

Kinetic study of *n*-heptane conversion on palladium or iridium supported on sulphated zirconia

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Abstract

The present paper continues and terminates our previous studies devoted to platinum supported on sulphated zirconia (Pt/SZ). More particularly, it deals with iridium or palladium supported on SZ (Ir/SZ or Pd/SZ) which kinetic data were determined for the *n*-heptane conversion. Both display similar catalytic behaviours since their kinetic data follow similar evolutions with the variations of temperature and hydrogen pressure. The results suggest that the catalysis is bifunctional at 150 °C and hydrogen pressures below 101,325 Pa, while it becomes acid with the increase of both temperature and hydrogen pressure. The main difference between Ir-or-Pd/SZ and Pt/SZ is the number of functions of the active metal–proton adduct site that are involved in the reaction at 150 °C and hydrogen pressures above 101,325 Pa. The metal–proton adduct is a single active site that gathers together two functions, the metal and the acid functions.

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1. Introduction

Sulphated zirconia (SZ) promotes the isomerization of aliphatic hydrocarbons to hydrocarbon mixtures having higher octane number [1]. Unfortunately, SZ rapidly deactivates [2]. Its performance is improved if it contains a transition metal. Platinum is the most investigated [3].

Pt supported on SZ (Pt/SZ) is a bifunctional catalyst, on which, generally, the isomerization reaction is believed to proceed according to the classical bifunctional mechanism [4]. Nevertheless, some modifications to this mechanism have been introduced, although, these ones do not dismiss the bifunctional nature of Pt/SZ [5–7]. Otherwise, the role of Pt in the presence of hydrogen is particularly debated. On the one hand, it is suggested that Pt catalyses the molecular hydrogen dissociation into a proton and a hydride [8,9]. On the other hand, it is supposed that Pt catalyses the molecular hydrogen dissociation into two hydrogen atoms, which spillover onto SZ and convert into a proton and a hydride [10,11].

A kinetic study can provide information about the hydrogen role and the catalyst behaviour. For example, recently, Løften and Blekkan [12] showed that, for the *n*-hexane conversion on Pt/SZ, the kinetic data obtained were in agreement with the values reported for a classical bifunctional mechanism.

The present paper is the continuation and the termination of our two previous papers. The first one reports the reactivity results of Pt, Pd or Ir supported on SZ for the conversion of alkanes [7]. The second one provides the kinetic data of the Pt/SZ catalyst [13]. Both underline that the metal–proton adduct $[H-(M_m)(H^+)_x]^{x+}$ is the active site for our catalysts in our experimental conditions. This adduct groups together the metal and the acid sites in a single ensemble and so has two functions. The present paper reports the kinetic study for the *n*-heptane conversion on 0.2 wt% Pd supported on SZ (Pd/SZ) and on 0.2 wt% Ir on supported SZ (Ir/SZ) under low (25,331–101,325 Pa) and high (119,990–399,967 Pa) hydrogen pressures. This study, especially, gives information about the behaviour of the catalysts in relation to the hydrogen concentration.

2. Experimental

The Pd/SZ and Ir/SZ catalysts were prepared according to a one step sol–gel synthesis. The catalytic reactions were carried

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out in pulse flow systems and the products were analysed by gas chromatographs. So as to get the maximum of kinetic information, the hydrogen pressure, the hydrocarbon partial pressure and the temperature were varied: 25,331–399,967 Pa, 667–5333 Pa and 150–250 °C. All the procedures have been described elsewhere [7,13].

The reaction rates r (nmol g⁻¹ s⁻¹) were determined by using the following equation:

$$r = \frac{Vd}{M\omega t} \ln \left(\frac{1}{1 - \alpha_T} \right)$$

where V (5×10^{-6} l) is the volume of the n -heptane injected, d (0.68 kg l⁻¹) the n -heptane density, M (100.21 g mol⁻¹) the n -heptane molecular weight, ω (0.1 g) the catalyst weight, t (s) the time for the hydrocarbon to pass through the catalyst and α_T is the total conversion (below 25% in all experiments). The calculations details have been given elsewhere [13]. The reaction orders in hydrogen n and in n -heptane m as well as the apparent activation energy E_A (kcal mol⁻¹) were determined by using the reaction rate r that can also be written as following power law:

$$r = k(P_{H_2})^n(P_{nC7})^m$$

$$k = A \exp \left(-\frac{E_A}{RT} \right)$$

3. Results

3.1. Reaction order in n -heptane

The orders in n -heptane were got, firstly, at the atmospheric pressure of hydrogen and at 170 and 240 °C, and secondly, at 240 °C for two hydrogen pressures, i.e. 101,325 and 299,975 Pa (Table 1). For both Ir/SZ and Pd/SZ, the orders are of 1 whatever the conditions (temperature and pressure) may be. In other words, the reaction rate is proportional to the n -heptane partial pressure and is independent of the reaction temperature. Such a value, i.e. $m \sim 1$, is generally noticed for the bifunctional catalysts and has already been reported for metal promoted SZs [11,12,14–16].

Table 1
Reaction orders in n -heptane

Catalyst	Temperature (°C)	Hydrogen pressure (Pa)	n -Heptane partial pressure (Pa)	Reaction order in n -heptane
Ir/SZ	170	101,325	667–5333	1.0 ± 0.1
	240	101,325	667–5333	1.0 ± 0.1
	240	299,975	667–5333	0.9 ± 0.1
Pd/SZ	170	101,325	667–5333	1.0 ± 0.1
	240	101,325	667–5333	1.0 ± 0.1
	240	299,975	667–5333	1.0 ± 0.1
Pt/SZ ^a	170	101,325	667–5333	1.00
	240	101,325	667–5333	1.00
	240	299,975	667–5333	1.00

^a From [13].

3.2. Reaction order in hydrogen

Table 2 shows the reaction orders in hydrogen that were obtained at 150, 200 and 250 °C, and in each case, at two different ranges of the hydrogen pressure (low pressures 25,331–101,325 Pa and high pressures 119,990–399,967 Pa). It is to note that, in general, for a bifunctional catalyst, a negative order in hydrogen is expected [17,18].

From Table 2, different points are remarkable for Ir/SZ and Pd/SZ:

- At 150 °C, the orders at the low hydrogen pressures are negative while the orders at the high hydrogen pressures are positive.
- With the increase of the reaction temperature, the orders at the low hydrogen pressures increase towards slightly positive values (0.2) while the orders at the high hydrogen pressures decrease towards zero.
- At 150 °C, the influence of hydrogen is the most important; at 250 °C, the hydrogen pressure has a small effect on the reaction rate at the low pressures and no influence at the high pressures; the orders got at 200 °C correspond to intermediate values.

The reaction orders of Ir/SZ and Pd/SZ vary as those of Pt/SZ varied [13]. Besides, one can remark that, at 150 °C and the low hydrogen pressures, the orders in hydrogen are similar for the three catalysts.

The most noteworthy difference between these three catalysts is observed for the orders in hydrogen got at 150 °C and the high hydrogen pressures, namely, 0.4 for both Ir/SZ and Pd/SZ and 0.8 for Pt/SZ.

It is to note that, for unpromoted SZ in n -hexane conversion, Løften and Blekkan [12] observed a positive order in hydrogen.

3.3. Apparent activation energy

The apparent activation energy for a conventional bifunctional metal–acid catalyst is in the range 20–30 kcal mol⁻¹ [19–22] while that for a superacidic catalyst is below 18 kcal mol⁻¹ [23]. For the n -hexane conversion on SZ,

Table 2
Reaction orders in hydrogen (667 Pa for the *n*-heptane partial pressure)

Catalyst	Temperature (°C)	Low hydrogen pressures (25,331–101,325 Pa)	High hydrogen pressures (119,990–399,967 Pa)
Ir/SZ	150	-0.6 ± 0.1	0.4 ± 0.1
	200	-0.2 ± 0.1	0.0 ± 0.1
	250	0.2 ± 0.1	0.0 ± 0.1
Pd/SZ	150	-0.5 ± 0.1	0.4 ± 0.1
	200	0.2 ± 0.1	0.0 ± 0.1
	250	0.2 ± 0.1	0.0 ± 0.1
Pt/SZ ^a	150	-0.50	0.80
	200	-0.35	0.20
	250	-0.15	0.00

^a From [13].

Coman et al. [24] found apparent activation energies below 19 kcal mol^{-1} at 120–240 °C, while Stepanov et al. [25] noticed, for the *n*-butane isomerization on SZ at 18–50 °C, values of $15\text{--}17 \text{ kcal mol}^{-1}$. For *n*-butane isomerization on Pt/SZ, Tomishige et al. [11] observed values of 25 kcal mol^{-1} at 200–267 °C and for a hydrogen/*n*-butane ratio of 99.

Table 3 shows the global apparent activation energies, the isomerization apparent activation energies and the cracking apparent activation energies. These values were graphically determined at temperatures between 150 and 250 °C and at hydrogen pressures of 101,325, 199,984 and 299,975 Pa. The following observations are noteworthy:

- (i) The isomerization apparent activation energies are lower than the cracking ones.
- (ii) At 101,325 Pa, the apparent activation energies of Ir/SZ and Pd/SZ are similar.
- (iii) At 199,984 and 299,975 Pa, the global apparent activation energies of Ir/SZ and Pd/SZ are similar while the isomerization and cracking apparent activation energies of Pd/SZ are slightly higher than the Ir/SZ ones.
- (iv) The apparent activation energies decrease with the increase of the hydrogen pressure from 101,325 to 199,984 Pa, while they are stable with a further increase to 299,975 Pa.

- (v) For each catalyst, the apparent activation energies got at 101,325 Pa agree with those generally found for the conventional bifunctional catalysts, while the values got at 199,984–299,975 Pa rather agree with those observed with the acid catalysts.

One can remark that the apparent activation energies of the three catalysts, i.e. Pt/SZ, Ir/SZ and Pd/SZ, follow quite similar evolutions with the increase of the hydrogen pressure.

4. Discussion

The kinetic data got with Ir/SZ and Pd/SZ for the *n*-heptane conversion are quite similar to those got with Pt/SZ in a previous study [13]. Løften and Blekkan [12], who investigated Ir/SZ and Pt/SZ, also remarked quite similar kinetic parameters for both. That is why one can consider that the mechanistic interpretations that were proposed to explain the catalytic behaviour of Pt/SZ in reference [13] can justify the catalytic behaviours of the present catalysts, i.e. Ir/SZ and Pd/SZ, as well. Yet one modification must be introduced.

Above all, it is important to mention the main conclusions that were put forward about the original catalytic behaviour of Pt/SZ [13]:

Table 3
Apparent activation energy (E_A) values (150–250 °C, 667 Pa for the *n*-heptane partial pressure)

Catalyst	Hydrogen pressure (Pa)	Global E_A (kcal mol^{-1})	Isomerization E_A (kcal mol^{-1})	Cracking E_A (kcal mol^{-1})
Ir/SZ	101,325	24 ± 1	16 ± 1	27 ± 1
	199,984	16 ± 1	9 ± 1	23 ± 1
	299,975	15 ± 1	8 ± 1	24 ± 1
Pd/SZ	101,325	23 ± 1	17 ± 1	30 ± 1
	199,984	18 ± 1	13 ± 1	29 ± 1
	299,975	16 ± 1	13 ± 1	21 ± 1
Pt/SZ ^a	101,325	31.0	28.0	38.0
	199,984	19.0	12.5	32.5
	299,975	18.5	11.5	32.5

^a From [13].

- (i) The metal–proton adduct is the active site, on which the *n*-heptane adsorption is associative.
- (ii) At the low hydrogen pressures (below 101,325 Pa) and 150 °C, the reactivity is controlled by both metal function and acid function: the catalysis is bifunctional.
- (iii) At the high hydrogen pressures (above 101,325 Pa) and at the temperatures higher than 150 °C, the reactivity is controlled by the acid sites: the catalysis is acid.

Besides, different kinetic models and different concepts (for more details and references, see reference [13]) were considered; these enabled to propose the following rate equations (where K' , K'' are constants [13] and Z the number of active sites involved in the reaction):

- (iv) At the low hydrogen pressures and 150 °C:

$$r_{LP} = K'(P_{H_2})^{-0.5}(P_{nC7})^1$$

- (v) At the high hydrogen pressures and 150 °C:

$$r_{HP} = K''(P_{H_2})^{Z/2}(P_{nC7})^1$$

The rate equation r_{LP} for the low pressures suggests an order in hydrogen of -0.5 . This value agrees with the orders in hydrogen of Ir/SZ and Pd/SZ got at 150 °C (Table 2). In the literature, negative orders in hydrogen were observed for Pt/SZ [11,14,26]. Recently, an order of -0.9 was noticed for Ir/SZ, which was then described as a conventional bifunctional catalyst [12].

At the high hydrogen pressures and 150 °C, the rate equation r_{HP} suggests a positive order in hydrogen. A positive order in hydrogen has already been reported for metal promoted SZ catalysts [8–10,15,16]. The explanation that was given to interpret such a value was that, rather than a classical bifunctional mechanism, it was an acid mechanism assisted by the metal function that, in fact, controlled the reaction. In the present case, the rate equation r_{HP} suggests an order of $Z/2$. Since the experimentally determined orders for Ir/SZ and Pd/SZ are of 0.4 (Table 2), a value for Z of ~ 1 can be deduced. This supposes then that a single function of the metal–proton adduct site is necessary for the *n*-heptane conversion. Note that this data differs from the value $Z \sim 2$ found for Pt/SZ [13]. Here, it is, one more time, important to mention the interpretation that was given in our previous paper to justify $Z \sim 2$ [13]:

- (vi) With Pt/SZ, the alkane transformation reaction needs two free sites; the first one is located on the metal function and the other one is on the acid function.

Now, if one returns to Ir/SZ and Pd/SZ, it is to remark that:

- The adsorption of molecular hydrogen on the polycrystalline surfaces of Ir is stronger than the adsorption on the polycrystalline surfaces of Pd and Pt [27].
- The adsorption of molecular hydrogen on the surfaces (1 1 0) and (1 1 1) of Pd is stronger than the adsorption on the surfaces (1 1 0) and (1 1 1) of Pt [27].

These two remarks suggest that the adsorption heats on Ir and Pd are higher than that on Pt. Hence, one can suppose that, at the high hydrogen pressures and a low temperature like 150 °C, the hydrogen species strongly adsorbed on Ir and Pd hinder the adsorption of the hydrocarbon on the metal sites. In consequence, the hydrocarbon activates on the acid sites, which are free. The free site ($Z \sim 1$) of the metal–proton adduct is then the acid site.

With the increase of the temperature, the catalysis becomes more and more acid.

For Ir/SZ and Pd/SZ, the transition from the low to the high hydrogen pressures is characterised by a decrease of the apparent activation energies from values complying with a classical bifunctional catalysis to values complying with an acid catalysis. Such an interpretation, i.e. a change in the reaction mechanisms, was initially suggested by Tomishige et al. [11]. In other words, with our metal supported on SZ catalysts, there is a transition from the bifunctional catalysis to the acid catalysis with the increase of the hydrogen pressure and/or the reaction temperature.

5. Conclusion

The present paper proposes the kinetic data relative to the Ir/SZ and Pd/SZ catalysts that were investigated for the *n*-heptane conversion. The reaction orders in *n*-heptane and in hydrogen and the apparent activation energies are given. The evolutions of these data with the variations of the hydrogen pressure and the reaction temperature are studied.

Ir/SZ and Pd/SZ display original kinetic features that are quite similar to those of Pt/SZ. These three catalysts have a particular catalytic behaviour that is explained by regarding the occupation of the active site, i.e. the metal–proton adduct. The excess of hydrogen (pressures higher than 101,325 Pa) and/or the temperature increase (beyond 150 °C) provoke a shift in the reactivity from the metal function of the adduct to the acid function. In other words, with these three catalysts, the catalysis is bifunctional at 150 °C and hydrogen pressures below 101,325 Pa, while it becomes acid with the increase of both. Nevertheless, the catalytic behaviours of Ir/SZ and Pd/SZ are not completely similar to that of Pt/SZ. At 150 °C and hydrogen pressures above 101,325 Pa, the number of free sites of the metal–proton adduct involved in the reaction is 1 for Ir/SZ and Pd/SZ (namely, the acid function) while it is 2 for Pt/SZ (namely, the metal function and acid function).

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