

Unique selectivity for the dimerization of propene on RhSn/SiO₂ catalysts: implications on the mechanism of C–C bond formation and cleavage on bimetallic catalysts

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Abstract

A series of bimetallic catalysts RhSn_x/SiO₂ ($x = 0.4, 0.7, 0.9, \text{ and } 1.4$) were synthesized by the reaction of the monometallic catalyst Rh/SiO₂ with Sn(*n*-butyl)₄ under hydrogen. Various chemical and spectroscopic methods indicated that the metals present were fully reduced, and that tin atoms rest on the surface, very slightly increasing particle size and producing isolated rhodium sites. The catalytic reactions of propylene/hydrogen mixtures in the presence of these bimetallic catalysts are compared with those of the monometallic Rh/SiO₂ catalysts. The mechanistically interesting reactions observed are those of carbon–carbon bond formation and cleavage. For the monometallic catalyst, olefin homologation and hydrogenolysis were observed, reactions which invoked the transfer of C₁ fragments from one olefin to another. For the bimetallic catalysts, a marked increase in the selectivity for C₆ products was observed. The presence of hydrogen is necessary to this reaction but selectivity for C₆ is enhanced when hydrogen is in deficit with respect to propylene. Selectivity for C₆ increases with the surface rhodium to tin, Rh^δ/Sn, ratio to a maximum at 0.9. Low temperature favors the formation of C₆ and C₂ products.

Keywords: Propylene; Dimerization; Rhodium; Tin; Bimetallic catalysts; Silica; Supported catalysts

1. Introduction

Numerous studies have demonstrated the remarkable properties of bimetallic catalysts composed of an iron group metal (groups 8, 9, or 10) and a group 14 metal (for example, tin). These catalysts, supported on silica or alumina, have been shown to be generally more stable, more active, and more selective than their monometallic analogs for reactions such as hydrogenation and dehydrogenation. Surface organometallic chem-

istry of metals (referred to herein by its French acronym, COMS/M) [1] is particularly well adapted to the determination of the process of the addition of tin to metallic surfaces. This method allows the utilization of a well controlled reaction of an organometallic complex of tin (tetrabutyl tin) with the metallic surface. Depending on the conditions of this reaction it is possible to graft stable organometallic fragments or tin atoms on the surface or to form highly dispersed alloys [2].

The hydrogenolysis and dehydrogenation of alkanes, the hydrogenolysis of ethers, the dissociation and reduction of carbon monoxide and

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nitric oxide are among the catalytic reactions which have been studied for bimetallic alloy catalysts prepared by COMS.

Coq and coworkers have shown that the hydrogenolysis of 2,2,3,3-tetramethylbutane (TeMB) on catalysts of the general formula MM'/Al_2O_3 ($M = Pt$, $M' = Sn, Zn, Al$, or $M = Rh$, $M' = Sn, Pb$) is very sensitive to the topology of the metallic surface [3]. It was shown that the addition of small quantities of tetrabutyl tin, diethyl zinc, or triethyl aluminum to small platinum particles favored the formation of isobutane. A similar effect was observed for rhodium catalysts modified by small amounts of lead or tin. The authors suggest that the added metal M' selectively inhibits reactions catalysed by sites of low coordination (edges and corners) which are relatively rare on small metal particles. These results and theoretical studies suggest that the atoms M' would be concentrated on corners and edges [4]. Catalysts SnM/Al_2O_3 having large tin contents behave like the small Rh or Pt particles but are nearly inactive for the hydrogenolysis of TeMB. This may be due to poisoning by tin.

Later studies by Coq and coworkers showed that the addition of larger amounts of tin to Pt/SiO₂ favored the nonselective ring decyclization of methylcyclopentane to *n*-hexane [5]. Margitfalvi and coworkers studied the dehydrogenation of methylcyclopentane (MCP) in the presence of hydrogen over catalysts PtSn/Al₂O₃ [6]. It was observed that benzene was formed at the same time on acidic sites of the support and on metallic sites. When tin is added to the support, the formation of benzene is greatly reduced.

Candy and coworkers showed that the hydrogenolysis of ethyl acetate to ethanol increased significantly as the tin content in the catalyst MSn/Al₂O₃ ($M = Rh, Ru, Ni$) increased. Contrary to expectations, it was observed that the rate of ethanol formation increased even for Sn/M ratios superior to 0.2 for nickel and rhodium based catalysts, and superior to 1 for the SnRu catalyst [7,8]. It seems thus that a simple geometric explanation for the effect of tin addition on this reaction is not sufficient to explain the results obtained. It

was proposed that a new type catalytic site was responsible for the reaction, a type of site which occurs more as the tin content of the bimetallic catalyst was increased.

Bimetallic catalysts prepared by COMS could perhaps provide an alternative to the 'three way' catalysts (based on Rh and Pt) currently used in the treatment of automobile exhaust gases. Iwasawa and coworkers recently reported the study of NO dissociation and reduction by H₂ over bimetallic catalysts RhSn/SiO₂ prepared by COMS [9]. These catalysts were prepared by the reaction of (CH₃)₄Sn with Rh/SiO₂ and have been shown to be more active than Rh/SiO₂. It was also reported that the activities of RhSn/SiO₂ catalysts prepared by COMS were superior to analogous bimetallic catalysts prepared by co-impregnation (5 times more active). Characterization of the surface of RhSn/SiO₂ systems by EXAFS [10] and by oxidation reactions have established that the tin atoms are found solely on the surface. As to the mechanism of the NO dissociation, it seems that the limiting factor for the monometallic catalyst is the presence of adsorbed hydrogen atoms while for the bimetallic systems, the slow step is the elimination (by hydrogen) of oxygen atoms bound to tin which had been formed by the dissociation of NO.

The study presented herein is directed toward the same objectives as those of the previously cited studies. We also search for bimetallic systems which are able to produce a better activity and, more significantly, better selectivity for a different catalytic process, the formation of carbon-carbon bonds. A significant undesired side reaction in industrial processes involving carbon-carbon bond formation is that of carbon-carbon bond cleavage: hydrogenolysis and hydrocracking reduces yields of products and of hydrogen. Coke formation reduces catalyst performance in many systems, notably in the dehydrogenation of isobutane to isobutene, a product used as feedstock in the production of methyl-*tert*-butyl ether, a fuel additive used in lead-free gasoline. Thus one would like to identify structures and conditions necessary to the formation of carbon-carbon

bonds while eliminating carbon–carbon bond cleavage reactions.

During the reaction of an olefin and hydrogen over a iron group (group 8, 9, 10) metal catalyst (for example, Rh) the formation and cleavage of carbon–carbon bonds are observed as parallel reactions to the principle reaction, hydrogenation. Mechanistic studies [11–14] have suggested that these parallel side-reactions are linked by a common dimetallo-cyclic intermediate.

If one assumes the formation of such a metallo-cyclic, with its implied presence of adjacent ‘active’ metal centers, the addition of inactive centers on the surface (like added tin) could inhibit the formation of such cycles and so enhance the selectivity of the catalyst with respect to hydro-carbon reactions. To verify this hypothesis we have prepared by COMS/M bimetallic catalysts Rh–Sn/SiO₂ in which the tin content varies over a wide range. We have studied the general characteristics of the reaction of propene/hydrogen over these catalysts. The detailed study of product distributions as a function of reaction parameters form the bulk of this work.

2. Experimental

XPS data was collected on an HP 5950a spectrometer calibrated with Si 2p_{3/2}. The CTEM images were obtained using a JEOL JEM 100 CX. The EDX study of bimetallic particles were performed on a HBS vacuum generator.

Infrared spectra of carbon monoxide adsorbed on the catalysts RhSn_x/SiO₂ were obtained on a Nicolet 10-MX FTIR spectrometer. A sample of the catalyst was pressed into a wafer which was carried in a moveable pyrex block within a sealed tube reactor equipped with CaCl₂ windows at one end. The cell is designed to permit thermal treatment of the sample, addition of known pressures of carbon monoxide, and treatment under vacuum in addition to infrared measurements.

2.1. Apparatus for catalytic tests

Catalytic reactions were carried out in a glass dynamic microreactor at atmospheric pressure. The reactor was a vertical U-tube equipped with a sintered glass on which a thin layer of catalyst was deposited. The reactor was placed in a cylindrical oven equipped with a thermostat. The temperature of the catalyst bed was measured with a thermocouple. The reactor was placed in line with gas sources (propene, hydrogen, and argon), corresponding flow meters, and a control panel and recorder, which allows the production of gas streams of a given propene/hydrogen mixtures of known composition.

The catalytic tests were performed as follows. The catalyst was treated at 300°C under a stream of pure hydrogen (1 l/h) for two hours. A stable temperature was then established under the flow of pure hydrogen. The propene/hydrogen mixture was allowed to flow through the catalyst for 5 min after which the product gas stream was sampled and analyzed by gas chromatography. The catalyst was then regenerated under pure hydrogen as above.

2.2. Preparation of the monometallic catalyst, Rh/SiO₂

The silica support was derived from commercial Degussa Aerosil 200 which was pretreated at 500°C under vacuum. The rhodium precursor, [ClRh(NH₃)₅]Cl₂ (Johnson Matthey) was transformed to [ClRh(NH₃)₅](OH)₂ by passage through an ion exchange resin (anionic Amberlite). This rhodium complex was reacted with the silica in a highly basic (pH = 10) ammoniated medium which, presumably by reaction with an ammonium surface entity, (SiO)(NH₄), produced the surface complex (≧SiO)₂[ClRh(NH₃)₅]. This was then treated with a nitrogen/oxygen mixture (10/1) between 25 and 350°C (1°C/min) to form Rh₂O₃/SiO₂. Reduction of this species at 350°C under hydrogen produces Rh/SiO₂.

The metal content of catalysts thus produced was around 2 wt% Rh. The average particle size (d_m) was determined by transmission electron microscopy (CTEM) to be 13 Å which corresponds to a dispersion of 85% (assuming all particles to be spheres of diameter d_m).

2.3. Preparation by COMS/M of the bimetallic catalysts, RhSn/SiO₂

The catalysts RhSn/SiO₂ were prepared by the reaction of Rh/SiO₂ with tetra-*n*-butyl tin. The reaction is performed under 30 mbar of hydrogen at temperatures from 50°C to 300°C, the temperature being increased by steps of 50°C after an hour at a given temperature. The hydrocarbons formed during the hydrogenolysis of butyl groups were extracted from the reaction environment by condensation in a liquid nitrogen trap. We have verified that this treatment was sufficient to totally hydrogenolyze the alkyl groups present.

3. Results

3.1. Characterization of the catalysts

Electron microscopy

Samples of Rh/SiO₂ and of RhSn/SiO₂ were examined by CTEM. Fig. 1 shows the distribution of particle sizes for these catalysts based on area containing over 250 metal particles. For the Rh/SiO₂, assuming spherical particles this corresponds to a dispersion of 85%. The expected slight increase in particle size due to the addition of tin to the surface was observed.

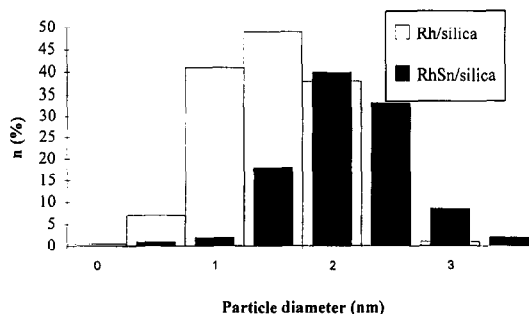


Fig. 1. Particle size distribution of Rh/SiO₂ as determined by CTEM.

Table 1

Sample	Rh 3d _{3/2}	Rh 3d _{5/2}	Sn 3d _{3/2}	Sn 3d _{5/2}
Rh ₂ O ₃ ^a	313.2	308.5		
Rh(0) metal ^a	311.5	307.0		
SnO ₂ ^a			494.9	486.4
SnO ^a			494.6	486.1
Sn(0) metal ^a			493.2	484.7
Rh/SiO ₂ ^b	311.6	306.9		
RhSn/SiO ₂ ^b	311.7	307.0	493.5	485.0

^a See ref. [15].

^b Sample treated at 500°C under hydrogen.

The EDX analysis of the sample of RhSn/SiO₂ for which the global Sn/Rh ratio as determined by elemental analysis was 0.7 indicated a ratio Sn/Rh^s on the surface of about 0.9. Isolated tin atoms on the surface of the silica were not observed. It is thus evident that tin has reacted only with the rhodium surface and that tin atoms rest on the surface.

X-ray photoelectron spectroscopy

Data obtained by in situ XPS for Rh/SiO₂ and RhSn/SiO₂ (Rh/Sn^s=0.9) are displayed in Table 1. The close agreement between the XPS emissions measured for these catalysts and literature values for the corresponding metals indicates that all metal atoms are reduced in the two catalysts.

Adsorption of hydrogen and carbon monoxide

The amount of hydrogen and of carbon monoxide adsorbed on samples of each catalyst were measured by volumetric techniques previously described in the literature [2]. Samples were pre-treated at 350°C under hydrogen then maintained at that temperature under vacuum (10⁻⁶ mbar) for four hours to desorb hydrogen. The isotherms of adsorption of the catalysts (obtained at 25°C, Fig. 2) are reproducible over 200 mbar for hydrogen and 20 mbar for carbon monoxide. Fig. 2 represents the adsorption capacity of catalysts RhSn_x/SiO₂ and shows clearly that the adsorption capacity falls quickly as the tin loading increases.

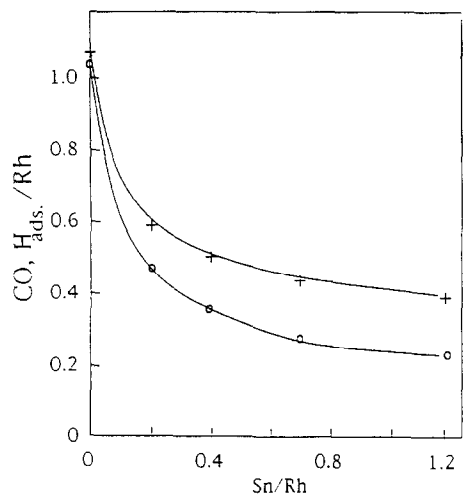


Fig. 2. Adsorption capacity of $\text{RhSn}_x/\text{SiO}_2$ of (O) CO and (+) H_2 as a function of the Rh/Sn ratio.

Infrared spectroscopic study of carbon monoxide adsorption

The infrared spectra obtained for Rh/SiO_2 and $\text{RhSn}_{0.8}/\text{SiO}_2$ after the adsorption of 10 mbar of CO are shown in Fig. 3. On the monometallic catalyst one can clearly discern two types of (CO) stretching vibration, one attributable to linear carbonyl ligands on Rh at 2059 cm^{-1} and the other to bridging carbonyl ligands on Rh at 1866 cm^{-1} . On the bimetallic catalyst the band corresponding to bridging carbonyl ligands does not appear, while the band corresponding to linear carbonyls is observed as a broader peak at 2008 cm^{-1} . This suggests that the number of sites in which rhodium atoms are adjacent has greatly diminished but that there are still rhodium atoms capable of supporting carbonyl coordination. Thus the addition of tin has effectively isolated the surface rhodium atoms from each other [16].

3.2. Characterization: Summary

After treatment under hydrogen at 300°C , the mono- and bi-metallic catalysts were composed of particles centered at 13 nm and 22 nm respectively, with a distribution of particle size quite narrow as demonstrated by electron microscopy. Metal atoms were shown in all cases to be reduced by X-ray photoelectron spectroscopy. For bimetallic systems the tin is always bound to rhodium

(EDX) and partially masks the rhodium. This was confirmed by the study of the adsorption of hydrogen, wherein it was shown that increasing tin content reduced the adsorptive capacity. The lack of an infrared absorbance in the region associated with the (CO) stretching of bridging carbonyls in the spectrum of CO-treated RhSn/SiO_2 suggests that rhodium centers are isolated from each other.

3.3. Catalytic reactions

Activity and stability of mono- and bi-metallic catalysts

To determine the stability and reactivity of Rh/SiO_2 and $\text{RhSn}_x/\text{SiO}_2$ catalysts, we studied the conversion of propene/hydrogen mixtures as a function of 'time on stream.' Two samples, one of Rh/SiO_2 and the other RhSn/SiO_2 ($\text{Sn}/\text{Rh}^s = 0.9$) were tested under identical conditions of flow (4 l/min), temperature (250°C), reactant composition ($P_{\text{H}_2}/P_{\text{C}_3\text{H}_6} = 1/1$) and catalyst mass (150 mg). Results are summarized in Fig. 4 and Fig. 5. For both types of catalyst the activity diminishes during the first five minutes on stream and stabilizes thereafter. Before arriving at this stable level of activity, the monometallic catalyst was more active than the bimetallic catalyst. The

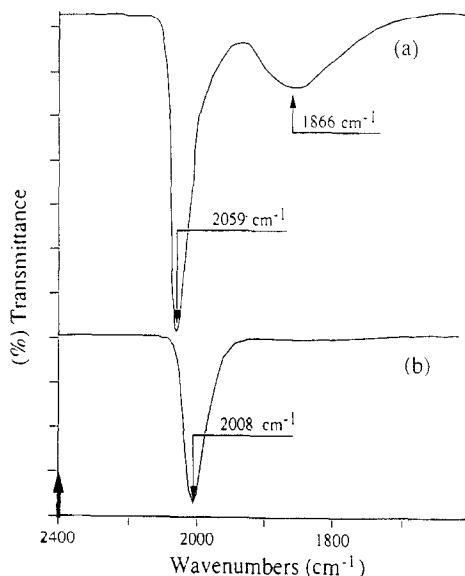


Fig. 3. Infrared spectra of CO adsorbed on (a) Rh/SiO_2 and (b) $\text{RhSn}_{0.8}/\text{SiO}_2$.

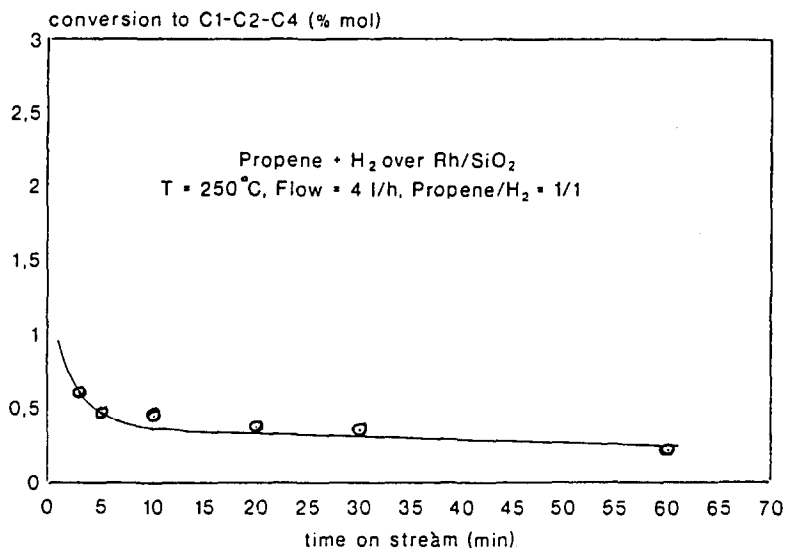


Fig. 4. Conversion of propylene to higher and lower hydrocarbons in the presence of Rh/SiO₂ as a function of time on stream.

relative reduction of activity is less for the bimetallic catalyst than for the monometallic.

The effect of the time on stream on the conversion of propylene into hydrogenolysis, homologation and dimerization products shows that the conversion is stabilized after four minutes on stream. In our studies of other parameters, we have therefore analyzed the product distribution after this plateau of activity is achieved, that is after five minutes of exposure of regenerated catalyst to the reactant mixture.

General characteristics of the reaction of propylene with hydrogen on Rh-Sn/SiO₂

When a mixture of propylene and hydrogen is passed over Rh-Sn/SiO₂ catalysts (Sn/Rh^s = 0.2; 0.4; 0.7; 0.9 and 1.4) at temperatures between the room temperature and 250°C several reactions occur: the hydrogenation reaction producing propane, the hydrogenolysis reaction producing C₁-C₂ hydrocarbons (methane, ethane and ethylene), the homologation reaction producing C₄-C₅-C₆ products and an important reaction of dimeriza-

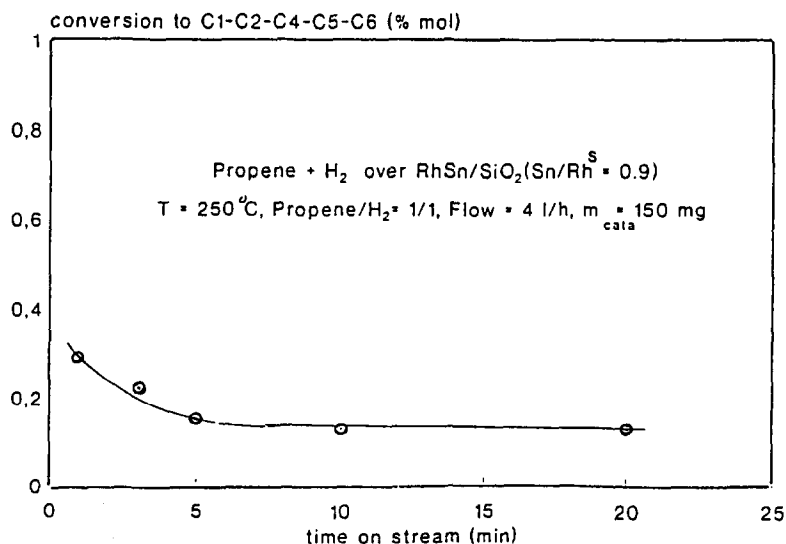


Fig. 5. Conversion of propylene to higher and lower hydrocarbons in the presence of Rh/SiO₂ as a function of time on stream.

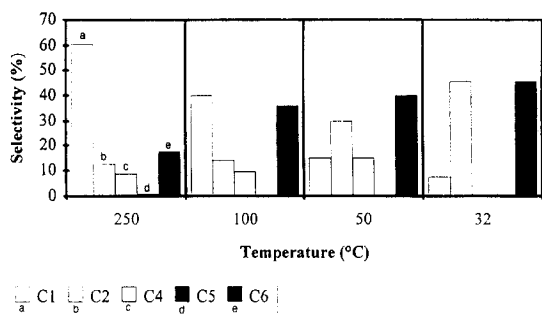


Fig. 6. The distribution of products (by number of carbons) observed for the reaction of propylene/hydrogen (3/1 at 32°C) over RhSn_{0.7}/SiO₂ at various temperatures.

tion producing C₆ hydrocarbons (shown for Sn/Rh^s=0.7 in Fig. 6). The latter reaction has not been observed in previous studies on monometallic catalysts [17,18]. In all experiments, hydrogenolysis and dimerization are the abundant reactions. At higher temperatures, methane formation by hydrogenolysis was the predominant reaction. At lower temperature it is the dimerization of propylene that predominates, the most abundant products being *n*-hexane, 2-methyl-pentane, 2-methyl-2-pentene and *trans*-3-hexene (Fig. 6).

Dimerization, hydrogenolysis and homologation are catalytic only in the presence of molecular hydrogen. However, the low $P_{H_2}/P_{C_3H_6}$ ratios favor the dimerization reaction and decrease the selectivity of the other competitive reactions on

the surface. In addition, the effect of contact time shows that the total conversion of propylene by the reactions involving the formation and breakage of C–C bond is proportional to contact time (Fig. 7). The study of the influence of contact time on the distribution of products showed that the olefins are the primary products in all of these experiments.

3.4. Parameters which influence the reaction of propylene and hydrogen

Sn/Rh ratio

For this study, samples RhSn_x/SiO₂ were prepared with calculated Sn/Rh^s ratios of 0.0, 0.4, 0.7, 0.9 and 1.4. A series of catalytic tests were conducted under identical conditions of contact time (gas flow rate: 4 l/h), hydrogen/propylene (1:3), and temperature (32°C), conditions chosen to enhance selectivity for the dimerization reaction. The results of these tests are summarized in Fig. 8. In general, as the Sn/Rh ratio is increased, the selectivity for C₆ hydrocarbons (*n*-hexane, 2-methylpentane, *trans*-3-hexene, 2-methyl-2-pentene, 2-methyl-1-pentene and 1-hexene) increases as the selectivity for C₂ products (ethane and ethylene) decreases. Up to Sn/Rh=0.9, the selectivity for C₁–C₅ hydrocarbons decreases as the amount of Sn is raised. From 0.9

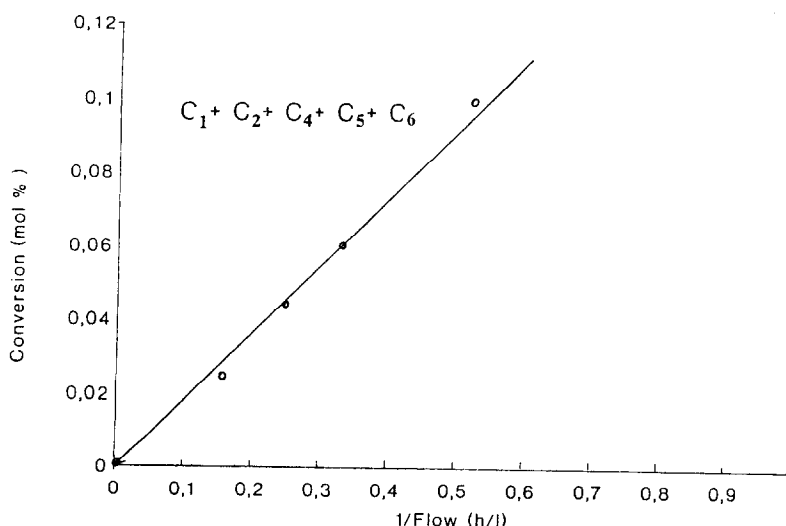


Fig. 7. Conversion of propylene to higher and lower hydrocarbons in the presence of RhSn_{0.7}/SiO₂ as a function of contact time.

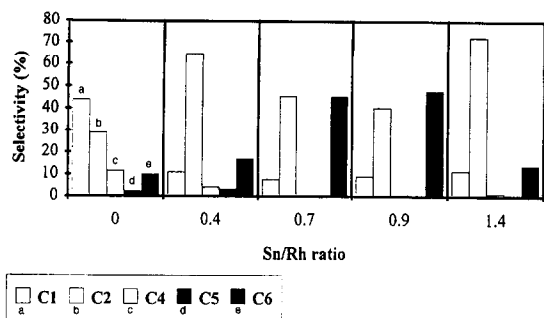


Fig. 8. The distribution of products (by number of carbons) observed for the reaction of propylene/hydrogen (3/1 at 4 l/h and 32°C) over $\text{RhSn}_{0.7}/\text{SiO}_2$ of various compositions.

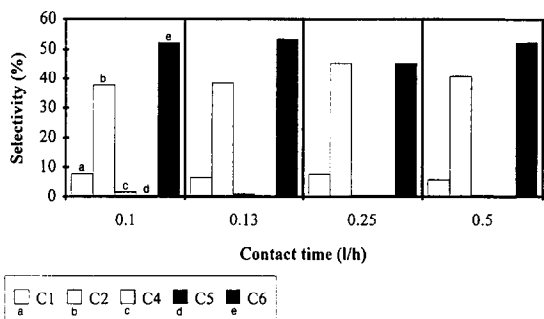


Fig. 9. The distribution of products (by number of carbons) observed for the reaction of propylene/hydrogen (3/1 at 32°C) over $\text{RhSn}_{0.7}/\text{SiO}_2$ at various gas stream flow rates.

to 1.4 a marked increase in selectivity for C_2 hydrocarbons was maintained whereas the proportion of C_6 products decreases dramatically. The latter passes from 50% for the catalyst $\text{RhSn}_{0.9}/\text{SiO}_2$ to 14% for $\text{RhSn}_{1.4}/\text{SiO}_2$.

Contact time

The effect of contact time was studied on $\text{Rh-Sn}/\text{SiO}_2$ with Sn/Rh ratio of 0.7 at room temperature and for the hydrogen/propylene ratio of 1:3. At this temperature, the influence of contact time has very little effect on the global distribution with respect to the number carbons of products (Fig. 9). In the C_6 products distribution there is a much sharper dependence on contact time. It was observed that at the shortest contact time, olefins were the predominant products (64% of C_6), especially *trans*-3-hexene (21% of C_6) and 2-methyl-2-hexene (27% of C_6). As the contact time was increased, the proportion of alkane products increased accompanied by slight changes in the distribution of olefinic products. It is clear that

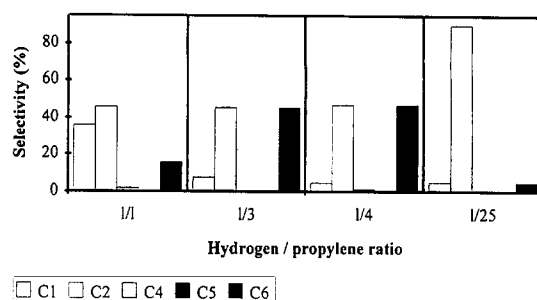


Fig. 10. The distribution of products (by number of carbons) observed for the reaction of various mixtures of propylene/hydrogen (at 4 l/h and 32°C) over $\text{RhSn}_{0.7}/\text{SiO}_2$.

increasing contact time favors the secondary hydrogenation and olefin isomerisation reactions

Temperature

For this study, a series of catalytic runs were conducted under identical conditions of contact time (gas flow rate of $41 \cdot \text{h}^{-1}$), Sn/Rh ratio (0.7) and hydrogen/propylene ratio (1:3) in range of temperatures of room temperature to 300°C (Fig. 6). High temperature leads to the increase in the selectivity for hydrogenolysis reactions.

Hydrogen/propylene ratio

The reduction of the partial pressure of hydrogen favors the dimerization reaction and disfavors the hydrogenolysis and clearly hydrogenation reactions (Fig. 10). There is also a decrease in the C_4 – C_5 products. A very low hydrogen to propylene ratio effectively suppresses the homologation reaction and greatly reduces the dimerization reaction. In the total absence of molecular hydrogen no catalytic reaction is observed.

4. Discussion

In the presence of hydrogen, $\text{Rh-Sn}/\text{SiO}_2$ catalyses the transformation of propylene into various olefinic and paraffinic compounds by hydrogenation, hydrogenolysis, homologation and dimerization. Although hydrogenation is the predominant reaction, we will neglect it in this discussion as we wish to concentrate on carbon-carbon bond formation and cleavage reactions. In

particular, we wish to explore the difference between the monometallic catalyst, Rh/SiO₂ and the bimetallic catalysts, RhSn_x/SiO₂. We shall discuss the dependence of these reactions on experimental parameters and mechanistic implications of these trends. Mechanisms suggested will be based on elementary transformations well known in organometallic chemistry [19].

4.1. Time on stream

The total conversion of propylene to higher and lower hydrocarbons decreases during the first five minutes of exposure the catalyst to the reactant stream and is steady thereafter. One could interpret this observation as an indication that there are very active sites on the surface which efficiently break carbon–carbon bonds leading to coking, effectively poisoning these sites.

4.2. Contact time

Changing contact time does not significantly affect product distributions in terms of carbon number (Fig. 7). This is an indication that the reaction is under kinetic control in the range of contact times studied. Contact time does however have a marked effect on olefin/paraffin ratio, with terminal olefins predominating at low contact time, and with olefins probably being the sole products at zero contact time (Table 2, Fig. 11). This effect has previously been discussed for the homologation/hydrogenolysis of linear olefins [11]. It is also remarked that as contact time is

shortened, the amount of 3-hexene and 2-methyl-2-pentene increases more sharply than the other C₆ olefins observed. A possible mechanistic conclusion based on this observation is included below.

4.3. Temperature

At high temperature the hydrogenolysis reaction predominates. At temperatures higher than 150°C and for any Sn/Rh ratio, propylene undergoes carbon–carbon cleavage (leading to methane, ethane and ethylene) and carbon–carbon formation (leading to olefinic and paraffinic C₄–C₅ and C₆ hydrocarbons). Although the conversions of propylene into C₄–C₅ hydrocarbons are small at high temperature, clear mechanistic links have been established between the homologation and hydrogenolysis reactions over supported monometallic catalysts [12,14]. The enhancement of the dimerization reaction by low temperature may indicate that a low entropy transition state (e.g., a multicentered state) may be involved. It has also been suggested that the coupling of carbenic fragments is favored by low temperature [20], a proposition which would tend to explain the high selectivity at low temperature for both the C₆ products (vide infra) and C₂ products (coupling of methylene fragments).

4.4. Hydrogen/propylene ratio

It is clear that hydrogen is necessary for carbon–carbon bond forming and cleavage reactions (no

Table 2
Distribution of primary products and fraction of olefins in the dimerization of propylene as function of contact time

Contact time (h · l ⁻¹)	% olefins in C ₆ products	Distribution of primary products in the dimerization reaction					
		2-Methyl-pentane	<i>n</i> -Hexane	<i>trans</i> -3-Hexene	<i>trans</i> -2-Hexene	2-Methyl-2-pentene	2-Methyl-1-pentene
0.083	64	13	23	21	8	27	8
0.125	51	20	29	13	5.5	26	6.5
0.250	46	25	28	12	4	25	6
0.500	24.5	35.5	40	5.5	2	14	3

$P_{C_3H_6}/P_{H_2} = 3/1$; room temperature; $m_{cat} = 150$ mg; $t = 5$ min.

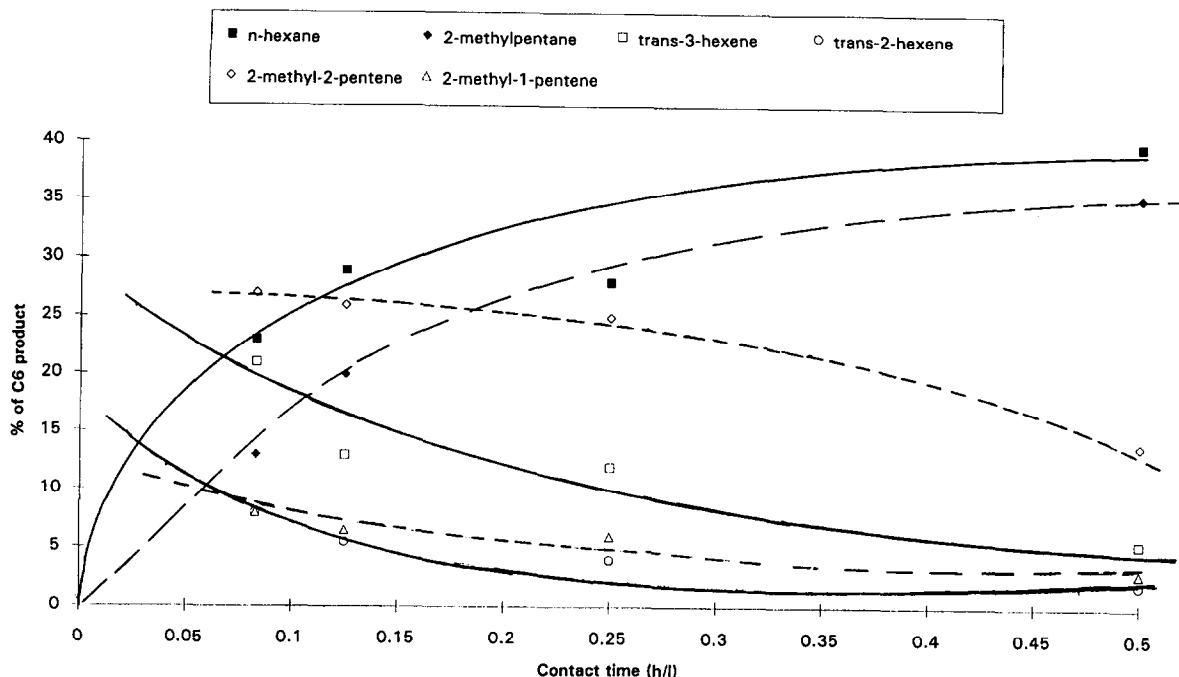


Fig. 11. The distribution of dimerization products as a function of contact time. Linear products are represented as solid lines, branched products as dotted lines.

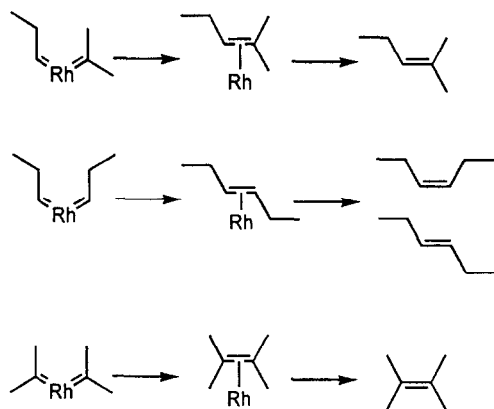
reaction is observed in the total absence of hydrogen, little reaction when the hydrogen/propylene ratio is 1/25), but a non-stoichiometric amount of hydrogen appears to be more favorable for these reactions.

4.5. Rh/Sn ratio

As the Sn/Rh ratio is increased up to 1, the proportions of C_1 and C_4 – C_5 hydrocarbons decrease while C_2 and C_6 selectivity increases. This suggests that the formation of C_4 – C_5 entities depends of the presence of C_1 fragment. Mechanisms already proposed for the monometallic catalysts explain quite well the formation of homologation and hydrogenolysis products [21]. In our laboratory we have performed, for several years, studies designed to investigate the possible mechanistic link between the hydrogenolysis and homologation of hydrocarbons and in particular of olefins. Studies on this topic have been completed for the homologation and the hydrogenolysis of linear butenes [16], linear and branched pentenes [10,12], cyclic pentenes [22,23] and

branched hexenes [24]. The homologation reaction depends on the formation of carbon–carbon bonds either by insertion of surface methylene into metal–alkyl bonds or by the direct coupling of surface methyldene to coordinated olefin. Thus the homologation reaction depends on the formation of C_1 surface fragments which can also be formed analogous mechanisms (either by methylene deinsertion from a metal propyl fragment or by γ -CH activation to form a metallacyclopentane and subsequent decyclization to form methylene and coordinated ethylene) [21]. It is the dimerization reaction and its relationship to the presence of surface tin which is unique to the bimetallic catalysts must be explored in this paper.

The principal dimerization products observed in the reaction of propylene and hydrogen are *n*-hexane, 2-methyl-pentane, *trans*-3-hexene, *trans*-2-hexene and 2-methyl-2-pentene. At low temperature and short contact time, *trans*-3-hexene and 2-methyl-2-pentene are the predominant primary products. The increased selectivity for the dimerization of propylene with increasing surface tin indicates that this reaction passes by a mech-



Scheme 1.

anism distinct from that of the hydrogenolysis/homologation reactions. In the literature, there are few examples which treat dimerization processes in heterogeneous catalysis [25].

There is one example in published by our laboratory related to propylene dimerization [13]. It was shown that the passage of ethylene/hydrogen mixtures over Ru/SiO₂ produced a number of reactions, among them apparently the direct dimerization of ethylene which, in turn, was favored at low temperature. The mechanism proposed at that time was the coupling reactions of ethylidene fragments, which still seems reasonable.

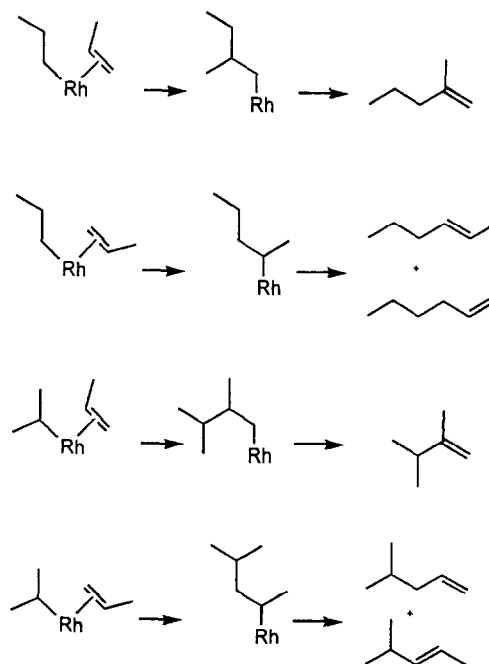
Propylene dimerization presents us with more mechanistic information than ethylene dimerization. Paraffins and olefins having the skeleton of *n*-hexane and 2-methylpentane are the major C₆ products. Olefins appear to be the majority if indeed not the sole dimerization products at zero contact time with *trans*-3-hexene and 2-methyl-2-pentene predominating. At least three mechanisms for propylene dimerization which lead to the formation of these products can be envisaged, the mechanisms being the coupling of two metal propylidene fragments, propylidene insertion into a metal-propyl bond, and direct coupling of two coordinated propenes.

(i) Coupling of two metal-propylidene fragments: The direct coupling of two propylene fragments (Scheme 1) has been observed for homogeneous reactions in electron poor complexes. The mechanism analogous to that which

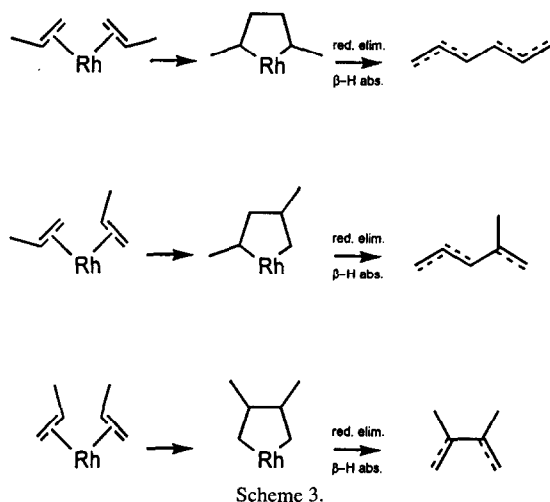
we previously suggested for ethylidene coupling. It is worth noting but not at all conclusive that the most abundant olefinic C₆ products at low contact time, 2-methyl-2-pentene (27%) and *trans*-3-hexene (21%), are formed directly by this mechanism.

(ii) Insertion of propylidene into metal-propyl fragment: Olefin insertion into a metal alkyl bond is a well documented organometallic reaction step. This carbon-carbon bond formation step would be followed by β -H elimination to leads to an olefin product (Scheme 2). Neither *trans*-3-hexene nor 2-methyl-2-pentene is directly formed by this mechanism.

(iii) Direct coupling of two coordinated propenes: Here two coordinated olefins couple to form a metallacyclopentane. The production of a mono-olefin product requires exactly one reductive elimination and one hydride abstraction before desorption into the product stream. Scheme 3 represents the wide variety of products possible (with potential double bond positions represented by dotted lines). Again, neither *trans*-3-hexene nor 2-methyl-2-pentene is directly formed by this mechanism.



Scheme 2.



4.6. Conclusions

On the bimetallic catalysts, $\text{RhSn}_x/\text{SiO}_2$ the reaction of propylene in the presence of hydrogen as a function of various experimental parameters was studied so as to provide information about the mechanism of the process of C–C bond formation and for comparison to our analogous study of the homologation and hydrogenolysis of propylene in the presence of hydrogen over monometallic Rh/SiO_2 . The parameters studied included the rhodium/tin ratio, the temperature of reaction, the propylene/hydrogen ratio, and the contact time. The reaction of propylene/hydrogen with $\text{RhSn}_x/\text{SiO}_2$ was selective for the dimerization of propylene under all conditions studied. This selectivity for dimerization increased as temperature was increased and as hydrogen pressure was decreased.

Hydrogenolysis and homologation reactions were observed but with very low selectivity compared to the selectivity for these reactions under analogous conditions with a monometallic Rh/SiO_2 catalyst. These reactions are believed to proceed by mechanisms invoking the formation or decomposition of dimetallacyclopentane intermediates.

Thus, we attribute the suppression of these processes on the bimetallic catalyst to the isolation of rhodium atoms from each other, which prevents the formation of these dimetallo-cycles. The mech-

anism of the dimerization of propylene cannot be closely related to that of common hydrogenolysis/homologation mechanism observed on metal surfaces.

The studies of the distribution of products as a function of contact time and of temperature are inconclusive due to the presence of multiple parallel reaction paths on the surface (hydrogenation, homologation/hydrogenolysis, dimerization). Three possible mechanisms for propylene dimerization are suggested, but it is perhaps the mechanism of the direct coupling of two coordinated two propylidene ligands coordinated to a single rhodium center that is the best supported by studies at low temperature and short contact time

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