Acetonylacetone conversion on $AlPO_4$–cesium oxide (5–30 wt%) catalysts

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Acetonylacetone underwent both acid- and base-catalyzed intramolecular cyclizations to 2,5-dimethylfuran and 3-methyl-2-cyclopenten-1-one, respectively, on pure $AlPO_4$, whereas its modification with increasing amounts of cesium oxide developed $AlPO_4$-based materials with increased basic properties and, hence, higher selectivities to the base-catalyzed cyclization process. However, the poisoning of surface acid and base sites indicated that acetonylacetone conversion into 3-methyl-2-cyclopenten-1-one can also be attributed to the joint participation of surface acid and base sites. So, acetonylacetone cannot be used for the simultaneous characterization of acidic and basic surface properties of acid–base heterogeneous catalysts.

Keywords: $AlPO_4$, $AlPO_4$–cesium oxide, 2,5-hexanodione conversion, activity, selectivity

1. Introduction

In a previous paper [1] we characterized the structure, texture and surface acidity of $AlPO_4$–cesium oxide catalysts and showed that 2-methyl-3-butyn-2-ol (MBOH) underwent dehydration to 3-methyl-3-buten-1-yne (acid activity) almost exclusively on pure $AlPO_4$, whereas its modification with increasing amounts of cesium oxide (5–30 wt%) developed $AlPO_4$–cesium oxide materials with increased basic properties and, hence, high selectivities (up to 99 mol%) to the base-catalyzed cleavage of MBOH yielding acetone and acetylene. Thus, as Lauron-Pernot et al. [2–4] indicate, the conversion of 2-methyl-3-butyn-2-ol can be used as a probe reaction for the simultaneous characterization of acidic and basic surface properties of solid catalysts. Also, there was no difference in product selectivity between Lewis (MgO) and Brønsted (KOH/SiO_2 and $Ca(OH)_2$) bases [5]. So, the MBOH test was independent of the nature of basic sites (Brønsted or Lewis) making it a global measure of basic properties.

Moreover, acetonylacetone, a 1,4-diketone (2,5-hexanedione), is known to undergo both acid- and base-catalyzed intramolecular cyclizations leading to 2,5-dimethylfuran and 3-methyl-2-cyclopenten-1-one, respectively, [6,7]. Also, Dessau [8] showed that the heterogeneously catalyzed conversion of 2,5-hexanedione over ZSM-5 closely paralleled the homogeneous reaction. Thus, with an acidic HZSM-5 catalyst, 2,5-dimethylfuran was produced at greater than 97% selectivity at conversions approaching 100%. In contrast, with a high-silica sodium-containing ZSM-5 catalyst, 3-methyl-2-cyclopenten-1-one was obtained with selectivities approaching 90% or better, even under complete conversion conditions. However, it was recently found that indeed, on basic catalysts such as MgO [9] and hydrotalcites [10], only the formation of 3-methyl-2-cyclopenten-1-one was observed, whereas on protonic zeolites [9] (HBEA, HFAU, HMFI and HEMT) both reaction products were obtained, indicating the existence of an acid mode (confirmed by ammonia poisoning) of formation of 3-methyl-2-cyclopenten-1-one that firstly implies internal aldolization and later on, dehydration on protonic sites. In the latter case, the reaction rate and the selectivity depend significantly on pore structure and on Si/Al ratio, i.e., on acidity.

The aim of the present work was to study the gas-phase (523–673 K) conversion of acetonylacetone over amorphous $AlPO_4$ and $AlPO_4$–cesium oxide (5–30 wt%) catalysts in order to test if acetonylacetone can be used as a sensitive molecule for the simultaneous characterization of acidic and basic surface properties of $AlPO_4$ solids, as in the case of the 2-methyl-3-butyn-2-ol probe molecule [1,11]. The work also includes the use of a typical oxide with surface base properties, MgO, and a commercial amorphous SiO_2–Al_2O_3 (13 wt% Al_2O_3, Si-235, Harshaw-Chemie) catalyst with fairly high acidity.

2. Experimental

2.1. Catalysts

$AlPO_4$ supports, with different pore volumes, were obtained by precipitation, from aluminum chloride and phosphoric acid aqueous solutions, with ethylene oxide (E) or propylene oxide (P), as described elsewhere [12]. $AlPO_4$–cesium oxide (5–30 wt% cesium oxide) catalysts were prepared by impregnation until incipient wetness using a methanolic solution of cesium acetate [1] or a

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Table 1
Textural properties and surface acidity vs. pyridine of $AlPO_4$ and $AlPO_4$–cesium oxide catalysts.

Catalyst	S_{BET} ($m^2\,g^{-1}$)	V_P ($ml\,g^{-1}$)	PY[a] ($\mu mol\,g^{-1}$)	Catalyst	S_{BET} ($m^2\,g^{-1}$)	V_P ($ml\,g^{-1}$)	PY[a] ($\mu mol\,g^{-1}$)
P-0	209	0.79	377 (23)	E-0	218	0.53	421 (33)
P-5CsAc	185	0.73	215	E-5CsAc	185	0.46	346
P-10CsAc	153	0.65	151	E-10CsAc	151	0.43	163
P-20CsAc	107	0.53	39	E-20CsAc	84	0.34	34
P-20CsCl	10	0.09	3	E-20CsCl	8	0.08	5
P-30CsAc	48	0.36	4	E-30CsAc	16	0.20	–[b]
MgO	23	0.09	–[b]	SiO_2–Al_2O_3	318	0.57	(81)

[a] Adsorption temperature 373 K; in parentheses: acidity values at 573 K.
[b] There was no adsorption of titrant agent.

methanol/water solution of cesium chloride [13]. The impregnated $AlPO_4$ were dried at 393 K (24 h) and then calcined at 873 K (3 h). Samples were called P (or E) followed by cesium oxide loading (in wt%) and indicating the cesium salt (5CsAc, 20CsAc, 20CsCl, and so on). Unmodified $AlPO_4$ (P-0 and E-0) were similarly prepared by placing them in methanol containing no cesium acetate or cesium chloride.

MgO was obtained by precipitation from the aqueous metal nitrate solution with aqueous ammonia. After filtration, washing first with water and later on with 2-propanol, and drying at 390 K for 24 h, it was calcined at 773 K for 3 h.

Commercial amorphous SiO_2–Al_2O_3 (13 wt% Al_2O_3, Si-235, Harshaw-Chemie) was calcined at 873 K for 3 h.

Surface areas and pore volumes of all catalysts were collected in table 1.

2.2. Surface acid properties

Surface acid properties were studied through adsorption of pyridine by using three procedures: pulse, TPD and DRIFT measurements [1]. In the present work the surface acidity (Brønsted and Lewis acid sites), measured in a dynamic mode by means of the gas-phase adsorption of pyridine (PY) at 373 and/or 573 K, using a pulse chromatographic technique, was also collected in table 1. As can be seen, the incorporation of cesium oxide leads to a progressive decrease in the number of acid sites as cesium oxide content increased. This decrease is greater for catalysts obtained from cesium chloride. Moreover, SiO_2–Al_2O_3 (13 wt% Al_2O_3) is highly acidic whereas MgO did not exhibit surface acidity.

2.3. Catalytic activity measurements

The catalytic properties of $AlPO_4$ and $AlPO_4$–cesium oxide catalysts in the conversion of acetonylacetone were studied by using a fixed-pulsed-bed reactor inserted between the sample inlet and the analytical column of a HP-5890-II GC with FID. Initially, a series of pulses of varying sizes were injected onto the catalyst in order to optimize the pulse size within the linear range of the adsorption isotherm. Thus, catalytic measurements were performed under the following conditions: acetonylacetone (liquid) volume/pulse size: 1 μl; reaction temperature 473–673 K (mostly 573 K); catalyst weight 10–30 mg in powder form; flow rate of nitrogen (except where otherwise specified) carrier gas 30 $ml\,min^{-1}$. A fresh catalyst was used in each run, and before use, the catalyst was pretreated by *in situ* heating under nitrogen (30 $ml\,min^{-1}$) for 1 h at 573 K.

Reaction products were analyzed by GLC with FID (HP-5890-II) and a stainless-steel column (2 m $\times$ 1/8″ i.d.) packed with 10% squalane/Chromosorb P-AW 60/80. Product characterization was performed by GC-MS (HP-5890 gas chromatograph coupled with a HP-5970 MSD quadrupole mass spectrometer) using a 25 m long cross-linked methyl silicone gum (0.2 mm $\times$ 0.32 μm film thickness) capillary column and products condensed in a cold trap. Also, retention times were compared to those of commercially available reagents. Reaction products were 2,5-dimethylfuran (DMF) and 3-methyl-2-cyclopenten-1-one (ONE).

Blank runs showed that under the experimental conditions used in this work, thermal effects could be ignored.

2.4. Poisoning experiments

The pulse poisoning technique, based on the poisoning of acid (with pyridine (PY)) and base (with acetic acid (AA), trichloroacetic acid (TCAA) and CO_2) sites, was also used for acetonylacetone conversion. In some cases, hexamethyldisilazane (HMDS) was also used as the poison of Brønsted acid sites [14,15]. Catalyst-poisoning experiments were carried out by pulses of pure probe molecule except in the case of TCAA (1 M in cyclohexane).

PY (Aldrich, Gold label 99.9%), HMDS (Merck, 99%), AA (Merck, 99%) and TCAA (Aldrich, 99+%) were used without further purification.

Poisoning experiments of basic sites with oxygen were also examined by using air as the carrier gas in the acetonylacetone conversion reaction process.

3. Results and discussion

Model reactions were recommended [16] as the best method for characterizing industrial acid catalysts. Thus,

reactions such as skeletal isomerization of 3,3-dimethyl-1-butene and cyclohexene, cracking–isomerization of 2-methyl-pentane and n-hexane or isomerization–disproportionation of o-xylene were used to characterize the acidity and acid strength of protonic sites [16]. In contrast, only scarce attention was paid to basic catalysts even though such materials show great potential for a number of industrially important reactions such as dehydrogenation of alcohols, isomerization of olefins or side chain alkylation of toluene. In this sense, the conversion of 2-methyl-3-butyn-2-ol, proposed by Lauron-Pernot et al. [2–4] as a probe reaction for the simultaneous characterization of acidic and basic surface properties, can also be used in the case of $AlPO_4$ solid catalysts [1,11].

Here we report on the results of acetonylacetone conversion on $AlPO_4$ and $AlPO_4$–cesium oxide (5–30 wt%) catalysts in order to test if this molecule can be selected as a dynamic method for the characterization of surface acid–base properties of $AlPO_4$-based materials.

3.1. Catalytic activities and product selectivities

In the above experimental conditions, acetonylacetone underwent both acid- and base-catalyzed intramolecular cyclizations to 2,5-dimethylfuran (DMF) and 3-methyl-2-cyclopenten-1-one (ONE), respectively, which accounted for more than 99.5 mol% of total selectivity.

On the other hand, as can be seen in figure 1(A), where a plot of acetonylacetone conversion (X_T) is shown as a function of the pulse number for the P-10CsAc catalyst (using nitrogen as the carrier gas), the conversion decreases steadily with the pulse number which, however, causes the selectivities to DMF and ONE to change only slightly. Moreover, when hydrogen was used as the carrier gas, acetonylacetone conversion and the reaction selectivities remained almost unchanged, compared to results in the nitrogen stream.

However, when air was used as the carrier gas, the deactivation of the catalyst with the pulse number (figure 1(B)) was less and, moreover, the reaction is highly selective to acid-catalyzed intramolecular cyclization to 2,5-dimethylfuran. Similar results were found for the remaining catalysts. This behaviour could be explained in similar terms to those used by Hattori et al. [17] in base-catalyzed 1-butene isomerization on the zeolite X–cesium oxide catalyst, where the reaction process was completely poisoned by the adsorption of oxygen. They concluded that the activity loss was due to the conversion of a part of the surface layers of the Cs_2O particles (encapsulated in the zeolite cavities) into the structures similar to those of the oxide such as Cs_2O_2, Cs_2O_3 and Cs_2O_4 (per- and superoxides) when oxygen molecules were adsorbed. Activity was gradually recovered as the oxygen-poisoned catalyst was outgassed at increasing temperatures.

In our case, the increase in 2,5-dimethylfuran selectivity (table 2) when air was used as the carrier gas could be explained by the conversion of supported Cs_2O into per- and superoxides. However, the attainment of similar acetonylacetone conversion with both carrier gases cannot be explained by the formation of such per- and superoxides.

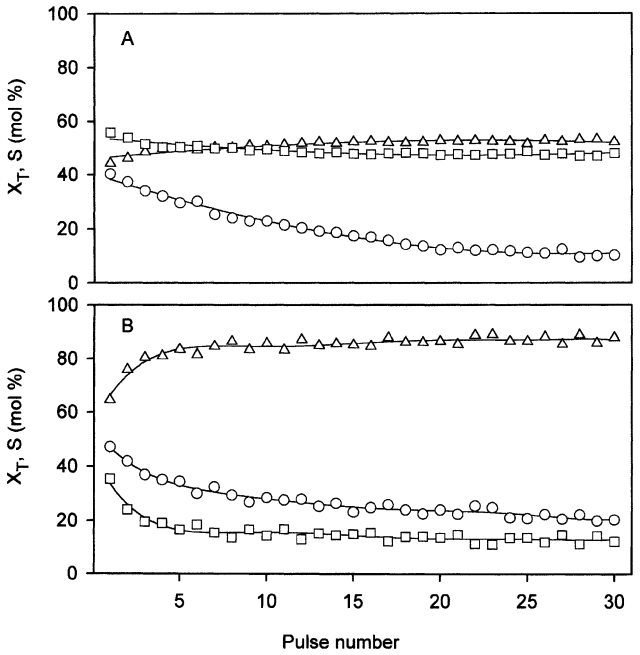

Figure 1. (○) Conversion (X_T) and product selectivities to (△) 2,5-dimethylfuran (S_{DMF}) and (□) 3-methyl-2-cyclopenten-1-one (S_{ONE}) for acetonylacetone reaction (at 573 K) over P-10CsAc catalyst as a function of the pulse number: (A) nitrogen as the carrier gas and (B) air as the carrier gas.

Table 2
Effect of carrier gas on the reaction selectivities (at 20 mol% acetonylacetone conversion) of $AlPO_4$ and $AlPO_4$–cesium oxide catalysts.[a]

Catalyst	Carrier gas	S_{DMF}	S_{ONE}
P-10CsAc	N_2	51.7	48.3
	H_2	52.4	47.6
	air	87.7	12.3
E-10CsAc	N_2	50.9	49.1
	H_2	50.1	49.9
	air	91.6	8.4

[a] Reaction temperature 573 K.

In order to compare the catalytic activity of different $AlPO_4$–cesium oxide catalysts we use nitrogen as a carrier gas and acetonylacetone conversions in the range 3–20 mol%. In these conditions and in the absence of diffusional influences and with pulse size always within the linear range of the adsorption isotherm, the acetonylacetone conversion reaction data in all catalysts were found to fulfill the rate equation for first-order kinetic processes in which the rate-determining step is the surface reaction. Besides, in this conversion range the catalytic activities and product selectivities did not change with pulse number. So, only the data for 3–20 mol% total conversion were used for the calculation of the apparent rate constants, k_a.

Catalytic activities, as apparent rate constants (k_a, at 573 K), of different catalysts on acetonylacetone conversion

Table 3
Apparent rate constants (k_a, 573 K) and reaction selectivities (at 10 and 20 mol% acetonylacetone conversion) of $AlPO_4$, $AlPO_4$–cesium oxide, MgO and SiO_2–Al_2O_3 catalysts.[a]

Catalyst	$k_a \times 10^6$ (mol atm/s m^2)	S_{DMF}		S_{ONE}	
		10 mol%	20 mol%	10 mol%	20 mol%
P-0	0.92	69.7	67.0	30.3	33.0
P-5CsAc	0.93	61.9	60.5	38.1	39.5
P-10CsAc	0.93	51.8	49.3	48.2	50.7
P-20CsAc	1.23	18.3	17.9	81.7	82.0
P-20CsCl[b]	1.04	4.7	–	95.3	–
P-30CsAc	1.69	1.9	2.0	98.1	98.0
E-0	1.07	64.0	62.2	36.0	37.8
E-5CsAc	1.08	62.8	60.9	37.2	39.1
E-10CsAc	1.09	52.8	50.9	47.2	49.1
E-20CsAc	1.38	18.2	15.3	81.8	84.7
E-20CsCl[b]	0.86	6.6	–	93.4	–
E-30CsAc	5.08	2.0	2.1	98.0	97.9
MgO	6.04	–	–	100.0	100.0
SiO_2–Al_2O_3	3.98	99.0	99.0	1.0	1.0

[a] Nitrogen as the carrier gas.
[b] Reaction temperature 673 K.

are collected in table 3. Reaction selectivities, at acetonylacetone conversions of 10 and 20 mol%, for all $AlPO_4$ and $AlPO_4$–cesium oxide catalysts, were also compiled in table 3.

As can be seen from table 3, the apparent rate constants for acetonylacetone conversion remained almost unchanged for cesium oxide loadings up to 10 wt%, but later on increased with the amount of cesium oxide. Moreover, in all cases, E-Cs catalysts exhibited higher activities than P-Cs ones. Moreover, from table 3 it can be seen that, on pure $AlPO_4$, acetonylacetone undergoes both acid- and base-catalyzed intramolecular cyclizations. Besides, the modification of $AlPO_4$ acid catalysts with increasing amounts of cesium oxide developed $AlPO_4$-based materials with increased basic properties and, hence, high selectivities to acetonylacetone base-catalyzed intramolecular cyclization yielding 3-methyl-2-cyclopenten-1-one. Thus, the incorporation of increasing amounts of cesium oxide to $AlPO_4$ produced a continuous decrease in DMF selectivity whereas ONE selectivity increased. Also, the selectivities for DMF and ONE did not show any change for acetonylacetone conversions lower than 20 mol%.

Moreover, for acid-catalyzed intramolecular cyclization, P-20CsCl and E-20CsCl catalysts are less selective than P-20CsAc and E-20CsAc ones, as corresponds to less acidic solids. However, with catalysts obtained from cesium chloride, higher temperatures and longer residence times were required (in order to obtain similar conversion levels) as compared to catalysts obtained from cesium acetate.

Furthermore, as can also be seen from table 3, $AlPO_4$ catalysts containing 30 wt% cesium oxide exhibited the same behaviour in acetonylacetone conversion as typical solid base catalysts, such as MgO, although the catalytic activities of $AlPO_4$–cesium oxide catalysts were lower than that of MgO.

3.2. Poisoning measurements

The poisoning of active sites of $AlPO_4$–cesium oxide catalysts in the acetonylacetone reaction was performed through the previous saturation of the acid sites with PY and HMDS and the basic sites with CO_2, AA and TCAA, according to the following procedure. After measuring the activity of the fresh catalyst at 573 K (in triplicate), the catalyst was saturated with the probe reagent in the nitrogen stream. After saturation, the bed was flushed with nitrogen at 573 K (1 h) to remove all traces of unreacted probe reagent. Then the activity of the catalyst was measured again.

The results obtained on the influence of probe reagents in product selectivities, at a reaction temperature of 573 K, are shown in table 4 for fresh E-10CsAc, E-20CsAc and E-30CsAc catalysts as well as after their poisoning with different probe reagents.

As expected, from table 4 it can be seen that acid reagents (CO_2, AA and TCAA) deactivated surface base sites thus affecting product selectivities by increasing the formation of 2,5-dimethylfuran. In this sense, TCAA poisoning developed catalysts with greater S_{DMF} values. Moreover, as was also expected, modification with NaOH resulted in the poisoning of acid sites and, hence, the S_{ONE} value increased. However, the poisoning of acid sites with PY or HMDS developed materials with lower selectivities to the acetonylacetone base-catalyzed intramolecular cyclization yielding 3-methyl-2-cyclopenten-2-one. Although the results from HMDS poisoning should be explainable by an increase in acidity (due to the fact that $AlPO_4$ catalysts were first deactivated by HMDS treatment but, later on, developed new surface hydroxyl sites and hence exhibited greater activities in catalyzed acid processes such as cyclohexene skeletal isomerization and cumene cracking [18,19]), those obtained from PY poisoning were re-

Table 4
Poisoning of active sites of $AlPO_4$–cesium oxide catalysts in acetonylacetone conversion (10–15 mol%).[a]

Catalyst	Poison	S_{DMF}	S_{ONE}
E-10CsAc	–	52.8	47.2
	AA	66.8	33.2
	TCAA	100.0	–
	NaOH	8.7	91.3
	PY	71.4	28.6
	HMDS	99.6	0.4
E-20CsAc	–	18.2	81.8
	CO_2	30.4	69.6
E-30CsAc	–	2.0	98.0
	AA	18.9	81.1
	TCAA	42.2	57.8
	PY	7.8	92.2
	HMDS	77.0	23.0

[a] Reaction temperature 573 K, nitrogen as the carrier gas.

ally surprising. These poisoning results seem to indicate that in the formation of 3-methyl-2-cyclopenten-2-one both acid and base surface sites participated jointly. Further research is in progress to clarify the poisoning of surface acid sites on $AlPO_4$–cesium oxide catalysts as well as to learn more about acetonylacetone conversion on acid–base catalysts.

4. Conclusions

The results presented above show that acetonylacetone (2,5-hexanodione) conversion is a good test reaction to confirm the acid or base surface properties of typical solid acid or base catalysts. However, acetonylacetone cannot be used as a sensitive molecule for the characterization of heterogeneous catalysts that exhibited simultaneously acidic and basic surface properties like $AlPO_4$–cesium oxide catalysts. In this sense, the conversion of 2-methyl-3-butyn-2-ol can indeed be used as a probe reaction for such simultaneous characterization [1,11]. Furthermore, acetonylacetone conversion confirms the base nature of $AlPO_4$ catalyst containing 30 wt% cesium oxide, whose behaviour was similar to that of MgO (acetonylacetone underwent base-catalyzed cyclization to 3-methyl-2-cyclopenten-1-one almost exclusively (>98 mol%)). Thus, the incorporation of cesium oxide allows us to obtain $AlPO_4$-based materials with tuned acid–base characteristics.

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References

[1] F.M. Bautista, J.M. Campelo, A. Garcia, R.M. Leon, D. Luna, J.M. Marinas, A.A. Romero, J.A. Navio and M. Macias, J. Mater. Chem., in press.
[2] H. Lauron-Pernot, F. Luck and J.M. Popa, Appl. Catal. 78 (1991) 213.
[3] C. Lahousse, J. Bachelier, J.C. Lavalley, H. Lauron-Pernot and A.M. Le Govic, J. Mol. Catal. 87 (1994) 329.
[4] F. Audry, P.E. Hoggan, J. Saussey, J.C. Lavalley, H. Lauron-Pernot and A.M. Le Govic, J. Catal. 168 (1997) 471.
[5] M. Huang and S. Kaliaguine, Catal. Lett. 18 (1993) 373.
[6] C.D. Hurd, O.E. Edwards and J.R. Roach, J. Am. Chem. Soc. 66 (1944) 2013.
[7] H. Hunsdiecker, Chem. Ber. 75 (1942) 455.
[8] R.M. Dessau, Zeolites 10 (1990) 205.
[9] N. Lavaud, P. Magnoux and M. Guisnet, in: *Third International Symposium on Acid–Base Catalysis*, Kerkrade, The Netherlands, 1997, O-23.
[10] A. Guida, M.H. Lhouty, D. Tichit, F. Figueras and P. Geneste, Appl. Catal. A 164 (1997) 251.
[11] F.M. Bautista, J.M. Campelo, A. Garcia, R.M. Leon, D. Luna, J.M. Marinas and A.A. Romero, React. Kinet. Catal. Lett. 65 (1998) 239.
[12] A. Blanco, J.M. Campelo, A. Garcia, D. Luna, J.M. Marinas and A.A. Romero, J. Catal. 137 (1992) 51.
[13] F.M. Bautista, J.M. Campelo, A. Garcia, R.M. Leon, D. Luna, J.M. Marinas, A.A. Romero, J.A. Navio and M. Macias, React. Kinet. Catal. Lett. 65 (1998) 245.
[14] A.J. van Roosmalen and J.C. Mol, J. Chem. Soc. Chem. Commun. (1980) 804.
[15] A.J. van Roosmalen, M.C.G. Hartmann and J.C. Mol, J. Catal. 66 (1980) 112.
[16] M.R. Guisnet, Acc. Chem. Res. 23 (1990) 392.
[17] F. Yagi and H. Hattori, Micropor. Mater. 9 (1997) 247.
[18] F.M. Bautista, J.M. Campelo, A. Garcia, D. Luna, J.M. Marinas and A.A. Romero, Appl. Catal. A 104 (1993) 109.
[19] F.M. Bautista, J.M. Campelo, A. Garcia, D. Luna, J.M. Marinas and A.A. Romero, Catal. Lett. 24 (1994) 293.