The Effect of Alkali Metal Promoters on the Stability and Coke Formation of Platinum-Based Propane Dehydrogenation Catalysts: A Kinetic Study

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ABSTRACT: *The kinetics of catalyst deactivation and coke formation during dehydrogenation of propane over supported Pt–based catalysts and, in particular, the effect of alkali metal promoters on catalyst activity and stability were studied. The analysis of propane conversion data showed that there is an optimum level of alkali metal promoter loading for both catalyst activity and stability. A model based on individual site poisoning was proposed for coke deposition kinetics. The model showed fair fits for coke formation data with time on stream. While the rate constant of coke formation was slightly affected by loading of Na as the neutralizing promoter, the ultimate coke amount was strongly dependent on the Na loading. It was found that coke formation sites should be different from active sites for the main reaction.*

KEY WORDS: *Propane dehydrogenation, Pt–based catalysts, Catalyst deactivation, Coke amount, Kinetics, Alkali metal.*

INTRODUCTION

Coke formation is the main cause of catalyst deactivation in many hydrocarbon conversion processes [1–3]. Coke deposits may amount to 15% or even 20% (w/w) of the catalyst and accordingly they may deactivate the catalyst either by covering of the active sites, and by pore blocking [3]. The latter could be important in severely diffusion–limited reactions exhibiting parallel fouling [4].

The dehydrogenation of lower paraffins such as propane and isobutane over Pt–based catalysts is an important commercial process in which coke formation plays a significant role in catalyst deactivation and, therefore, in process design due to the need for frequent catalyst regeneration [5, 6]. Coke formation could occur both due to the decomposition of the hydrocarbons involved or dehydro–condensation reactions over the residual acidic sites of the support. The former is reduced by using tin as the promoter while the latter is minimized

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by addition of alkaline promoters such as alkali metals (Li, Na and K) [7,8].

Tin and alkali metals can reduce the coverage of coke on the Pt active site of Pt/γ–Al$_2$O$_3$ propane dehydrogenation catalyst. Sn and Sn–alkali metal promoted catalysts show higher excess mobile electrons than the unpromoted ones. The excess mobile electrons enhance hydrogen spillover on the catalyst surface, thus reducing the amount of coke deposits [9].

The addition of alkali metal promoters to Pt–Sn/Al$_2$O$_3$ dehydrogenation catalyst also improves the performance via suppression of acid–catalyzed side reactions (cracking, isomerization and polymerization) by neutralizing the residual acid sites of the support. The additional effects might be modifying the active metal dispersion and increasing the fraction of bare metallic Pt surface after carbon deposition [10]. The promoting effect depends on the alkali metal involved.

Casella et al. [11] studied lithium-modified Pt-Sn/γ–Al$_2$O$_3$ catalysts for isobutane dehydrogenation. On the monometallic platinum catalysts, when lithium was added after the metallic precursor, a system having a high dispersion was obtained. In this case, platinum presents an important modification in its electronic properties. When lithium was added before the metal precursor compounds, the dispersion of the resulting systems was markedly lower, due to the modification of the textural properties and of the acidity of the support. This lower dispersion is responsible for a lower catalytic activity, for both mono and bimetallic catalysts.

Zhang et al. [12] studied the effect of Na addition to Pt-Sn/ZSM–5 catalysts on coke formation as a function of time-on-stream and Na loading. The results showed the suppression of coke deposition upon addition of Na to the catalyst. Their data were used in this work to study coke formation kinetics on Pt–based dehydrogenation catalysts.

Songbo et al. [13] studied the effect of K promoter on the performance of Pt–Sn–K/γ–Al$_2$O$_3$ catalyst in dehydrogenation of hexadecane. Their results showed that the addition of K decreased the interaction of SnO$_x$ species with Al$_2$O$_3$, promoted the reduction of SnO$_x$ and decreased the amount of strong acidic centers of the catalyst. Thus, the side reactions on the catalyst were inhibited, and the selectivity to mono-olefins was increased. The stability of the catalyst was slightly

enhanced by the addition of K because of the increased resistance to coke formation on the catalyst. However, the synergistic effect of active sites and acidic sites was weakened by the excess addition of the K promoter, which results in a decrease in the activity and a low stability of the catalyst.

The concentration at which the carbon on the surface begins to inhibit further deposition is a strong function of the catalyst formulation. For example, while on a Pt/Al$_2$O$_3$ catalyst, the rate of formation starts slowing down at a carbon content of about 2 wt %, on a bimetallic Pt–Sn/Al$_2$O$_3$ catalyst the coking rate remains unchanged up to about 7 wt% carbon [14].

The rate of coke formation has an important role in the design of catalyst regeneration units and its operating conditions. Unfortunately, the determination of real–time coke deposition is difficult especially for fixed–bed reactors. On the other hand, the catalyst activity can be easily calculated from reactor output. Consequently, a correlation for coke formation versus time–on–stream or catalyst activity for dehydrogenation of light alkanes could be very useful from a practical point of view.

In this work, the kinetics of catalyst deactivation and coke formation in propane dehydrogenation over Pt-based catalysts is studied to develop a correlation between catalyst activity and coke amount. The effect of addition of alkali metals as neutralizing agent of acidic sites of the support which are considered as the main coke formation sites is also studied.

THEORETICAL SECTION

The catalyst activity, *a*, defined as the ratio of the reaction rate –*r'* to its initial value (Eq. 1), is commonly used as a measure of active sites available for reaction.

$$a = \frac{-r'(t)}{-r'(t = 0)} \tag{1}$$

Using a first order kinetics for the main reaction and an independent first–order decay law for catalyst deactivation,

$$-\frac{da}{dt} = k_d a \tag{2}$$

the following relation has been proposed to obtain deactivation rate constant, k_d, from propane conversion, *X*, versus time data [15-17].

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$$\ln\frac{1-X}{X} = k_d t + \ln\frac{1-X_0}{X_0} \qquad (3)$$

where X_0 is the time–zero conversion, a measure of catalyst activity. A plot of Eq. (3) will give k_d and X_0. More sophisticated and more accurate correlations have been also proposed [18]. However, Eq. (3) suffices for catalyst screening purposes.

While catalyst decay rate laws, mostly empirical, are often available in the literature, corresponding correlations for coke formation rates are rather scarce.

The amount of coke, C_C, after time–on–stream t obeys the empirical *Voorhies* relation [19], which holds for a wide–variety of reactions:

$$C_C = At^n \qquad (4)$$

where A is a constant depending on the feedstock, reactor type and reaction conditions and *n* is an exponent with a value close to 0.5 which corresponds to coke formation rate proportional to the reciprocal of coke amount. In this equation the amount of coke formed on the catalyst is assumed to be independent of the hydrocarbon feed rate, a hypothesis that has not been confirmed by all authors [3]. Further, the empirical nature of the relation makes its application limited.

In the generalized Monolayer-Multilayer Coke Growth Model (MMCGM) [20], coke content in the catalyst versus time can be described taking into account a simultaneous formation of coke over the surface of the catalyst and a multilayer coke deposition. Therefore, the total coke formation rate must be described as the addition of monolayer and multilayer coke growth.

$$\frac{dC_C}{dt} = \frac{dC_m}{dt} + \frac{dC_M}{dt} \qquad (5)$$

with

$$r_{C_m} = \frac{dC_m}{dt} = k_1\left(C_{max} + C_m\right)^h \qquad (6)$$

and

$$r_{C_M} = \frac{dC_M}{dt} = k_2 C_m^n \left(C_{max} + C_m\right)^m \qquad (7)$$

where C_m and C_M are the coke concentration in monolayer and multilayer, respectively, and C_{max} is the maximum coke concentration in monolayer.

Resasco [14] proposed a kinetic expression for the rate of carbon formation as a function of the partial pressures of olefin and hydrogen. The expression predicts a strong inhibition of coke formation by both a negative term in the numerator, which reflects the elimination of carbonaceous deposits by hydrogenation and a term in the denominator that result from the competition for adsorption sites.

Different functionalities between catalyst activity and amount of coke have been proposed. The following deactivation functions were suggested by *Dumez & Froment* [21]:

$$a = \left(1 - \alpha C_C\right)^n \qquad n = 1 \text{ or } 2 \qquad (8)$$

$$a = \left(1 + \alpha C_C\right)^n \qquad n = -2 \text{ or } -1 \qquad (9)$$

$$a = \exp\left(\alpha C_C\right) \qquad (10)$$

The dehydrogenation of propane has been shown not to be intraparticle diffusion–limited [22]. Further, the fact that both the reactants and products can contribute in coke formation implies that coke formation should be uniform within the pellet. In this case, rate of coke formation could be considered to be proportional to unfouled coke formation sites:

$$\frac{dC_C}{dt} = k_c(C_{C\infty} - C_C) \qquad (11)$$

In which $C_{C\infty}$ showing the ultimate coke amount is a measure of potential coke formation sites. Integration using the initial condition of no coke deposition results in:

$$\ln(1 - C_C / C_{C\infty}) = -k_c t \qquad (12)$$

Therefore, a plot of Eq. (12) should result in straight line passing through the origin. Since $C_{C\infty}$ is unknown, it could be obtained by a trial and error procedure for a given data set. The slope of the resulting lines will give the rate constant of coke formation.

Upon integration of Eq. (2) with $a(0)=1$,

$$a = \exp(-k_d t) \qquad (13)$$

and eliminating time between Eqs. (12) and (13), one obtains:

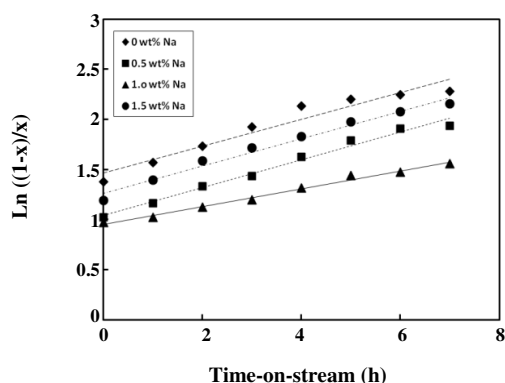$$a = \left(1 - \frac{C_C}{C_\infty}\right)^{k_d/k_c} \qquad (14)$$

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Fig. 1: Plots of Eq. (3) for different Na loadings over Pt–Sn/AlSBA catalyst (experimental data from [23], T=590 ºC, H_2/HC=0.25 mol/mol).

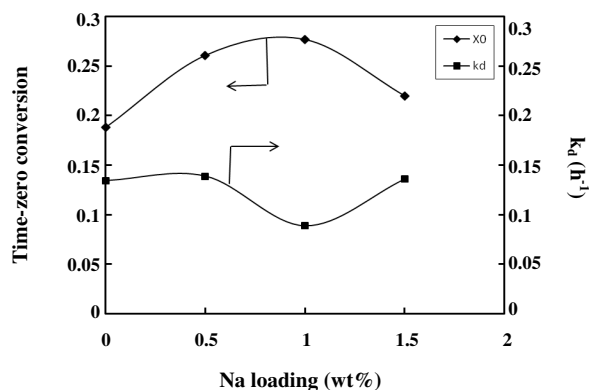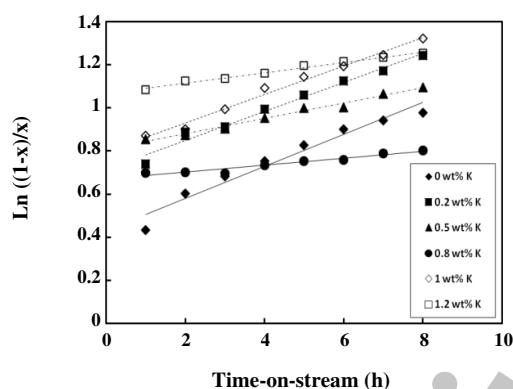*Fig. 2: Plots of Eq. (3) for different K loadings over Pt–Sn/ZSM–5 catalyst (experimental data from [24], T=590 ºC, H_2/HC=0.25 mol/mol).*

Fig. 3: Effect of Na loadings of Pt–Sn/AlSBA catalyst on time–zero conversion and deactivation rate constant (T=590 ºC, H_2/HC=0.25 mol/mol).

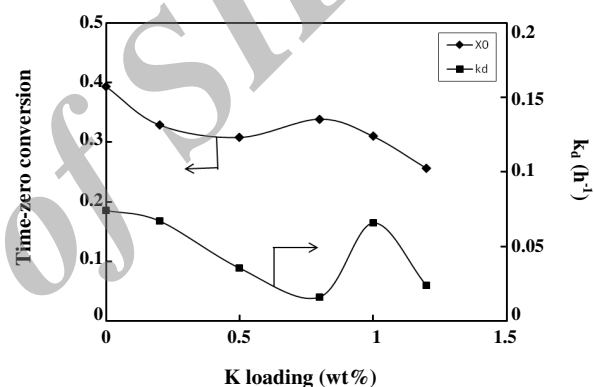*Fig. 4: Effect of K loadings of Pt–Sn/H–ZSM5 catalyst on time–zero conversion and deactivation rate constant (T=590 ºC, H_2/HC=0.25 mol/mol).*

Which relates the catalyst activity to the amount of coke deposited. Equation (14) is in the form of *Dumez & Froment* function (Eq. (8)) with $\alpha=1/C_C$ and $n=k_d/k_c$. It can be used to estimate coke amounts from catalyst activities at any time. The catalyst activity can be calculated from propane conversions data.

RESULTS AND DISCUSSION
Catalyst activity

Figs. 1 and 2 show plots of Eq. (3) for different loadings of Na and K for Pt–Sn/AlSBA (Si/Al=20) and Pt–Sn/ZSM–5 catalysts, respectively. Fair fits are observed. They illustrate that alkali metal loading has a pronounced effect on catalyst activity and stability. Figs. 3 and 4 show time-zero convesrions and rate

constants of deactivations versus alkali metal loading for Na and K, respectively, derived from the interceps and slopes of Fig. 1 and 2. Figs. 3 and 4, althought somewhat different, show that cataxst activity (time–zero conversion) passes a peak at certain level of alkali metal loading while deactivation rate constant passes a minimum at nearly the same loading. Consequently, there is an optimum level of alkali metal loading beyond which both activity and stabillity suffer by further loading. Excess alkali metal could destroy the balance of metal function and acid properties, weakening the interaction of Pt and Sn, and thus the catalytic performance declines [25].

In Fig. 4, for example, the Pt–Sn–K(0.8%)/ZSM–5 catalyst sample possesses the best ratio between the number of active sites and the number of acid sites.

However, with continuous addition of K, the character of Pt active sites changes. In these cases, the Pt metal dispersions are reduced by the excess addition of K (after the content is 0.8%). As a result, the multiple interactions between Pt, SnO_x and K^+ can coexist and the catalytic performance can be affected because these interactions between the three components are considered to be responsible for the stabilization of Pt in its oxidized state [24,26].

Coke formation

Fig. 5 shows plots of Eq. (14) for different values of k_d/k_c ratio. For a ratio close to unity, the coke amount varies linearly with catalyst activity implying that active sites and coke forming sites are the same. A ratio smaller than unity results in positive deviation, which is desirable, as high levels of catalyst activity are retained for higher levels of coke deposition. In the extreme case, the reaction and coke formation sites are different and coke formation rate is much higher than active (Pt) site coverage.

The data of ref [12] were used to fit coke formation rate expressions. Fig. 6 shows that the carbon deposition favorably obeys Voorhies correlation for different Na loadings. A series of nearly parallel straight lines are obtained. However, the exponents are about 0.3, smaller than the typical value of 0.5, which indicates that coke formation strongly inhibits coke deposition. *Jinxiang et al.* [27] obtained good fits for isobutane dehydrogenation over Pt and Pt–Sn/Al$_2$O$_3$ catalysts but *n* was close to 0.5.

Fig. 7 shows plots of Eq. 12 for different Na loadings. Fair fits are observed, however, the intercept is slightly below the origin. It could be explained by the fact that at the beginning of the reaction the catalyst is highly active but less selective resulting in extensive side reactions and very fast deactivation [14]. After a short period of time, the highly active hydrogenolysis sites are selectively deactivated leaving dehydrogenation sites which promote the main reaction. The lower the amount of sodium doped, the higher is the rate of catalyst deactivation. Interestingly, however, the rate constant of coke formation is only slightly affected by the Na loading. In contrast, the ultimate coke amount strongly depends on Na loading, decreasing in an exponential–like manner after an initial nearly–linear dependence (Fig. 8). The fact that the linear relation does not hold for higher Na contents, and that coke formation continues even
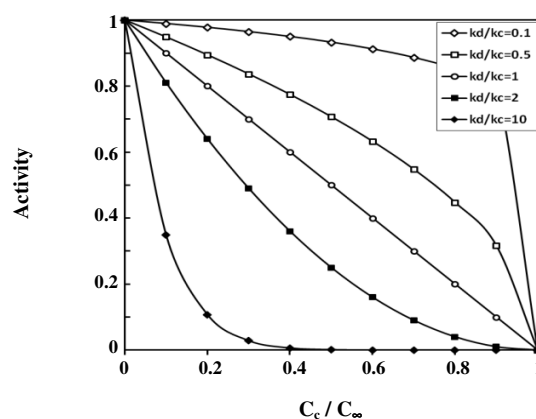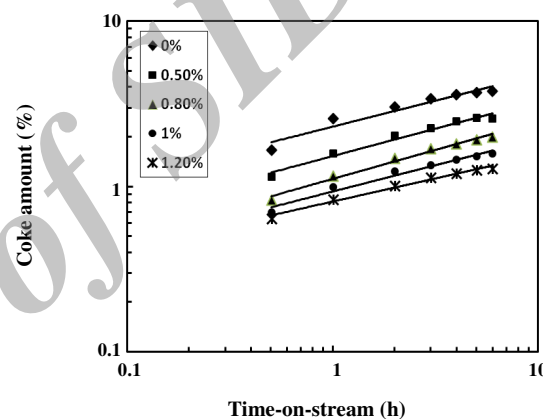

Fig. 5: Typical plots of Eq. (14).

Fig. 6: Voorhies plots for coke formation on promoted Pt/ZSM–5 catalysts of different Na loadings (wt%) (T=590 ºC, H$_2$/HC=0.25 mol/mol).

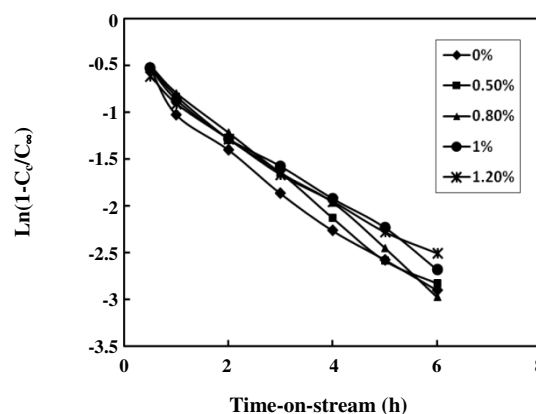*Fig. 7: Plots of Eq. 12 for different loadings of sodium (T=590 ºC, H$_2$/HC=0.25 mol/mol).*

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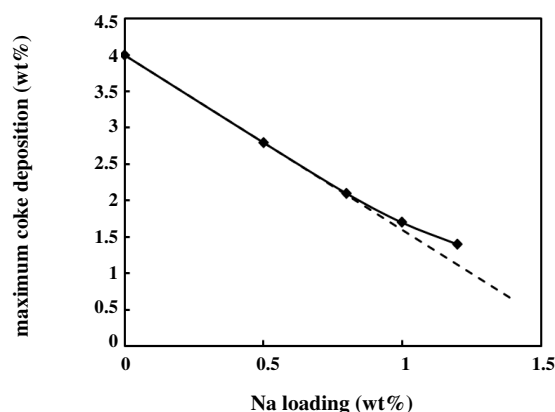**Fig. 8: The effect of sodium addition on ultimate coke amount (T=590 ºC, H_2/HC=0.25 mol/mol).**

when acid sites are totally blocked, implies that sites other than acidic sites, i.e. certain metallic sites; as well as thermal decomposition, should have a contribution on coke formation.

The extrapolation of linear portion in Fig. 8 gives an intercept at near 1.7 wt% Na loading, equivalent to 740 μmol/g Na. This is of the same order of magnitude as total acidity of the zeolite support.

In addition to blocking acid sites, Na can modify Pt dispersion, promoting H_2 spillover and diminish even coke formation on active metal sites [10]. In this way, the formation of bare Pt surface increase after coke deposition. However, too high alkaline loading bring about Pt–Sn segregation which is undesirable [25].

Earlier woks showed the applicability of Eq. (13) to dehydrogenation on Pt based catalyst with a value of about 0.02 h^{-1} for k_d [28] (see also Fig. 3 and 4 giving k_d in the range of 0.02 to 0.14 h^{-1}). Having 0.5 h^{-1} for k_c from the above results, the exponent of Eq. (11) is in the order of 0.04 to 0.3 which are smaller than unity. These results further confirm the view that coke formation is possible on sites other than active sites, e.g. acid sites of the support.

CONCLUSIONS

Addition of alkali metal promoters to supported Pt-based propane dehydrogenation catalysts can improve the catalyst performance. There is an optimum level of alkali metal loading, within 0.5-1 wt% range, which results in the highest catalyst activity and stability. The rate of coke formation over the catalyst can be explained

by a first–order rate expression from which the *Dumez & Froment* type relation for functionality of catalyst activity with coke amount can be derived theoretically. Unlike ultimate coke amount which decreases by alkali metal loading, the rate constant of coke formation is slightly affected by alkaline promoter loading. Although the coke amount strongly depends on acid site concentration of the support, the analysis of the model results illustrated that other sites as well as thermal decomposition could play a role in coke formation.

Nomenclature

A	A constant defined by Eq. (4), kg/h^n
a	Catalyst activity
C_C	Coke amount, kg/kg catalyst
C_∞	Ultimate coke amount, kg/kg catalyst
C_m	Coke concentration in monolayer, kg/kg catalyst
C_M	Coke concentration in multilayer, kg/kg catalyst
k_C	Rate constant for coke formation, h^{-1}
k_d	Rate constant for deactivation of catalyst, h^{-1}
r'	Rate of disappearance of reactant (propane) per mass of catalyst, mol/(kg·h)
t	Time on stream, h
X	Conversion of propane

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