

Proposal for a common reactive adsorbate for ethylbenzene and indenic compounds in the conversion of *n*-propylbenzene over a precoked silica-supported platinum catalyst

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Abstract

The effect of moderate sintering of the platinum particles of a precoked Pt/SiO₂ catalyst on the transformation of *n*-PB was investigated under reforming conditions (773 K, 5 bar, and H₂/HC = 5). The results showed that the larger the platinum particles, the greater the formation of cyclic compounds. Furthermore, a concentration balance between the ethylbenzene and the cyclic compounds was revealed, suggesting a common reactive adsorbate for both reaction products. According to a previously proposed reactive adsorbate for ethylbenzene and the results of studies of Pt/SiO₂ and PtSn/SiO₂ catalysts, a reactive adsorbate was proposed for the formation of the cyclic compounds. This latter reactive adsorbate, which results from the reactive adsorbate leading to ethylbenzene, is consistent with either a decrease in the size of the Pt ensembles or an increase in the electron density of the platinum particles of the Pt/SiO₂ catalyst sample with the smaller particles after coke deposition. It is still uncertain as to whether the concentration balance phenomenon is due to a geometric ensemble effect, a change in the electronic density of the platinum clusters, or both. The studies with a tin-promoted catalyst were discussed in relation to this new finding and a detailed reaction network for the transformation of *n*-PB over metallic sites is proposed.

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1. Introduction

The scission of the carbon–carbon bond, as affected by hydrogen, occurs in many processes in petroleum refineries [1]. The C–C bond scission is a desired reaction of fluid catalytic cracking or hydrocracking processes, the objective of which is to decrease the molecular weight of the feedstocks. In other refining processes, such as isomerization or reforming, the C–C bond scission is a side reaction, which lowers the yield of the desired products. In the reforming process, hydrogenolysis can either take place in the naphtha feed, which consists mainly of paraffins and naphthenes, or with respect to alkyl aromatics, thus leading to the formation of benzene and other aromatics. However, new envi-

ronmental regulations in 2005 will strictly limit the content of benzene in gasoline; thus, refiners want to gain a better understanding of such side reactions of the reforming process [2] in order to lower the level of benzene.

Relatively few studies have been performed on C–C bond scission of the alkyl chain of alkylaromatic compounds [3–7], in contrast to the number of studies on the hydrogenolysis of alkanes. Among the latter, the study of ethane has received most attention [8–10], although the hydrogenolysis of alkanes other than ethane has been the subject of numerous studies as well [11–14].

Dehydrogenation of the reacting alkane occurs before hydrogenolysis of the C–C bond [8–16]. However, the influence of the nature of the adsorbed intermediates on the degree of dehydrogenation of the C–C bond is still being investigated [10–14,16]. A systematic study of the hydrogenolysis reactions of 14 aliphatic hydrocarbons, ranging from C₄ to C₈, led Leclercq et al. to conclude that 1,3-

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diadsorbed species were favored over an alumina-supported platinum catalyst [11]. Nevertheless, these authors could not rationalize all their hydrogenolysis results by a single mechanism based upon such 1,3-intermediates species only. Thus, 1,2-, 1,4-, and 1,5-diadsorbed species could all play a role in hydrogenolysis reactions as well. Few studies of alkylaromatic compounds have described the nature of the corresponding adsorbed species [4,7] which are fundamental to gaining an understanding of hydrogenolysis of the alkyl chain.

The transformation of *n*-PB, a model alkylaromatic molecule, was investigated over monofunctional catalysts (acid or metallic) [17]. That work showed that hydrodealkylated products (benzene, toluene, and ethylbenzene) form over the metallic sites along a parallel pathway, suggesting the involvement of different adsorbed species, which occupy specific patches of platinum atoms. Based on the dehydrogenated compounds detected in the gas phase in the course of the reaction, adsorbed intermediates were suggested to explain the formation of ethylbenzene and toluene. These hydrodealkylated products require an adsorption site with two adjacent platinum atoms. Concerning the formation of benzene, a sequence of elementary steps, adapted from that proposed by Grenoble [4] for toluene hydrodealkylation, involving a unique platinum atom has been suggested. In this previous work, we exclusively focused our attention on dehydrogenated and hydrodealkylated products. However, reaction products issuing from cyclization and isomerization reactions were also detected.

In the present paper, the influence of limited sintering of the platinum particles of a precoked silica-supported platinum catalyst on the transformation of *n*-PB is investigated under reforming conditions (773 K, 5 bar total pressure, $H_2/HC = 5$). The results reveal a concentration balance phenomenon between ethylbenzene and the cyclic compounds. A common reactive adsorbate is proposed to explain this phenomenon. In addition, this study gives a new explanation concerning the results reported in our previous study over a tin-promoted catalyst [17]. A detailed reaction network of *n*-PB transformation is also proposed according to the present results and the conclusions drawn from the above-cited reference [17].

2. Experimental

Grace X254 silica (BET specific surface area $540 \text{ m}^2 \text{ g}^{-1}$, grain size 1–3 mm) was used as a support. The Pt/SiO₂ catalyst (0.48 wt% Pt) was prepared by means of the excess impregnation technique of the silica carrier with an ammonia solution of platinum dihydroxotetramine $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$ (Johnson Matthey). After drying at 353 K overnight, the catalyst was calcined ex situ in flowing air ($1 \text{ L h}^{-1} \text{ g}_{\text{catalyst}}^{-1}$) for 2 h at 673 K. Before carrying out the catalytic measurements, the catalyst samples were calcined in situ in flowing

air ($1 \text{ L h}^{-1} \text{ g}_{\text{catalyst}}^{-1}$) for 2 h at 773 K and then reduced in flowing hydrogen for 2 h at 773 K.

For the sake of comparison, the results obtained over a tin-promoted catalyst [17] will also be reported in this paper. This PtSn/SiO₂ catalyst (0.48 wt% Pt and 0.23 wt% Sn) was prepared by impregnating the Pt/SiO₂ catalyst with an aqueous solution of Me₃SnCl (Aldrich). After drying at 353 K overnight, the catalyst was calcined in situ in flowing air ($1 \text{ L h}^{-1} \text{ g}_{\text{catalyst}}^{-1}$) for 2 h at 773 K and then reduced in flowing hydrogen for 2 h at 773 K.

Reference [17] gives a more detailed description of the characterization of the catalysts. The silica-supported platinum catalyst was also characterized by means of transmission electron microscopy (TEM) with a JEOL JEM100 CXII instrument. The microscope was operated at 100 kV with a tungsten filament. The powered catalyst was embedded in epoxy resin and cut into thin slices (70 nm) with an ultramicrotome equipped with a diamond knife. Distributions were calculated by counting about 700 and 800 metallic particles for the 0.3-g and the 0.8-g samples, respectively.

Catalytic measurements were carried out using commercial *n*-propylbenzene (Fluka, purum $\geq 98\%$), without further purification, as a reactant. Liquid *n*-propylbenzene was delivered to the catalytic device by means of a high-pressure piston pump (Gilson 307). The hydrogen flow and the total pressure were controlled by a mass-flow controller (Brooks 5850 TR) and a back-pressure regulator (Brooks 5866), respectively.

Reactions were carried out using either 0.3 or 0.8 g of the silica-supported platinum catalyst (0.16–0.20 mm) in a fixed-bed microreactor at a temperature of 773 K and a total pressure of 5 bar. Catalytic measurements were performed on the stabilized catalyst. The contact time varied from 0.4 to 4.0 s, maintaining a hydrogen-to-hydrocarbon molar ratio of 5. The reaction products were analyzed by means of an on-line gas chromatograph (HP 4890, FID), and the identification of the products was confirmed by GC-MS (HP 5890-HP 5971A) analysis and injection of the standards. GC and GC-MS analyses were performed using a PONA (paraffins–olefins–naphthenes–aromatics) capillary column (Hewlett Packard, 50 m long, 0.20 mm inner diameter, 0.5 μm film thickness).

3. Results and discussion

To study the influence of moderate sintering of the platinum particles on the transformation of *n*-PB under reforming conditions, a single batch of Pt/SiO₂ catalyst was used to avoid any bias that might have occurred due to catalyst synthesis. For this purpose, two silica-supported platinum catalyst samples of different weight were used and the sintering of the metal particles was induced by means of the catalyst activation steps (oxidation and reduction). It is well known that both oxidative thermal treatment and water release in the course of the reduction step, water acting as a sintering

agent, can affect the particle size distribution of supported metal catalysts [18]. Since the batch of the Pt/SiO₂ catalyst was calcined *ex situ* up to 673 K followed by additional *in situ* calcination of the two samples up to 773 K, particle sintering probably occurred during the subsequent reduction step. In that case, the heavier the catalyst sample and, thus, the higher catalyst bed height (2.7 times higher for the 0.8-g sample compared to the 0.3-g sample), the greater the exposure of the catalyst bed to the released water and, thus, the greater the extent of sintering of the platinum particles. After activation, the catalyst samples were removed from the reactor. The catalyst samples were homogenized before being analyzed by TEM. The reason is that the sintering process may not have occurred uniformly along the catalyst bed since the bottom part should have been submitted to the highest water exposure in the course of the reduction activation step. As a result, a more pronounced sintering of the platinum particles should have occurred in the bottom layer of the catalyst bed rather than in the upper layer. Since the catalytic *n*-PB transformation depends on the mean platinum particle-size distribution, it was of the utmost importance to ensure that the sample studied by TEM was representative of the mean particle distribution of the catalyst bed through a thorough homogenization of the sample.

The particle-size distribution measured by TEM is rather narrow for the 0.3-g sample, with a maximum around 1.5 nm (Fig. 1a). On the other hand, the distribution for the 0.8-g

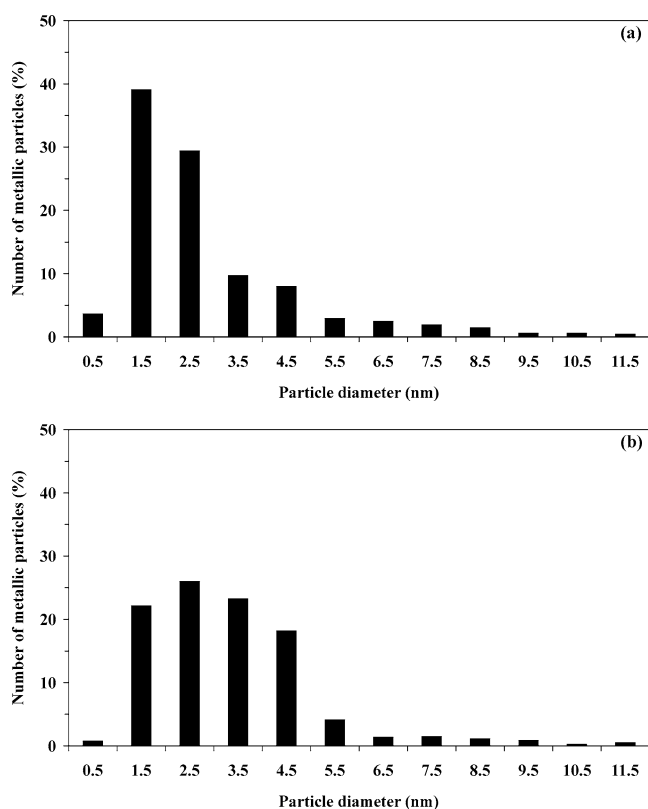


Fig. 1. Particle-size distributions for two amounts of Pt/SiO₂ sample loaded in the reactor: (a) 0.3 g and (b) 0.8 g.

sample is broader with a maximum shifted to bigger particle size (2.5 nm, Fig. 1b). For both samples, the presence of very large metallic particles drastically decreases the platinum dispersion. The platinum dispersion was estimated from the mean particle diameter assuming a cubo-octahedral shape for the metallic particles [19]. Dispersion is then 36 and 31% when considering the mean particle diameters of 2.8 and 3.3 nm for the 0.3- and 0.8-g samples, respectively. The dispersion estimated for the 0.3-g sample coincides with that determined by means of H₂–O₂ titrations (37.5%) [17]. These observations are consistent with the sintering of the metallic particles of the 0.8-g sample. As expected, the platinum particles are bigger in the 0.8-g sample than in the 0.3-g sample.

The effects of the weight of the catalyst sample and, thus, of the size of the platinum particles on the formation of hydrodealkylated, indane, indene, and 2-ethyltoluene products from the conversion of *n*-PB are shown as a function of time on stream in Figs. 2 and 3. For the sake of comparison, the deactivation trends were studied with a comparable contact time (about 1.5 s) for both samples by adjusting the reactant flow rates to the weight of the catalyst sample.

Considering first the hydrodealkylated products, a decrease of the concentration of the three reaction products is observed in Fig. 2 for both platinum particle sizes. Such a decrease can reasonably be ascribed to a deactivation of the metallic phase by coke deposition [20]. Fig. 2 also shows that the formation of both toluene and benzene follows a comparable decrease whatever the platinum particle size and that the concentration of each product is identical after stabilization (680 min on stream). The most striking difference is the much lower concentration of ethylbenzene over the heavier catalyst sample with the larger platinum particles.

Concerning the cyclization and isomerization products (Fig. 3), a concentration decrease, comparable to that previously reported for hydrodealkylated products [17], is observed for indane and 2-ethyltoluene, whereas the indene concentration is stable after only a few minutes on stream.

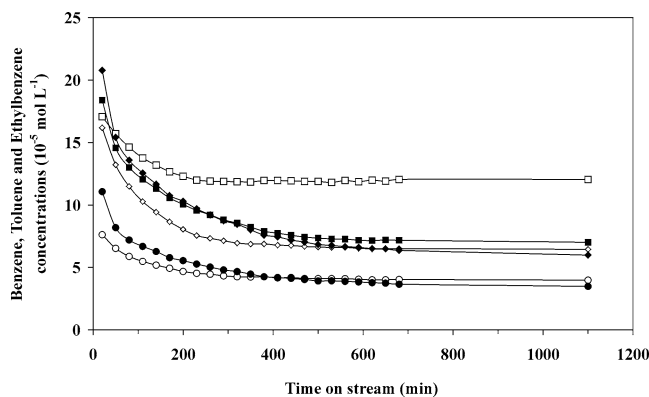


Fig. 2. Concentrations of hydrodealkylated products versus time on stream, in the conversion of *n*-propylbenzene at 773 K, 5 bar, and H₂/HC = 5, as a function of the Pt/SiO₂ sample weight loaded in the reactor: ■, ethylbenzene; ◆, toluene; and ●, benzene (open symbols, contact time of 1.56 s) 0.3 g and (full symbols, contact time of 1.50 s) 0.8 g.

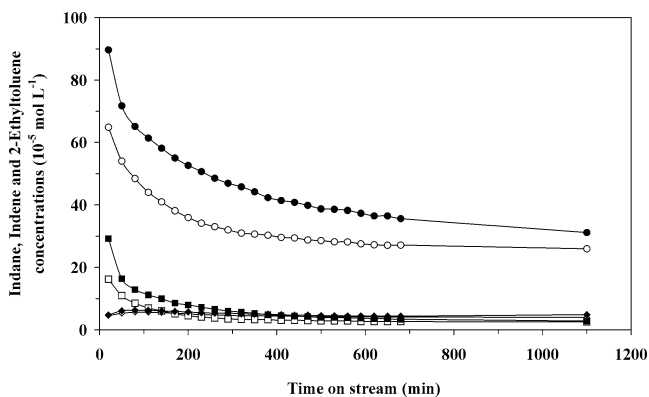


Fig. 3. Concentrations of indane, indene, and 2-ethyltoluene versus time on stream, in the conversion of *n*-propylbenzene at 773 K, 5 bar, $H_2/HC = 5$, as a function of the Pt/SiO₂ sample weight loaded in the reactor: ●, indane; ■, indene; and ◆, 2-ethyltoluene (open symbols, contact time of 1.56 s) 0.3 g and (full symbols, contact time of 1.50 s) 0.8 g.

Table 1

Product concentrations ($10^{-5} \text{ mol L}^{-1}$) at 10% conversion of *n*-propylbenzene over a Pt/SiO₂ catalyst at 773 K, 5 bar, and $H_2/HC = 5$

Reactions	Products	Pt/SiO ₂ sample weight (g)	
		0.3	0.8
Cyclization	Indene	4.0	4.9
	Indane	26.0	31.2
Dehydrogenation	Phenyl-2-propene	1.4	1.5
	Z-Phenyl-1-propene	3.2	3.4
	E-Phenyl-1-propene	11.5	11.6
Isomerization	Isopropylbenzene	1.7	1.6
	Ortho-xylene	0.7	0.6
	2-Ethyltoluene	2.5	2.8
Hydrodealkylation	Benzene	4.0	3.5
	Toluene	6.5	6.0
	Ethylbenzene	12.1	7.0

Data recorded after 1100 min on stream at contact times of 1.56 and 1.50 s for the 0.3- and 0.8-g Pt/SiO₂ samples, respectively.

After deactivation of the metallic phase, comparable concentrations are found for indene and 2-ethyltoluene over both samples, whereas the indane concentration is significantly higher over the catalyst sample (0.8 g) with the larger platinum particles.

Table 1 lists the concentrations of all the reaction products resulting from the conversion of *n*-PB after stabilization of the metallic phase. At comparable conversion of the reactant (10%), a higher formation of the cyclic compounds occurs at the expense of ethylbenzene over the catalyst sample (0.8 g) with the larger platinum particles.

This interesting finding prompted us to study the dependence of the concentrations of the products resulting from *n*-PB transformation as a function of contact time over both samples. Catalytic measurements of the above-noted reaction products are shown in Figs. 4–6. As reported elsewhere [17], there is a linear dependence of concentration on the contact time (from 0.35 to 4.00 s) for the disappearances of *n*-PB (Fig. 4) and dehydrogenated products (Fig. 6), and

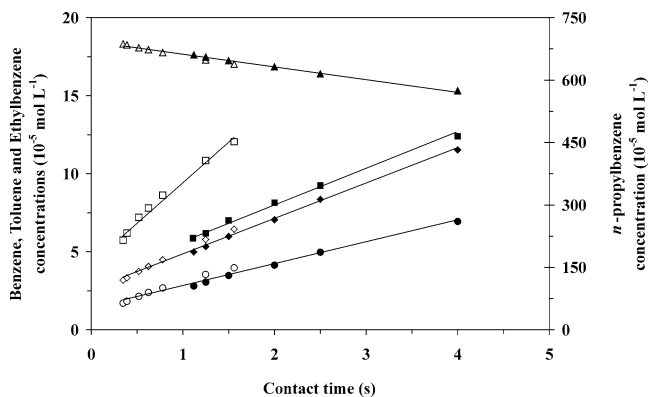


Fig. 4. Concentrations of *n*-propylbenzene and hydrodealkylated products versus contact time, in the conversion of *n*-propylbenzene at 773 K, 5 bar, and $H_2/HC = 5$, as a function of the Pt/SiO₂ sample weight loaded in the reactor: ▲, *n*-propylbenzene; ■, ethylbenzene; ◆, toluene; and ●, benzene (open symbols) 0.3 g and (full symbols) 0.8 g (data recorded for 420 min of run after a deactivation period of 680 min on stream).

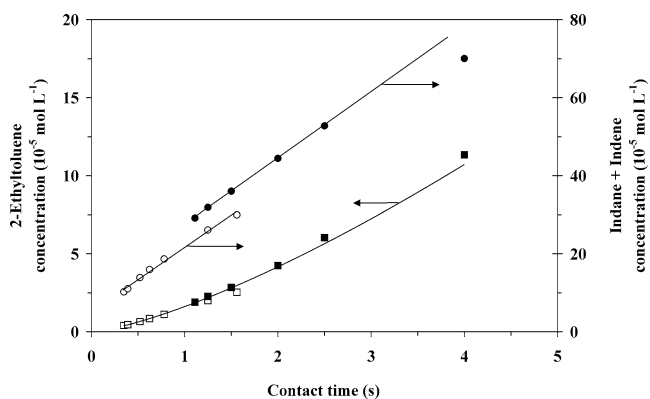


Fig. 5. Concentrations of cyclic compounds (indane + indene) and 2-ethyltoluene versus contact time, in the conversion of *n*-propylbenzene at 773 K, 5 bar, and $H_2/HC = 5$, as a function of the Pt/SiO₂ sample weight loaded in the reactor: ●, indane + indene; and ■, 2-ethyltoluene (open symbols) 0.3 g and (full symbols) 0.8 g (data recorded for 420 min of run after a deactivation period of 680 min on stream).

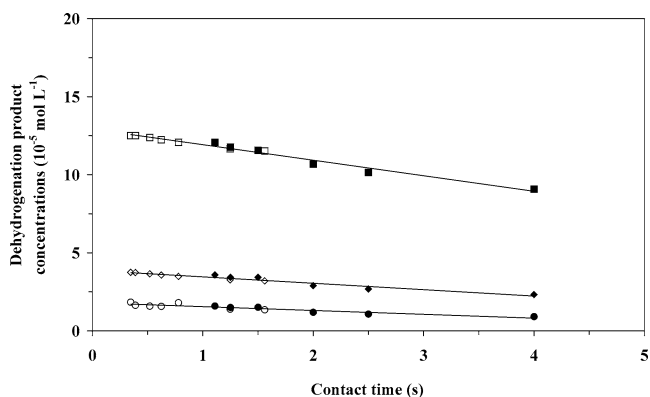


Fig. 6. Concentrations of dehydrogenated products versus contact time, in the conversion of *n*-propylbenzene at 773 K, 5 bar, and $H_2/HC = 5$, as a function of the Pt/SiO₂ sample weight loaded in the reactor: ■, *E*-phenyl-1-propene; ◆, *Z*-phenyl-1-propene; and ●, phenyl-2-propene, (open symbols) 0.3 g and (full symbols) 0.8 g (data recorded for 420 min of run after a deactivation period of 680 min on stream).

the formation of all other reaction products (Figs. 4 and 5), except 2-ethyltoluene. These observations suggest an apparent zero-order reaction.

The concentrations of toluene and benzene do not depend on the size of the platinum particles since comparable concentrations were obtained over the wide range of contact times studied (Fig. 4). On the other hand, ethylbenzene shows a singularly different behavior. A clear break in its formation rate along with a significant decrease of this formation rate over the larger platinum particles is observed (Fig. 4, 0.8-g catalyst sample). Such a break is not observed for 2-ethyltoluene (Fig. 5) or for the dehydrogenated products (Fig. 6). However, an inverse break compared with that observed for ethylbenzene is found for the cyclic compounds (indane and indene), the concentrations of which were lumped together in Fig. 5 for the sake of clarity. The catalyst sample (0.8 g) with the larger platinum particles shows an increased formation rate of cyclic products, which counterbalances the decreased formation rate of ethylbenzene. In other words, the sum of the concentrations of ethylbenzene and the cyclic compounds remains unaffected when the mean size of the platinum particles is changed.

From the above-noted results, it is very likely that a common initially reactive adsorbate can explain the observed concentration balance phenomenon for ethylbenzene and the cyclic compounds. This common intermediate would preferentially lead to ethylbenzene, but may also lead to the cyclic compounds.

To further understand this phenomenon, one must remember that the metallic phase of both samples suffered a deactivation process by coke deposition. The surface of the metallic particles has been described as being continuously and mostly covered by a strongly bound carbonaceous deposit coexisting with uncovered patches of platinum surface atoms [21]. These latter patches of platinum atoms are the so-called "Pt ensembles" or "Pt domains" introduced by Sachtler and co-workers [22], as well as Stephan and Ponec [23] to account for the differences found in the adsorption of H₂ and CO, respectively, over platinum-based films. Platinum ensemble size effects were then invoked by Puddu and Ponec [24] to explain the much slower hydrogenation of benzene compared to that of cyclohexene over Pt and Pt–Au catalysts. Afterward, the ensemble concept was considered to explain the selectivity of hydrocarbon reactions over alloys [25,26], and in particular in the case of supported bimetallic platinum–tin catalysts [27–33]. The authors of these studies concluded that one of the effects of tin promotion is to enhance the isolation of the platinum atoms through dilution by tin atoms [28–33]. The addition of tin therefore decreases the size of the Pt domains.

Significant changes of the selectivity in hydrocarbon reactions were also reported after catalyst deactivation [26,34–36]. Sárkány and Ponec and co-workers have concluded that the size of the Pt domains is diminished by a geometric effect by coke deposition, comparable to that of a promoter addi-

Table 2

Hydrodealkylation and cyclization formation rates of *n*-propylbenzene over silica-supported platinum catalysts (0.8-g sample weight) at 773 K, 5 bar, and H₂/HC = 5

Reactions	Products	Formation rates (10 ⁻⁵ mol L ⁻¹ s ⁻¹)	
		Pt/SiO ₂	PtSn/SiO ₂
Hydrodealkylation	Benzene (B)	1.43	2.15
	Toluene (T)	2.26	0.44
	Ethylbenzene (EB)	2.25	1.68
	B + T + EB	5.94	4.27
Cyclization	Indane + indene	16.89	0.47

Data recorded for 420 min of run after a deactivation period of 680 min on stream.

tion such as tin, over platinum and iridium catalysts [34–36] or alloys [26].

To better understand the results of this study over the two Pt/SiO₂ samples, let us first recall the results obtained for the effect of the tin promoter reported in our previous work [17]. In that work, little attention had been paid to the formation of the cyclic compounds since the main goal was to investigate the distribution of the hydrodealkylated products in the transformation of *n*-PB, and in particular the formation of benzene, over the metallic and acidic functions [17]. Table 2 lists the effects of adding tin to a silica-supported platinum catalyst on the rates of formation of hydrodealkylated and cyclic products. Over the unpromoted catalyst, the rate of formation of the cyclic compounds (indane and indene) is almost three times higher than that of the global reaction rate of hydrodealkylation. In addition, the most striking difference between the two catalysts is that the rate of formation of the cyclic compounds is almost zero over the tin-promoted catalyst, whereas 30 and 25% decreases are found for the global hydrodealkylation and ethylbenzene formation rates, respectively. According to a recent study by Humblot et al. [31] over identical catalytic systems, these decreases can be assigned to geometric considerations and to a decrease in the size of the Pt ensembles with the addition of tin as a promoter. One can therefore reasonably conclude that the size of the Pt ensembles required for the formation of cyclic compounds; thus, the corresponding steric hindrance of the reactive adsorbate must be higher than that involved for the formation of ethylbenzene. Moreover, it can be concluded that the Pt domains required for the formation of cyclic compounds have almost completely disappeared over the tin-promoted catalyst. As reported by Dadyburjor and Ruckenstein [14], this latter conclusion does not necessarily mean that the size of the Pt domains has become too small to prevent the occurrence of reactions involving reactive adsorbate of lower steric hindrance than that engaged for the cyclization reaction.

In accordance with the chemical nature of the dehydrogenated compounds detected in the gas phase, an adsorbed phenylpropene species has been suggested (Fig. 7a) to explain the formation of ethylbenzene [17]. Such a diadsorbed

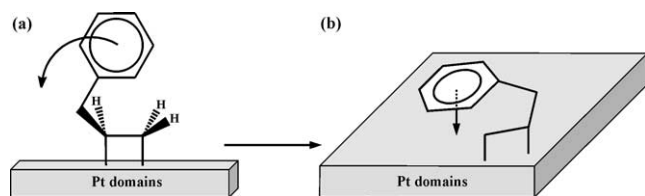


Fig. 7. Adsorbed reactive intermediate species for the formation of: (a) ethylbenzene and (b) indane and indene.

intermediate species was considered according to a 1,2-adsorption mode. The 1,3-adsorption mode, suggested to be favored for the hydrogenolysis of alkanes over a platinum catalyst from the work of Leclercq et al. [11], was not considered for the following reasons: (i) If a 1,3-diadsorbed intermediate species were involved in the formation of hydrodealkylated compounds, it is very likely that the selectivity of hydrodealkylated products would have been the same over both the unpromoted and the promoted catalysts, which is not the case in the present studies (Table 2 and [17]). The reason for that is that the addition of tin to a silica-supported platinum catalyst [31] and coke deposition on platinum [26–28,34–36] were both shown to lead to a decrease in the size of the platinum ensembles. Note that Leclercq et al. [11] were unable to rule out the involvement of 1,2-diadsorbed species and other diadsorbed species. (ii) It must be emphasized that the conclusion of Leclercq et al. [11], that the 1,2-adsorption mode is not favored over platinum surfaces, in contrast to the 1,3-adsorption mode, has been drawn on the basis of initial reaction rates. Thus, the authors assumed that their conclusion is valid in the case of a carbon-free platinum surface only, which obviously exhibits much larger platinum domains than those exhibited in the present study. Our results were obtained on stabilized catalysts, i.e., pre-coked platinum surfaces.

In order to explain the formation of cyclic products, it is likely to assume that the aromatic ring of the adsorbed phenylpropene species, involved in the formation of ethylbenzene, bends toward the particle surface leading to a “flat” adsorbed intermediate, as indicated in Fig. 7b. Such a species would be adsorbed on the Pt by the aromatic nucleus in a π -type interaction as well as by the alkyl chain; the latter adsorption mode is involved in the formation of ethylbenzene (Fig. 7a). Such an adsorbed species would, therefore, require larger Pt ensembles than needed for the reactive adsorbate of ethylbenzene. One can add that the adsorbed phenylpropene species is thought to occur with smaller Pt ensembles only when the “flat” adsorption of the aromatic ring is hindered. According to these two adsorbed intermediate species, the difference between the two Pt/SiO₂ samples of different weight could be ascribed to a lowering of the size of the Pt ensembles over the catalyst sample with the smaller particles. Given the modest difference in the formation rate of the cyclic compounds of the two Pt/SiO₂ samples (Fig. 5), the size of the Pt domains is likely to be only a little lower over the Pt/SiO₂ with the smaller platinum particles (0.3-g sample). This conclusion is supported

by the equal formation rates of benzene and toluene over both Pt/SiO₂ samples (Fig. 4). A more pronounced decrease in the size of the Pt domains should have resulted in a significant increase of the benzene formation rate and a decrease of that of toluene, as shown in Table 2 which compares benzene and toluene formation rates between unpromoted and tin-promoted platinum catalysts.

In addition to the geometric effect of coke deposition, Barbier et al. [37] reported an electronic effect. The chemical structure of coke has been ascribed to the formation of polyaromatic compounds of high molecular weight [38]. Consequently, it was suggested that the electron density of the platinum clusters is enhanced following coke deposition [37], in agreement with the work of Hlavathy and Tétényi [39]. These authors showed that the adsorption of light alkanes/alkenes on a platinum surface leads to changes in the work function, indicating electron transfer from the adsorbed hydrocarbons to the platinum. This electronic effect is not inconsistent with the above-proposed flat adsorbed reactive adsorbate involved in the formation of the cyclic compounds (Fig. 7b). The higher the dispersion and, thus, the smaller the platinum particles, the higher the electron density of the particles following coke deposition. This increase in the metallic electron density of the platinum clusters of the catalyst with the smaller platinum particles is consistent with an unfavored adsorption of the aromatic ring of the ethylbenzene reactive adsorbate (Fig. 7a) to lead to the cyclic reactive one (Fig. 7b). This electronic effect can also account for the observed decrease of the formation of cyclic compounds over the 0.3-g Pt/SiO₂ sample (Table 1, Figs. 3 and 5).

According to this finding, a common reactive adsorbate for the formation of ethylbenzene and the cyclic compounds such as indane and indene, a new explanation for the results obtained in our previous study [17] may be suggested. The increase in the rate of formation of benzene and the decreases of that of toluene and ethylbenzene over the PtSn/SiO₂ catalyst (Table 2) are consistent with an isolation effect of tin. *n*-PB adsorption sites consisting of single or two adjacent ensembles of platinum atoms were suggested for the formations of benzene or toluene and ethylbenzene, respectively. The reason for the more drastic decrease of the formation rate of toluene compared to that of ethylbenzene is not obvious, because both compounds involve comparable ensembles of two adjacent platinum atoms. Two assumptions can be suggested to account for this disparity: First, differences in steric hindrance of the chemisorbed intermediates may be invoked. The adsorbed intermediate involved in the formation of toluene has a much higher steric hindrance (due to the phenyl and methyl groups [17]) than the adsorbed intermediate leading to ethylbenzene (Fig. 7a). Second, it is well known that an aromatic ring attracts electrons through an inductive effect. This effect is the more pronounced for the alkyl C–C bonds closest to the aromatic ring. Consequently, electron withdrawal is probably more important for the termi-

nal C–C bond (involved in the formation of ethylbenzene) than for the central C–C bond (involved in the formation of toluene). It is assumed, therefore, that the weakening of the C–C bond involved in the formation of ethylbenzene is greater than that involved in the formation of toluene. This assumption may also apply to the preferential hydrogenolysis of terminal alkyl C–C bonds over the Pt/SiO₂ catalyst, as reported for studies performed with *n*-PB over supported Rh catalysts [6] or with alkylbenzene molecules other than *n*-PB over supported Pt and Ni catalysts [7]. However, the above-noted concentration balance between ethylbenzene and the cyclic compounds also explains the slight decrease in the formation rate of ethylbenzene compared to that of toluene with tin addition (Table 2). Indeed, the formation rate of the cyclic compounds shows a strong decrease. The decrease in the size of the platinum ensembles over the tin-promoted catalyst prevents the formation of cyclic compounds but does not hinder the formation of ethylbenzene. It can also be added that the size of the Pt domains must be strongly diminished by tin addition since a decrease of the formation rate of ethylbenzene is observed after all. An increase of the formation rate of ethylbenzene could have been expected on the basis of the concentration balance phenomenon revealed in this work over the two Pt/SiO₂ samples. Finally, the negligible deactivation reported over the tin-promoted catalyst [17] is in agreement with the limited formation of cyclic compounds and the greater resistance of the tin-promoted catalysts to deactivation by coke [28,29].

As noted above, the behavior of 2-ethyltoluene differs significantly from the other reaction products (Figs. 4–6). The concentration of 2-ethyltoluene is not linearly dependent on contact time (Fig. 5). From a kinetic point of view, such a trend indicates that 2-ethyltoluene is related to the further transformation of a previous reaction product. Moreover, the concentration of 2-ethyltoluene is rather low. Thus, one must take a careful look at the other reaction products to determine the involved primary product that transforms to 2-ethyltoluene. The concentration of the cyclic compounds, measured at a contact time of 4.0 s, is a little lower than expected from an apparent zero-order plot (Fig. 5). This suggests that 2-ethyltoluene originates from the further reaction of the cyclic compounds. This would be in agreement with the work of Csicsery, who studied the transformation of 2-ethyltoluene over supported platinum catalysts [40]. In that work, the formation of indane and the subsequent formation of *n*-PB took place along the opposite reaction pathway. The isomerization of 2-ethyltoluene to *n*-PB, thus, occurred through the formation of the cyclic compounds such as indane [40]. Our conclusion is further supported by the unique detection of 2-ethyltoluene, ruling out the possibility that 2-ethyltoluene formed through dealkylation–alkylation processes. This would have indeed led to other isomers such as either 3- and 4-ethyltoluene or diethylbenzenes and propylethylbenzenes. The proposed reaction pathway is also consistent with the absence of

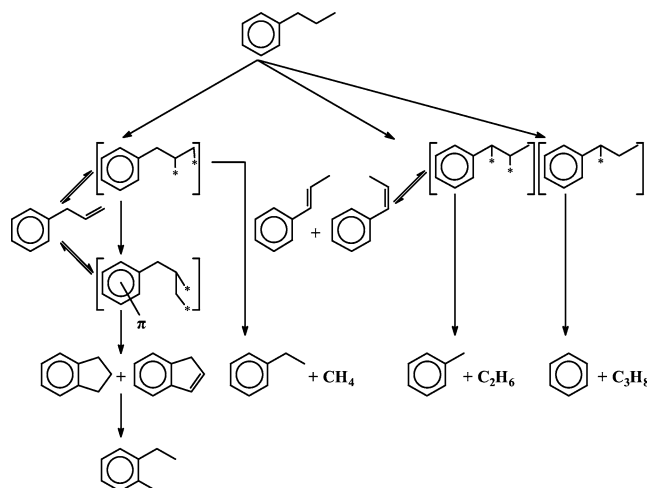


Fig. 8. Detailed reaction network of the transformation of *n*-propylbenzene over metallic sites, * and [] symbols representing a platinum atom adsorption site and an undetected reactive adsorbate, respectively.

2-ethyltoluene over the tin-promoted catalyst, for which the formation of cyclic compounds suffered a drastic decrease [17].

The studies of the transformation of *n*-PB over a metallic platinum phase, promoted by tin or not ([17], and this study), led us to propose the reaction network shown in Fig. 8.

4. Conclusion

The effect of moderate sintering of the platinum particles of a precoked Pt/SiO₂ catalyst on the transformation of *n*-PB was investigated under reforming conditions (773 K, 5 bar, and H₂/HC = 5). The results showed that the larger the platinum particles, the greater the formation of cyclic compounds. Furthermore, a concentration balance between ethylbenzene and the cyclic compounds was revealed, suggesting a common reactive adsorbate for both reaction products. According to a previously proposed reactive adsorbate for ethylbenzene and the results of studies of Pt/SiO₂ and PtSn/SiO₂ catalysts [17], a reactive adsorbate was proposed for the formation of the cyclic compounds. This latter reactive adsorbate, which results from the reactive adsorbate leading to ethylbenzene, is consistent with either a decrease in the size of the Pt ensembles or an increase in the electron density of the platinum particles of the Pt/SiO₂ catalyst sample with the smaller particles after coke deposition. It is still uncertain as to whether the concentration balance phenomenon is due to a geometric ensemble effect, a change in the electronic density of the platinum clusters, or both.

The studies with a tin-promoted catalyst [17] were discussed in relation to this new finding and a detailed reaction network for the transformation of *n*-PB over metallic sites is proposed.

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