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NO reduction with CH_4 or CO on $Pt/ZrO_2–CeO_2$ catalysts

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Abstract

Catalytic properties of platinum supported on $ZrO_2–CeO_2$ were studied in the NO reduction by CO or CH_4 as a reducing agent. The catalysts were characterized by means of N_2 adsorption, SEM, XRD, TPR and 2-propanol decomposition. Pt/CeO_2 catalyst showed a higher surface area than the $Pt/ZrO_2–CeO_2$ and Pt/ZrO_2 catalysts. All samples showed irregular shape and cumulus size. The PtO_2 reduction causes spill over of hydrogen onto the support inducing a concurrent reduction of platinum oxide and the ceria-rich support. The monoclinic and tetragonal phases of the ZrO_2 and the cubic phase of the CeO_2 were identified in the catalysts. 2-Propanol reaction on ZrO_2 sample showed high selectivity towards propene, this is due to the acid properties of this material. The reduction of the NO was dependent of the reducing agent on the catalysts. When CH_4 was used for NO reduction, the catalysts that contain zirconia in the support showed the highest catalytic activity. The NO reduction with CO produced a shift to higher temperature, on this reaction the ceria-content catalysts showed the best catalytic activity. The highest selectivity toward N_2 was showed when CH_4 was used as a reduction agent for the NO reduction. While, the highest N_2 yield was observed on Pt/ZrCe-70 catalysts for both reactions.

Keywords: $Pt/ZrO_2–CeO_2$; SCR; NO + CO; NO + CH_4; Catalytic activity; TPR

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1. Introduction

Nitric oxide (NO) is one of the major air pollutants particularly in the modern big cities. It is estimated that 35–38 × 10^6 t of NO are released from the exhaust gases of automobiles every year in the world. NO causes severe environmental hazards and is very harmful to the human being health. The common methods of NO treatment include liquid or solid absorption, selective catalytic reduction of NO with NH_3 and electronic irradiation. However, all these methods result in incomplete NO treatment and cause secondary pollutants. Selective catalytic reduction (SCR) by hydrocarbons (HC), and specifically by CH_4, seems to be the technology of choice. The noble metals are responsible for the elimination of CO, HC and reduction of NOx from exhausted gases. Several studies were reported aiming to diminish the Rh contents and also to eliminate them by substitution with other less expensive elements or rare transition metals. The reduction of NO by CO is catalyzed by precious metals; in particular Rh is used in three way conversion catalysts [1]. The scarcity and high price of Rh, however, promoted the investigations to develop novel catalyst systems; low-Rh content or non-Rh catalysts such as MO-supported Pt catalyst [2,3] or catalysts using the first transition metals as main catalytic components. Although platinum is considered the best metal candidate for the SCR reactions, doubts exist concerning the type of the support to be used. For this reason, since 1980s, scientists have been looking for highly efficient DeNOx catalysts to eliminate NO through reductive mechanisms. CeO_2 has been widely used in purifying vehicle exhausts and became the most important rare oxides for controlling NOx. CeO_2 increases the dispersion of active components and thermal stability of the support, and enhances the migration and exchange of oxygen species in the reactions by storing and releasing oxygen of CeO_2 so as to improve CO, HC oxidation and NOx reduction [4,5]. CeO_2 support would be sintered after

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calcinations at 750 °C [6], in the solid solution of ZrO_2–CeO_2, the replacement of some Ce atoms by other cations led to the microstain and lattice defect of CeO_2 yielding a better catalytic activity at low temperatures, thermal stability and higher redox potential than pure CeO_2 [7–9]. Due to this fact a strong effort has been directed to increase the overall efficiency of CeO_2 in these applications and recently a new generation of mixed oxides based on CeO_2 and ZrO_2 has been developed [10–12]. Martínez-Arias et al. [13] studied the influence of NO into CO oxidation over $CuO/CeZrO_4$. They assumed that both the copper oxide and the support components of the interface are involved to some extent in the reaction.

In this work we studied the effect of CO or CH_4 as a reduction agent in the catalytic properties of the Pt supported in ZrO_2–CeO_2 for NO reduction.

2. Experimental methods

2.1. Preparation of catalytic materials

2.1.1. Single oxides

ZrO_2 was prepared by a sol–gel method from zirconium (IV) propoxide (Fluka) as a precursor in *n*-propanol (Aldrich) solution and acid catalyst (HNO_3) (Baker) in constant stirring. The solution was processed at reflux temperature and deionized water was added drop wise to complete hydrolysis. Reflux continued for 50 min and then cooled to room temperature. The mixture was aged for 24 h and the residual liquid was removed by decanting. The synthesis of CeO_2 proceeded by combustion method by heating cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$) (Sigma) at 100 °C for 1 h in air stream and then burned at 700 °C for 5 h.

2.1.2. The mixed oxides

ZrO_2–CeO_2 (50 and 70 wt.% of CeO_2 in mixed oxides) were prepared as follows: $(Ce(NO_3)_3) \cdot 6H_2O$ at an appropriate composition to yield (50 and 70 wt.%) was dissolved at room temperature in *n*-propanol then the HNO_3 and Zr-propoxide were added. The solution was processed at reflux temperature and deionized water was added drop wise to complete hydrolysis. Reflux continued for 50 min and then cooled to room temperature. The mixture was aged for 24 h and the residual liquid was removed by decanting. The molar ratio used for the synthesis was: propoxide/alcohol/H_2O/HNO_3 was 1:4:4:0.33. A xerogel was obtained after heating at 100 °C for 24 h. Aliquots of the xerogel were first heated 1 h at 100 °C under an air stream and then burned at 700 °C for 5 h.

The prepared supports were impregnated with the Pt-$(acac)_2$ (Merck) at an appropriate concentration to yield 1 wt.% of Pt in all catalysts. The samples were dried at 100 °C for 1 h and then burned at 500 °C for 2 h in air stream, and reduced with H_2 at 500 °C for 1 h. The labelling of different catalysts will be referred as Pt/ZrO_2, Pt/CeO_2 and Pt/ZrCe-*n*, were Zr = ZrO_2, Ce = CeO_2, *n* = 50, 70 wt.% of CeO_2 in mixed oxide, respectively.

2.2. Characterization

Total surface area was calculated by the BET method from N_2 adsorption by the single point method using a 30% N_2/He gas mixture, recorded at the temperature of liquid nitrogen. X-ray diffraction (XRD) powder patterns were recorded in a Siemens D-5000 diffratometer, using Cu Kα ($\lambda = 0.15406$ nm). The morphology and chemical composition analysis of the samples were performed in a Philips XL-30, with a resolution of 3.5 nm, fitted with an energy dispersive X-ray spectrometer (EDAX). The analysis was performed in equipment conditions of 25 kV acceleration voltages, obtaining the images with the backscattering electron signal. Before the analysis, the samples were fixed on an aluminium specimen holder with an aluminium tape. The TPR experiments were performed in a multitask unit RIG-100 from in situ Research Inc. For TPR runs, the sample (0.1 g) was placed in the reactor and purged with Ar at room temperature and then heated at a rate of 10 °C/min in presence of a 5% H_2/Ar gas mixture (30 ml/min). 2-Propanol (Aldrich, 99.9%) decomposition was determined in a continuous flow reactor. 0.05 g of the sample was reactivated in He in a flow of 60 ml/min, from room temperature to 300 °C at a rate of 10 °C/min, remaining at this temperature for 1 h. The sample was brought up to the reaction temperature (200 °C) in He 60 ml/min. The partial pressure of the 2-propanol was 100 Torr. The effluent gas of the reactor was analyzed by gas chromatography using TCD. A 2-m packed Porapack Q was used at 115 °C to separate the reaction products from the isopropanol decomposition.

2.3. Catalytic tests

The steady-state activity in the reduction of NO to N_2 in the presence of CH_4 or CO was studied in a flow reactor equipped with an on-line gas chromatograph (using TCD). The amount of the catalyst was 0.05 g and the total flow rate (STP) was 100 ml/min. A thermocouple in contact with the catalytic bed allowed the control of the temperature inside the catalyst. The feed composition for the test was adjusted by a mass-flow controller attached inside of the RIG-100 in order to obtain a mixture consisting of 2500 ppm of NO and 2500 ppm of CH_4 or CO in He. Before each activity test, the catalyst was reduced in situ by heating the catalyst in a stream of 60 ml/min H_2, from room temperature to 400 °C at a rate of 10 °C/min, remaining at this temperature 1 h. The catalyst was brought up to the reaction temperature in He and the reaction mixture was introduced. The activity test was performed at different temperatures from 200 to 500 °C in steps of 50 °C. The effluent gas from the reactor was separated using a 4-m packed carbosphere and molecular sieve 5A columns used at 85 °C to separate the reaction products from the NO + CH_4 or NO + CO reactions.

The activity of the catalyst is defined as C_{NO} (%), the percent conversion of NO to all products.

$$C_{NO} = \frac{[NO]_{in} - [NO]_{out}}{[NO]_{in}} \times 100$$

The selectivity towards N_2 (mol of N_2 produced) is given by:

$$\%S = \frac{[N_2]_{out}}{2[NO]_{in}} \times 100$$

The subscripts in and out indicate the inlet and the outlet concentrations of the reactants or products.

3. Results and discussion

3.1. BET specific surface area

Table 1 summarizes the BET specific surface area of the supports and the catalysts after different thermal treatments. CeO_2 support exhibited a higher value of specific surface area (ca. 43 m^2/g) than the mixed oxides and ZrO_2. When the ceria content goes up to 50 and 70 wt.% on the mixed oxide the surface area values are close to 30 m^2/g. Pt impregnation on the supports causes a decrease in the surface area, this behaviour could be attributed to the blockade of the pores in the support by the Pt, as well as to the thermal treatments, but the tendency in the surface area was maintained. The Pt/ZrO_2 catalyst showed the lowest surface area, as well as flat facets and the largest cumulus size [14] related to the highest degree of sinterization.

3.2. XRD analysis

Fig. 1 shows the XRD patterns of the Pt/ZrO_2–CeO_2 catalysts. All the samples, showed diffraction peaks characteristic of crystalline materials. Monoclinic and tetragonal phases were identified in the Pt/ZrO_2 sample. Broad XRD peaks were observed for Pt/ZrCe-50, this pattern showed a segregation of phases, cubic CeO_2 and tetragonal ZrO_2. This result could be attributed to the fact that the water from cerium precursor can hydrolyze the Zr-propoxide, promoting the phases segregation between the zirconia and the ceria. XRD pattern of Pt/ZrCe-70 and Pt/CeO_2 showed a cubic phase of CeO_2. None of the cases observed by this technique presented evidences of phase corresponding to the Pt. This is due to the low concentration of the metal (1.0 wt.%) or because the particle size of the Pt is below of the detection limit of the technique.

Table 1
BET surface area of Pt/ZrO_2–CeO_2 catalysts (m^2/g)

Support	Surface area	Catalyst	Surface area
ZrO_2	19	Pt/ZrO_2	15
ZrCe-50	28	Pt/ZrCe-50	23
ZrCe-70	30	Pt/ZrCe-70	27
CeO_2	43	Pt/CeO_2	36

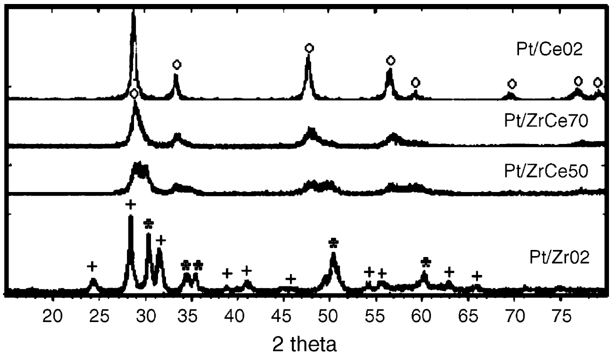

Fig. 1. XRD patterns of the Pt/ZrO_2–CeO_2 catalysts after different thermal pre-treatments: [+] monoclinic (ZrO_2); [*] tetragonal (ZrO_2); [○] cubic (CeO_2).

3.3. Temperature-programmed reduction

Fig. 2 shows the TPR profiles obtained from the calcined Pt/ZrO_2–CeO_2 catalysts. Three reduction peaks were observed on ceria-rich samples, while in the zirconia-rich catalysts only two reduction peaks were observed. The relative intensities of the peaks strongly depend on the CeO_2 content. The Pt/ZrO_2 catalyst showed a peak of around 220 °C and another at higher temperature, starting at 650 °C. The reduction peaks of ceria-rich catalysts shifted toward lower temperature in comparison with the Pt/ZrO_2 sample. Pt/CeO_2 sample showed a shoulder at 77 °C and three reduction peaks at 115, 240 and 400 °C. Pt/ZrCe-50 catalyst showed reduction peaks at 110, 190 and 390 °C. The hydrogen uptake for the peak centred at 110 °C was much larger than expected for the reduction of all platinum. This peak is likely due to a concomitant reduction of PtOx crystallites and the synergistically reduced ceria. On the other hand, the presence of reduction peaks at 90, 140 and

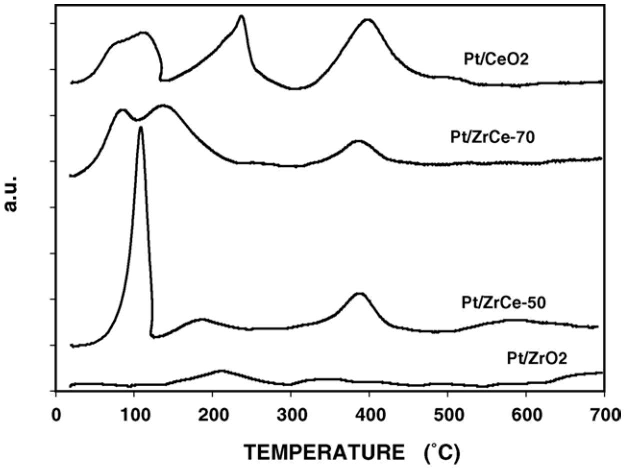

Fig. 2. TPR profiles of calcined Pt-loaded ZrO_2–CeO_2 catalysts.

Table 2
Characteristic reduction temperature peaks of the Pt/ZrO_2–CeO_2 catalysts

Catalysts	Peak 1 (T_{max}) (°C)	Peak 2 (T_{max}) (°C)	Peak 3 (T_{max}) (°C)	Peak 4 (T_{max}) (°C)	PtO_2 reduction (%) from peak 1
Pt/ZrO_2	220	Star at 650	–	–	30
Pt/ZrCe-50	110	190	390	–	176
Pt/ZrCe-70	90	140	390	–	74
Pt/CeO_2	77 (shoulder)	115	240	400	63

390 °C were observed on the Pt/ZrCe-70 sample. This last peak appeared at the characteristic reduction temperature of all ceria-rich catalysts. During the TPR study the metal particles caused spill over of hydrogen onto the support inducing a concurrent reduction of both the platinum oxide and the surface of CeO_2 [10,15–17]. In the ceria-rich samples the reduction of the support depends strongly on the CeO_2 loaded in the catalysts, this phenomena caused a large H_2 consumption. The amount of H_2 consumption by the reduction peaks is reported in Table 2. The apparent lack of the H_2 consumption in the platinum oxide reduction (Table 2) could be related to the fact that in the calculation none of the following phenomena are considered: (a) platinum oxide is reduced at sub-ambient temperatures; (b) some platinum oxide interacts strongly with the support, therefore, it is reduced at higher temperatures. The reduction at 500 °C for the ceria-rich catalysts caused a SMSI (strong metal support interaction) effect, due to this, it was not possible to determinate the Pt dispersion by CO or H_2 chemisorption in these samples. For the Pt/ZrO_2 catalyst the dispersion of Pt was 7%. Even when it was not possible to determine the dispersion in the ceria-rich catalysts, it is assumed that the values should be close to the Pt/ZrO_2 catalyst, because of surface area in all catalysts is similar (Table 1).

3.4. 2-Propanol reaction

Dehydration of 2-propanol to propene is widely used to characterize the acidity of the oxides [18]. Some reports indicate that dehydrogenation of 2-propanol to acetone can also reveal basicity [19]. However, this issue remains unclear since acetone formation can occur by a redox mechanism, particularly at low temperature [20]. In Table 3, the selectivity and reaction rate for 2-propanol decomposition are presented. After 3 h of isopropanol decomposition (4% of 2-propanol in He and 60 ml/min) the reaction rate with CeO_2 happened to be half as with the ZrO_2 and ZrCe-50 samples (Table 3). However, the zirconia showed the highest selectivity to propene and water, whereas on ZrCe-50 and CeO_2, formation of acetone (about 50%) is also observed. 2-Propanol dehydrates on ZrO_2 showing its more pronounced acidic character than ZrCe-50 and CeO_2 samples. For the Pt/ZrO_2 catalyst, Mariscal et al. [21] showed by DRIFT that the sample exhibited important acid properties.

Table 3
2-Propanol decomposition on ZrO_2–CeO_2 samples

Sample	Reaction time (min)	Propene (%)	Acetone (%)	Ra ($\times 10^7$ mol/s/g)
ZrO_2	205	93	7	6.53
ZrCe-50	207	48	52	6.54
CeO_2	200	49	51	3.05

3.5. Catalytic activity

Fig. 3 shows the total NO conversion with CH_4 versus temperature over the Pt/ZrO_2–CeO_2 catalysts. The light-off temperature for all samples is near to 300 °C. The catalytic activity on the catalysts with ZrO_2-content is similar and, the NO conversion reached 100% at 350 °C. In the Pt/CeO_2 sample the catalytic activity was less than the other catalysts and, the NO conversion reached 100% at 400 °C. Pérez-Hernández et al. [22] studied the NO reaction on Pt/ZrO_2–TiO_2 samples and they found that the NO conversion reached 100% at 500 °C on the Pt/ZrO_2 catalyst. For this system, Mariscal et al. [21] showed by DRIFT the presence of isocyano (–N≡C) and isocyanate (–NCO) species stable on Pt supported on zirconia-rich catalysts for NO + CH_4 reaction. For Ru/γ-Al_2O_3 catalysts the temperature in which the NO conversion reached 100% was at 450 °C [23].

Fig. 4 shows the influence of the CO on the NO reduction over Pt/ZrO_2–CeO_2 catalysts. The use of CO instead of CH_4 as a reducing agent produces in the NO conversion a 50 °C shift to higher temperatures. The light-off temperature for all catalysts is near to 350 °C. In these catalysts, the NO conversion reached 100% at 400 °C except the Pt/ZrO_2

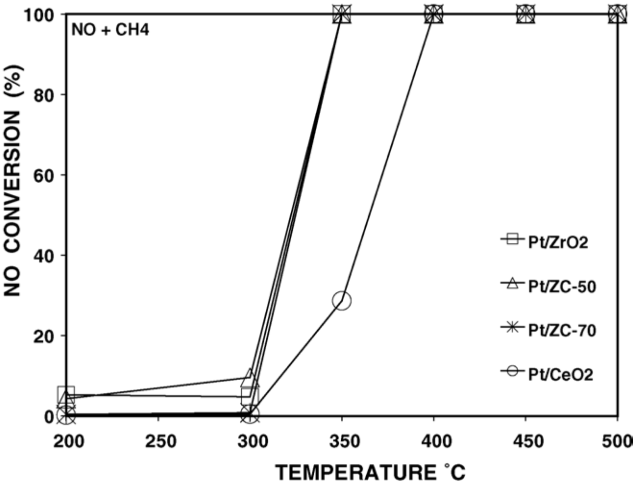

Fig. 3. NO conversion percent profiles vs. T (°C) for the NO + CH_4 reaction over Pt/ZrO_2–CeO_2.

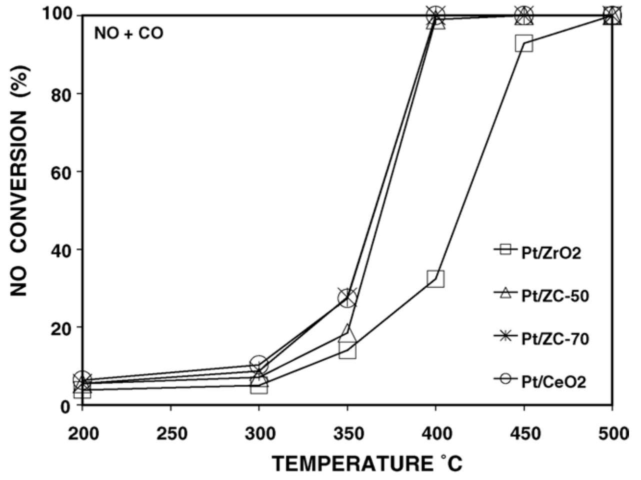

Fig. 4. NO conversion percent profiles vs. *T* (°C) for the NO + CO reaction over Pt/ZrO_2–CeO_2.

sample which reach that conversion at 500 °C. A peculiarity in the Pt/ZrO_2 and Pt/CeO_2 catalysts is their catalytic behaviour for NO reduction with CO or CH_4. The catalytic activity on NO + CO reaction, increased slowly with the reaction temperature for the Pt/ZrO_2 sample, while in the same catalyst, its catalytic activity for NO + CH_4 reaction increased faster when the temperature is rising. An opposite behaviour was observed for the Pt/CeO_2 sample. This suggests that the presence of the acid–basic sites on the catalysts are important for the NO + CO reaction; while in the acid properties seem to be important in the catalysts for NO reduction with CH_4. Several studies have demonstrated the importance of the acidic sites in the NO + CH_4 reaction [21,24,25]. Other authors have reported that the role of acid sites is to promote the NO oxidation step [26–28] on NO reduction with HC. For the reduction of NO by CO on Pt-MoO_3/γ-Al_2O_3 catalysts, da-Silva and Schmal [29] suggest the existence of synergy between Pt and Mo, in which platinum maintains the surrounding molybdenum particles in its more active form and suggested significant changes of surface sites during the reaction. Xie et al. [30] reported on Ba/MgO catalysts that the rate of NO reduction was higher with CH_4 than CO (at the same amounts of CO or CH_4 employed). This behaviour was observed in this work.

3.5.1. Selectivity

The products for the NO + CH_4 reaction were N_2, N_2O, CO_2 and H_2O; the formation of CO was not detected at any of the reaction temperatures. In the case of the NO + CO reaction the detected products were N_2, N_2O and CO_2. The N_2 (mol%) selectivity on the NO reduction with CH_4 or CO as a reducing agent gradually increases with the reaction temperature in all catalysts and followed nearly the same trend as the overall activity. However, the selectivity for each catalyst is different (Table 4). For the NO + CH_4 reaction the Pt/CeO_2 catalyst was more selective towards N_2 than the Pt/ZrO_2 sample when NO conversion reached 100% at 400 °C and 350 °C, respectively. In the Pt/ZrCe-70 catalyst the selectivity towards N_2 was higher than the Pt-supported on single oxides. The Pt/ZrCe-70 sample showed a better N_2 yield than the other samples after 350 °C. At high temperature the selectivity toward N_2 is near 100% in all catalysts. Balint et al. [23] showed that NO is selectively reduced by CH_4 to N_2 and CH_4 is selectively oxidized by NO to CO_2 and H_2O over Ru nanoparticles supported on γ-Al_2O_3. In our case the products of the methane oxidation with NO were CO_2 and H_2O. Chin et al. [26b] studied the NO + CH_4 reaction on Pd supported on tungstated zirconia, they observed that selectivity towards N_2O was very low, particularly for the catalyst supported on the acidic materials. Liotta et al. [31] studied the NO reduction with C_3H_6 in presence of O_2 on Pt/$Ce_{0.6}Zr_{0.4}O_2$ catalyst as a function of the reduction temperature. Enhancement of the activity was found for the catalyst pre-treated in hydrogen at 350 °C as compared to the sample pre-treated at 800 and 1050 °C. However, no differences were reported in terms of the selectivity to N_2, at the temperature of maximum NO conversion.

Table 4
Effect of the temperature on N_2 selectivity when CH_4 or CO is used for the NO reduction

Temperature (° C)	N_2 selectivity (%)							
	Pt/ZrO_2		Pt/ZC-50		Pt/ZC-70		Pt/CeO_2	
	CH_4	CO	CH_4	CO	CH_4	CO	CH_4	CO
200	11	4	23	10	4	9	6	10
300	10	4	21	10	10	11	8	12
350	34	7	89	15	88	20	17	18
400	56	15	100	35	100	74	83	41
450	100	67	98	94	99	98	98	96
500	96	100	97	100	100	100	100	100

On the other hand, when CO is used as a reducing agent for the NO conversion, the N_2 selectivity was modified in all the catalysts. Table 4 shows that the Pt/ZrCe-70 catalyst was the more selective towards N_2 in all the studied reaction temperatures. For this reaction, the Pt/ZrO_2 catalyst showed a low selectivity towards N_2 respect to the Pt/CeO_2 sample as in the NO + CH_4 reaction, when NO conversion reached nearly 100%.

The selectivity toward N_2 on the Pt/ZrO_2 base catalyst when NO achieves a 100% conversion was 34 and 67% at 350 and 450 °C in presence of CH_4 or CO, respectively. At the same NO conversion on the other base catalyst, Pt/CeO_2, the N_2 selectivity was 83 and 41% at 400 °C in presence of CH_4 or CO, respectively. However, at higher temperatures the selectivity towards N_2 is nearly 100% in all catalysts.

4. Conclusions

Catalytic supports were prepared by sol–gel and Pt/ZrO_2–CeO_2 catalysts by the classic impregnation method.

The catalytic activity was determined by the NO reduction in presence of CO or CH_4 as a reducing agent. The catalytic activity of the Pt/ZrO_2–CeO_2 catalysts as a function of the reaction temperature for the NO + CO reaction showed that the ceria-content catalysts were the most active, while for the NO reduction, where CH_4 was used as a reduction agent, the zirconia-content in the catalysts were the most active (for this reaction the NO conversion shifted towards to lower temperatures). The results obtained in the decomposition of 2-propanol as a model reaction to determine the acid–basic properties in the samples, allowed to establish that the zirconia sample presents important acidic properties while the ceria and the ZrCe-50 sample showed acid–basic properties, result that can be correlated with the catalytic activity of the catalysts. In this context, the presence of the acid–basic sites on the catalysts seemed to be important for the NO + CO reaction. While the acid properties seem to be important in the catalysts for NO reduction with CH_4, as well as, of the support, however, the intermediary of the reaction cannot be rule out. The N_2 selectivity was larger for the NO reduction with CH_4 than CO as a reducing agent. Finally the Pt/ZrCe-70 catalyst was the most selective to N_2 than the all catalysts tested in this work.

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