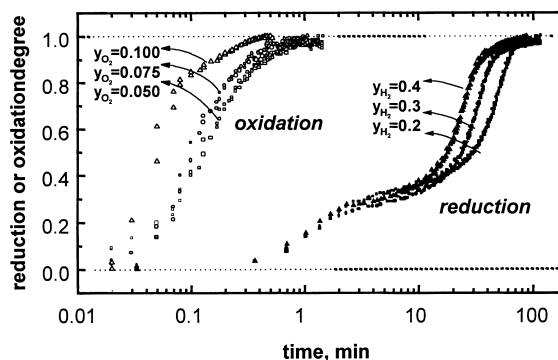

Fig. 1. XRD patterns for fresh and used MoO_3/MgO catalysts.

Fig. 3. Variation of the reduction (or reoxidation) degree of MoO_3/MgO catalyst with the time on stream under different hydrogen (or oxygen) partial pressures and 550°C.
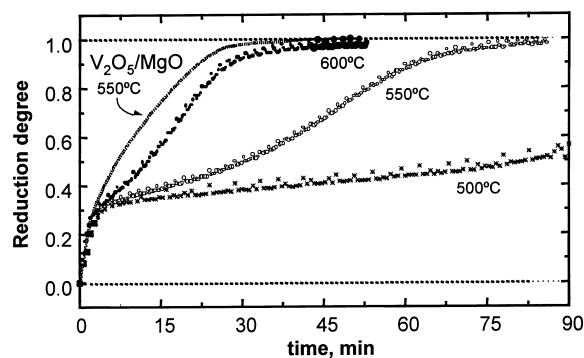
Fig. 4. Variation of the degree of reduction of MoO_3/MgO catalyst with the time on stream at different temperatures under 20 kPa of H_2. The corresponding curve for V_2O_5/MgO at 550°C is also shown for comparison.

Table 2
Butane conversion and product distribution under the reference conditions of Table 1 (time on stream of 120 min)

O_2/C_4H_{10}[a]	X-C_4H_{10}[b]	S-C_4H_6[c]	S-C_4[d]	S-CO_x[e]	S_{others}[f]
Cofeed mode					
0.5	43.0	24.9	58.2	24.8	17.0
1.0	57.4	19.9	53.5	31.1	15.4
2.0	72.5	12.7	33.7	55.6	10.7
3.0	83.0	8.4	19.9	72.8	7.3
4.0	92.4	7.1	11.7	82.8	5.5
Separate feeds					
0.5	31.5	38.0	65.8	22.4	11.8
1.0	42.3	41.1	61.1	30.7	8.2
2.0	68.7	43.0	49.4	45.6	5.0
3.0	75.4	19.9	23.5	71.3	5.2
4.0	80.6	11.4	14.3	80.5	5.2

[a] O_2/C_4H_{10} molar ratio.
[b] Butane conversion.
[c] Selectivity to butadiene.
[d] Selectivity to C_4-olefins (1-butene, 2-butene, and butadiene).
[e] Selectivity to CO and CO_2.
[f] Selectivity to C_1, C_2, and C_3 hydrocarbons.

overall oxidation/reduction cycle. It may be noticed that the experiments were carried out using H_2 instead of butane to avoid problems of coke deposition on the catalyst. However this conclusion (i.e. that catalyst reduction is the controlling step) stands since H_2 is a more powerful reducing agent than butane.

We must notice that the rate of reduction in MoO_3/MgO is also considerably lower than that observed for V_2O_5/MgO under comparable reduction conditions [7]. This is consistent with the TPR results in Fig. 2 where it can be seen that very little catalyst reduction of Mo-sites takes place at 550°C. Fig. 4 shows the MoO_3/MgO reduction curves for different temperatures at a fixed hydrogen partial pressure. From a comparative purpose, the reduction of V_2O_5/MgO at 550°C and the same hydrogen partial pressure is also shown. It can be seen that only at 600°C, the degree of reduction obtained with MoO_3/MgO approaches the reduction curve of V_2O_5/MgO at 550°C. Thus, the experiments in the TZFBR with MoO_3/MgO catalyst were therefore carried out at 600°C.

Table 2 shows the results obtained in the TZFBR after 2 h of operation with fresh catalyst under different oxygen/hydrocarbon ratios (R_{oh}), other conditions as in Table 1. It can be seen that in the CFBR (cofeed mode), butane conversions are higher due to the fact that oxygen and butane are premixed and supplied at the bed entrance. However, the increase in conversion is accompanied by a decrease in the selectivity to dehydrogenation products in general, and in particular to butadiene. In the TZFBR (separate feed

mode), the lower butane conversion is compensated by a higher selectivity. The maximum yields to total dehydrogenation products and to butadiene (the most valuable product) obtained in the CFBR at $R_{oh}=1.0$ were 27.5 and 11.4%, respectively. This compares with yields of 33.9 and 29.5, respectively, in the TZFBR obtained at $R_{oh}=2.0$. It is interesting to note that in the TZFBR, both the conversion and the selectivity to butadiene increase with R_{oh} up to $R_{oh}=2$. As will be shown next, this is due to the fact that for $R_{oh}=2$ and lower, an effective separation of oxidation and reduction zones is achieved, i.e. the oxygen fed to the reactor is consumed below the butane inlet.

Fig. 5 shows the oxygen and hydrocarbon concentration profiles along the bed. For $R_{oh}=0.5$, there is a clear segregation of butane and oxygen: oxygen disappears from the gas phase at least 2 cm (or 18% of reactor volume) before the butane inlet. As R_{oh} increases while other operating conditions are maintained, the amount of oxygen available in the reoxidation zone increases, and zone separation becomes less distinct. The limit occurs at $R_{oh}=2$ (Fig. 5), where overlapping of the oxygen and hydrocarbon-containing zones is incipient. At $R_{oh}=4$, butane and oxygen coexist in the gas phase throughout the bed, which causes the drop in selectivity shown in Table 2. The maximum in the
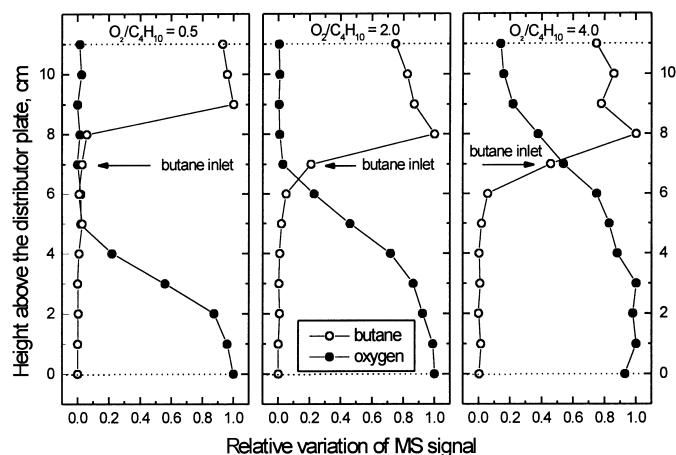
Fig. 5. Oxygen (●) and n-butane (○) concentration profiles for different R_{oh} values. Other conditions as in Table 1.

yield to butadiene takes place precisely at $R_{oh}=2$ with a sharp decrease for higher values of R_{oh} as can be seen in Fig. 6. This figure also shows that the variation of butadiene yield with R_{oh} is comparable to that obtained with V_2O_5/MgO at 550°C [5], other conditions being the same. This indicates the role of the reduction stage in the overall catalytic performance, since as shown in Fig. 4 the reduction rates of V_2O_5/MgO at 550°C are similar to those obtained for MoO_3/MgO at 600°C.

Fig. 7 compares the performance of the TZFBR with that of the CFBR and the fixed bed reactor loaded with the same catalyst. It can be seen that the TZFBR always gives a higher selectivity for the same conversion, while the selectivity–conversion plots of the CFBR and the fixed bed reactor follow the same trend. This shows the benefits of the segregation of the oxidation and reduction zones for this system. This was already shown by the experiments of Vrieland and Murchison [6], who used segregation in time (pulse experiments) instead of segregation in space, but the TZFBR results demonstrate that it is also possible to obtain continuous operation while avoiding the simultaneous presence of oxygen and hydrocarbons in the gas phase.

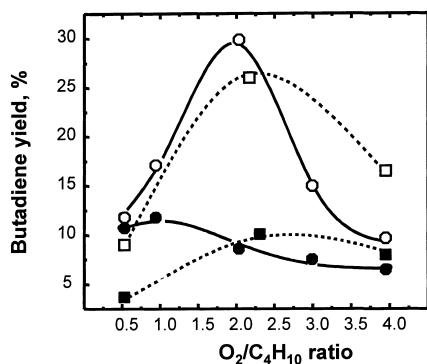Fig. 8 summarizes the catalytic results obtained on MoO_3/MgO catalyst in the three types of reac-

Fig. 6. Variation of the yield of butadiene with the O_2/butane ratio for the TZFBR (○, □) and the CFBR (●, ■) reactors on MoO_3/MgO catalyst at 600°C (○, ●) and on V_2O_5/MgO catalyst at 550°C (□, ■).
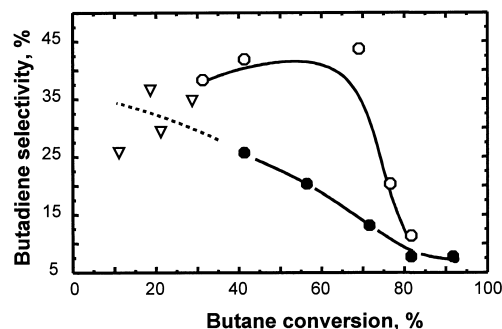

Fig. 7. Variation of the selectivity to butadiene with the n-butane conversion for the three types of reactor obtained during the OXDH of n-butane on MoO_3/MgO at 600°C: TZFBR (○); CFBR (●); fixed bed (▽).
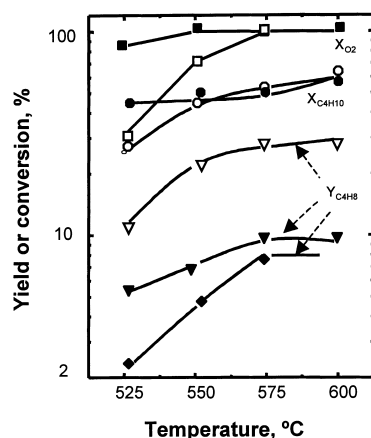
Fig. 8. Variation of the conversion of n-butane ($\bigcirc$, $\bullet$) and oxygen ($\square$, $\blacksquare$) and the yield to butadiene ($\blacktriangledown$, $\triangledown$, $\blacklozenge$) with the reaction temperature for the three types of reactor used in this work: TZFBR ($\bigcirc$, $\square$, $\triangledown$); CFBR ($\bullet$, $\blacksquare$, $\blacktriangledown$); fixed bed ($\blacklozenge$).

tor as a function of temperature. At temperatures below 575°C, oxidation and reduction processes in the TZFBR are slow, and zone segregation does not take place under the conditions given in Table 1. In this case, it can be seen that, even under those conditions, the butadiene yield is higher to that obtained in the CFBR, i.e. the lower butane conversion is compensated with a higher selectivity to butadiene.

At temperatures of 575°C and above, zone separation is achieved. In this case, similar butane conversions are achieved in both reactors, although a better selectivity to butadiene is obtained in the TZFBR. Thus, more than double of butadiene yields is obtained at 600°C in the TZFBR.

Catalyst deactivation was the main problem observed with the use of MoO$_3$/MgO in the TZFBR. This can be related to catalyst sintering as indicated by the higher crystallinity of the main crystalline phases (XRD analysis of the used catalyst) and the loss of catalyst surface area (25% of the initial BET area is lost after 84 h of use). The evolution of both the *n*-butane conversion and the selectivity to the main reaction products with the time on stream is given in Fig. 9. It can be seen that not only the butane conversion but also the selectivity to dehydrogenation products decreases with the time on stream. Thus, amorphous and highly dispersed MgMoO$_4$ on the surface of MgO could be the active and selective catalyst in the system studied.
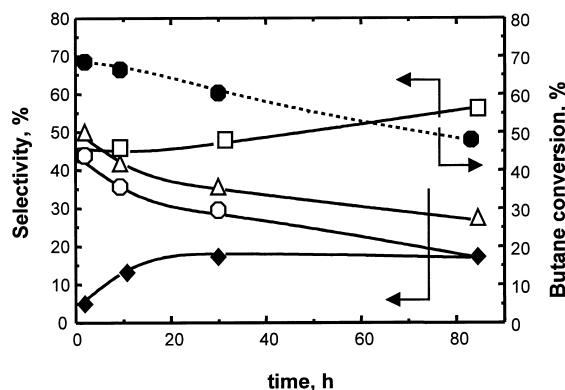

Fig. 9. Variation of the conversion of *n*-butane and the selectivity to the main reaction products with time on stream in the TZFBR. Experimental conditions as in Table 1. Symbols: *n*-butane conversion ($\bullet$); selectivity to C$_4$-olefins ($\triangledown$); butadiene ($\bigcirc$); CO$_x$ ($\square$) and others ($\blacklozenge$).

Similar models have been proposed for V$_2$O$_5$/MgO catalysts [8–10].

In summary, the principle of zone segregation works well with MoO$_3$/MgO catalysts, giving a clearly better performance with respect to both conventional fluidized bed and fixed bed reactors. However, V$_2$O$_5$/MgO seems to be a superior catalyst for oxidative dehydrogenation of butane in the TZFBR. It showed a stable behaviour over the range of conditions investigated, and its performance at 550°C was comparable to that of the MoO$_3$/MgO catalyst operated at 600°C.

Acknowledgements

References

[1] J. Coronas, J. Santamaría, Catal. Today 51 (1999) 377.
[2] R.M. Contractor, D.I. Garnett, H.S. Horowitz, H.E. Bergna, G.S. Patience, J.T. Schwartz, G.M. Sisler, Stud. Surf. Sci. Catal. 82 (1994) 233.
[3] R. Ramos, J. Herguido, M. Menéndez, J. Santamaría, J. Catal. 163 (1996) 218.
[4] J. Soler, J.M. López Nieto, J. Herguido, M. Menéndez, J. Santamaría, Catal. Lett. 50 (1998) 25.

[5] J. Soler, J.M. López Nieto, J. Herguido, M. Menéndez, J. Santamaría, Ind. Eng. Chem. Res. 38 (1999) 90.

[6] G.E. Vrieland, C.B. Murchison, Appl. Catal. A 134 (1996) 101.

[7] J.M. López Nieto, J. Soler, P. Concepción, J. Herguido, M. Menéndez, J. Santamaría, J. Catal. 185 (1999) 324.

[8] A. Corma, J.M. López Nieto, N. Paredes, J. Catal. 144 (1993) 425.

[9] X. Gao, P. Ruiz, Q. Xin, X. Guo, B. Delmon, J. Catal. 148 (1994) 56.

[10] A. Pantazidis, A. Burrows, C.J. Kiely, C. Mirodatos, J. Catal. 177 (1998) 325.