Iranian Journal of Organic Chemistry Vol. 2, No. 1 (2010) 320-326

IranJOC
Iranian Journal of
Organic Chemistry

Synthesis and characterization of VPO catalysts with the different ratio of P/V in organic medium for partial oxidation of n-butane to maleic anhydride

M. R. Tousi,[a*] V. Mahdavi[b]
[a]*Department of Chemistry, Islamic Azad University, Ghaemshahr Branch, Ghaemshahr, Iran*
[b]*Department of Chemistry, Faculty of Science, University of Arak, Arak, Iran*

Abstract: In this paper, vanadium phosphorus oxide (VPO) catalysts were synthesized with the different P/V ratio (0.5, 1.0, and 2.0) in organic medium. The structure of catalysts were characterized by XRD, SEM, AA, and BET instruments. The activity and selectivity of those synthesized VPO catalysts were investigated with partial oxidation of *n*-butane to maleic anhydride.

Keywords: VPO catalyst; Vanadium; Butane; Maleic anhydride; Partial Oxidation.

Introduction

The world demand for maleic anhydride (MA) has been increased because it is widely used for production of unsaturated polyesters, succinic anhydride, maleic acid, 1, 4-butanediol, THF, and butirolactone. Moreover, it is used as an additive of lubricant oils in food and pharmaceutical industries. Historically, MA was prepared by oxidation of benzene over V_2O_3–MoO_3 catalysts with a good selectivity. This process, however, was limited in 1970's due to the environmental problems of benzene consumption and replaced by oxidation of light alkanes such as n-butane. Vanadium phosphorus oxide (VPO) catalysts with vanadyl pyrophosphate [$(VO)_2P_2O_7$] as the major component (VPP) are effective for the oxidation of n-butane to maleic anhydride [1]. In recent year, many studies have been reported the results of catalytic activity of VPO catalysts supported on the different materials such as SiO_2, TiO_2, Al_2O_3, MCM-41, and SBA-15 [2-7].

Some papers have investigated the effect of promoters on the activity of VPO [8, 9]. The aim of these articles was the enhancement of activity or selectivity of VPO catalyst for increasing MA production. There are two general methods for preparation of VPO catalysts according to the type of medium used for catalyst synthesis: aqueous and organic. A number of aqueous synthesis methods are such as impregnation of aqueous solution of $VO(H_2PO_4)_2$ [10], aqueous solution of V(III) and phosphoric acid [11], vanadium oxalate [12], and ammonium metavanadate [13]. It is generally accepted that VPO catalysts prepared in an organic medium have better structure for catalytic oxidation of n-butane [14]. In this way, isobutanol and benzyl alcohol usually has been used as a solvent [15-17].

It has been found that the P/V atomic ratio plays an important role in the reaction over VPO catalysts [18]. However, there is a lack of the clear discussion about the structure of these catalysts and details of the conversion in different condition. In the present study we have prepared VPO catalysts with the different P/V ratio in organic medium and developed previous data about the catalytic activity of them for MA production. Moreover, we have investigated some instrumental analysis of VPO catalysts for the relation of catalytic structure and the activity, based on the obtained results.

Results and discussion

Characterization

Table 1 shows the details of BET and AA measurements of the catalysts. It can be seen that the surface area of the catalyst increases by increasing the P/V ratio. Maximum ratio of P/V in the bulk of catalyst is 1.12 while this ratio in the solution is 2.0.

---

*Corresponding author. Fax: +(98) 123 2240090; Tel.: +(98) 123 2244111 E-mail: *mrtoosi@gmail.com*

XRD patterns of three catalysts are shown in figure 1. The crystallinity of VPO-0.5 is lower than other catalyst. By increasing the P/V ratio, the crystallinity increases. In figure 2, the pattern of XRD for non-calcinated catalyst represents the phase of $VOHPO_4.0.5H_2O$ with the orthorhombic structure [19]. After calcinations, the XRD pattern represents that the main phase is $(VO)_2P_2O_7$ [204-mahdavi] with the small amount of $VOPO_4$ phase. Therefore, the oxidation state of V^{+4} is predominant after calcination. Mechanism of its formation is the reduction of vanadium alkylate by organic solvent (isobutanol and benzyl alcohol) which is convert to the $VOHPO_4.0.5H_2O$ after reaction with H_3PO_4. This is also observed in figure 3 for VPO-2 but the $VOPO_4$ phase does not exist in this pattern.

The SEM micrographs of the catalysts are shown in figure 2. It can be seen that by varying the P/V ratio, the morphology of the catalyst changes. The shape of VPO-0.5 crystal is platelet, while the VPO-1 and VPO-2 catalysts contain the particles without any identified shape.

Table 1. Analysis results of the prepared catalysts.

Catalyst	P/V in solution	P/Vin catalyst[a]	BET($m^2.g^{-1}$)[b]
VPO-0.5	0.5	0.47	3.4
VPO-1	1.0	0.94	4.2
VPO-2	2.0	1.12	4.5

[a] From AA analysis

[b] From N_2 adsorption measurements

Figure 1. XRD pattern of VPO catalysts, A: before calcination, B: after calcination.

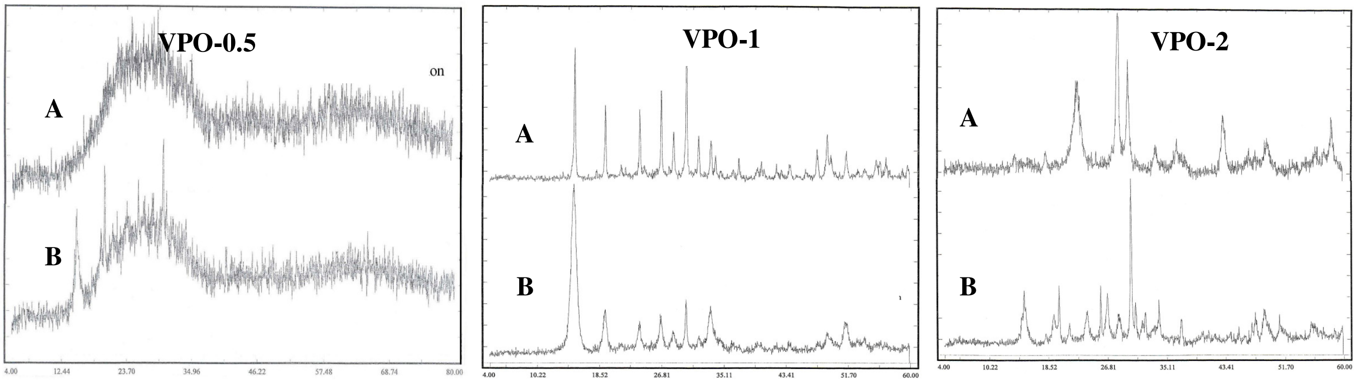
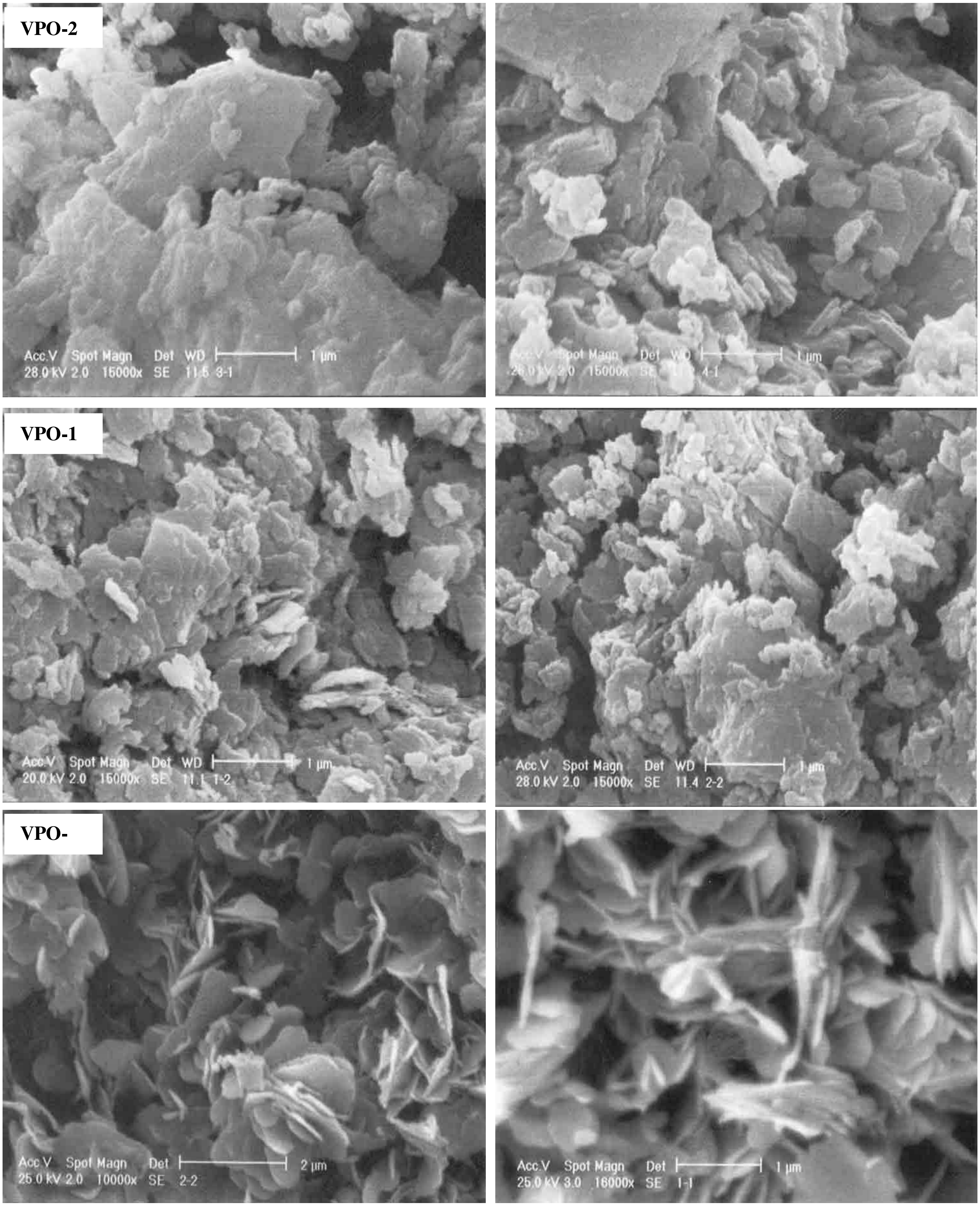


Figure 2. SEM micrographs of the prepared catalysts, before calcination (left) and after it (right).



Conversion and selectivity

Figure 3 shows the results of MA selectivity and conversion of the reaction at the different GHSV (Gas Hourly Space Velocity). It isobserved that at the low conversion of *n*-butane (lower temperature) the reaction is not sensitive to the GHSV. However, in the higher conversion (at higher temperature), by rising GHSV, the MA selectivity decreases, especially for VPO-0.5 catalyst.

Figure 3. Activity and selectivity of the catalysts at the different amount of GHSV.

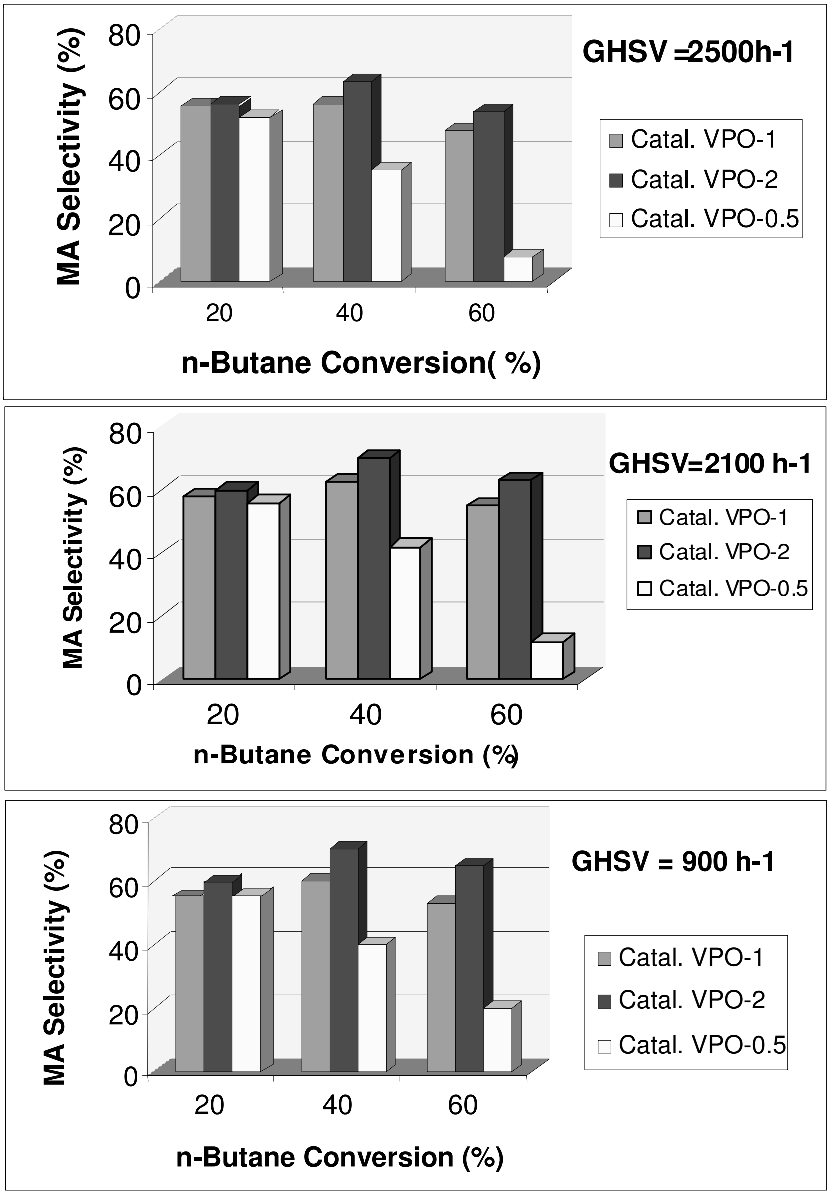


Table 2 shows the results of conversion and selectivity for n-C_4 oxidation over VPO-0.5. The conversion of reaction increases by rising the temperature. However, the MA selectivity decreases. Maximum of selectivity for MA is 60% at the temperature of 335°C. At the higher temperature, the selectivity of CO_x (the product of total oxidation) increases. From results obtained for yield of reaction (yield for MA = conversion × MA selectivity), it can be seen that the maximum yield of MA production is 17.49 at 380°C.

Table 2. Details of n-butane partial oxidation over VPO-0.5 catalyst. (GHSV=2100 h^{-1} and P=1.0 atm)

Temperature (^{o}C)	Conversion (%)	S_{MA} (%)	$S_{CO2 + CO}$ (%)	Yield (%)
335	7	51	49	35.7
360	17	60	40	10.2
380	33	53	47	17.49
410	38	46	54	17.48
430	42	41	59	17.22
450	47	35	65	16.45

The conversion and selectivity of MA production over VPO-1 are shown in Table 3. Similar to VPO-0.5, by raising the temperature, the conversion increases. Maximum selectivity and yield of MA are 66% at 360°C and 34.22% at 410°C, respectively.

Table 3. Details of *n*-butane partial oxidation over VPO-1 catalyst. (GHSV=2100 h^{-1} and P=1.0 atm)

Temperature (°C)	Conversion (%)	S_{MA} (%)	$S_{CO2 + CO}$ (%)	Yield (%)
335	16	56	44	8.96
360	30	66	34	19.8
380	44	61	39	26.84
410	59	58	42	34.22
430	63	54	46	34.02
450	68	47	53	31.96

The results of MA production over VPO-2 catalyst (Table 4) show that the selectivity and yield reach to the maximum at 380°C (72%) and 430°C (44.66%), respectively.

Table 4. Details of *n*-butane partial oxidation over VPO-2 catalyst. (GHSV=2100 h^{-1} and P=1.0 atm)

Temperature (°C)	Conversion (%)	S_{MA} (%)	$S_{CO2 + CO}$ (%)	Yield (%)
335	19	52	48	9.88
360	35	67	33	23.45
380	50	72	28	36
410	59	65	35	38.35
430	77	58	42	44.66
450	83	49	51	40.67

It can be seen that by rising the P/V ratio, the conversion increases. Moreover, the maximum selectivity and yield of MA shifts to the higher temperature. The effect of P/V ratio is related to the acidity of the VPO catalyst as an important property in MA production [20]. At the presence of Lewis acid sites (V^{4+}) the H-abstraction occurs and the cleavage of C–H bond occurs on Bronsted acid sites (P–OH). Bronsted acidity favors the stabilization of intermediates and the generation of an organic surface species that is involved in oxygen activation [21].

Conclusion

We have studied the preparation of VPO catalysts in the organic medium and the optimum conditions for the best activity and selectivity for MA synthesis from n-butane oxidation. We have found that the organic medium synthesis is a favorable method for production of the catalyst. Both of the activity and selectivity are directly dependent to the P/V ratio in the structure of the catalyst. This effect is related to the increasing the surface area and crystallity of VPO sample and enhancement of the acidity of Bronsted (P–OH) and Lewis acid sites (V^{4+}).

Experimental

Preparation of the catalysts:

Three catalysts by different P/V ratio were prepared in "organic medium". $VOHPO_4.0.5H_2O$, as a precursor of VPO was prepared with a suspension of the desired amounts of V_2O_5 and H_3PO_4 in isobutanol (60%) and benzyl alcohol (40%) using a reflux system at 105°C for 6 h. After it, the suspension was washed with acetone and then dried at room temperature for 16 h and then placed in oven at 120°C for 12 h. The calcinations of the catalysts were performed at the tubular microreactor under the gas stream containing N_2 (80%) and O_2 (20%) with GHSV (Gas Hourly Space Velocity) of 5100 h^{-1} at 500°C for 6 h. In this way, three catalyst having P/V ratio of 0.5, 1.0, and 2 were prepared, which were named VPO-0.5, VPO-1, and VPO-2, respectively.

Catalyst characterization:

The surface area of the samples was measured by N_2 adsorption at -196°C with a Micromeritics ASAP 2010 apparatus. X-ray powder diffraction patterns were recorded using a Philips PW800 X-ray diffractometer with Cu $K\alpha$ radiation. SEM was done using a Philips XL-30 electron microscope for determination of the morphology and the particle shape in catalyst. The atomic absorption (AA) analysis was performed using Varian Techtron1000 for determination of P/V ratio.

Catalytic evaluation

Catalytic reactions were carried out at atmospheric pressure in a continuous fixed-bed glass microreactor (i.d. 10 mm) packed with 1.0 g catalyst, giving a catalyst-bed depth of ca. 10 cm. The bed temperature was kept constant within ±1°C as checked with a K-type thermocouple traveling along the bed axis. After the catalyst was pretreated in a N_2 flow (30 ml min^{-1}), the reactant gas containing 2% n-butane and 98% air (80% N_2+20% O_2) was introduced into the reactor with a desired space velocity. The effluent from the reactor was analyzed on-line with Shimadzu 8A gas chromatograph equipped with Porapak-N column and the thermal conductive detector (TCD). In order to observe the effect of temperature on the conversion, the reaction was carried out with the different catalysts in various temperatures between 335 and 430°C. All experiments were carried out during 600 min of TOS (time of stream). Moreover, the reaction was performed at the different GHSV (gas hourly space velocity) of *n*-butane for the evaluation of its effect on the conversion and MA selectivity.

References:

[1] Centi, G.; Trifiro, F.; Ebner, J. R.; Franchetti, V. M. *Chem. Rev.* **1988**, *88*, 55.

[2] Marc, J.; Ledoux, C. C.; Cuong, P. H.; Vincent, T.; Kostantinos, K.; Patrick, M.; Jan, L. *J. Catal.,* **2001**, *203*, 495.

[3] Buenoa, J. M. C.; Bethkeb, G. K.; Kung, M. C.; Kung, H. H. *Catal. Today,* **1998**, *43*, 101.

[4] Zhou, Z. Q.; Xu, H. Y.; Ji, W. J.; Chen, Y. *Catal. Lett.* **2004**, *96*, 221.

[5] Nie, W. Y.; Wang, Z. Y.; Ji, W.J.; Chen, Y.; Au, C. T. *Appl. Catal. A* **2003**, *244*, 265.

[6] Nie, W. Y.; Wang, X. S.; Ji, W. J.; Yan, Q. J.; Chen, Y.; Au, C. T. *Catal. Lett.* **2001**, *76*, 3.

[7] Xiao, C. Y.; Chen, X.; Wang, Z. Y.; Ji, W. J.; Chen, Y.; Au, C. T. *Catal. Today* **2004**, *93*, 223.

[8] Pierini, B. T.; Lombardo, E. A. *Catal. Today* **2005**,*107*, 323.

[9] Carrara, C.; Irusta, S.; Lombardo, E.; Cornaglia, L. *Appl. Catal. A,* **2001**, *217*, 275.

[10] Bethke, G. K.; Wang, D.; Bueno, J. M. C.; Kung, M. C.; Kung, H. H. *The Third World Congress on Oxidation Catalysis, Elsevier, Amsterdam*, **1997**, p. 453.

[11] Overbeek, R. A.; Warringa, P. A.; Crombag, M. J. D.; Visser, L. M.; van Dillen, A. J.; Geus, J. W. *Appl. Catal. A* **1996**, *135*, 209.
[12] Wachs, I. E.; Saleh, R. Y.; Chan, S. S.; Chersich, C. C. *Appl. Catal.* **1985**, *15*, 339.
[13] Bond, G. C.; Bruckman, K. *Faraday Disc. Chem. Soc.* **1981**, *72*, 235.
[14] Lombardo, E. A.; Sanchez, C. A.; Cornaglia, L. M. *Catal. Today* **1992**, *15*, 407.
[15] Sanchez, F. J. C.; Lopez-Sanchez, J. A.; Wells, R. P. K.; Rhodes, C. *Catal. Lett.* **2001**, *77*, 189.
[16] Landi, G.; Lisi, L.; Volta, J. C. *Catal. Today* **2004**, *91*, 275.
[17] Ji, W. J.; Xu, L. J.; Wang, X. S.; Hu, Z.; Yan, Q. J.; Chen, Y. *Catal. Today* **2002**, *74*, 101.
[18] Ballarini, N.; Cavani, F.; Cortelli, C.; Ricotta, M.; Rodeghiero, F.; Trifiro, F.; Fumagalli, C.; Mazzoni, G. *Catal. Today* **2006**, *117*, 174.
[19] Busca, G.; Cavani, F.; Centi, G.; Trifiro, F. *J. Catal*. **1986**, *99*, 400.
[20] Abon, M.; Volta, J.-C. *Appl. Catal. A* **1997**, *157*, 173.
[21] Centi, G.; Colinelli G.; Busca G. *J. Phys. Chem.* **1990**, *94*, 6813.