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Applied Catalysis A: General 248 (2003) 279–289
APPLIED CATALYSIS A: GENERAL
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Sintering and redispersion of Pt/γ-Al_2O_3 catalysts: a kinetic model

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Accepted 19 February 2003

Abstract

The sintering and redispersion kinetics of a Pt/Al_2O_3 naphtha reforming catalyst have been studied. The effect of the operating conditions, temperature, and oxygen and HCl concentration on the sintering and redispersion rates have been investigated. It was found that the rate of sintering depends on temperature and oxygen partial pressure. The rate of redispersion depends both on oxygen and HCl concentrations. A new kinetic model to study the sintering and redispersion phenomena has been developed. The model considers the evolution of the metallic dispersion as a reversible process and includes the effect of the operating conditions on the dispersion variation rate.

Keywords: Pt/Al_2O_3-Cl naphtha reforming catalysts; Sintering; Redispersion; Kinetic modeling; Deactivation; Regeneration

1. Introduction

Sintering is one of the main causes of deactivation of bifunctional Pt/Al_2O_3-Cl naphtha reforming catalysts [1]. It mainly occurs during catalyst regeneration performed under oxidizing atmospheres because the reaction is highly exothermic and forms water [2]. The sintering of Pt crystallites may be partially prevented by adding chlorinated compounds to the oxidizing mixtures [3]. Thus, the normal regeneration procedure involves a rejuvenation step, in which the metallic fraction of the aged catalyst is restored with a redispersion treatment with O_2/HCl/H_2O/N_2 mixtures at 673–773 K [3–5].

Sintering and redispersion of Pt/Al_2O_3 catalysts have been widely investigated [6,7]. Nevertheless, in most cases both phenomena, sintering and redispersion, have been studied individually and often under experimental conditions which are not usually employed at industrial level [8,9].

It has been pointed out that, in most of cases, sintering data attain a non-zero residual dispersion after a finite sintering time and therefore kinetic models which allow for the prediction of the presence of this residual dispersion should be used [10,11]. These models are called generalized power-law equations (GPLE) [10,11] or deactivation models with residual activity (DMRA) [12,13]. In general reviews on sintering kinetics [14,15], Bartholomew has shown that the use of generalized power-law equations provides a more comprehensive analysis of sintering kinetic data than the simple power law expression (SPLE). Furthermore, an inadequate kinetic model can result in

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0926-860X/$ – see front matter
doi:10.1016/S0926-860X(03)00300-4

misleading conclusions about the deactivation mechanism and lead to systematic errors in estimating intrinsic parameters, such as activation energies [13].

While sintering kinetics has been extensively investigated [10,11,14,15], few works have been devoted to the redispersion (reactivation) kinetics of sintered (deactivated) catalysts [16,17].

In this paper we present a new kinetic model to study simultaneously the sintering and redispersion of metal supported catalysts. This model has been developed to explain the effect of the main operating conditions (i.e. the chlorine and oxygen concentration in the oxidizing atmosphere, the temperature, etc.) on the dispersion variation rate under simulated industrial conditions. In addition, this kinetic model is a generalization of other deactivation models previously proposed for sintering [11,14,18].

2. Experimental

2.1. Catalyst preparation

A catalyst containing 0.6% Pt and 0.9% Cl was prepared as previously described [12]. A high purity γ-Al_2O_3 powder (Cyanamid Ketjen CK-300) was impregnated at 303 K with an aqueous solution containing H_2PtCl_6 and HCl. After impregnation, the sample was dried for 12 h at 393 K and heated in flowing air to 773 K. Then, the Cl content was regulated using a gaseous mixture of HCl, water, and air. Finally, the sample was purged with N_2 and reduced in flowing H_2 for 8 h at 773 K.

2.2. Hydrogen chemisorption

Accessible platinum fractions were determined by hydrogen chemisorption. Prior to the Pt dispersion measurements, the samples were reduced under flowing hydrogen during 2 h at 773 K and then evacuated at the same temperature. The double isotherm method was used [19], the first isotherm gave the total gas uptake and the second, obtained after 1 h of evacuation at room temperature, the weakly adsorbed gas. By difference, the amount of strongly adsorbed H_2, $(HC)_i$, was determined. A stoichiometric ratio of $(HC)_i/\text{Pts} = 1$, where Pts implies a Pt atom on surface, was used. The volumetric adsorption experiments were performed in a conventional glass vacuum apparatus equipped with an MKS Baratron pressure gauge. The pressure range of isotherms was 0–50 torr and extrapolation to zero pressure was used as a measure of the gas uptake on the metal.

2.3. Sintering procedure

Sintering treatments using fresh catalysts (initial dispersion, $D_0 = 65\%$) were performed with O_2/N_2 mixtures at temperatures ranging from 673 to 873 K. The effect of the O_2 partial pressure was examined using oxygen concentrations varying from 0.1%, corresponding to industrial regeneration conditions, to 100% ($p_{O_2} = 0.001$, 0.02, 0.21 and 1 atm).

2.4. Redispersion procedure

Redispersion treatments of a previously aged catalyst were carried out in a flow system at 773 K employing $HCl/O_2/H_2O/N_2$ mixtures of different compositions. Water and HCl were continuously added to O_2/N_2 gas mixtures by employing a motor-driven syringe. To avoid water condensation the gaseous mixture was kept at a temperature higher than 353 K, before entering to the reactor. The initial dispersion of the sintered sample was 12%. The effects of the O_2 partial pressure and of the HCl concentration were studied. The O_2 partial pressure was varied from 0 to 100% and the HCl concentration from 0.0005 atm to 0.003 atm.

3. Results and discussion

3.1. Sintering

Sintering experiments were carried out at constant temperature, varying the sintering time. Figs. 1 and 2 show the time-evolution of the relative dispersion as a function of sintering temperature for $p_{O_2} = 0.001$ atm and $p_{O_2} = 0.21$ atm, respectively. These figures reveal that: (i) for the same sintering time, the relative dispersion decreases with increasing sintering temperature, and (ii) the dispersion of sintered catalysts decreases as a function of time until attaining an asymptotic dispersion value, always different from zero. This value would correspond to a pseudo-stationary state, called

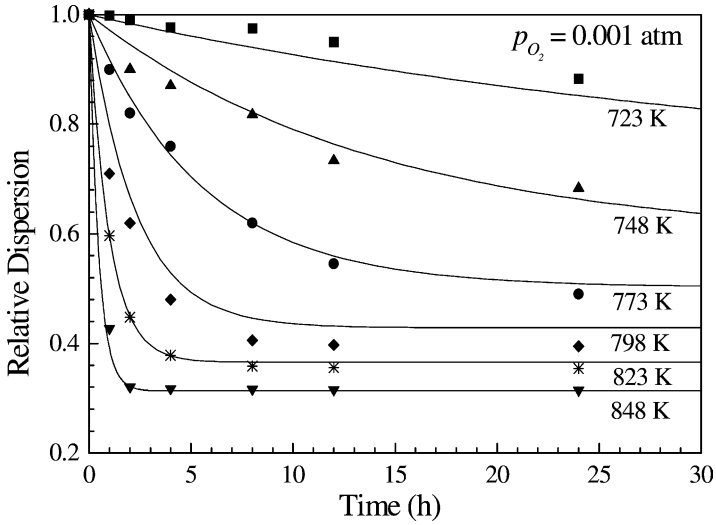

Fig. 1. Influence of the temperature on the sintering rate, $p_{O_2} = 0.001$ atm.

residual dispersion. Thus, a higher sintering temperature produces an increase of the sintering rate and a decrease of the residual dispersion. An increase in the oxygen concentration decreases the rate of sintering.

As has already been said, because the dispersion attains a pseudo-steady state value, deactivation models with residual dispersion should be used [10–15]. In a previous paper [18], we have developed a Sintering Kinetic Model, which provides a quantitative relationship between the operational variables involved during the process and the kinetic parameters. This model is in fact an extension of the kinetic model proposed by Fuentes and Ruiz-Treviño [10,11]. The sintering rate was expressed as function of the relative dispersion, $D_r = D/D_0$, as

$$\frac{dD_r}{dt} = \psi_D (D_r - D_{rr})^n \quad (1)$$

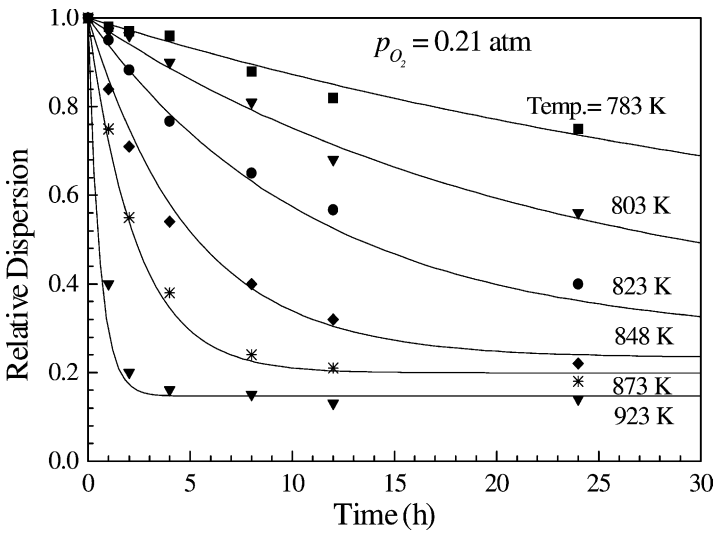

Fig. 2. Influence of the temperature on the sintering rate, $p_{O_2} = 0.20$ atm.

In this expression, ψ_D is the deactivation function of sintering, D_0 the initial dispersion, D_{rr} the relative residual dispersion attained at $t \to \infty$ and n the deactivation kinetic order of sintering. As regards the value of n, it has been demonstrated that all the sintering data published in the literature can be satisfactorily fitted using either $n = 1$ or 2. The discrimination between these two values is still an open question as was pointed out by Fuentes [20] and, for both orders, mechanistic and/or mathematical explanations have been proposed [20,21]. In the present case, we have selected the value of $n = 1$ because we obtained the best fit of the data using this value, but the quality of the fitting using $n = 2$ was almost the same. Recently, Lif et al. [22] in a study of sintering kinetics of a Ni/γ-Al_2O_3 catalyst, have also assumed a value of $n = 1$ taking into consideration the best fit obtained with this sintering order.

Taking into account the above considerations, the explicit relationship between D_r versus time for $n = 1$ is

$$D_r = \frac{D}{D_0} = D_{rr} + (1 - D_{rr}) \exp(-\psi_D t) \tag{2}$$

It was found that both parameters, ψ_D and D_{rr}, depend on the operating conditions (p_{O_2} and temperature), according to the following empirical expressions [18].

$$\psi_D = k_{D_0} \exp\left(-\frac{E_D}{R}\left(\frac{1}{T} - \frac{1}{823}\right)\right) p_{O_2}^{\beta} \tag{3a}$$

$$\psi_D = 0.0615 \exp\left(-\frac{157.8}{R}\left(\frac{1}{T} - \frac{1}{823}\right)\right) p_{O_2}^{-0.51} \tag{3b}$$

$$D_{rr} = D_{S_0} \exp\left(\frac{Q_S}{R}\left(\frac{1}{T} - \frac{1}{823}\right)\right) p_{O_2}^{\gamma} \tag{4a}$$

$$D_{rr} = 0.324 \exp\left(\frac{38.6}{R}\left(\frac{1}{T} - \frac{1}{823}\right)\right) p_{O_2}^{-0.058} \tag{4b}$$

Eqs. (3b) and (4b) reveal that both ψ_D and D_{rr} decrease as the p_{O_2} increases, indicating that high oxygen pressure inhibits the sintering process. This fact could be explained by considering the higher stability of the Pt^{+4} species as the p_{O_2} increases [18]. The activation energy was 132.6 kJ/mol, which is similar to the values reported by Fuentes and Gamas [11] and Bartholomew [14,15], for the sintering of Pt/Al_2O_3 catalysts under air. The parameter D_{rr} is slightly influenced by p_{O_2} and decreases as the temperature increases. The temperature dependence of the residual relative dispersion was well fitted using a Vant'Hoff type equation [18]. However, the parameter Q_S involved in Eq. (4a) has no clear physical meaning.

3.2. Redispersion

Sintered catalysts were redispersed under HCl/O_2/H_2O/N_2 mixtures at different temperatures. The highest catalyst redispersion was attained when the temperature was between 753 and 773 K. A kinetic study on the redispersion of a Pt/Al_2O_3 catalyst was, therefore, performed at 773 K.

The effect of the oxygen concentration during redispersion of a sintered catalyst at a fixed HCl partial pressure is shown in Fig. 3. An increase in the O_2 concentration produces an increase in the redispersion rate and the steady state value of the dispersion also increases. It should be noted that when the O_2 concentration is zero an additional sintering of the metallic phase takes place (see Fig. 3). This fact demonstrates that the simultaneous presence of the HCl and oxygen is required to produce the redispersion of the aged catalyst.

The effect of the HCl partial pressure on the redispersion process was also investigated. Fig. 4 shows that the higher the HCl concentration, the higher the redispersion rate and a higher final value of the dispersion is attained.

3.3. Kinetic model of sintering-redispersion

In most cases, sintering and redispersion have been studied individually in spite of the fact that both processes can be considered as a part of a single process. In recent works [23–25], employing "in situ" EXAFS spectroscopy we have clearly shown that a $[Pt(OH)_4Cl_2]^{2-}$ hydroxychlorinated complex is the key species for the sintering/redispersion process. This hydroxychlorinated species is responsible for the redispersion of the metallic fraction. Hence, the operating conditions, i.e. temperature, O_2 partial pressure, H_2O partial pressure, chlorine concentration, determine the equilibrium between the surface species, which is the key to whether sintering or redispersion of Pt particles occurs. Therefore, the

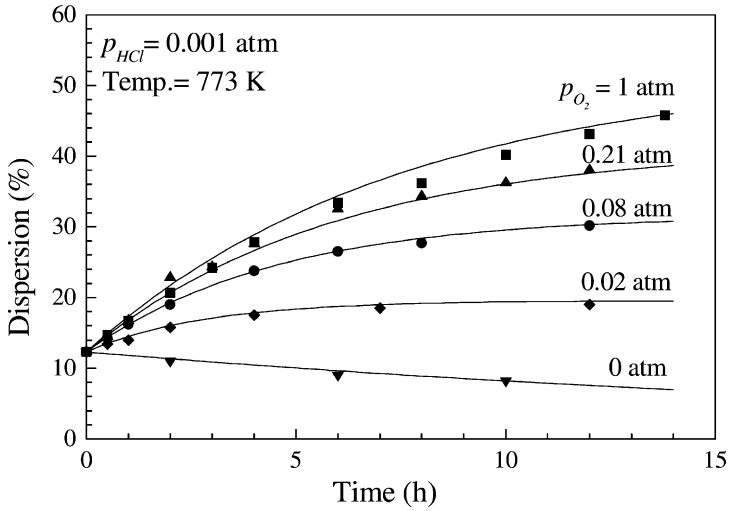

Fig. 3. Influence of p_{O_2} on the redispersion rate.

evolution of the metallic dispersion should be considered as a reversible process and a unique kinetic model should be able to analyze both sintering and redispersion data. This new kinetic model assumes the sintering-redispersion phenomenon as a first-order reversible process. Therefore, the net variation rate of the metallic dispersion can be written as

$$\frac{dD}{dt} = \psi_R(D_T - D) - \psi_S D \tag{5}$$

ψ_R and ψ_S are the kinetic functions of redispersion and sintering, respectively. The term D_T corresponds to the maximum allowable catalyst dispersion. Ideally the catalyst could attain a value of 100% but we assume that D_T takes the initial value of the dispersion before the sintering treatments. In our case the value of D_T is equal to 56%.

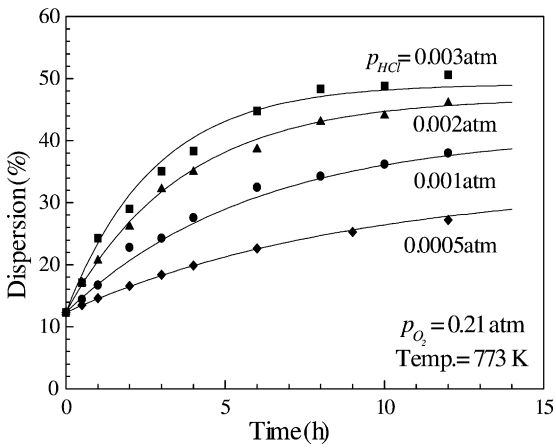

Fig. 4. Influence of p_{HCl} on the redispersion rate.

The term $(D_T - D)$ represents the driving force for the redispersion process and the term D, the driving force for the sintering process. Consequently, if $\psi_R(D_T - D) > \psi_S D$ a redispersion process occurs while if $\psi_R(D_T - D) < \psi_S D$ the sintering of the catalyst is observed.

The variation rate of the catalyst dispersion can also be re-written as

$$\frac{dD}{dt} = -(\psi_R + \psi_S)D + \psi_R D_T \tag{6}$$

and finally, the following equation can be derived

$$\frac{dD}{dt} = \psi_G(D - D_{SS}) \tag{7}$$

where

$$\psi_G = \psi_R + \psi_S \tag{8}$$

and

$$D_{SS} = D_T \frac{\psi_R}{\psi_R + \psi_S} \tag{9}$$

It is important to note that Eq. (2) (for $n = 1$) and Eq. (7) are mathematically equivalent in form. However, now it is quite straightforward to assign a

physical meaning to the kinetic parameters involved in Eqs. (7)–(9). Moreover, the deactivation function of sintering, ψ_D, used in Eq. (2) is, in fact, the sum of the kinetic functions for sintering and redispersion in this Sintering-Redispersion Kinetic Model, as indicated by Eq. (8). In addition, assuming that the dispersion attains a pseudo-steady state when $t \to \infty$, the following expression can be derived

$$\frac{dD}{dt} = 0 \Leftrightarrow D_{SS} = D|_{t\to\infty} = D_T \frac{\psi_R}{\psi_R + \psi_S} = D_T \frac{K_{RS}}{1 + K_{RS}} \quad (10)$$

Therefore, this model allows the prediction of the final steady dispersion from the values of ψ_R, ψ_S and D_T.

The parameter K_{RS} in Eq. (10) represents the equilibrium constant for the sintering-redispersion process.

$$K_{RS} = \frac{\psi_R}{\psi_S} = \frac{D_{SS}}{(D_T - D_{SS})} \quad (11)$$

Thus, high K_{RS} values should be obtained during redispersion experiments while low ones should be obtained during sintering. If K_{RS} tends to zero, the residual dispersion also tends to zero, attaining the maximum theoretical degree of sintering. On the other hand, when K_{RS} tends to ∞, the final dispersion tends to D_T, which represents the maximum degree of redispersion.

The dependence with time of the catalyst dispersion can be obtained integrating Eq. (7).

$$D = D_{SS} + (D_0 - D_{SS}) \exp(-\psi_G t) \quad (12)$$

The above expression can be re-written in terms of the parameters corresponding to the Sintering-Redispersion Kinetic Model.

$$D = D_T \left(\frac{\psi_R}{\psi_R + \psi_S}\right) + \left(D_0 - D_T \left(\frac{\psi_R}{\psi_R + \psi_S}\right)\right) \times \exp(-(\psi_R + \psi_S)t) \quad (13)$$

D_0 corresponds, as in Eq. (2), to the initial dispersion of the catalyst and must be determined experimentally. In the present case $D_0 = 12.3\%$. The term D_T corresponds to the maximum allowable catalyst dispersion.

Assuming that the kinetic functions of redispersion, ψ_R, and sintering, ψ_S, depend on the operating conditions, temperature and atmosphere, it can be written that

$$\psi_R = k_{R_0} \exp\left(-\frac{E_R}{RT}\right) p_{HCl}^{n_R} p_{O_2}^{m_R} \quad (14)$$

$$\psi_S = k_{S_0} \exp\left(-\frac{E_S}{RT}\right) p_{HCl}^{n_S} p_{O_2}^{m_S} \quad (15)$$

In the present work the effect of H_2O on sintering-redispersion has not been investigated. However, it could also be included in both kinetic functions, ψ_R and ψ_S, in a similar manner as has been done for O_2 and HCl. The above equations are empiric expressions based on power-law kinetics. However, Langmuir–Hinshelwood kinetics usually obtained from mechanistic developments can also be used [26].

Substituting the above expressions in Eq. (9), the evolution of D_{SS} as a function of the operating conditions can be obtained.

$$D_{SS} = D_T \frac{K_{RS}}{1 + K_{RS}} = D_T \frac{k_{RS_0} p_{HCl}^{\alpha} p_{O_2}^{\beta} \exp(-E_{RS}/RT)}{1 + k_{RS_0} p_{HCl}^{\alpha} p_{O_2}^{\beta} \exp(-E_{RS}/RT)} \quad (16)$$

In the above equation the terms k_{RS_0}, α, β and E_{RS} are given by

$$k_{RS_0} = \frac{k_{R_0}}{k_{S_0}}; \quad \alpha = n_R - n_S; \quad \beta = m_R - m_S; \quad E_{RS} = E_R - E_S \quad (17)$$

The parameters α and β represent the observable orders of the residual dispersion with respect to HCl and O_2, respectively. According to the above expressions, the values of α and β can be positive, zero or negative, depending on the relative values of the kinetic orders in Eqs. (14) and (15). The term E_{RS} represents the observable activation energy for the parameter D_{SS}. Again, depending on the relative values of the activation energies involved in the sintering and redispersion processes, the value of E_{RS} can be positive, negative or zero.

As has been pointed out, the Sintering-Redispersion Kinetic Model must be able to explain both the sintering and the redispersion data. Thus, during sintering treatments it is logical to assume that $K_{RS} \ll 1$. This implies that in Eq. (16), the term

$k_{RS_0} p_{HCl}^{\alpha} p_{O_2}^{\beta} \exp(-E_{RS}/RT) \ll 1$, and therefore D_{SS} can be simplified to

$$D_{SS} \cong D_T (k_{RS_0} p_{HCl}^{\alpha} p_{O_2}^{\beta}) \exp\left(-\frac{E_{RS}}{RT}\right) \quad (18)$$

Eq. (18) is mathematically equivalent to Eq. (4), but it should be emphasized that the parameters involved in Eq. (18) have a clear physical meaning. The term $D_T(k_{RS_0} p_{HCl}^{\alpha} p_{O_2}^{\beta})$ in Eq. (18) is equivalent to the term $(D_{S_0} p_{O_2}^{\beta})$ in Eq. (4); and the parameter E_{RS} in Eq. (18) is equivalent to the parameter Q_S in Eq. (4). Hence, the negative value for the parameter Q_S can be easily explained by assuming that the sintering activation energy is higher than the corresponding activation energy for the redispersion process. In addition, according to the Sintering-Redispersion Kinetic Model, the negative dependence of the residual dispersion with respect to oxygen implies that the kinetic order with respect to oxygen for ψ_S (exponent m_S, Eq. (15)) is higher than that for ψ_R (exponent m_R, Eq. (14)).

In order to calculate the kinetic parameters, ψ_R and ψ_S, we have used Eq. (13) to fit the experimental data displayed in Figs. 1–4. The results of these fittings are shown in Figs. 5–8. Figs. 5 and 6 show the effect of oxygen partial pressure and temperature on the values of ψ_R and ψ_S during sintering treatments. Fig. 5 reveals that both parameters decrease as the oxygen concentration increases. This fact indicates that, under sintering conditions, the increase in oxygen concentration inhibits not only the sintering step, as already pointed out by our previous Sintering Kinetic Model [16], but also inhibits the redispersion step. Probably both phenomena are the consequence of the stabilization of Pt^{+4} surface species at high oxygen concentrations [16]. However, ψ_S has higher values than ψ_R and therefore the sintering process prevails over redispersion. Regarding the effect of temperature, Fig. 6 shows that both parameters increase with the temperature following an Arrhenius-type dependence. In this figure, the values of ψ_G and D_{SS}, calculated using Eqs. (8) and (9), are also represented. It can be seen that both terms also follow Arrhenius-type dependences (in the case of D_{SS} a negative dependence) indicating that the approximation followed in Eq. (18) is correct.

As regards the redispersion results, the influence of oxygen and HCl concentrations on ψ_R and ψ_S during redispersion treatments is shown in Figs. 7 and 8.

In Fig. 7 it can be seen that an increase of p_{O_2} does not modify the value of ψ_R but strongly diminishes ψ_S. Therefore, the main effect of O_2 during redispersion is the inhibition of the intrinsic sintering rate, having little effect on the redispersion step. Paradoxically, both facts result in a net process of redispersion as shown in Fig. 3.

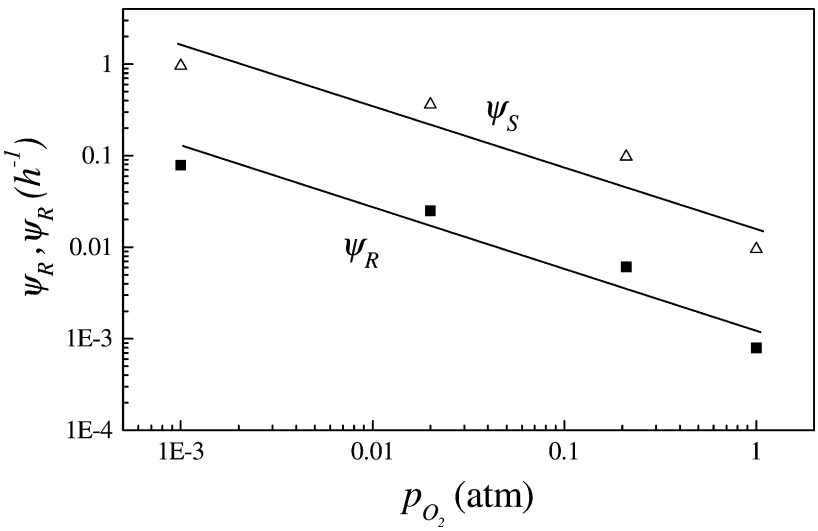

Fig. 5. Influence of temperature on the sintering-redispersion kinetic parameters during sintering.

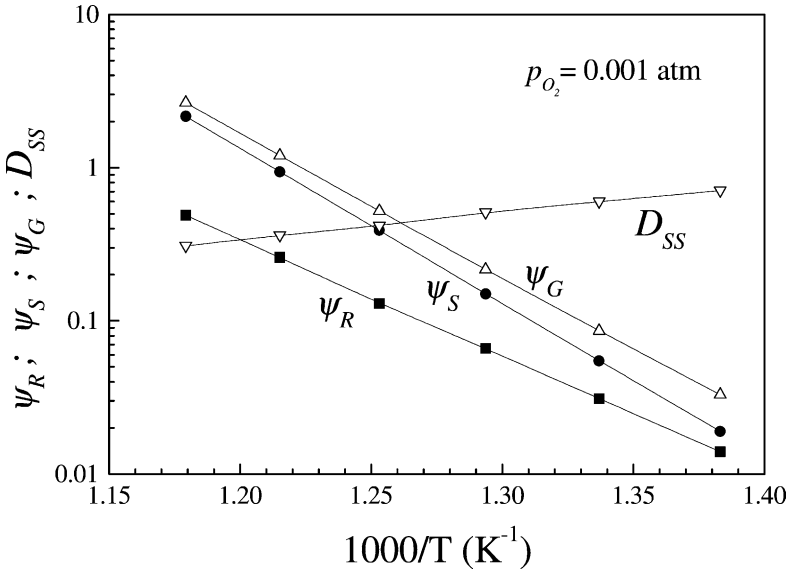

Fig. 6. Influence of p_{HCl} on the sintering-redispersion kinetic parameters during sintering.

In Fig. 8 it is shown that an increase of p_{HCl} produces a slight decrease on the intrinsic rate of sintering, but strongly increases the intrinsic rate of redispersion. Consequently, the most important effect of HCl during the redispersion experiments is the promotion of the redispersion process, while the sintering step is only slightly inhibited. Accordingly, both facts result in a net process of redispersion as shown in Fig. 4.

In our experimental conditions during sintering treatments, the kinetic functions of sintering and redispersion only depend on the temperature and oxygen concentration. Therefore, Eqs. (14) and (15) are

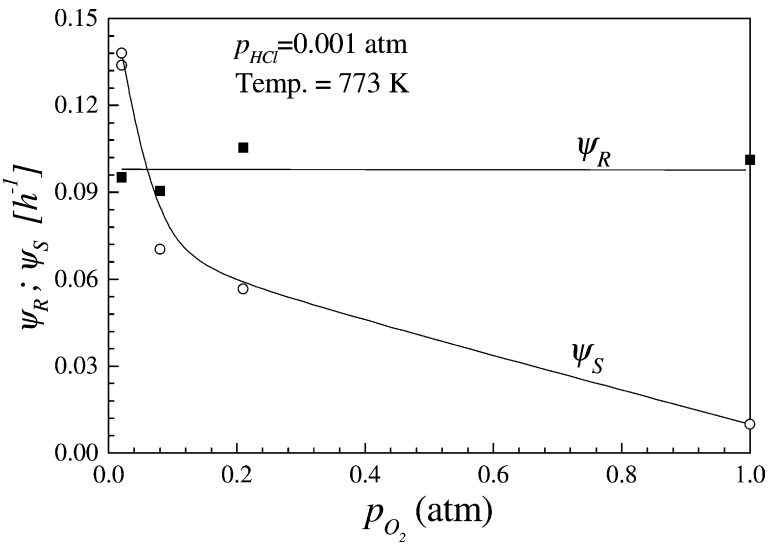

Fig. 7. Influence of p_{O_2} on the sintering-redispersion kinetic parameters during redispersion.

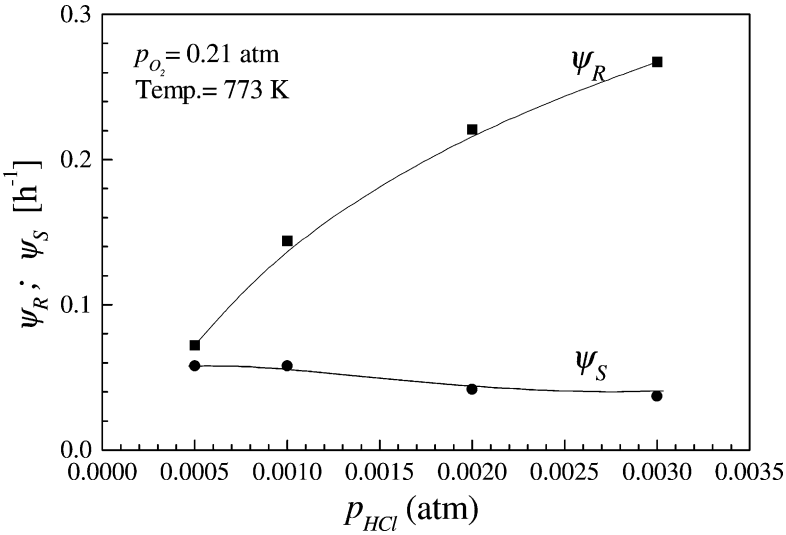

Fig. 8. Influence of p_{HCl} on the sintering-redispersion kinetic parameters during redispersion.

expressed as

$$\psi_{\mathrm{R}} = k_{\mathrm{R}_0} \exp\left(-\frac{E_{\mathrm{R}}}{R}\left(\frac{1}{T} - \frac{1}{823}\right)\right) p_{\mathrm{O}_2}^{m_{\mathrm{R}}} \tag{19}$$

$$\psi_{\mathrm{S}} = k_{\mathrm{S}_0} \exp\left(-\frac{E_{\mathrm{S}}}{R}\left(\frac{1}{T} - \frac{1}{823}\right)\right) p_{\mathrm{O}_2}^{m_{\mathrm{S}}} \tag{20}$$

In the above equations 823 K was used as the reparametrization temperature and therefore k_{R_0} and k_{S_0} correspond to the values of ψ_{R} and ψ_{S} at this temperature.

As regards redispersion treatments, given that the temperature was kept constant during these experiments, ψ_{R} and ψ_{S} depend only on the HCl and oxygen concentrations. Therefore, in this case this dependence is expressed as

$$\psi_{\mathrm{R}} = k_{\mathrm{R}}\, p_{\mathrm{HCl}}^{n_{\mathrm{R}}} \tag{21}$$

$$\psi_{\mathrm{S}} = k_{\mathrm{S}}\, p_{\mathrm{HCl}}^{n_{\mathrm{S}}} p_{\mathrm{O}_2}^{m_{\mathrm{S}}} \tag{22}$$

The intrinsic kinetic parameters of the sintering-redispersion model (k_{R_0}, k_{S_0} E_{R}, E_{S}, m_{R} and m_{S} for sintering and k_{R}, k_{S}, n_{S}, m_{R} and m_{S} for redispersion) can also be obtained by non-linear multivariable regression of experimental data using Eqs. (13), (19) and (20) for sintering and Eqs. (13), (21) and (22) for redispersion. The intrinsic kinetic parameters calculated in this way are summarized in Tables 1 and 2. In addition, the solid lines in Figs. 1–4 show that the Sintering-Redispersion Kinetic Model satisfactorily fits all the data.

The values reported in Table 1 are in good agreement with the kinetic parameters previously obtained [18]. The negative dependence of D_{rr} with respect to oxygen (Eq. (4), $\gamma = -0.058$) is related to the fact that both ψ_{R} and ψ_{S} decrease as the oxygen concentration increases ($m_{\mathrm{R}} = -0.78$, $m_{\mathrm{S}} = -0.69$), but the kinetic order for redispersion is lower than for sintering ($m_{\mathrm{R}} - m_{\mathrm{S}} = -0.09$). In addition, the values of both kinetic orders, m_{R} and m_{S}, are similar to the value of the parameter β in Eq. (3) ($\beta = -0.51$). As regards, the intrinsic kinetic constants, value of k_{S_0} is nearly six times higher than the value of k_{R_0}, indicating the prevalence of the sintering over the redispersion under these working conditions.

Table 1
Kinetic parameters of sintering-redispersion model

Parameter	Values ± S.E.
k_{R_0} [a]	$3.47 \times 10^{-3} \pm 5.2 \times 10^{-4}$
m_{R}	-0.78 ± 0.04
E_{R} (kJ/mol)	136.0 ± 8.8
k_{S_0} [b]	$2.05 \times 10^{-2} \pm 2.1 \times 10^{-3}$
n_{S}	-0.69 ± 0.05
E_{S} (kJ/mol)	185.8 ± 7.1

Sintering experiments.
[a] $[k_{\mathrm{R}_0}] \equiv \mathrm{h}^{-1}\ (\mathrm{atm\ O_2})^{0.78}$.
[b] $[k_{\mathrm{S}_0}] \equiv \mathrm{h}^{-1}\ (\mathrm{atm\ O_2})^{0.69}$.

Table 2
Kinetic parameters of sintering-redispersion model

Parameter	Values ± S.E.
k_{R_0} [a]	18.25 ± 0.94
n_R	0.72 ± 0.03
k_{S_0} [b]	$4.45 \times 10^{-4} \pm 7.68 \times 10^{-5}$
n_S	−0.495 ± 0.025
m_S	−0.73 ± 0.10

Redispersion experiments.
[a] $[k_{R_0}] \equiv h^{-1}\ (\text{atm HCl})^{-0.72}$.
[b] $[k_{S_0}] = h^{-1}\ (\text{atm HCl})^{0.73}\ (\text{atm } O_2)^{0.495}$.

Regarding the activation energies, the value of the parameter Q_S (38.6 ± 1.3 kJ/mol) is also in quite good agreement with the difference between E_S and E_R ($E_S - E_R = -49.7$ kJ/mol). Besides, the value of E_D in Eq. (3) (157.8 ± 8.2 kJ/mol) is of the same order as the activation energies for ψ_R and ψ_S (185.7 and 136.0 kJ/mol, respectively). These values are in agreement with the values of activation energies involved in this type of process [11,14,20].

In Table 2 the parameters of Eqs. (21) and (22) are presented, corresponding to redispersion data. These parameters are in agreement with the results shown in Figs. 7 and 8. In this fitting the value of m_R has been fixed to zero, according to the results presented in Fig. 7. However, to verify this assumption further, the experimental data were also fitted leaving the parameter m_R free in the optimization procedure. In this case, the value of this parameter was $m_R = -0.027 \pm 0.021$, being therefore statistically non-different from zero. This means that, in fact, ψ_R depends only on the HCl concentration ($n_R = 0.72$). The negative exponents of ψ_S ($n_S = -0.69$, $m_R = -0.73$) indicate that the sintering process is strongly inhibited under these conditions.

Finally, it is important to note that, as far as we know, this is one of the few systematic studies on sintering and redispersion kinetics of supported metal catalysts reported in the literature, which allows for the establishment of a relationship between the intrinsic kinetic parameters and the operating conditions.

4. Conclusions

The sintering-redispersion of the metallic crystallites in Pt/γ-Al_2O_3 catalysts can be considered as a reversible phenomenon. According to this hypothesis a new Sintering-Redispersion Kinetic Model has been proposed. This model explains the results obtained by previous sintering models, and allows us to assign a physical meaning to the intrinsic kinetic parameters.

The proposed kinetic model fits satisfactorily all the experimental data obtained during the sintering and redispersion experiments, allowing the determination of the influence of the operating conditions on the dispersion variation rate during sintering experiments as well as during redispersion experiments. The influence of the operating conditions is included in the main parameters of this model: $\psi_{R,}$ the kinetic function of redispersion and $\psi_{S,}$ the kinetic function of sintering.The sintering experiments show that the net rate of sintering depends on temperature and oxygen concentration. When the oxygen concentration increases, the net rate of sintering (ψ_S) decreases. However, the increase in oxygen concentration inhibits not only the sintering step but also inhibits the redispersion step, as a consequence of the stabilization of Pt^{+4} surface species at high oxygen concentrations. It was found that both kinetic functions, ψ_R and ψ_S, follow an Arrhenius law with the temperature.

The redispersion experiments show that the net rate of redispersion depends both on oxygen and HCl concentrations. The main effect of O_2 during redispersion is the inhibition of the intrinsic sintering rate, having little effect on the redispersion step. Finally, the most important effect of HCl during the redispersion experiments is the promotion of the intrinsic redispersion rate, having a little effect on the sintering step.

Acknowledgements

The authors acknowledge financial support from DGI-MCYT, Madrid, Spain (Grant PPQ2001-2479). The authors are very gratefully to Mr. E. Rincon for his contribution on obtaining experimental data.

References

[1] J.P. Franck, G. Martino, Progress in Catalytic Deactivation, in: J.L. Figueiredo (Eds.), NATO, Advance Study Institutional Series, E54, 1982, p. 355.
[2] W. Callender, J.J. Miller, in: Proceedings of the VIIIth International Congress on Catalysis, Deshema, Frankfurt am Main, vol. II, 1984, p. 481.

[3] T.F. Garetto, A. Borgna, E.R. Benvenutto, C.R. Apesteguia, in: Proceedings of the 12th Iberoamerican Symposium on Catalysis, vol. 1, 1990, p. 585.
[4] R.M.J. Fiedorow, S.E. Wanke, J. Catal. 37 (1975) 432.
[5] F.M. Dautzenberg, H.B.M. Wolters, J. Catal. 51 (1978) 26.
[6] E. Ruckenstein, in: S.A. Stevenson, J.A. Dumesic, R.T.K. Backer, E. Ruckenstein (Eds.), Metal-Support Interactions in Catalysis, Sintering and Redispersion, Nostrand Reinhold, New York, 1987.
[7] S.C. Fung, Catal. Today 53 (1999) 325.
[8] T.J. Lee, Y.G. Fim, J. Catal. 90 (1984) 279.
[9] K. Foger, H. Jaeger, J. Catal. 92 (1985) 62.
[10] G.A. Fuentes, F.A. Ruiz-Treviño, in: Proceedings of the Natural AIChE Meeting, New York, 15–25 November 1987.
[11] G.A. Fuentes, E.D. Gamas, Stud. Surf. Sci. Catal. 68 (1991) 637.
[12] A. Borgna, T.F. Garetto, A. Monzón, C.R. Apesteguía, J. Catal. 146 (1994) 69.
[13] A. Monzón, E. Romeo, A. Borgna, Chem. Eng. J. (2003), in press.
[14] C.H. Bartholomew, Appl. Catal. 107 (1993) 1.
[15] C.H. Bartholomew, Stud. Surf. Sci. Catal. 88 (1994) 1.
[16] R.W. Rice, C.C. Chen, J. Catal. 103 (1987) 140.
[17] S.C. Fung, in: Proceedings of the 17th North American Catalysis Society Meeting (NACS 2001), Toronto, Canada, 3–8 June 2001.
[18] T.F. Garetto, A. Borgna, A. Monzón, J. Chem. Soc. Faraday Trans. 92 (1996) 2637.
[19] J.R. Sinfelt, J.L. Cartier, D.F.C. Yates, J. Catal. 24 (1972) 283.
[20] G.A. Fuentes, in: Proceedings of the XV Iberoamerican Symposium on Catalysis, vol. 1, Córdoba, Argentina, 1996, p. 105.
[21] C.H. Bartholomew, Catal. R. Soc. Chem. 10 (1994) 41.
[22] J. Lif, M. Skoglundh, L. Löwendahl, Appl. Catal. 228 (2002) 145.
[23] F. Le Normand, A. Borgna, T.F. Garetto, C.R. Apesteguía, B. Moraweck, J. Phys. Chem. 100 (1996) 9068.
[24] A. Borgna, T.F. Garetto, C.R. Apesteguia, B. Moraweck, J. Catal. 186 (1999) 433.
[25] A. Borgna, F. Le Normand, T.F. Garetto, C.R. Apesteguía, B. Moraweck, Stud. Surf. Sci. Catal. 126 (1999) 179.
[26] T.F. Garetto, A. Borgna, A. Monzón, C.R. Apesteguia, in: Proceedings of the 14th Iberoamerican, Symposium on Catalysis, vol. 1, 1994, p. 63.