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TRANSIENT AND ISOTOPIC STUDIES OF THE OXYGEN TRANSPORT AND EXCHANGE DURING OXIDATIVE COUPLING OF METHANE ON Sr PROMOTED La_2O_3

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Isotopic transient techniques were applied to study oxidative coupling of methane over lanthanum oxide and strontium promoted La_2O_3 catalysts. Results of the $^{18}O_2/^{16}O_2$ isotopic exchange experiments indicate that Sr promotion increases oxygen uptake from the lattice of the catalyst. Oxygen self diffusion coefficients, which were determined for the series of lanthana catalysts, reach a maximum for the 1% Sr/La_2O_3. Steps of $^{18}O_2$ in the presence of a steady flow of methane over Sr/La_2O_3 catalysts, indicate that surface and bulk oxygen appear in the reaction products before gas-phase $^{18}O_2$. Steps of CO_2 over catalysts in which lattice oxygen has been exchanged with $^{18}O_2$, show that gas/solid exchange involves over 50% of the lattice oxygen. Under reaction conditions, methane pulses with no gas-phase oxygen yield negligible amounts of products which indicates that methane interacts with lattice oxygen only in the presence of the gas-phase oxygen.

Keywords: Oxidative coupling of methane, La_2O_3, isotopic exchange

1. Introduction

Lanthanum oxide is considered to be one of the most active oxidative coupling catalysts. Hicks et al. [1–3] have reported that the catalyst promoted with 1% Sr exhibits higher activity than the unpromoted La_2O_3. A number of research groups [4,5], have suggested that the species responsible for the activation of methane in rare earth metal oxides is O^- or its thermodynamically more stable form, O_2^{2-}, i.e. an oxygen atom trapped in an anion vacancy. Although, several papers have been published concerning catalytic behavior of lanthanum oxide catalysts, little attention has been given to the role of oxygen and the pathways of lattice and gas-phase oxygen during activation of methane on these materials. These issues can be resolved by transient experiments consisting of isotopic switches, pulses, and steps of reactants as is demonstrated in this paper. Pulsing of reactants over degassed samples of the catalyst is a fast and simple way to determine surface response to the wide range of operating conditions [6]. Isotopic switches of the reactants are considered to be very useful during mechanistic studies of the reaction pathways without affecting steady-state equilibrium [5,7]. Determination of the oxygen self-diffusion coefficients in the unpromoted and Sr-promoted La_2O_3 could help explain the higher activity of the strontium doped catalysts.

2. Experimental procedure

Strontium promoted La_2O_3 catalysts were prepared by wet impregnation from a solution of strontium nitrate followed by calcination at 600°C. Prior to each experiment a sample of the catalyst was pretreated in oxygen flow for one hour at 750°C. Since the surface area of the La_2O_3 supplied by Alfa products was significantly smaller than the surface area of the hydrothermally treated catalyst, unpromoted lanthanum oxide used during these experiments was first introduced into the deionized water and later calcined in oxygen flow.

Steady state activity measurements as a function of the ratio of the total flow rate to the mass of the catalyst (which can be easily converted to the gas space velocity calculated at STP conditions) were conducted in 9 mm i.d. quartz reactors at 750°C. Methane and oxygen were diluted in helium, and fed into the reactor at a total flow rate of 100 cc/min. The methane to oxygen mole ratio was kept at two, the reactant partial pressure $P^* = (P_{CH_4} + P_{O_2})/P_{TOT}$ was adjusted at 0.48, and the space velocities were varied by using different volumes of catalysts. Gas analysis was conducted using a Carle gas chromatograph equipped with TC detector with helium as a carrier. A detailed description of the sampling and analytical techniques can be found elsewhere [8].

The reactor used in transient and isotopic studies was a 4 mm i.d. quartz tube designed to minimize dead volumes. In order to keep oxygen conversion low, isotopic switch experiments in the presence of methane were conducted at 700°C, using 0.01 g of catalysts. In order to avoid interactions with reversibly adsorbed oxygen, which might have remained after calcination, the catalysts were degassed in helium flow over a period of 30 min. Oxygen and methane flow rates were adjusted at 1 and 4 cc/min respectively. Gases were diluted in helium, so the total flow rate was 60 cc/min. Oxygen diffusion measurements were conducted at 750°C using 0.01 g of catalysts and at 0.5 cc/min $^{18}O_2$ isotope flow. In order to obtain a fast response to a step of oxygen, a total flow of a helium carrier of 120 cc/min was used.

To generate pulse and step changes of reacting species concentrations within the carrier flow, a combination of four-way and six-way valves was utilized. A detailed description of the reaction apparatus can be found elsewhere [9]. During the step mode operation, at time equal "zero" a flow of helium was switched to the flow of the reactant (isotopic oxygen) and helium for the diffusion coefficient measurements, or to the flow of methane and isotopic oxygen diluted in helium for the analysis of products during oxidative coupling reaction. A $CO_2/^{18}O$ step exchange experiment was conducted at 700°C, total flow rate of 120 cc/min, by introducing a step of CO_2 at a flow rate of 4 cc/min, on 0.01 g of catalyst which had been previously exchanged with $^{18}O_2$. Experiments were terminated when an equilibrium between the surface and the gas-phase products was established. All experiments were reproducible within an experimental error of 5%.

For all transient and isotopic measurements, gases were analyzed by a UTI quadrupole mass spectrometer equipped with a fast-response continuous inlet system. Mass to charge ratios of 15, 26, 28, 32, 34, 36, 44, 46, and 48 were used for the analysis of CH_4, C_2H_4, C_2H_6, $^{16}O_2$, $^{16}O/^{18}O$, $^{18}O_2$, $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$ after appropriate calibration.

3. Results and discussion

Catalytic activity of the unpromoted and 1% Sr promoted lanthanum oxide can be found in fig. 1. It is seen that at low space velocities, due to oxygen conversion close to 100%, methane conversion is similar for both catalysts; clearly, at these reaction conditions it is rather difficult to distinguish their difference in catalytic activity. However, when the volume of the catalyst was decreased i.e. decreasing the contact time, a decrease in both methane and oxygen conversions was observed. It is evident that at a constant space velocity, strontium promotion significantly increases methane conversion. Selectivity for unpromoted and promoted catalysts did not change with varying residence times and remained constant at 55 and 57% for La_2O_3 and 1% Sr/La_2O_3 respectively.

Fig. 2 displays 1% Sr/La_2O_3 response to the step of $^{18}O_2$ isotope at 750°C. It is seen that after a time delay corresponding to the reactor dead volume, a large signal of $^{16}O_2$ released from the lattice of the catalyst can be observed. This quickly released $^{16}O_2$ corresponds to the oxygen adsorbed on the catalyst surface and also subsurface oxygen immediately below. The $^{16}O_2$ signal reaches a maximum and then decreases to a value close to that of the initial background. On the other hand, the $^{16}O^{18}O$ signal does not follow the same response but stays constant at much higher level due to the diffusion of the oxygen from the bulk of the oxide. Steady flow of the $^{18}O_2$ isotope (no gas-solid exchange) can be regained approximately 5 min after introducing it into the reactor. A similar response was observed for the unpromoted catalyst and for the 2% Sr/La_2O_3. In order to determine the degree of the oxygen exchange from the lattice of the catalyst, an oxygen mass balance was written for each of the oxygen species present in the system. The results of these calculations are shown in table 1. They indicate that Sr promotion increases $^{18}O/^{16}O$ exchange capacity, which reaches a maximum for the 1% Sr/La_2O_3 catalyst. The oxygen exchange increased by ~ 10% for the 1% Sr promoted lanthanum oxide compared to the unpromoted catalyst. The amount of the exchanged oxygen accounts for 69, 79, and 72% of the total amount of lattice oxygen present in La_2O_3, 1% Sr/La_2O_3, and in the 2% Sr/La_2O_3 respectively. For the purpose of comparison table 1 presents results of

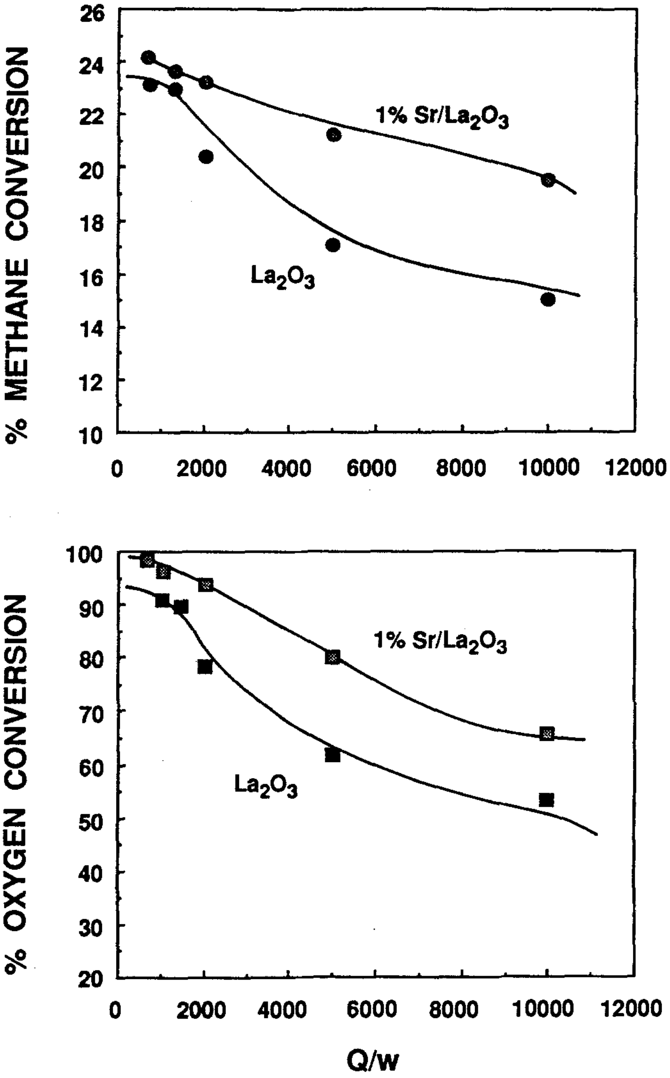

Fig. 1. Methane and oxygen conversions as a function of the flow to mass ratio for the oxidative coupling reaction on La_2O_3 and on 1% Sr/La_2O_3 catalysts at 750°C.

exchange measurements for the magnesium oxide. It is seen that only 7% of lattice oxygen in MgO is exchanged with the isotope.

The above experiments also allow for the determination of the oxygen self-diffusion coefficients within the lattice of the catalyst. D_0 can be calculated from the $^{16}O^{18}O$ flux, after the exchange reaction reaches equilibrium. The method used to determine diffusion coefficients was similar to that of Peil et al. [10], who recently studied isotopic exchange reactions on Li promoted MgO and Sm_2O_3. It is seen that (table 1), the 1% Sr/La_2O_3 catalyst exhibits the highest value of the D_0 which is equal $1.9 * 10^{-14}$ cm^2/sec. The observed trend indicates again that Sr

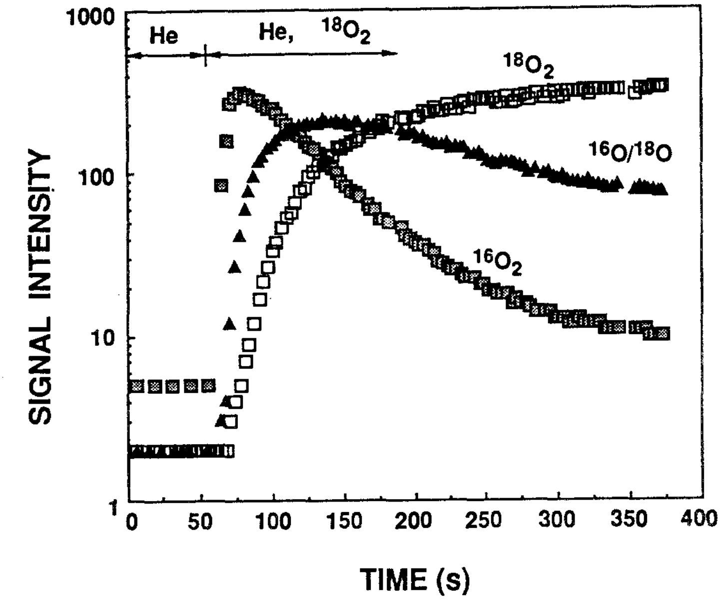

Fig. 2. $^{18}O/^{16}O$ isotopic exchange on 1% Sr/La_2O_3 catalyst, $T = 750°C$.

promotion has a significant influence on the bulk properties of the lanthanum oxide. Zhen et al. [11] proposed that for the lanthanum oxide structure, a strontium dopant forms defect pairs with the oxygen vacancies, which increase the oxygen conductivity. These authors also reported that the 1% Sr/La_2O_3 oxide exhibited the highest oxygen conductivity and the minimum activation energy for conduction among a series of samples of La_2O_3 doped with alkaline earth oxides. The differences in oxygen uptake observed during the isotopic oxygen exchange experiments reported here, are most likely due to the increase in oxygen vacancies. An improvement in the activity of the catalysts with higher number of oxygen vacancies suggests that during the oxidative coupling reaction, methane is activated by the oxygen trapped in an anion vacancy.

It is extremely difficult to determine exactly what is an active site for the selective methane activation since most likely there is an equilibrium between O^- and O^{2-} oxygen species present in the system [12,13]. Since the participation of

Table 1
Results of the exchange experiments

	B.E.T. area	% of O_2 exch.	$D_0 * 10^{-15}$ (cm^2/s)
MgO	32.57	7.33	0.02
La_2O_3	5.03	68.9	9.83
1% Sr/La_2O_3	6.86	79.0	18.86
2% Sr/La_2O_3	7.64	72.0	11.18

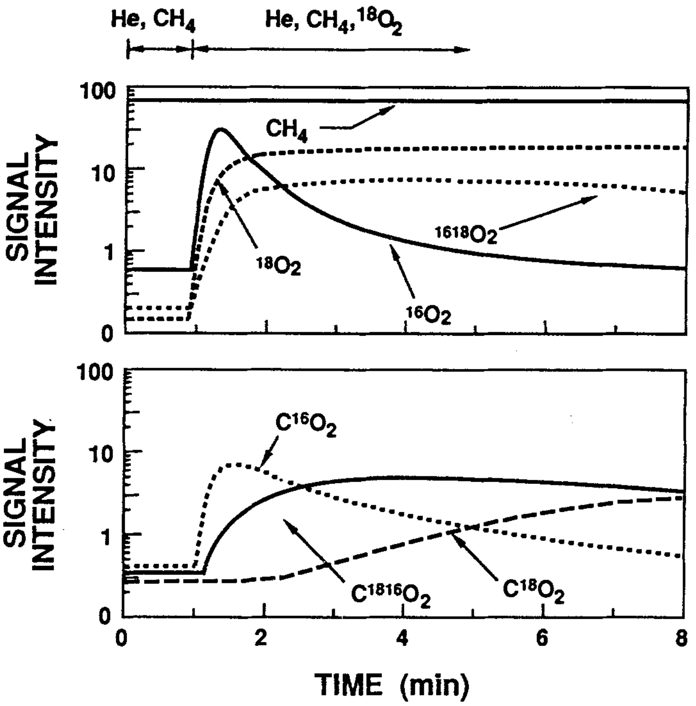

Fig. 3. Step of methane and oxygen over 1% Sr/La_2O_3 catalyst saturated with oxygen 18 at 750°C.

the bulk oxygen in the exchange reaction is significant, an increase of the oxygen self-diffusion coefficient allows for the faster transport of oxygen anions to the surface of the catalyst, which may be responsible for an increase of methane conversion during reaction. Among the different alkali and alkali earth metals which were applied as lanthana dopants, Sr promoted lanthanum oxide exhibits the best catalytic properties for the catalytic oxidative coupling of methane [2,3,14]. An important factor, which affects the structure of the promoted La_2O_3 is the match of the atomic radii between the dopant and the lanthanum atoms. In the case of alkali earth metals the best match is achieved for the strontium promoter. This may explain why it yields the maximum concentration of ion vacancies [11]. Recently Tong et al. [15] reported that due to the mismatch between atomic radii of sodium and lanthanum ions, sodium carbonate/sodium oxide phase largely covers the surface of the lanthana causing a significant drop of its catalytic activity. They also proposed a different mechanism for the formation of methyl radicals, which does not involve bulk oxygen of the lanthana phase.

In order to probe the oxygen pathway during activation of methane on lanthana, additional experiments were conducted using a step change of $^{18}O_2$ on a steady methane/helium flow over 1% Sr/La_2O_3 at 750°C. Fig. 3 displays the various responses observed, showing clearly that despite the high volume of $^{18}O_2$

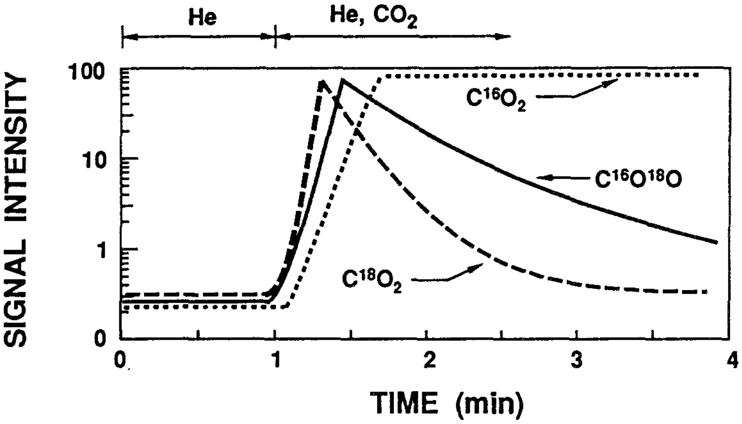

Fig. 4. Step of CO_2 over 1% Sr/La_2O_3 catalyst saturated with ${}^{18}O_2$.

present in the gas phase, a major source of oxygen detected in the carbon dioxide, comes from the ${}^{16}O$ present only in the lattice of the catalyst. After ${}^{16}O$ is depleted, the amount of the $C^{18}O_2$ product increases and reaches a steady value. Isotopic oxygen balance indicates that almost 50% of the exchanged oxygen can be detected in the reaction products, suggesting that surface and bulk oxygen are involved in the reaction with methane. It is also interesting to note that despite the presence of the ${}^{18}O_2$ in the gas phase, the delay of the $C^{18}O^{16}O$ signal is ten seconds, whereas the $C^{18}O_2$ signal appears after thirty seconds.

In order to determine the catalyst ability to exchange lattice oxygen with unselective products of the oxidative coupling reaction, a step of CO_2 was introduced into the reactor over the 1% Sr/La_2O_3 catalyst with lattice oxygen previously exchanged with ${}^{18}O$, where at least 80% of the initial amount of ${}^{16}O$ oxygen was exchanged with the isotope. Results of the step experiment presented in fig. 4 show that the primary product of the exchange reaction is $C^{18}O_2$ followed by the $C^{16}O^{18}O$. It can be seen that signals for these species drop sharply due to the depletion of oxygen 18 present in the lattice. It is interesting to note that the relaxation time of the $C^{16}O^{18}O$ signal exceeds that of $C^{18}O_2$ due to the bulk diffusion of the oxygen species. A rough estimation of the amount of oxygen 18 exchanged with gas phase carbon dioxide suggests that almost 80% of all isotope present in the lattice participates in the exchange reaction. Since CO_2 also reacts with oxygen surface species which participate in methane activation, it is possible that this interaction can have an effect on the selectivity of C_2 hydrocarbons. This experiment shows clearly that CO_2 undergoes rapid isotopic exchange with lattice oxygen and that the appearance of labelled $C^{18}O_2$ in the previous experiment could be the result of this exchange rather than the direct oxidation of methyl radicals by surface or lattice oxygen.

When methane pulses were introduced over Sr promoted La_2O_3 with *no gas-phase oxygen* present in the system, the catalyst response was significantly

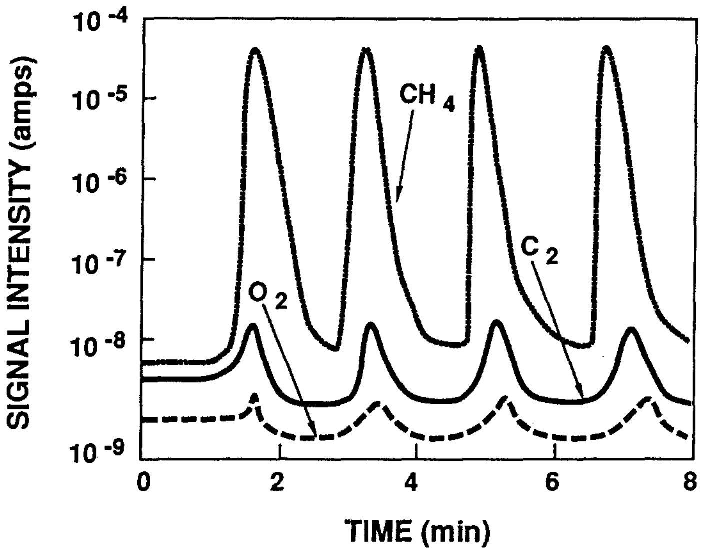

Fig. 5. Methane pulses in the absence of gas phase oxygen on 1% Sr/La_2O_3 catalyst.

different, yielding no oxy-derivative products, (fig. 5). The small amount of C_2 hydrocarbons detected in the effluent gases comes from trace impurities present in the methane feed. It is interesting to note that the small amount of oxygen present in the helium carrier, which is referred to as an oxygen trace level (~ 10 ppm), can restore lattice oxygen which reacts with gas phase reactants [6]. On lanthana catalysts, when oxygen is not present in the gas phase, lattice oxygen does not interact with methane. A similar type of behavior was also observed for the unpromoted lanthanum oxide. When the methane pulse experiment was repeated at 850°C (not shown here), a small amount of CO_2 was detected in the reaction products. This can be explained by an increase in the oxygen mobility at higher temperatures, and by the difference in thermal stability of the lanthana carbonates present on the surface of lanthanum oxide [16].

The results of the isotope exchange experiments show that on lanthanum oxide catalysts, lattice oxygen plays a major role during the oxidative coupling of methane. Transient and isotopic data show that while only 7% of lattice oxygen is exchanged in MgO, about 70% can be exchanged in La_2O_3. Strontium promotion increases the oxygen diffusivity by increasing a number of oxygen anion vacancies. It is also found that oxygen is detected in the reaction products only when gasphase oxygen is present in the system. This behavior indicates that the pathway for oxygen interaction with the surface might be as follows:

$$\tfrac{1}{2}O_{2g} \rightleftharpoons O_a \rightleftharpoons O_l \underset{-2e}{\overset{+2e}{\rightleftharpoons}} O^{2-} \underset{-e}{\overset{+e}{\rightleftharpoons}} O^-.$$

O_a are oxygen atoms adsorbed on the surface, which are able to diffuse into the lattice to form O^{2-} anions and which in term can equilibrate with O^- species.

It is still not possible, however, to ascertain uniquely which of the oxygen anions can selectively activate methane. In the absence of gas-phase oxygen, oxygen anions probably are not mobile within the lattice of La_2O_3 and do not yield C_2 products. Oxygen exchange between gas phase CO_2 and the lattice oxygen is very fast and could lead to erroneous conclusions regarding the oxidation of methyl radicals.

Acknowledgments

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References

[1] J.M. DeBoy and R.F. Hicks, J. Catal. 113 (1988) 517.
[2] J.M. DeBoy and R.F. Hicks, J. Chem. Soc., Chem. Commun. (1988) 982.
[3] J.M. DeBoy and R.F. Hicks, Ind. Eng. Chem. Res. 27 (1988) 1577.
[4] C-H. Lin, K.M. Campbell, J-X. Wang and J.H. Lunsford, J. Phys. Chem. 90 (1986) 534.
[5] A. Ekstrom and I.A. Lapszewicz, J. Phys. Chem. 93 (1989) 5230.
[6] E.E. Miro, Z. Kalenik, J. Santamaria and E.E. Wolf, Catal. Tod. 6 (1990) 511.
[7] J. Happel and R.S. Csuha, J. Catal. 20 (1971) 132.
[8] G.S. Lane and E.E. Wolf, J. Catal. 113 (1988) 144.
[9] E.E. Miro, J. Santamaria and E.E. Wolf, J. Catal. 124 (1990a) 451.
[10] K.P. Peil, J.G. Goodwin and G. Marcelin, J. Catal. (1990) submitted.
[11] Y.S. Zhen, S.J. Milne and R.J. Brook, High Tech Ceram. (1987) 1989.
[12] E.R.S. Winter, J. & E. Sturge, J. Chem. Soc. (1968) 2890.
[13] V.B. Kazansky, Kinet. Katal. 18 (1977) 43.
[14] G.J. Hutchings, M.S. Scurell and J.R. Woodhouse, Chem. Soc. Rev. 18 (1989) 251.
[15] Y. Tong, M.P. Rosynek and J.H. Lunsford, J. Catal. 126 (1990) 291.
[16] T. Le Van, M. Che, M. Kermarec, C. Louis and J.M. Tatibouet, Catal. Lett. 6 (1990) 395.