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Ethylbenzene Dehydrogenation in the Presence of Carbon Dioxide over Metal Oxides

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1. Introduction

1.1 The use of carbon dioxide for chemicals manufacture

Because of the harmful effects to the environment, there is an increasing concern worldwide for decreasing the amount of atmospheric carbon dioxide. The average temperature of the earth, caused by greenhouse gases, has been increased in such a value that can cause catastrophic events. Several solutions have been proposed to overcome this problem, but they basically involve two approaches: (i) the decrease of carbon monoxide emissions or (ii) the application in innovative technologies to capture and use it. Both alternatives have been studied and discussed and several applications have been proposed (Song, 2006).

The global chemical industry uses about 115 million metric tons of carbon dioxide every year as feedstock in a variety of synthetic processes. This number is insignificant compared to 23.7 billion metric tons estimated annual global emissions of the gas caused by human activities, primarily the burning of fossil fuels. In addition, the total anthropogenic emissions of carbon dioxide, approximately 45%, remain in the atmosphere, as a result of a gradual accumulation of carbon dioxide (Ritter, 2005).

It is believed that the amount of carbon dioxide used by chemical industry could easily be tripled using current technologies, but that still does not solve the problem, since only its use by the chemical industry is not enough to significantly reduce carbon dioxide emissions. Because of the scale of the problem, different strategies need to be used simultaneously, including increasing the efficiency of current processes, as well as the capture and use or storage of carbon dioxide generated by burning fossil fuels and using renewable fuels and energy sources. As a result of the development of the chemistry based on carbon dioxide, a reduction in the use of toxic products in chemical industry is expected with an improvement in health and safety (Ritter, 2005). Therefore, there is a significant effort of scientific and technological community to discuss the use of carbon dioxide in different applications which would provide its elimination from the air and its reuse as raw material for manufacturing other products.

Carbon dioxide can be conveniently used as carbon and/or oxygen sources for the synthesis of chemicals through several processes, both as solvent and/or as reactants. It has potential applications in supercritical conditions, in direct carboxylation reactions, in the conversion of natural gas to liquid (GTL technology) and in methanol synthesis (Aresta and Dibenedetto, 2004). Other studies have shown the use of carbon dioxide as an oxidant in the dehydrogenation of ethane (Murata et al., 2000; Nagakawa et al., 1998), propane (Wang et al., 2000), isobutene (Shimada et al., 1998) and ethylbenzene (Mimura et al., 1998), as well as in methane dry reforming (Wang et al., 2000) and oxidative coupling of methane (Nishiyama and Aika, 1990). Currently, most intermediates in the petrochemical industry are produced from alkenes and aromatics, but their consumption is growing and the existing production capacity is inefficient to provide this market. In addition, alkenes are obtained from cracking processes of natural gas and naphtha which however are very expensive, due to the need of separation and purification of the products (Ogonowski and Skrzynska, 2005).

1.2 The advantages of using carbon dioxide in dehydrogenation reactions

Currently, light alkenes (C₂-C₄) are obtained by thermal cracking of natural gas and naphtha as well as by catalytic cracking that occurs during oil refining. In addition, they can be produced by catalytic dehydrogenation of hydrocarbons, which has considerable industrial impact, since it provides a route to get the valuable alkenes from low cost feedstock. This process has also the advantage of producing only the desired products, making the plants cheaper to construct and less complicated to operate. Besides alkenes, the dehydrogenation of alkanes can be used to produce hydrogen and oxygenates such as aldehydes and ketones (Nishiyama and Aika, 1990). All these chemicals are important intermediates for the production of polymers, rubbers, detergents and solvents, among other products.

The dehydrogenation of hydrocarbons is reversible and limited by thermodynamic equilibrium and thus the reaction is often performed at high temperatures to increase the conversion. However, this condition leads to hydrocarbons cracking, decreasing the selectivity of the process. These difficulties can be overcome by supplying heat to the reaction by the oxidation of the produced hydrogen or by using an oxidant in the presence of a catalyst, able to perform an oxidation reaction. The reaction thus becomes exothermic and can be carried out at low temperatures, making negligible the formation of cracking products. Another advantage is that the conversion is not strongly limited by thermodynamic factors and then oxidizing agents, such as molecular oxygen, nitrous oxide, halogens, elemental sulfur and carbon dioxide can be used. The use of molecular oxygen or nitrous oxide as oxidants effectively reduces the reaction temperature under atmospheric pressure. Nevertheless, the reaction presents several problems, such as the need of removing the heat of reaction and of controlling the selectivity due to the production of carbon oxides, besides the undesirable flammability of reaction mixtures. Among the oxidizing agents, carbon dioxide has been shown to be the most promising one to be used in dehydrogenation reactions (Bhasin et al., 2001; Krylov et al., 1995; Corberán, 2005).

Chromium oxide (Cr₂O₃) has been used as a commercial catalyst for decades, in the dehydrogenation of light alkanes while chromium-doped hematite is the classical catalyst for ethylbenzene dehydrogenation (Nishiyama and Aika, 1990; Santos et al., 2006; Rangel et al., 2003; Ramos et al., 2008). However, the toxicity of Cr⁺⁶ ion requires a special care in the

preparation, use and disposal of these catalysts and then there is an interest for developing new green technologies for replacement of these solids. Therefore, several other systems were studied such as cerium oxide (Ikenaga et al., 2000), manganese oxide (Burri et al., 2006), titanium oxide, vanadium oxide (Burri et al., 2007; Chen et al., 2006) and zirconium oxide among others (Park et al., 2000).

The mechanism of the dehydrogenation reactions of alkanes C₂-C₇ with carbon dioxide over oxide catalysts proved to be different for light and heavy alkanes. The reaction occurs via a redox mechanism but the activation of carbon dioxide can occur by its direct interaction with the reduced catalysts or through the formation of a complex intermediate or by its interaction with the coke produced on the catalyst surface. In the dehydrogenation of ethane and propane, for instance, the removal of oxygen from the oxide-based catalyst occurs as a result of the interaction of the catalyst with the reagent and with the hydrogen which was removed from the alkane molecule. In the case of dehydrogenation of butanes and isobutanes, the reaction occurs through the direct dehydrogenation of alkane followed by the oxidation of hydrogen while for n-heptane both the oxidative function of the catalyst and carbon dioxide lead to coke oxidation. Therefore, it is essential to select catalysts able to adsorb and activate carbon dioxide. The properties of acidic carbon dioxide favor the choice of catalysts with basic properties. However, the alkali and alkaline earth oxides are inefficient because they form carbonate species. Metal oxides of moderate basicity are required and must participate in the redox process with the reduction of carbon dioxide (Krylov et al., 1995).

The effect of carbon dioxide on the propane and isobutane dehydrogenation is small as compared to ethane dehydrogenation, this can be related to the lower reaction temperatures (600 °C) required to obtain significant conversions, since the dissociation energies for CH₂ or CH groups in propane and isobutane are lower than for CH₃ group in ethane. On the other hand, for ethylbenzene dehydrogenation the produced alkenes contain allylic hydrogen, which has a dissociation energy lower than the starting alkanes. Therefore, the abstraction of hydrogen from the allylic position may favor the formation of coke precursors and the catalyst deactivation cannot be avoided, thereby decreasing the alkenes yield (Wang and Zhu, 2004).

1.3 Ethylbenzene dehydrogenation in the presence of carbon dioxide

Styrene is one of the most used intermediate for organic synthesis, being used as feedstock in the production of synthetic rubbers, plastics and resins copolymers, among other products of high commercial value (Sakurai et al., 2002). This monomer can be obtained by several routes, but the ethylbenzene dehydrogenation in the presence of steam is the main commercial route to produce this monomer. This process allows to supply 90% of the global production of styrene, which is approximately 13 x 10⁶ t/year (Sakurai et al., 2002; Cavani and Trifiró, 1995).

Despite being widely used around the world for several years, the ethylbenzene dehydrogenation in the presence of steam (Equation 1) still has some drawbacks, the main one related to the endothermicity and the equilibrium limitation of reaction. As a result, the typical conversion is low, rarely exceeding 50%, even in processes performed at high temperatures (Cavani and Trifiró, 1995). Side reactions also occur, leading to the production of toluene, benzene and coke, which affect the yield of the process and may lead to the

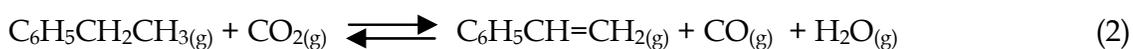
catalyst deactivation (Styles, 1987; Shreve and Brink, 1997). Other problems include the need for recycling of reagents and the use of low ratios steam/ethylbenzene (Cavani and Trifiró, 1995; Styles, 1987; Shreve and Brink, 1997).



In industrial processes, the catalyst deactivation is minimized by the addition of large amounts of steam, which also shifts the equilibrium increasing the styrene production and eliminates or prevents the formation of coke. In addition, steam oxidizes the catalyst keeping it in a state of highly selective oxidation to styrene (Shreve and Brink, 1997; Herzog et al., 1984).

The most widely used catalysts in ethylbenzene dehydrogenation in the presence of steam are inorganic oxides with promoters (Cavani and Trifiró, 1995; Shreve and Brink, 1997). However, iron oxides containing potassium and chromium oxide are superior to any other known system and have been used in commercial plants, since the first process, for nearly 70 years. Since that time, both the catalyst and the process have undergone several improvements, such as the introduction of beds with radial flow and the use of poison inhibitors (Shreve and Brink, 1997). Several works have been carried out (Santos et al., 2006; Rangel et al., 2003; Ramos et al., 2008; Miyakoshi et al., 2001; Liao et al., 2008) aiming to improve the iron-based catalysts or to find new alternatives systems and process conditions (Holtz et al., 2008; Oliveira et al., 2008; Morán et al., 2007; Ohishi et al., 2005).

A promising alternative to overcome these problems is to perform the process in the presence of carbon dioxide instead of steam. In this case, there is a consumption of $1.5\text{-}1.9 \times 10^8$ cal instead of 1.5×10^9 cal per mol of styrene produced, among other advantages of the new process (Mamedov, 1994). In this case, the produced hydrogen is removed as steam by the reverse water gas shift reaction shifting the equilibrium to the formation of dehydrogenation products, as shown in Equation 2. In addition, carbon dioxide removes the coke deposits formed during reaction (Mamedov, 1995).



Several authors (Cavani and Trifiró, 1995; Shreve and Brink, 1997; Herzog et al., 1984) have shown that the commercial catalysts based on iron oxide are not satisfactory for ethylbenzene dehydrogenation in the presence of carbon dioxide. Thus, extensive studies have been carried out in order to develop catalytic systems that can operate effectively in the presence of carbon dioxide. Mimura and Saito (Mimura and Saito, 1999; Mimura and Saito, 2000; Saito et al., 2003) and others (Badstube et al., 1998; Dziembaj et al., 2000), for instance, have investigated iron oxide catalysts promoted with alkali metals supported on alumina and charcoal, respectively, for ethylbenzene dehydrogenation, noting the increased selectivity to the products in the presence of carbon dioxide. Also, the use of carbon dioxide have been studied on iron oxide supported on zirconium oxide and zeolites (Park et al., 2002; Chang et al., 2004), vanadium oxide catalysts and vanadium-antimony supported on alumina (Vislovskiy et al., 2002; Park et al., 2003), in which there was the increased catalytic activity, according to the catalyst. From these studies, they have observed that the effect of carbon dioxide on the activity, selectivity and stability for ethylbenzene dehydrogenation depends on the kind of the catalyst. In the case of zirconia, the positive effect of carbon dioxide was found to be highly dependent on the crystalline phase at 550 °C, the tetragonal one has presented high activity and selectivity to styrene (Vislovskiy et al., 2002). This

finding was related to differences in specific surface area of the solids and its affinity with carbon dioxide associated with the surface basic sites (Pereira et al., 2004; Sun et al., 2002). In other works, zirconium oxide (Vislovskiy et al., 2002), mixed oxides of zirconium with titanium or manganese (Park et al., 2000) and mixed oxide of zirconium and cerium supported on SBA-15 (Burri et al., 2006) have led to around 65% of conversion and 95% of selectivity to styrene. On the other hand, Jurczyk and Kania (1989) have found a relationship between the acidic or basic properties and the selectivity of the catalysts by studying binary oxides supported on alumina.

Activated carbons-based catalysts have also proved to be active in ethylbenzene dehydrogenation in the presence of carbon dioxide. Badstube et al. (2000), for instance, have investigated catalysts based on iron supported on activated carbon in ethylbenzene dehydrogenation coupled with the reverse of water gas shift reaction and have found high activity and selectivity to styrene at 550 °C. In addition, Sakurai et al. (2000) have studied active-carbon supported vanadium catalysts at 450-650 °C and also have noted high conversion (67.1%) and selectivity to styrene (80%) at 550 °C. They also found that ethylbenzene conversion in the presence of carbon dioxide was 14% higher than in the presence of argon. Moreover, we have found (Oliveira et al., 2008) that spherical activated carbon-supported copper are promising catalysts for ethylbenzene dehydrogenation in the presence of carbon dioxide. The catalyst with the lowest amount of copper was the most promising one, showing high activity and resistance against deactivation, being able to work up to 600 °C.

In spite of the several studies addressed to metal oxides-based catalysts for ethylbenzene dehydrogenation in the presence of carbon dioxide, there is not a systematic comparison of their behavior in ethylbenzene dehydrogenation. In the present work, we compare the activity and selectivity of lanthana, magnesia, niobia, titania and zirconia aiming to state the individual contribution of these pure oxides to the performance of the catalysts for ethylbenzene dehydrogenation in the presence of carbon dioxide.

2. Experimental

2.1 Catalysts preparation

Commercial niobium oxide (Nb_2O_5) and titanium oxide (TiO_2) in rutile phase were kindly supplied by CBMM (HY 340) and Millenium (T-568), respectively. Lanthanum oxide (La_2O_3), magnesia (MgO) and zirconia (ZrO_2) were prepared in the laboratory.

Zirconium oxide was obtained by the hydrolysis of zirconium oxychloride (250 mL, 1 mol.L⁻¹) with ammonium hydroxide (8 % w/w). These solutions were added simultaneously (10 mL.min⁻¹) to a beaker containing 50 mL of distilled water, keeping the system under stirring at room temperature. After addition of the reactants, the pH was adjusted to 10 by adding a concentrated ammonium hydroxide solution (30% w/w). The sol was aged for 24 h under stirring and centrifuged at 2500 rpm, for 4 min. The gel obtained was then washed with distilled water. The steps of washing and centrifugation were repeated until no chloride ions detected in the supernatant anymore. The gel was dried at 120 °C, for 12 h, ground and sieved in 100 mesh. In the case of lanthanum oxide and magnesium oxide, lanthanum nitrate and magnesium nitrate solutions (250 mL, 1 mol.L⁻¹) were used, respectively, following the method described.

All solids were heated ($10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$) under air flow ($50\text{ mL}\cdot\text{min}^{-1}$) up to $750\text{ }^{\circ}\text{C}$ and kept at this temperature for 5 h to get the L (lanthana), M (magnesia), N (niobia), Z (zirconia) and T (titania) samples.

2.2 Catalysts characterization

Samples were characterized by X-ray diffraction (XRD), specific surface area (S_g) and porosity measurements, thermoprogrammed reduction (TPR) and thermoprogrammed ammonia desorption (NH_3 -TPD).

The XRD powder patterns of the solids were obtained in a Shimadzu model XD3A equipment, using $\text{CuK}\alpha$ ($\lambda=1.5420\text{ nm}$) radiation and nickel filter, in a 2θ range between 10 - 80° , with a scanning speed of $2^{\circ}/\text{min}$.

The specific surface area and porosity measurements were carried out by the BET method in a Micromeritics model TPD/TPR 2900 equipment, using a 30% N_2/He mixture. The sample was previously heated at a rate of $10^{\circ}\cdot\text{min}^{-1}$ up to $170\text{ }^{\circ}\text{C}$, under nitrogen flow ($60\text{ mL}\cdot\text{min}^{-1}$), remaining 30 min at this temperature. The TPR profiles were obtained in the same equipment. The samples (0.25 - 0.3 g) were heated from 27 and $1000\text{ }^{\circ}\text{C}$, at a rate of $10^{\circ}\cdot\text{min}^{-1}$, under flow of a 5% H_2/N_2 mixture.

The Micromeritics model TPD/TPR 2900 equipment was also used for the acidity measurements by desorption of ammonia (NH_3 -TPD). The sample was heated at $110\text{ }^{\circ}\text{C}$, under nitrogen flow, during 30 min and then saturated with ammonia, injecting this gas through a calibrated loop. After cooling at room temperature, the temperature programmed desorption began, heating the solid from 30 up to $770\text{ }^{\circ}\text{C}$, under a heating rate of $10^{\circ}\cdot\text{min}^{-1}$, using argon as gas carrier ($45\text{ mL}\cdot\text{min}^{-1}$).

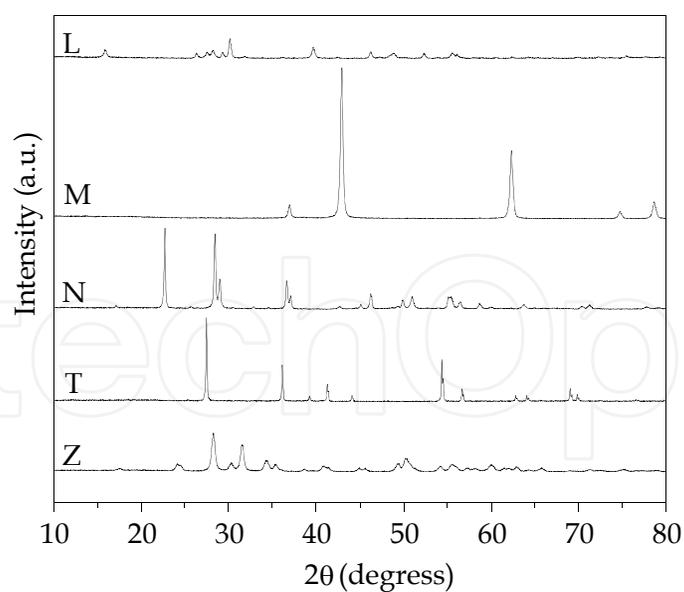
2.3 Catalysts evaluation

In the catalysts evaluation, the sample (0.3 g) was placed in a fixed bed microreactor and the system was heated under nitrogen flow ($20\text{ mL}\cdot\text{min}^{-1}$) up to the reaction temperature ($600\text{ }^{\circ}\text{C}$). The nitrogen flow was then interrupted and a gaseous mixture containing ethylbenzene and nitrogen (coming from a saturator with ethylbenzene at $77\text{ }^{\circ}\text{C}$) was mixed with a carbon dioxide stream in a chamber and then fed to the reactor. The experiments were performed at atmospheric pressure, using a carbon dioxide to ethylbenzene molar ratio of 10. The gaseous effluent was monitored continuously by a Varian model 3600-X chromatograph with ionization flame detection system, in injection intervals of 30 min. The reaction conditions was adjusted to eliminate the diffusion limitations and to get stable values of 10% of conversion with a commercial catalyst at $600\text{ }^{\circ}\text{C}$.

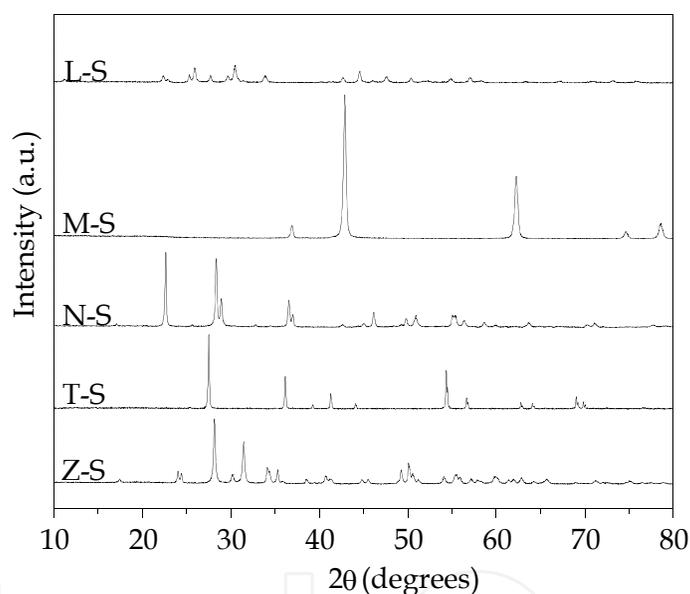
3. Results and discussion

3.1 X-ray diffraction

The X-ray diffractograms of the catalysts before (fresh) and after (spent) ethylbenzene dehydrogenation in the presence of carbon dioxide are displayed in Figure 1. It can be seen that fresh lanthana is made of a mixture of hexagonal lanthanum oxide, La_2O_3 (JCPDS 83-1354) and lanthanum hydroxide, $\text{La}(\text{OH})_3$ (JCPDS 83-2034) while the spent catalyst has only lanthanum oxide.



(a)



(b)

Fig. 1. X-ray diffractograms of the catalysts (a) before and (b) after ethylbenzene dehydrogenation in the presence of carbon dioxide. L= lanthana; M= magnesia; N= niobia; T= titania; Z= zirconia.

On the other hand, the other samples did not go on phase transition during reaction, indicating that they are stable under ethylbenzene dehydrogenation in the presence of carbon dioxide. Moreover, no significant widening or narrowing of the peaks for the fresh and spent catalysts was noted, indicating no change in crystallinity and/or particles size.

For the magnesium-containing solid, cubic magnesium oxide, MgO (JCPDS 87-0652) was found in the catalysts while the monoclinic phase of niobium oxide, Nb₂O₅ (JCPDS 74-0298) was detected for N sample. The tetragonal phase of titanium oxide (rutile), TiO₂ (JCPDS 88-1172) was found for T sample. Zirconium oxide (ZrO₂) showed a typical profile of the monoclinic phase (JCPDS 86-1450) but with several peaks coincident with those of the

tetragonal (JCPDS 88-1007) or cubic (JCPDS 81-550) phases and then the presence of these phases cannot be discarded.

3.2 Thermoprogrammed reduction

Figure 2 shows the reduction profiles of the catalysts. As we can see, the L sample shows a curve with only one reduction peak around 636 °C, which can be related to the reduction of nitrate species and/or the reduction of lanthanum oxide (Santos et al. 2005; Hoang et al., 2003).

On the other hand, the solid based on niobium (N sample) displays a curve with two reduction peaks, the first one at 645 °C can be attributed to the formation of carbon monoxide and dioxide produced from the carbon residue of the precursor, used in the commercial preparation. The second peak, at 894 °C, is related to the reduction of Nb⁺⁵ to Nb⁺⁴ species (Pereira et al., 2000).

The sample containing titanium (T sample) displays a curve with a small and broad reduction peak at 487 °C, assigned to a small reduction of titania (Lenzi et al., 2011). The solid based on magnesium oxide (M sample) presents a curve with a reduction peak centered at 318 °C, related to the reduction of nitrate species and another in the range of 400-850 °C. The curve of zirconium oxide (Z sample) presents two reduction peaks, the first centered at 665 °C and the second one centered at 786 °C (Maity et al., 2000). These results are in agreement with previous works (Santos et al. 2005; Hoang et al., 2003; Pereira et al., 2000; Lenzi et al., 2011; Maity et al., 2000) and indicate that the reducibility increases in the sequence T < N < Z < L < M.

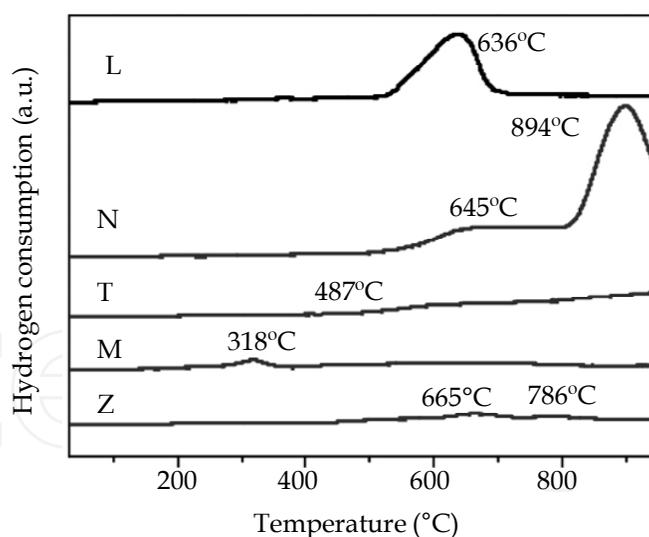


Fig. 2. Curves of thermoprogrammed reduction of the catalysts. L= lanthana; M= magnesia; N= niobia; T= titania; Z= zirconia.

3.3 Specific surface areas and porosity

All samples showed type III isotherms, as shown in Figure 3, which are typical of macroporous solids. Magnesia and zirconia showed curves with a small hysteresis loop (type H3), indicating the presence of some mesopores.

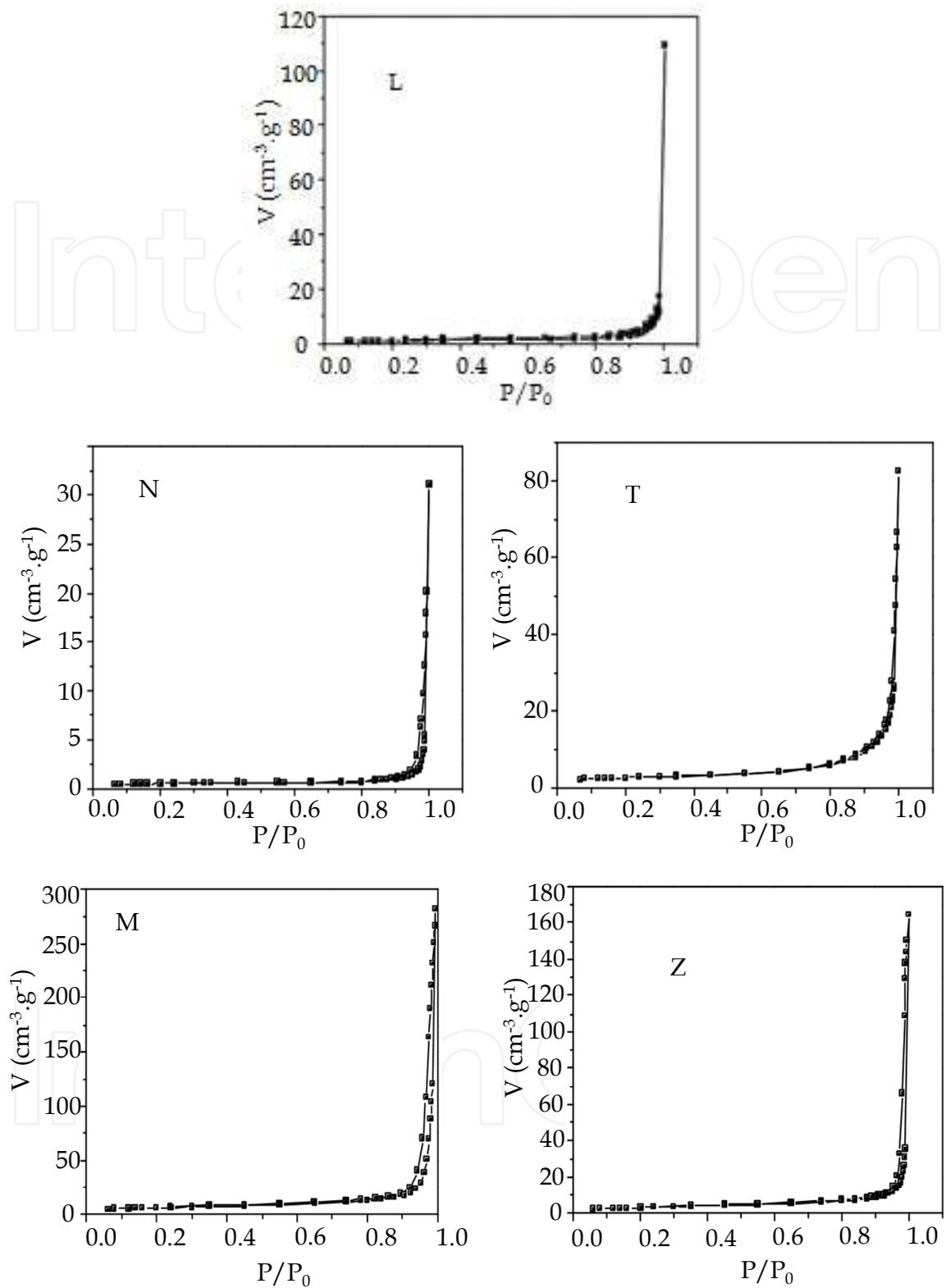


Fig. 3. Adsorption/desorption nitrogen isotherms of the samples. L= lanthana; M= magnesia; N= niobia; T= titania; Z= zirconia.

The specific surface areas of fresh and spent catalysts are shown in Table 1. All fresh catalysts showed low values, this can be assigned to the high calcination temperature of the

solids. During reaction, the specific surface area of titania, magnesia and zirconia showed no significant change, indicating that they were stable under the reaction conditions.

On the other hand, lanthana and niobia showed an increase of this parameter after ethylbenzene dehydrogenation, a fact that can be related to the reduction of the solids during reaction, by carbon monoxide (Equation 2) producing smaller and/or more porous particles. The easiness of these samples for going on reduction is confirmed by the reduction thermoprogrammed profiles, which showed that lanthanum oxide and niobium oxide have consumed the highest amount of hydrogen.

3.4 Thermoprogrammed ammonia desorption

The profiles of temperature programmed desorption of ammonia (NH₃-TPD) for the catalysts are shown in Figure 4 and the total number of moles of ammonia desorbed by the samples is shown in Table 2. As previously stated (Ohishi et al., 2005), the amount of ammonia desorbed below 200 °C is related to weak acidic sites; in the range of 200-350 °C it corresponds to moderate acidic sites, while in temperatures higher than 350 °C it can be associated to strong acidic sites.

Samples	Sg (m ² .g ⁻¹)	Sg* (m ² .g ⁻¹)
L	3.0	15
N	1.6	3.4
T	10	9.2
M	21	18
Z	11	12

Table 1. Specific surface areas of the catalysts before (Sg) and after (Sg*) ethylbenzene dehydrogenation. L= lanthana; M= magnesia; N= niobia; T= titania; Z= zirconia.

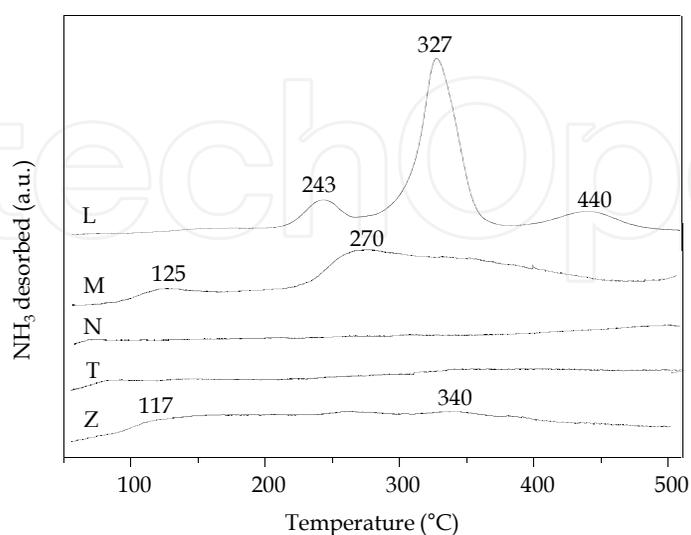


Fig. 4. Curves of thermoprogrammed ammonia desorption for the catalysts. L= lanthana; M= magnesia; N= niobia; T= titania; Z= zirconia.

Samples	$n(\text{NH}_3) \times 10^5 \text{ (g}^{-1}\text{)}$
L	20.89
M	3.10
N	0.73
T	0.72
Z	2.79

Table 2. Total acidity of the catalysts, expressed as number of moles of ammonia, $n(\text{NH}_3)$ desorbed per gram of catalyst. L= lanthana; M= magnesia; N= niobia; T= titania; Z= zirconia.

Niobia and titania showed a very low hydrogen consumption (Table 1), indicating almost the absence of acidic sites. For zirconia and magnesia weak and moderate sites were detected, which correspond to a low ammonia consumption. For lanthana, the amount of ammonia desorbed is much greater than for other oxides, showing that it is the most acidic solid. The desorption peaks are centered at 243, 327 and 440 °C and the most sites are those of moderate strength.

3.5 Activity and selectivity of the catalysts

All catalysts were active in ethylbenzene dehydrogenation, in the presence of carbon dioxide, as shown in Figure 5. In the beginning of reaction, lanthana was the most active one followed by the others in the order: $L > Z > M \cong N > T$. This behavior can be related to both the intrinsic activity of these solids and their specific surface areas. As these catalysts are mass,

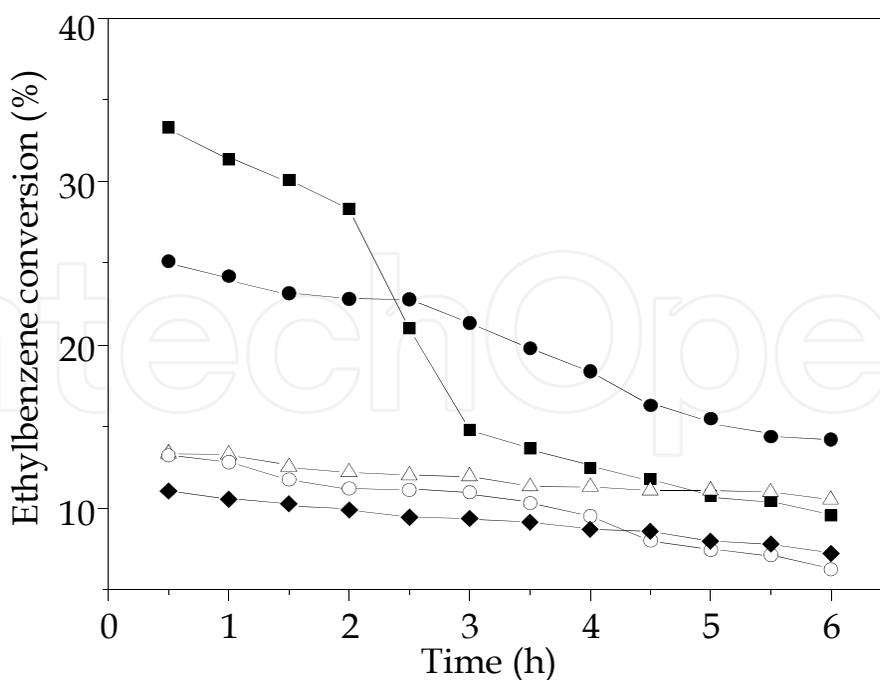


Fig. 5. Ethylbenzene conversion as a function of time over the catalysts during dehydrogenation reaction in the presence of carbon dioxide. (■) L= lanthana; (Δ) M= magnesia; (○) N= niobia; (◆) T= titania; (●) Z= zirconia.

Sample	$a_i \times 10^3$ (mol.g ⁻¹ .h ⁻¹)	$a_i/S_g \times 10^4$ (mol.m ⁻² .h ⁻¹)	$a_f \times 10^3$ (mol.g ⁻¹ .h ⁻¹)	$a_f/S_g \times 10^4$ (mol.m ⁻² .h ⁻¹)	ΔX (%)
L	3.8	12.7	1.1	0.7	23.5
N	1.5	9.2	10.7	2.3	4.8
T	1.3	1.3	1.1	1.2	1.6
M	2.9	1.4	2.5	1.4	1.9
Z	2.7	2.5	1.6	1.3	10.6

Table 3. Initial (a_i) and final (a_f) activity, initial (a/S_g) and final (a^*/S_g) specific surface area of the catalysts and the drop in conversion (ΔX) during ethylbenzene dehydrogenation in the presence of carbon dioxide. $\Delta X = X(\text{initial}) - X(\text{final})$. L= lanthana; M= magnesia; N= niobia; T= titania; Z= zirconia.

their intrinsic activity can be conveniently expressed as the activity per specific surface area. As shown in Table 3, the intrinsic activity decreases in the order: $L > N > T \cong M \cong Z$, indicating that titania, magnesia and zirconia have the same activity in ethylbenzene dehydrogenation while lanthana and niobia showed the highest values, a fact that is closely related to the kind of metallic oxide. In addition, it is well known the ability of lanthana for adsorbing carbon dioxide (Yue et al., 2007) favouring the activity in the reaction. Niobia showed the lowest activity due to its low specific surface area, since it has intrinsic activity close to zirconia.

During ethylbenzene dehydrogenation, all catalysts go on deactivation but in different ways, according to their kind (Figure 5 and Table 3). The lanthanum-based sample showed the highest deactivation, the conversion decreases sharply after 2 h of reaction achieving values close to magnesia, at the end of reaction. On the other hand, zirconia deactivates slowly during reaction while the other samples deactivates even more slowly.

Zirconia was the most selective catalysts towards styrene production, as shown in Figure 6, while titania was the least selective one; the other samples showed similar intermediate values of selectivity. During reaction, the selectivities change according to the kind of the catalysts, in such way that at the end of reaction the selectivity decreases in the order: $Z > M \cong L > T > N$. This finding suggests that the active sites go on transformations during reaction probably related to changes in acidity. As found previously (Qiao et al., 2009), the selectivity of the catalysts in ethylbenzene dehydrogenation is closely related to the acidity/basicity of the sites.

The selectivities of the catalysts to benzene and toluene are shown in Figures 7 and 8, respectively. As we can see, titania and niobia were the most selective catalysts to toluene, in agreement with the results of ammonia desorption. According to previous authors (Qiao et al., 2009), if the basic sites are strong enough to remove the β -hydrogen, the rupture of the lateral bond C-C will be favored and then the toluene selectivity will increase. On the other hand, if the acidity is high, the α -hydrogen will be preferentially removed, the phenyl-C bond will be favored and benzene selectivity will increased. Therefore, benzene and toluene are formed on different kinds of sites.

The selectivities to benzene and toluene change during ethylbenzene dehydrogenation, as noted in Figures 7 and 8. It is interesting to note that after 5 h of reaction, the selectivity of niobia to toluene increased sharply as the expenses of a decrease in ethylbenzene selectivity. It suggests that the basicity of niobia increases even more during reaction.

The values of styrene yield as a function of reaction time in ethylbenzene dehydrogenation are shown in Figure 9. One can note that the values follow the same tendency as the conversion both in the beginning and in the end of reaction. Zirconia led to the highest yield, followed by lanthana, which leads to yield similar to magnesia and lightly higher than titania and niobia.

These results show that zirconia is the most promising catalyst for ethylbenzene dehydrogenation in the presence of carbon dioxide, as compared to lanthana, niobia, titania and magnesia. These findings are mostly related to the kind of oxide as well as to the acidic/basic properties of the catalysts.

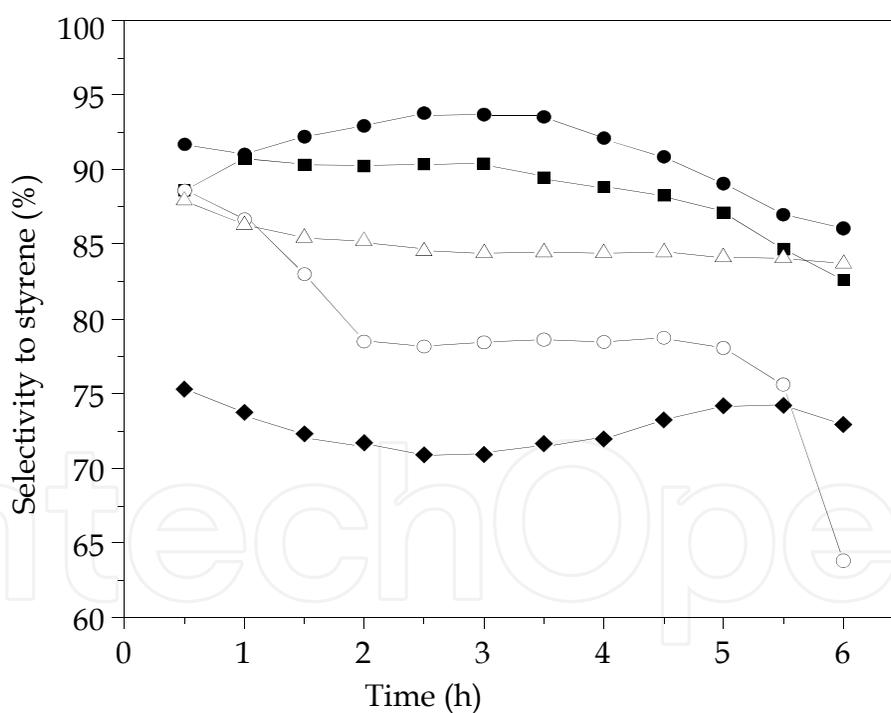


Fig. 6. Selectivity of the catalysts to styrene as a function of time during dehydrogenation reaction in the presence of carbon dioxide. (■) L= lanthana; (Δ) M= magnesia; (○) N= niobia; (◆) T= titania; (●) Z= zirconia.

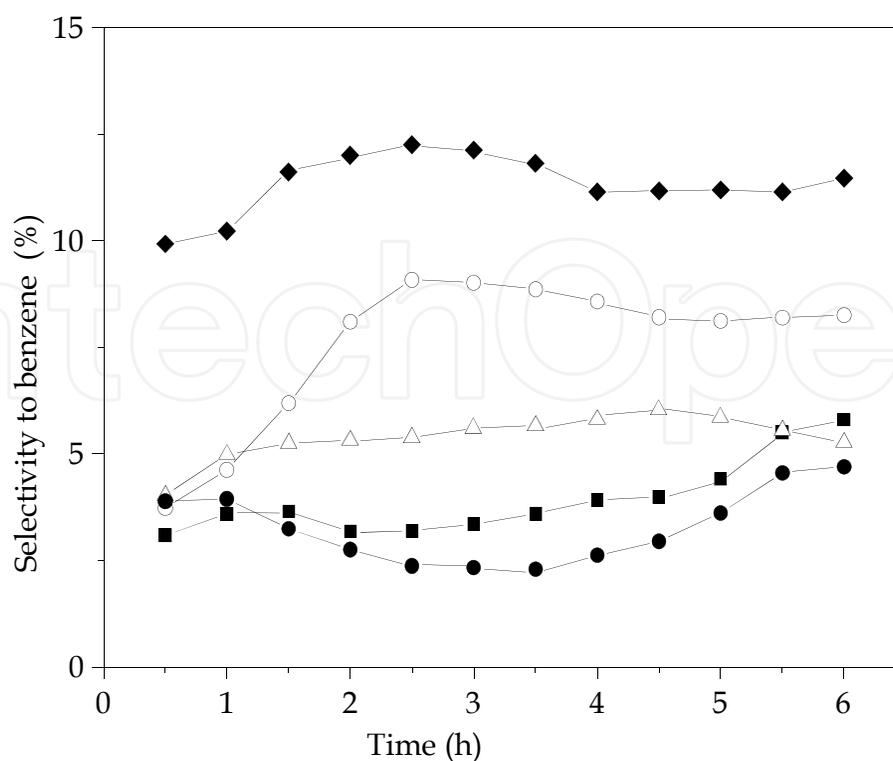


Fig. 7. Selectivity of the catalysts to benzene as a function of time during dehydrogenation reaction in the presence of carbon dioxide. (■) L= lanthana; (△) M= magnesia; (○) N= niobia; (◆) T= titania; (●) Z= zirconia.

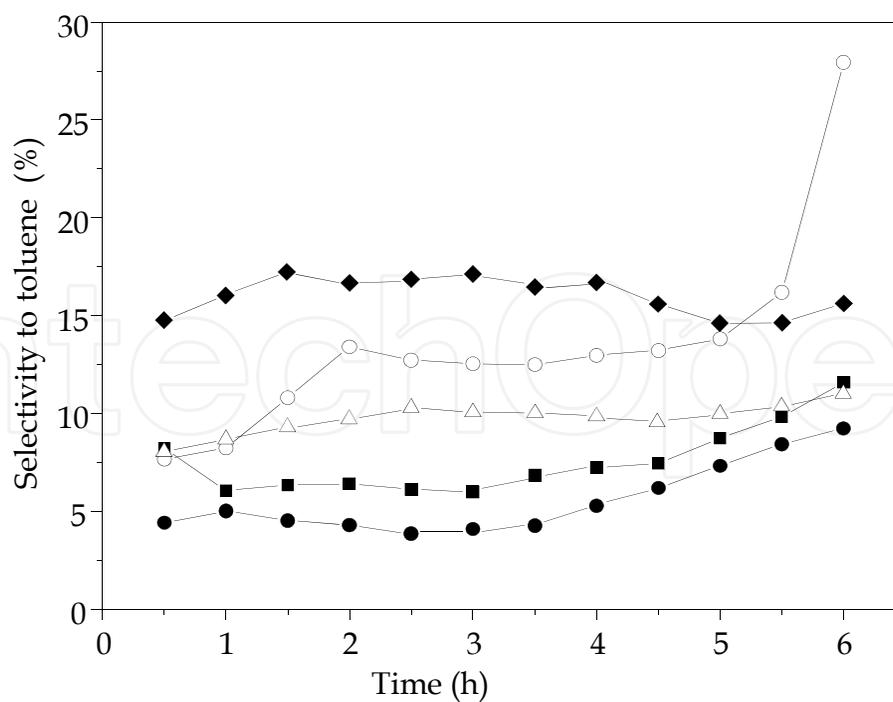


Fig. 8. Selectivity of the catalysts to toluene as a function of time during dehydrogenation reaction in the presence of carbon dioxide. (■) L= lanthana; (△) M= magnesia; (○) N= niobia; (◆) T= titania; (●) Z= zirconia.

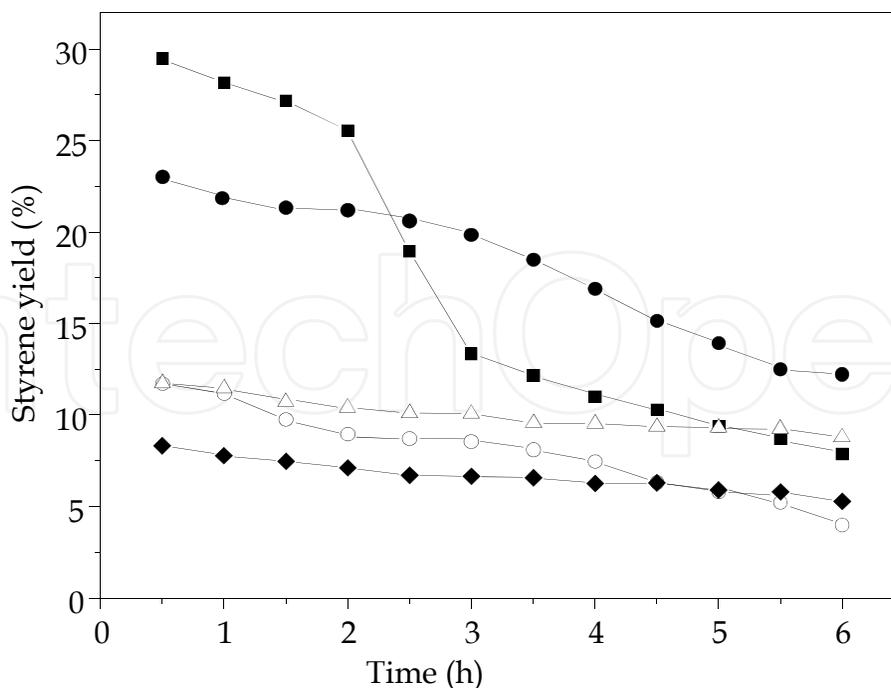


Fig. 9. Styrene yield as a function of time over the catalysts during ethylbenzene dehydrogenation in the presence of carbon dioxide. (■) L= lanthana; (Δ) M= magnesia; (o) N= niobia; (♦) T= titania; (●) Z= zirconia.

4. Conclusion

Metal oxides such as lanthana (La_2O_3), magnesia (MgO), niobia (Nb_2O_5), titania (TiO_2) and zirconia (ZrO_2) are catalytically active in ethylbenzene dehydrogenation in the presence of carbon dioxide to produce styrene. These solids are stable during reaction, showing the same phases before and after reaction, except for the lanthanum-based solid, which went on phase transition during reaction. Except for zirconia and titania, all specific surface areas changed during reaction. All catalysts have shown styrene selectivities higher than 60 % and were typically basic, producing more toluene than benzene. Zirconia was the most active and selective catalyst and this was related to its highest intrinsic activity. It was also the most selective to styrene, leading to the highest styrene yield. Therefore, it is the most promising catalyst to produce styrene by ethylbenzene dehydrogenation in the presence of carbon monoxide, among the samples studied.

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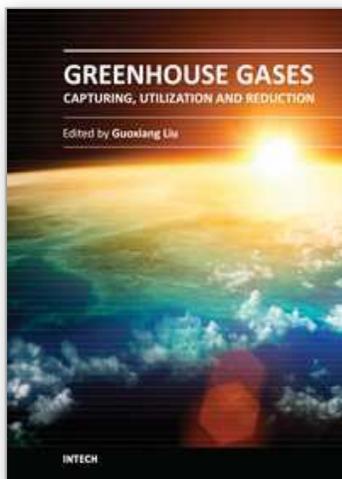
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