CHARACTERIZATION AND BEHAVIOUR OF PT CATALYSTS SUPPORTED ON BASIC MATERIALS IN DRY REFORMING OF METHANE

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Abstract - Different basic materials, such as K-L zeolite, $K-Al_2O_3$, K-Mg/Al mixed oxide and MgO, were used as supports of Pt-catalysts for the dry reforming of methane (DR) reaction. The effects of the distribution of basic strength in the support on the metal-support properties and catalyst performance were evaluated. The density of strong and the total basic sites decreased as follows: MgO>K(Mg-Al) >$K-Al_2O_3$>K-L. The total basic sites decrease from 214 to 23 µmol CO_2. g^{-1}, for MgO and KL, respectively. Pt catalysts supported on materials with high density of strong basic sites such as MgO were the most adequate for the DR reaction. An increase in the dehydrogenation velocity of 12.1 to 25.2 mol h^{-1} g^{-1} was observed between Pt/KL and Pt/MgO, which indicates a higher metallic dispersion of the latter catalyst. With respect to the DR reaction, both catalysts have a similar CO_2 conversion, but the CH_4 conversion and the H_2/CO ratio increase from 71.1 to 83.0 % and 0.5 to 0.73, respectively. The best catalytic behaviour of Pt/MgO would be related with the good interaction between the metal and the basic support. The methane conversion and the H_2/CO ratios obtained by DR reaction correlate quite well with the basicity of the different catalysts.
Keywords: Dry reforming of CH_4; H_2 production; Syngas; Platinum acetylacetonate (II); Mg/Al mixed oxide; Alkaline metal-doped materials.
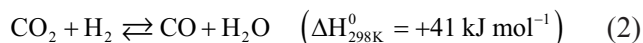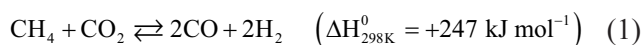
INTRODUCTION

The transformation of methane into syngas, a more valuable product, has attracted noticeable interest since high conversions and selectivities can be obtained. Steam reforming (SR) is the most common process that has been used for years on an industrial scale. However, this is an endothermic process with a very important energy requirement. An alternative is the methane reforming with CO_2 or dry reforming (DR) that has aroused a lot of interest due to its green nature (Hileman, 1998). The operating cost analysis of this process compared to others has shown its usefulness

(Stagg and Romeo, 1998; Ballarini and de Miguel, 2005). The syngas produced by this reforming reaction is used as feedstock for various chemical processes, such as fuel cells fed with H_2, methanol synthesis and Fischer-Tropsch synthesis (Seo and Young, 2009; de Miguel and Vilella 2012). Besides, the DR of methane not only has the advantage of providing a H_2/CO ratio equal to 1, more appropriate for carbonylation and hydroformylation reactions, and lower operating costs compared to the processes of SR and oxidative reforming (OR), but also brings a contribution to environmental preservation, because it consumes carbon dioxide, which is one of the greenhouse gases

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(van Keulen and Hegarty, 1997; de Miguel and Vilella, 2012). Thus, this process is presented as a promising alternative to obtain both synthesis gas as well as hydrogen. The main reactions in the DR process are:

$$CH_4 + CO_2 \rightleftarrows 2CO + 2H_2 \quad \left(\Delta H^0_{298K} = +247 \text{ kJ mol}^{-1}\right) \quad (1)$$

$$CO_2 + H_2 \rightleftarrows CO + H_2O \quad \left(\Delta H^0_{298K} = +41 \text{ kJ mol}^{-1}\right) \quad (2)$$

The second reaction is always present at high temperatures and it is called the reverse water gas shift reaction (RWGS).

Great research efforts are being done in order to develop catalysts with good activity, selectivity and stability for the DR reaction. The major drawbacks and limitations of this process are the serious catalyst deactivation due to coke formation and the operation temperature, that presents an important requirement of energy due to the highly endothermic reaction (Arandiyan and Parvari, 2008; Khalesi and Arandiyan 2008). The main cause of coke formation in DR is due to the fall off of the hydrogenating activity of carbon precursors caused by metallic sintering. This is accentuated by the high operating temperature required by thermodynamics. As it is not possible to change the thermodynamics of the reactions, we must find a more stable metallic catalyst which promotes hydrogenating activity. The challenge is based on finding active catalysts with low coke formation.

Two ways are possible to decrease the rate of coke formation: i) use noble metals of greater hydrogenating capacity and greater metal-support interaction to maintain a high dispersion or ii) use basic supports. The deactivation reaction could be controlled with basic supports that would favour the dissociation of CO_2 into CO and O, this last specie being responsible for the metallic surface cleaning (Stagg et al, 1998). In this work we have tried both ways to improve the catalytic stability.

Noble metals (Rh, Ru, Pt and Ir) have shown improved activity since they are more active and less sensitive to the deactivation by carbon deposition than Ni (Rostrup-Nielsen and Hansen, 1993). Besides, the use of metallic catalysts based on noble metals, although it is more expensive than the utilization of non-noble metals such as Ni, presents advantages with respect to the activity and stability of the metallic phase for reactions with CO_2, as in the case of dry reforming of methane. Moreover, noble metals can also be used for this reaction to promote the Ni catalysts in order to increase the resistance to deactivation (Pakhare and Spivey, 2014; de Miguel et al., 2012).

Some researchers have greatly enhanced the catalytic activity and stability of catalysts by adding some components to the alumina support to inhibit sintering and phase transformation. To overcome these drawbacks, recently we reported the addition of alkaline (Na, K) and alkaline earth (Mg) metals to γ-Al_2O_3 (Ballarini and Basile 2012). In the literature, numerous metallic oxides such as Al_2O_3, SiO_2, MgO, BaO, CaO, TiO_2, ZrO_2 and CeO_2 have been investigated as supports for dry reforming of methane (Fan and Abdullah 2009; Mehran Rezaeia and Meshkania 2014; Ballarini et al., 2005; Nagaoka et al., 2004; Ozkara-Aydinoglu et al., 2009; Sadykov at al., 2011; Garcia-Dieguez et al., 2010; Ozkara-Aydinoglu and Aksoylu, 2011; Ozkara-Aydinoglu and Aksoylu, 2013; Adans et al., 2017).

It is well known that the introduction of Pt into porous alumina is carried out by impregnation with an aqueous solution of H_2PtCl_6 precursor. Previous works on H_2PtCl_6 (Berdala and Freund, 1986; Shelimov and Lambert 1999; Womes and Cholley, 2005) have shown that the interaction between the metallic precursor and the surface depends critically on the nature of the surface sites. For the impregnation of Pt on a basic support, $Pt(NH_3)_4(NO_3)_2$ or platinum acetylacetonate [$Pt(acac)_2$] can be used as a precursor. In contrast to $Pt(NH_3)_4(NO_3)_2$, there is little information about the interaction between $Pt(acac)_2$ and alumina. Womes et al. (2003) showed that the interaction between $Pt(acac)_2$ and alumina surfaces is weak but, after calcination at 623 K, there is a complete decomposition of the complexes and an oxidation of all platinum to Pt^{4+}, thus leading to a dispersed state. An alternative route to obtain well-dispersed Pt on the alumina is by impregnating the alumina with a solution of $Pt(acac)_2$ in organic solvents such as toluene, benzene or dichloromethane (Coq and Crabb 1994; Walter and Coq 1995; de Menorval and Chaqroune 1997; Gandao and Coq 1996; Reyes and Pecchi 1997, Al-Doghachi et al., 2015).

This work studies the influence of the use of different basic supports on the catalytic performance in dry reforming of methane of Pt-catalysts prepared by the impregnation with an organometallic precursor (platinum acetylacetonate (II) solution in toluene:acetone (1:1)). The acidity-basicity of the supports was studied by temperature-programmed desorption of NH_3 or CO_2, and 2-propanol decomposition. Catalysts were characterized by test reactions of the metallic phase (cyclohexane dehydrogenation), temperature-programmed reduction and FTIR spectroscopy of the adsorbed CO in order to find a relationship between the catalyst metallic structure and the catalytic performance (activity, selectivity and stability) in the Dry Reforming reaction.

MATERIALS AND METHODS

Catalysts preparation

Several supports were used, viz:

i) Commercial γ-Al_2O_3 (Cyanamid Ketjen, CK-300; S_{BET}: 190 m² g⁻¹) was added as a reference.

K doped γ-Al$_2$O$_3$ (S$_{BET}$: 176 m^2 g^{-1}) was prepared by impregnation of CK-300 with 1 wt% KOH (Merck, p.a.) aqueous solution using an impregnating volume relative to the weight of alumina of 1.4 cm^3 g^{-1}. Before the doping, the support was calcined for 3 h at 773 K. The support was named K-A.

ii) Commercial KL zeolite (Union Carbide, SK-45; S$_{BET}$: 245 m^2 g^{-1}) was calcined in air at 873 K for 3 h.

iii) Commercial MgO (Alfa Aesar 99.95%) was hydrated with water and the resulting Mg(OH)$_2$ was calcined in N$_2$ for 18 h at 773 K, the resulting support having S$_{BET}$: 160 m^2 g^{-1}.

iv) Synthesized mixed oxide K(Mg-Al) (S$_{BET}$: 160 m^2 g^{-1}) prepared by co-precipitation of magnesium and aluminium nitrates at 333 K. The pH was adjusted to 10 with aqueous solution of K$_2$CO$_3$ + KOH. The precipitate was repeatedly washed with hot demineralized water and dried at 353 K. Then it was impregnated with a solution of KOH and calcined in air at 773 K. The mixed oxide had a molar Mg/Al ratio = 1.3 with 1wt% K. This support was named as K(Mg-A).

The supports were homogenized, pelletized and crushed to 35 and 80 mesh particle size. All solids were heated at a rate of 3 K. min^{-1} under air flow to 573 K and held at this temperature for 1 h. Then, they were heated at a rate of 7 K. min^{-1} to 773 K and kept at this temperature for 2 h.

The catalysts were prepared by impregnation of the supports with a solution of platinum acetylacetonate (II) 97% dissolved in a solution of toluene and acetone (1:1) to obtain Pt loading of 1 wt.%. Then they were stabilized for 12 h at room temperature and then heated from 303 K (at 3 K. min^{-1}) to 393 K and maintained at this temperature for 12 h. Calcinations of the materials were carried out under a flow of air with a heating rate of 3 K min^{-1} until 623 K and held at this temperature for 3h. The catalysts obtained were labelled as: Pt/KA, Pt/KL, Pt/MgO and Pt/K(Mg-A).

Characterization of the samples

The supports were characterized by determination of specific surface area and pore volume, NH$_3$ and CO$_2$ adsorption and desorption experiments and 2-propanol (IPA) dehydrogenation reaction.

The specific surface was measured in a volumetric system from N$_2$ adsorption isotherms obtained at 77 K. The specific surface area (BET method) and porosity measurements were performed in a model ASAP 2020 Micromeritics apparatus on 0.3 g of samples, which were outgassed by heat under vacuum (10^{-6} Torr) at 523 K for 30 h before the nitrogen adsorption.

The basic character and total basic site densities (nb) of the supports (0.3 g) were determined by CO$_2$ adsorption and desorption experiments. The CO$_2$ adsorption was carried out at room temperature using a flow of CO$_2$ (5%)/N$_2$ (50 cm^3 min^{-1}), and the desorption was studied by Temperature Programmed Desorption (TPD) from 298 K up to 1023 K at 5 K min^{-1} using a thermal conductivity detector to measure the response.

The measurements of the density of acid sites for the different supports were also determined by using TPD of NH$_3$. The samples were first treated with helium ($\sim$ 100 cm^3 min^{-1}) at 673 K for 0.5 h and exposed to a gas stream of 1.1% NH$_3$/He at room temperature until all NH$_3$ was adsorbed. Then the temperature was raised to 673 K at a rate of 10 K min^{-1} and the NH$_3$ concentration in the effluent was measured in the mass spectrometer (MS).

The basic properties of the supports were also determined by the isopropanol (IPA) dehydrogenation reaction to acetone at 523 K and atmospheric pressure in a flow reactor, using a N$_2$/IPA molar ratio equal to 12 and a WHSV of 32 h^{-1}. The conversion was kept at similar conversions level (10-15%).

Platinum catalysts were characterized by temperature programmed reduction (TPR), cyclohexane dehydrogenation test reaction (DCH) and FTIR spectroscopy to study the characteristics of metallic particles.

Temperature programmed reduction analysis were done in a Micromeritics TPD/TPR 2900 device. Previously catalysts were calcined at 623 K in air flow with (160 ml min^{-1}) for 3 h. Before the tests, N$_2$ flow was passed. 0.5 g of catalyst were heated at 6 K min^{-1} from room temperature up to 1173 K under a reductive mixture of H$_2$(5 v/v%)/N$_2$ (10 cm^3 min^{-1}).

The test reaction of the metallic phase (DCH) was carried out in a differential flow reactor at 1 bar with a H$_2$/CH molar ratio of 16 and WHSV=12.6 h^{-1}. The reaction temperature was 573 K for the reaction. The reaction products were analysed by gas chromatography with a Chromosorb column and a FID detector. The catalysts (0.1 g) were previously reduced at 823 K under flowing H$_2$ (60 cm^3 min^{-1}).

The interaction between Pt atoms and the supports can change the electronic state of metallic active sites. This effect was studied by infrared spectroscopy of adsorbed CO. The CO-FTIR spectra were recorded at room temperature in a Perkin Elmer Spectrum One spectrometer, in the range 4000-400 cm^{-1} with a resolution of 4 cm^{-1}. A self-supported wafer of 0.05 g of the reduced sample was successively outgassed at 10^{-4} bar at 773 K for 30 min to eliminate water and then reduced with a hydrogen flow at 723 K for 30 min. After reduction, the cell was outgassed at 10^{-10} bar and kept at 773 K for 30 min, cooled down to room temperature and the first spectrum was taken. After recording the IR spectra, the samples were contacted with 0.04 bar of CO for 5 min and then a new spectrum was recorded. The bands of the chemisorbed CO were obtained by subtraction of both spectra.

CATALYTIC ACTIVITY IN CH$_4$ DRY REFORMING

The dry reforming reaction of CH$_4$ was carried out in a continuous reactor with 0.2 g of catalyst. The catalyst was previously reduced in situ at 823 K for 3 h then it was kept in He flow to reach the reaction temperature (1023 K), similar to those of industrial operation of these catalysts. Moreover additional experiments at 873, 923 and 973 K (in conditions far from the thermodynamic equilibrium) were carried out. The reactor was fed with 20 cm^3 min^{-1} of CH$_4$ and CO$_2$ with molar ratio equal to 1. The reaction time was 200 min. The reaction products were analysed on-line using a Varian Star 3400 CX gas chromatograph, equipped with a TCD and a column Carboxem 1006. After the reaction, the content of coke deposited on the catalyst was verified by temperature programmed oxidation (TPO) measurements.

Methane conversion (XCH$_4$), CO$_2$ conversion (XCO$_2$) and CO/H$_2$ ratio were calculated as follows using the gas composition measured by GC:

$$X_{CH_4} = \frac{F_{CH_{4in}} - F_{CH_{4out}}}{F_{CH_{4in}}} \times 100 \qquad (3)$$

$$X_{CO_2} = \frac{F_{CO_{2in}} - F_{CO_{2out}}}{F_{CO_{2in}}} \times 100 \qquad (4)$$

RESULTS AND DISCUSSION

Table 1 shows the BET surface area and the pore volume values of the different supports. The KL zeolite displayed the highest value of Sg (245 m^2 g^{-1}), while the remaining supports showed similar values between 160 and 176 m^2 g^{-1}. With respect to the porosity, the mean pore volume was around 0.5 cm^3.g^{-1}, except for the K(Mg-Al) sample that displayed a slightly higher Vp (0.663 cm^3 g^{-1}).

The measurements of the density of acid sites of the supports were studied by temperature-programmed desorption of NH$_3$. Table 1 shows that the acidity value of the KL zeolite is only comparable with that of the pure alumina (A) without promoter. In the

other supports, ammonia was not chemisorbed, so the acidity appears to be negligible.

The basicity of the supports was studied by TPD-CO$_2$ and the test reaction of 2-propanol dehydrogenation. Figure 1 shows the TPD-CO$_2$ desorption profiles for the different supports. The profiles of the different sites overlap, hence they were deconvoluted in order to determine the distribution of the basic strength sites of the different materials. In this figure, three types of basic sites can be observed. A weak basicity (nbW), with a peak of desorption centred at 403 K; a medium basicity (nbM), with a desorption peak at 513 K and a strong basicity (nbS), with a desorption peak at 643 K. The curves of desorption were deconvoluted into three Gaussian or Lorenzian curves in order to quantify the area corresponding to the different basic sites. The density of the total basic sites (nb) was determined by integration of the area under the corresponding desorption profiles of the different supports. KL zeolite shows a low density of weak and medium basic sites that desorb CO$_2$ below 573 K (Fig.1). The K doped alumina (KA) shows weak and medium basic sites with a CO$_2$ desorption up to 623 K, and the mixed oxide (K(Mg-Al) with a desorption curve that reached up to 743 K, displays an important amount of weak and medium basic sites and low amount of strong basic sites. On the other hand, MgO does not show weak basic sites (desorption peak at 423 K), but it displays an intermediate zone of medium basic sites and an important desorption peak at very high temperatures (673 K) corresponding to very strong basic sites. The total number of basic sites (nb) is presented in Table 1 and follows the decreasing tendency: MgO > K(Mg-Al) > KA > KL.
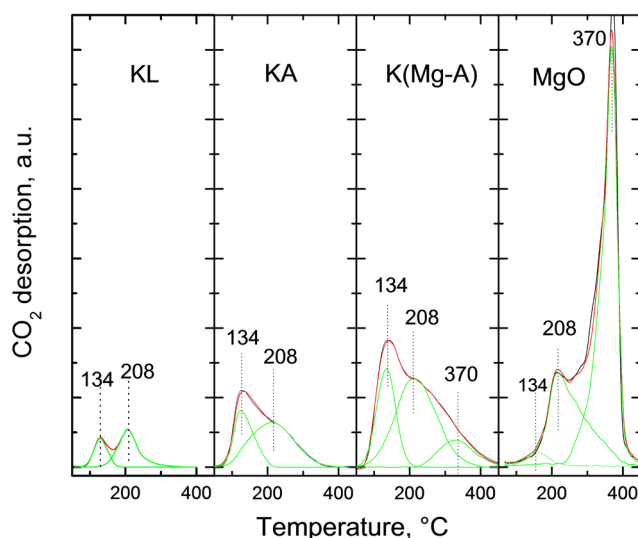
Table 1. Values of specific surface area (Sg), pore volume (Vp) and density of acid (n$_a$) and basic (nb) sites of the different supports.

Support	Sg (m²/g)	Vp (cm³/g)	n$_a$ (μmol/g)	n$_b$ (μmol/g)
A	190	0.500	101	3
KL	245	0.520	90	23
KA	176	0.492	-	62
K(Mg-Al)	160	0.663	-	130
MgO	160	0.517	-	214

Figure 1. TPD-CO$_2$ profiles of the supports: KL zeolite, MgO, Al$_2$O$_3$-K (KA) and mixed oxide K(Mg-Al) in Weak basicity (nbW), Medium basicity (nbM) and Strong basicity (nbS).

It is known that acetone production from the 2-propanol dehydrogenation reaction can be carried out on the basic sites of different strength for a catalyst (Gervasini and Auroux 1991). Hence, the study of this reaction on the different supports lets one know the basicity of the materials. Figure 2 also shows the acetone/propylene ratio for the different supports. The basic site density follows the same order as that found from CO_2 desorption, this meaning that the mixed oxide K(Mg-Al) shows a higher quantity of basic sites than the doped alumina (AK), while the zeolite (KL) has the lowest basicity. Hence, the values of basicity determined by desorption of carbon dioxide agreed with those obtained by the dehydrogenation of 2-propanol. With respect to the data corresponding to MgO, this catalyst is inactive for isopropanol dehydrogenation. Hence, this reaction test is not adequate to know the basic character of determined oxides like MgO since it does not occur on basic oxides without redox properties (Lahousse and Bachelier, 1994). Although both A-K and K(Mg-Al) do not have redox properties, they could activate the hydrogen at the reaction temperature, while MgO cannot at that temperature.

After deposition of Pt on the different supports, the chemical analysis results (Table 2) showed that the platinum contents of the catalysts were near to the nominal loadings. The characeristcs of the metallic
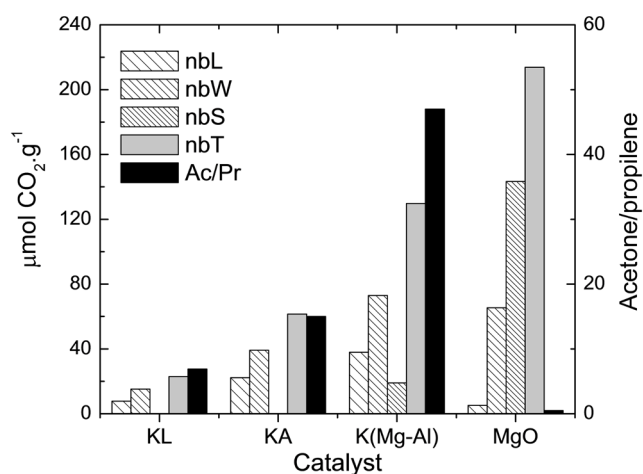
function were analyzed by different techniques, such as test reaction, TPR and FTIR.

In orden to determine the metallic dispersion, the catalysts were evaluated by the CHD reaction. This reaction is a structure-insensitive reaction, which is carried out on one site of metallic surface, and it can be considered as an indirect measurement of exposed metallic sites on the catalysts (Blakely and Somorjai, 1976). Table 2 also shows the values of initial reaction rates for cyclohexane dehydrogenation. The values have an experimental error lower than 5%. In all cases, the only product of the reaction of conversion of cyclohexane was benzene. The sample of Pt supported on MgO showed the highest value, followed by Pt/K(Mg-Al) and Pt/KA. Finally, the Pt/KL catalyst, with the lowest basicity, displayed the lowest value. Hence the use of basic MgO as a support of Pt catalysts prepared from organometallic precursors favours the dispersion of the metallic phase, as it has been previously reported (Gamba and Colella, 2001).

The TPR profiles (Figure 3) of the monometallic platinum catalysts supported on KL, KA, K(Mg-Al) and MgO show Pt reduction zones at temperatures between 573 and 773 K. From these profiles it can be ensured that, for all catalysts, Pt is in metallic state at the reduction temperature (823 K) previous to the dry reforming reaction.

IR spectra of adsorbed CO on the different reduced catalysts (Figure 4) show two absorption bands in the CO vibration zone at v_{CO} = 1800-1755 cm^{-1} and at v_{CO} = 1900-2200 cm^{-1} that correspond to both the bridge and linear CO adsorption on Pt particles, respectively (Morterra and Aschieri; 2008). The band
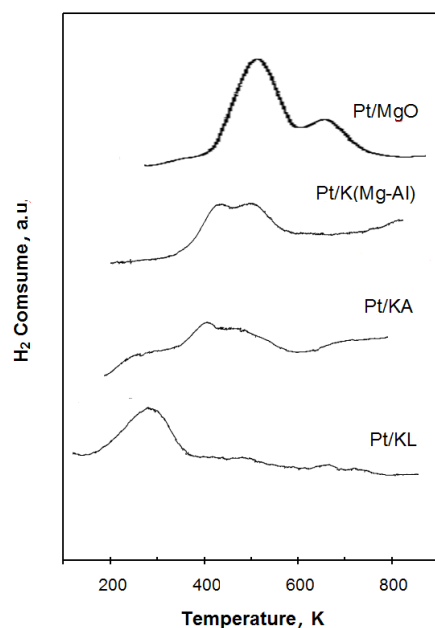

Figure 2. Acetone/propylene ratio obtained from the 2-propanol decomposition reaction and Density of the basic sites (nb) determined from TPD-CO_2 profiles of the supports: KL zeolite, MgO, Al_2O_3-K (KA) and mixed oxide K(Mg-Al).

Table 2. Pt content and initial rate of cyclohexane dehydrogenation reaction of the Pt-catalysts.

Catalysts	Pt loading (%)	r^o (573 K) (mol g^{-1} h^{-1})
Pt/KL	0.85	12.1
Pt/KA	0.99	21.5
Pt/K(Mg-Al)	0.87	22.6
Pt/MgO	0.95	25.2

Figure 3. TPR profiles of Pt-catalysts supported on KL zeolite, MgO, Al_2O_3-K (KA) and mixed oxide K(Mg-Al).
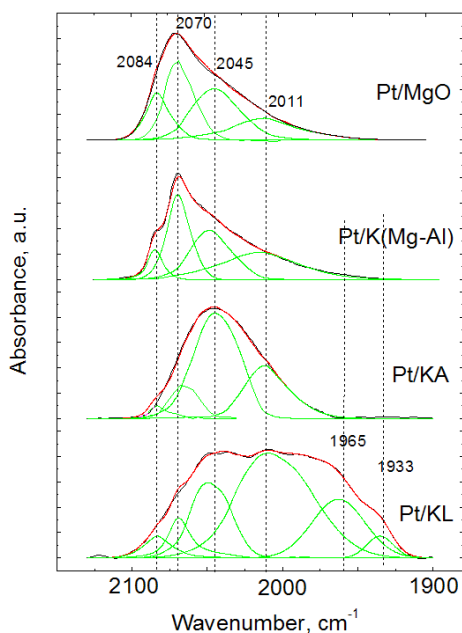
Figure 4. FTIR spectra of adsorbed CO on the Pt-catalysts supported on KL zeolite, MgO, Al_2O_3-K (KA) and mixed oxide K(Mg-Al).

that gives more information about Pt interaction with the support is the linear CO adsorption one. Because of this, Figure 4 only shows the bands corresponding to the linear CO adsorption of the catalysts. This band is composed of different peaks whose position and intensity are modified according to the electronic density of the metallic particles reduced on the surface, this depending on the metal-support (M-S) interaction. In supports with low M-S interaction, this band has a maximum at $v_{CO} = 2075$ cm^{-1} corresponding to the adsorbed CO over Pt^0 (Kustov and Kazansky, 1994). When the metallic dispersion is high and the interaction of the particles with the support is strong, there exist different intensity signals at $v_{CO} > 2075$ cm^{-1} that correspond to CO adsorbed on electrodeficient Pt, $Pt^{\delta+}$ (Ivanov and Kustov, 1998). When the metallic cluster is large and it was deposited on a basic support, there exist different intensity signals at $v_{CO} < 2075$ cm^{-1} that correspond to CO adsorbed on electroexcedent Pt, $Pt^{\delta-}$ (Yu and Kustov, 1999). These signals are very well defined in Pt/KL catalysts due to their crystalline structure and are found at $v_{CO} = 2045$, 2011, 1965 and 1933 cm^{-1} (Arcoya and Seoane, 2005). The zeolitic structure of KL favors the interaction between the weak and medium basic centers of the support with the Pt particles, generating large electroexcedent Pt metal centers. In the other supports, in spite of having more medium and strong basic centers (Fig.1), the electronic transfer from basic centers to metallic particles of Pt is less efficient, possibly due to the amorphous character of the support. The deconvolution of CO-FTIR signals of the Pt/MgO catalyst (which has a high density of

strong basic centers) shows that there is an increase in the signal at 2084 cm^{-1} (with respect to the other catalysts), thus indicating the strongest interaction between Pt and the basic support. It is known that by increasing the metal-support interaction, the dispersion of the metallic phase is more likely to be higher.

The catalytic properties of the Pt-catalysts were evaluated in the methane dry reforming to produce syngas (CO + H_2) at 1023 K (industrial conditions). It is worth mentioning that, at this temperature, the more active catalysts reach conversions near the thermodynamic equilibrium. All catalysts were stable through the 200 min reaction time. The deposited carbon contents were analysed after the reaction, which were negligible in all cases (< 0.01 wt% C). The catalytic behaviour of the different catalysts at 1023 K is shown in Figures 5 and 6 and Table 3. Figure 5 shows the evolution of the CO_2 and CH_4 conversions and the H_2/CO ratios in the products as a function of time-on-stream (TOS). Figure 6 shows the concentrations of H_2, CO and H_2O in the product as a function of time-on-stream in the dry reforming of methane. Table 3 shows the average values of CO_2 and CH_4 conversions and the H_2/CO ratios obtained for the different catalysts. The Pt catalysts supported on KL, KA and K(Mg-Al) show similar CO_2 conversions of about 92 %, while for Pt/MgO the conversion is higher (about 94%). It can be observed that methane conversions and H_2/CO ratios decreased in the following order: Pt/MgO> Pt/K(Mg-Al) $\cong$ Pt/KA > Pt/KL. These catalysts were prepared with supports of similar areas but different distribution of basic sites. In this sense, the methane and CO_2 conversions and the H_2/CO ratios correlate well with the basicity of the catalysts. In this sense, the worst catalytic performance of Pt/KL catalyst corresponded to the metallic sample supported on a material with the lowest basicity (KL zeolite). On the other hand, the catalyst supported on the material with the highest basicity (MgO) displays the highest CO_2 ($\cong$ 94%) and CH_4 (83%) conversions, and the highest H_2/CO ratio (0.73). Figure 7 shows the results of additional activity measurements in dry reforming at lower temperatures (873, 923 and 973 K) to confirm the correlation between the catalytic behaviour and the support basicity. At these temperatures the conversions keep away from the thermodynamic equilibrium. These tests were performed with samples of the highest and lowest basicity (Pt/MgO and Pt/KL, respectively). It can be

Table 3. Average CH_4 and CO_2 conversion and H_2/CO ratio for the Pt-catalysts.

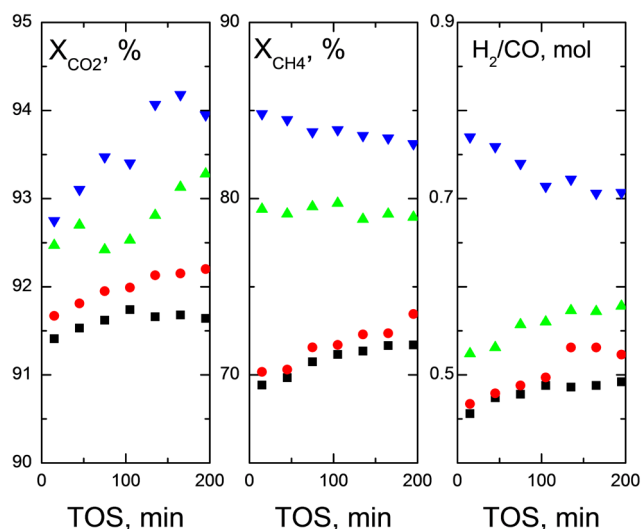| Catalysts	X_{CH4} (%)	X_{CO2} (%)	H_2/CO
Pt/ KL	71.1	91.5	0.50
Pt/ KA	75.0	92.0	0.52
Pt/ K(Mg-Al)	79.0	92.8	0.58
Pt/ MgO	83.0	93.6	0.73

Figure 5. Conversion of CO_2 and CH_4 and the H_2/CO ratio in the products as a function of time-on-stream (TOS) in the dry reforming of methane. Symbols: (▼) Pt/MgO; (▲) Pt/K(Mg-Al); (●) Pt/KA and (■) Pt/KL.
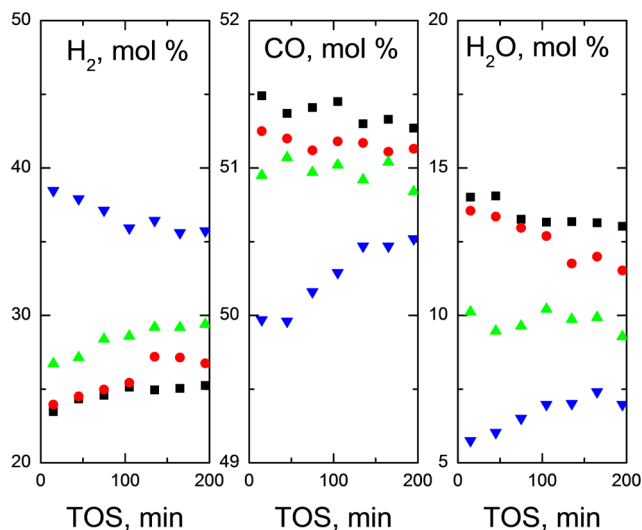

Figure 6. Concentration (as mol%) of H_2, CO and H_2O in the product as a function of time-on-stream in the dry reforming of methane. Symbols: idem Fig 5.

Figure 7. Conversion of CO_2 and CH_4 and the H_2/CO ratio in the products as a function of the reaction temperature in the dry reforming of methane.

is lower than MgO and higher than zeolite KL, have an intermediate catalytic behaviour in the DR reaction. The Pt/MgO shows a very good catalytic performance for the DR reaction compared with other results reported in the literature (Fan et al., 2009).

It is important to highlight the high H_2/CO ratio (0.73) obtained in the product stream for the Pt/MgO catalyst, much higher than those obtained for the other catalysts. Considering that the theoretical H_2/CO molar ratio produced by the dry reforming reaction ($CH_4 + CO_2 \rightarrow CO + H_2$) is equal to one, the decrease of this value is associated with the reverse water-gas shift reaction (RWGS). This undesirable reaction ($CO_2 + H_2 \leftrightarrows CO + H_2O$) consumes part of the H_2 produced by reforming, which reacts with CO_2 to yield CO and water. In this sense, the results indicate the importance of the Pt catalyst supported on the basic MgO, since it would inhibit the RWGS reaction, thus producing a higher H_2/CO ratio than the other catalysts. Figure 7 shows the evolution of the molar concentration of H_2, CO and H_2O in the products as a function of time-on-stream. In agreement with the above results, it can be observed that the Pt catalyst with the higher density of strong basic sites (Pt/MgO catalyst) displays the higher yield of H_2 and the lower yield of CO and H_2O. This is because this catalyst inhibits the RWGS, thus leading to an increase of the H_2/CO ratio.

CONCLUSIONS

From the results presented and discussed above, the following conclusions can be drawn:

(i) A good adsorption of platinum acetylacetonate (II) was obtained during the impregnation step on several supports with different distribution of basic sites. At the reduction temperature (823 K) previous to the dry reforming reaction and in the presence of H_2, Pt is reduced to the metallic state.

observed that, at a lower temperature, the more basic catalyst (Pt/MgO) displays much higher conversions and generates a higher H_2/CO ratio than the least basic catalyst (Pt/KL). Moreover, the differences between the conversions of both catalysts increase at lower temperatures, in conditions far from the equilibrium.

The better catalytic behaviour of the Pt/MgO catalyst could be related with the strong interaction between the metallic phase, prepared from an organic precursor, and the most basic support, thus leading to the highest metallic dispersion (Gamba and Colella, 2001). In this sense, the interaction of Pt with the basic sites of the support should be very important for this reaction. The Pt catalysts supported on Pt/KA and Pt/KL, whose basicity
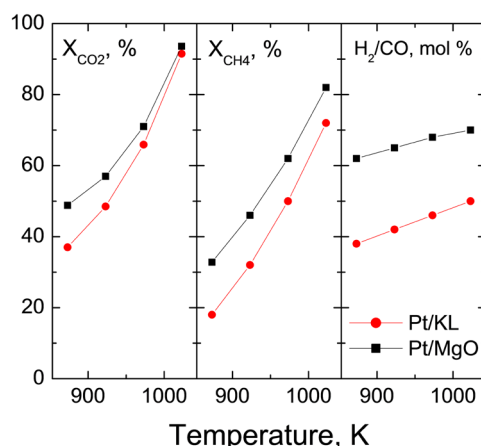
(ii) The monometallic Pt-catalysts supported on the different materials showed a good and stable activity along the reaction time (both CH_4 and CO_2 conversions have high and constant values).

(iii) The use of a lightly basic zeolite, like KL, as a catalytic support was not adequate for this reforming reaction because the catalyst shows both the lowest methane and CO_2 conversions and H_2/CO molar ratio.

(iv) Pt catalysts supported on MgO, with high amounts of strong basic sites displayed very good metallic dispersion, the best catalytic behaviour in dry reforming with respect to activity, and produced the highest H_2/CO ratio of 0.73.

(v) The methane conversion and the H_2/CO ratios obtained for the DR reaction followed a similar tendency corresponding to the basicity of the catalysts.

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