

Influence of the reactant concentration in selective hydrogenation of 1,3-butadiene over supported gold catalysts under alkene rich conditions: A consideration of reaction mechanism

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Abstract

This article is about the reaction of selective hydrogenation of 1,3-butadiene performed in an excess of alkenes (propene/butadiene ratio = 100) over supported gold catalysts, so as to mimic the conditions of purification of light alkenes (C4 cuts) from the presence of impurities (highly unsaturated compounds, 1-3%). Gold was found highly selective (close to 100%, no propane or butane formation) for the hydrogenation of butadiene to butenes at 100% conversion of butadiene. The influence of the concentrations of the various reactants, i.e. hydrogen, butadiene and propene, on the rates of butadiene and propene hydrogenation was investigated, and the apparent reaction orders were deduced from the dependence of rate on partial pressure in the gas phase. The reason for the high selectivity of gold catalysts is that the reaction of hydrogenation of alkenes occurs at much higher temperature (0.1% conversion at 300°C) than that of selective hydrogenation of butadiene (100% at T <170°C).

Moreover, the presence of propene has only a limited influence on the reaction of butadiene hydrogenation, while butadiene has no influence on propene hydrogenation; the two reactions of hydrogenation hardly influence each other. Hydrogen dissociation is the rate limiting step of the reaction (partial order of 0.7 and 1 with respect to H₂ for butadiene and propene hydrogenation, respectively), responsible for the low activity of gold. The catalytic properties of gold were compared to those of palladium-based catalysts, and reasons for their different behaviour were discussed.

Introduction

This work follows a study on the catalytic properties of supported gold catalysts in the selective gas phase hydrogenation of 1,3-butadiene performed in an excess of propene (propene/butadiene ratio = 100) (1). These reaction conditions were chosen to mimic those of purification of light alkenes (C4 cuts) from the presence of impurities of alkenes (1-3%). In that paper, it was shown that gold catalysts were very selective to hydrogenate 1,3-butadiene into butenes without hydrogenating alkenes, i.e., butenes and propene. It was found that the reactivity of propene and butenes was the same, which validated the choice of replacing butene by propene that we did for analytical reasons. However, gold catalysts were found to be much less active but much more selective than the palladium-based catalysts which are used today in industry for that type of reaction, and it was anticipated that the reaction mechanism was different (1). It was also found that the gold particle size and gold loading had no influence on the TOF (expressed per surface gold atoms). In contrast,

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Running title: kinetics of selective hydrogenation of butadiene over gold catalysts

the method of preparation had an influence, and this was related to the amount of chlorines contained in the samples. The samples prepared by deposition-precipitation in which the amount of chlorine was below the detection limit of analysis (≤ 200 ppm), were more active than the samples containing more chlorine, such as those prepared by impregnation in excess of solution or by anion adsorption.

To go further in the study of this reaction, and to deepen the comparison between the catalytic properties of gold and those of palladium-based catalysts, i.e., the conclusion of our former paper (1) that gold behaves differently from palladium-based catalysts, the present paper reports a study on the influence of the partial pressure of the reactants on the reaction rate, i.e. a rather basic study of the kinetics of the reaction of hydrogenation of butadiene over gold catalysts with the determination of the apparent orders of reaction with respect to the reactants and of the apparent activation energy.

Only a few kinetics studies on selective hydrogenation of single unsaturated hydrocarbons over gold catalysts have been reported up to now: the first one in 1973 on the hydrogenation of butadiene over Au/Al₂O₃ (2), the second one on the hydrogenation of propene over Au/SiO₂ (3, 4), and the third one on the hydrogenation of acetylene and ethylene over Au/Al₂O₃ (5). They were complicated by the fact that these studies were often performed over deactivated gold catalysts or containing large gold particles. More details are given in Discussion Section A.

The present study was mainly performed with gold supported on alumina prepared by deposition-precipitation with urea (1 wt% Au), after activation under hydrogen at 300°C. In such conditions, the samples contain very small gold particles (~2 nm) and a low level of chlorine (≤ 200 ppm). Because of the impossibility to reach a pseudo-stationary state at temperature above 150°C because of long-lasting slow deactivation, the kinetic study (determination of the apparent orders of reaction with respect to the reactants from the dependence of rate on partial pressure in the gas phase) was performed under the same condition as in our first paper (1), i.e., at increasing reaction temperature, and using a fresh sample for each experiment. The issue of the deactivation will be developed in another paper.

Experimental

A. Catalyst preparation

The catalysts were prepared by deposition-precipitation with urea (DPU) as described previously (6, 7), so as to reach a gold loading of 1 wt%. A 300 mL solution containing HAuCl₄ (5.10⁻⁴ M, Acros Chemicals), 0.9 g of urea ($C_{\text{Urea}} \sim 100 \times C_{\text{Au}}$) and the alumina support (3 g of AluC Degussa, 110 m².g⁻¹, δ -type) was prepared, and stirred at 80°C for 16 h in a dark, closed reactor. Titania (P25, Degussa, 50 m².g⁻¹) was also used for some experiments (Results Section C). After DPU, the solid was separated by centrifugation, washed four times with deionised water (with centrifugation between each washing). After the third washing, a few drops of silver nitrate were added to the washing solution, and did not show any AgCl precipitation. The samples were then dried under vacuum at RT for 12 h, and stored at RT under vacuum in a desiccator, away from light in order to prevent any uncontrolled reduction of gold (8).

Chemical analyses of Au, Cl and metal cation of the support were performed by inductively coupled plasma atom emission spectroscopy at the CNRS Center of Chemical Analysis (Vernaison, France). The Au weight loading of the samples was expressed in gram of Au per gram of sample: $\text{wt\% Au} = [m_{\text{Au}} / (m_{\text{Au}} + m_{\text{support}})] \times 100$.

B. Catalytic reaction

The reaction of hydrogenation was carried out with 100 mg of catalyst (sieve fraction, 125-200 μm) in a plug flow microreactor in pyrex (4 mm of internal diameter, catalyst bed around 18 mm high). This type of reactor allowed better reproducibility of catalytic results than CSTR-type reactor with such small amount of catalyst. Moreover, we could not perform kinetic study in isothermal conditions because of long-lasting slow deactivation. The kinetics measurements were performed at low butadiene and propene conversion ($\leq 15\%$) to avoid too high concentration gradient in the catalysts bed, and to be able to consider that the concentrations were constant in the entire catalytic bed. The catalysts were activated in situ, under pure H₂ (100 mL.min⁻¹) from RT to 300°C (2°C.min⁻¹) and kept about 30 min at 300°C. In a few cases, (see Results Section C), activation was also performed at 400 and 500°C and under air. Then, the catalysts were cooled to room temperature under pure H₂, and the standard reaction mixture consisting of 0.3% butadiene, 30% propene and 20% hydrogen in He

(49.7%) was introduced with a total flow rate of 50 mL.min⁻¹ (STP conditions), which corresponds to a space velocity of 30 L.g⁻¹.h⁻¹ (GHSV =20 000 h⁻¹). The catalysts were heated under this gas mixture at a rate of 1°C.min⁻¹, up to 300°C. Gas analysis at the outlet of the reactor was performed every 15 min, i.e., every 15°C, between 30 and 300°C. It was checked that with the slow heating rate chosen, the activity was stable, at least at temperatures lower than 150°C since stronger deactivation occurs at higher temperature. The analysis of reaction products was performed by gas chromatography (Perichrom PR 2100, FID detector) using a 7.5 m column (1/8 inch) filled with sebaconitrile 25% Chromosorb PAW 80/100 Mesh). Retention times and sensitivity factors for the reactants and products were calibrated using several gas mixtures. Software Winilab 4.0 was used for data acquisition and extraction of the concentrations of the different gases detected. Alumina alone did not show activity, only 20 ppm of butadiene being hydrogenated at 300°C. Tests were also made to check that under these catalytic conditions and at low conversion, internal and external diffusion limitations could be neglected. To estimate the influence of the external diffusion, we changed the flow rate and the mass of catalyst, keeping the flow rate/mass ratio constant (25 mL.min⁻¹ and 50 mg, 50 mL.min⁻¹ and 100 mg, and finally 100 mL.min⁻¹ and 200 mg). To examine the influence of the internal diffusion, we changed the average

size of the catalyst grain: 50-125 µm, 125-200 µm and 200-315 µm. For these experiments, the other parameters were maintained constant. All these experiments led to the same catalytic activities, only when a 200-315 µm cut was used, a lower apparent activity showed internal limitations. Numerous tests of repeatability and reproducibility were performed to validate the experimental results. For a series of tests performed with samples of the same batch, experimental error is estimated to be 5%. For instance, for two Au/Al₂O₃ samples arising from the same batch, activity at 60°C was equal to 4.9 and 4.7 µmol.s⁻¹.g_{Au}⁻¹. However when the samples arise from different batches, the variation of activity can be larger, 4.0 and 5.0 µmol.s⁻¹.g_{Au}⁻¹ (see Table 1). Except when this is mentioned, the results reported in this article arise from the same catalyst batch. Note that the carbon balance is 100% within the limit of the accuracy of the GC measurement.

The activities of the catalysts expressed in µmol.s⁻¹.g_{metal}⁻¹ were compared at 60°C, i.e. at low conversion so deactivation can be neglected. Since at this temperature, the activities were very low, it was not possible to calculate them with enough accuracy from the GC data, thus they were calculated from the apparent activation energy measured from the straight part of the Arrhenius plot of the ln(activity) versus 1/T. We could check in the 75-120°C range of temperature, that the fit between experimentally

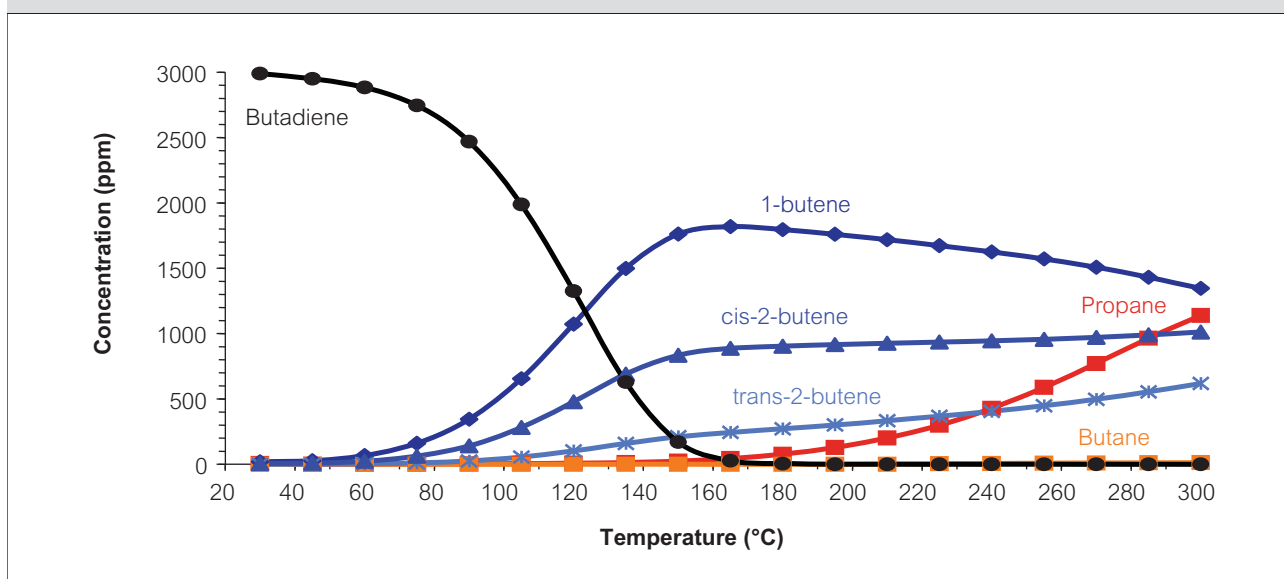
Table 1

Reactant studied	Concentrations (%)			Butadiene hydrogenation at 60°C Activity (µmol.s ⁻¹ .g _{metal} ⁻¹)
	Butadiene	H ₂	Propene	
hydrogen	0.30	5	30	1.4
	"	10	"	1.7
	"	20	"	5.0
Propene ¹	0.30	20	30	4.0
	"	"	20	4.9
	"	"	10	5.2
	"	"	0	5.3
Butadiene	0.10	20	30	4.1
	0.20	"	"	3.9
	0.30	"	"	5.0

¹ Unique case where the sample arises from another batch

Influence of the reactant concentrations on the activity of DPU Au/Al₂O₃ catalyst (1 wt% Au) activated under H₂ at 300°C under hydrogen in butadiene hydrogenation at 60°C

Figure 1



Reactivity of $\text{Au}/\text{Al}_2\text{O}_3$ catalyst (DPU, 0.9 wt % Au and <200 ppm Cl, activation in H_2 at 300°C, standard reaction conditions: 0.3% butadiene, 30% propene and 20% hydrogen in He): Evolution of the concentrations of butadiene and products as a function of the reaction temperature

determined values of activity and values derived from the Arrhenius plot was excellent. Then, we extrapolated the calculation of the activity at 60°C.

Results

A. Catalytic behaviour of DPU $\text{Au}/\text{Al}_2\text{O}_3$ catalyst

Figure 1 reports the typical catalytic behaviour of a DPU $\text{Au}/\text{Al}_2\text{O}_3$ catalyst in the standard conditions described in Experimental, i.e., the evolution of the concentrations of the reactant and products as a function of the reaction temperature. Such kind of catalysts contains gold metal particles of around 2 nm after activation. Butadiene is totally converted into butenes at ~170°C without formation of butane (<5 ppm) and without significant formation of propane (~100 ppm). Even at 300°C, the amounts of butane and propane formed do not exceed ~15 and ~1500 ppm, respectively, which corresponds to conversions of 0.5% for both butadiene and propene. This result also indicates that the reactivity of propene is similar to that of butenes. Figure 1 also shows that 1-butene is the main product, and that the proportions in the different butenes vary as follows: 1-butene > *cis*-2-butene > *trans*-2-butene with an increasing proportion of *trans*-2-butene as reaction temperature increases (see also Figure 9 in ref. (1)). It is worth noting that the reactions of butadiene hydrogenation and propene hydrogenation operate in two different ranges of temperature.

The gold activity was around $5 \mu\text{mol}\cdot\text{s}^{-1}\cdot\text{g}_{\text{Au}}^{-1}$ at 60°C (Table 1), which is low compared for example with that of palladium in hydrogenation of acetylene, which is about $100 \mu\text{mol}\cdot\text{s}^{-1}\cdot\text{g}_{\text{Pd}}^{-1}$ at 30°C or with that of a $\text{Ag-Pd}/\text{Al}_2\text{O}_3$ catalyst, which is $160 \mu\text{mol}\cdot\text{s}^{-1}\cdot\text{g}_{\text{Pd}}^{-1}$ at 60°C (9).

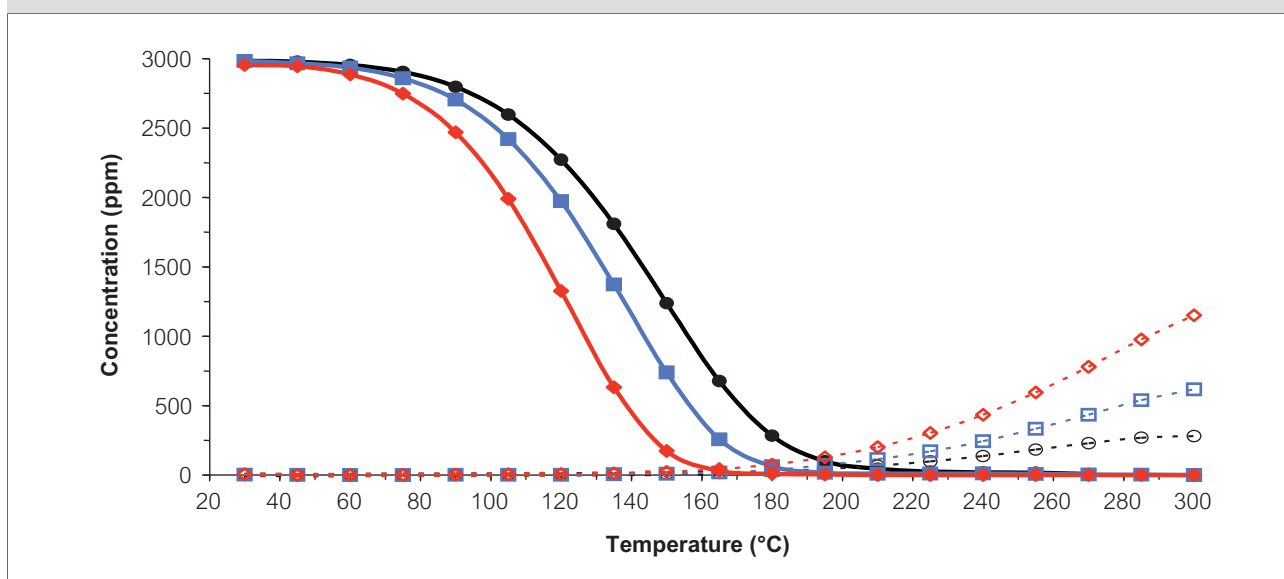
B. Influence of the reactant concentrations on the rates of butadiene and propene hydrogenation

1. Influence of the hydrogen concentration

The influence of the hydrogen concentration (5, 10 and 20%) on the hydrogenation of butadiene (0.3%) in the presence of propene (30%) is reported on Figure 2. For a given reaction temperature, the conversion of butadiene increases when the hydrogen concentration increases, and Table 1 shows that the activity at 60°C in butadiene hydrogenation increases as well. The logarithm of the activity plotted versus the logarithm of the hydrogen partial pressure at the different reaction temperatures (30, 45, 60, 75, 90°C) give straight lines (Figure 3A), the slope of which equal to 0.7, indicates that the apparent order for hydrogenation of butadiene with respect to hydrogen is equal to 0.7.

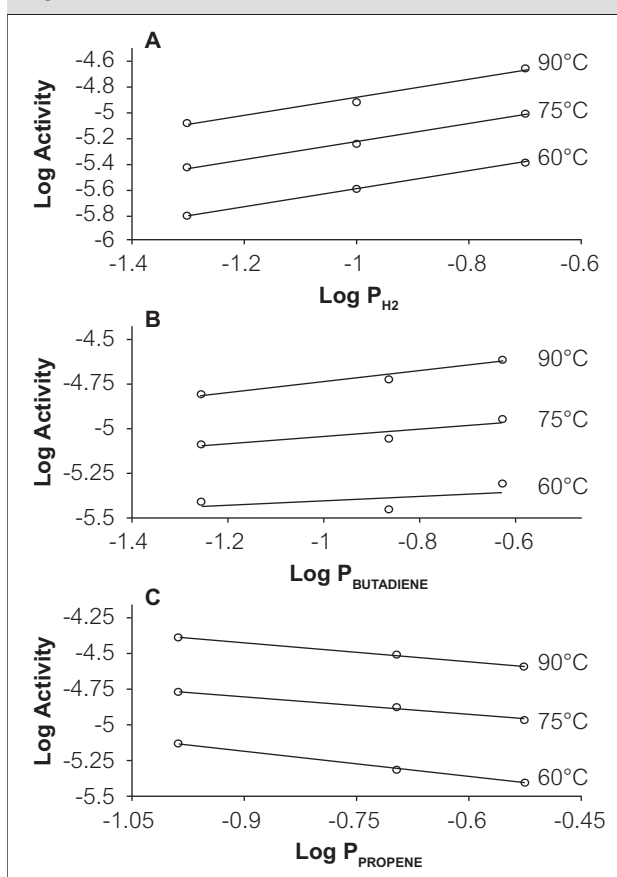
Figure 2 also shows that the amount of alkanes formed increases with the hydrogen concentration. The logarithm of the activity in propene hydrogenation

Figure 2



Comparison of the reactivity of Au/Al_2O_3 in butadiene hydrogenation as a function of the hydrogen concentration (full symbols and plain lines: butadiene concentration; open symbols and dotted lines: alkane concentration); H_2 : 5% (● ○), 10% (■ □) and 20% (◆ ◇)

Figure 3



Plot of the logarithm of activity versus the logarithm of the partial pressure of hydrogen (A), butadiene (B), propene (C)

versus the logarithm of the hydrogen concentration plotted at 240, 255, 270, 285 and 300 °C, also give straight lines, the slope of which varies from 0.8 to 1.0, which indicates that the order with respect to hydrogen is around 1 for propene hydrogenation.

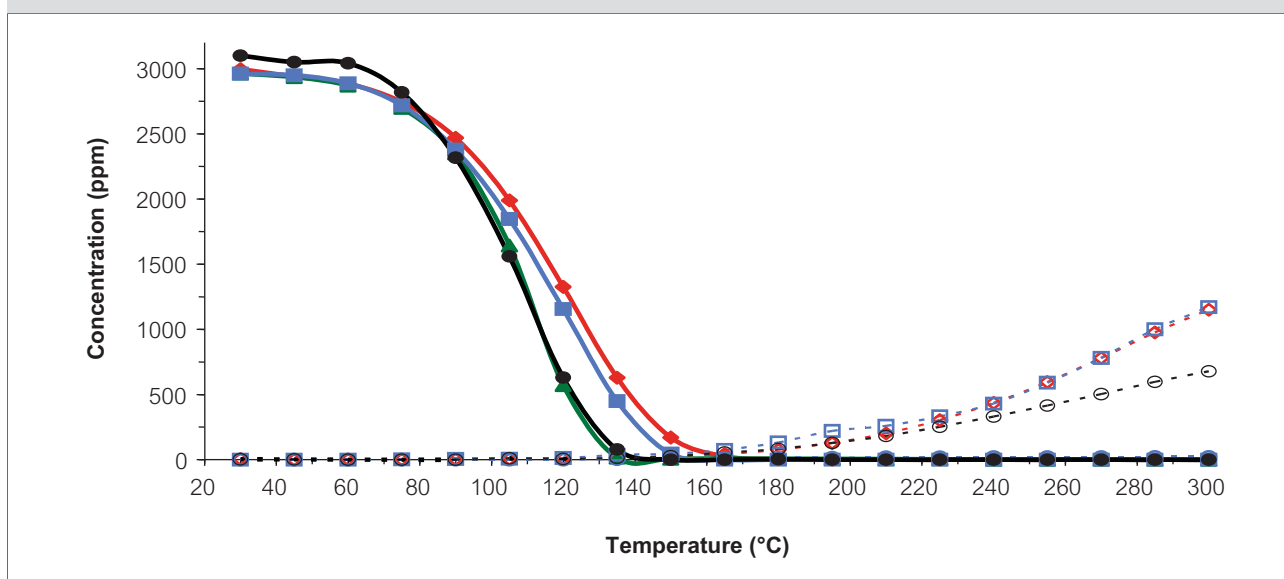
2. Influence of the propene concentration

The influence of the propene concentration (30, 20, 10 and 0%) on the hydrogenation of butadiene (0.3%) was also investigated. Figure 4 shows that the butadiene conversion slightly increases as propene concentration decreases. The increase in activity at 60 °C with propene concentration is not drastic either (Table 1). The influence of propene is therefore rather weak if one keeps in mind that 30% propene corresponds to a concentration 100 times as high as that of butadiene.

The plot of the logarithm of the activity in butadiene hydrogenation versus the logarithm of the propene partial pressure at 60, 75 and 90 °C gives straight lines with roughly the same slope of -0.4 (Figure 3B).

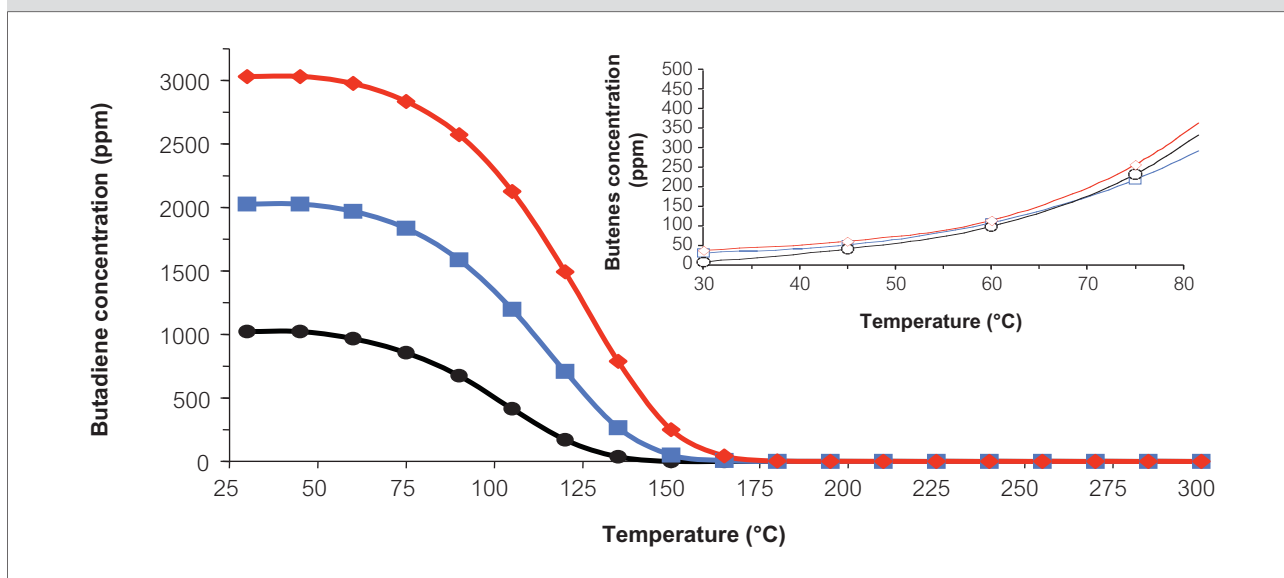
The slightly higher activity of the gold catalysts in hydrogenation of butadiene when propene was removed from the reaction mixture (Figure 4), and the negative order with respect to propene indicate a competition of adsorption between propene and butadiene and/or hydrogen on the gold surface sites.

Figure 4



Comparison of the reactivity of Au/Al_2O_3 in butadiene hydrogenation as a function of propene concentration (full symbols and plain lines: butadiene concentration; open symbols and dotted lines: alkane concentration); Propene : 0% (▲), 10% (●) 20% (■) and 30% (◆)

Figure 5

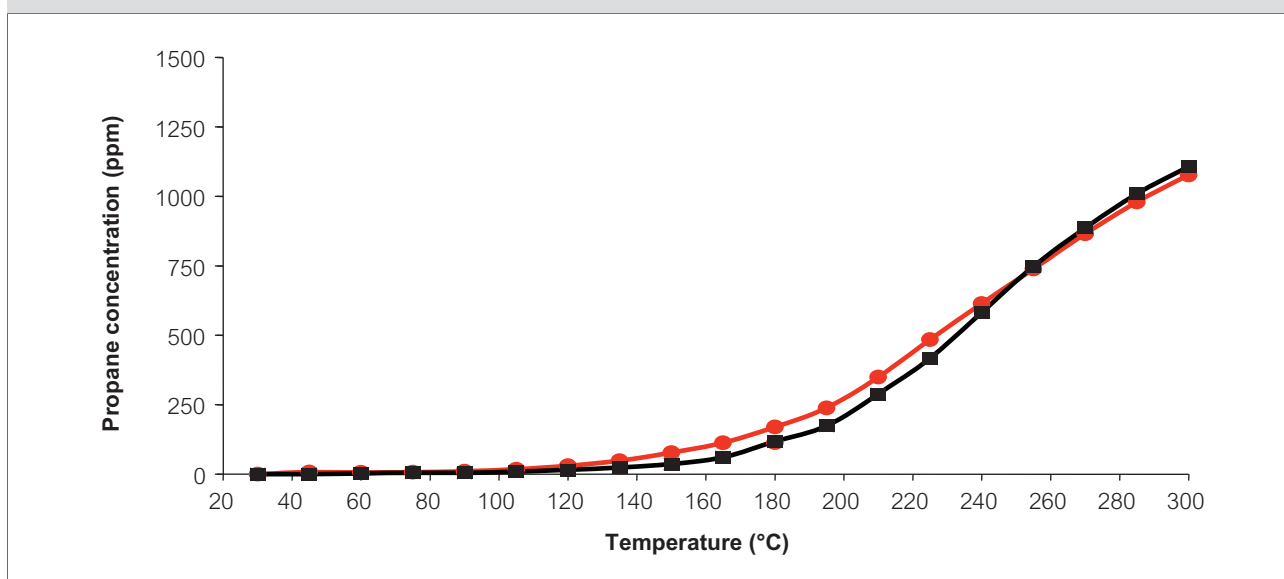


Comparison of the reactivity of Au/Al_2O_3 in butadiene hydrogenation as a function of butadiene concentration: 0.1% (●), 0.2% (■) and 0.3% (◆). Insert: Evolution of the butenes concentration as a function of the reaction temperature; butadiene concentration: 0.1% (○), 0.2% (□) and 0.3% (◇)

It seems that adsorbed propene limits the access of the gold sites to the other reactants. However, propene is probably weakly adsorbed, otherwise butadiene hydrogenation would be inhibited. In other words, alkene adsorption on the catalytic sites is not a parameter limiting the reaction rate.

Figure 4 also shows a dependence of the activity in hydrogenation of propene when the propene concentration varies. This will be discussed in Discussion Section A.

Figure 6



Comparison of the reactivity of Au/Al_2O_3 catalysts in propene hydrogenation in the presence (●) or absence of butadiene (■)

3. Influence of the butadiene concentration

The influence of the butadiene concentration (0.1, 0.2 and 0.3%) was investigated in the presence of propene. Figure 5 shows that as expected the lower the percentage of butadiene the lower the temperature for 100% conversion of butadiene, but the activity does not significantly change (Table 1). Moreover the proportions in the different butenes are similar, and the amount of butane formed does not significantly change (~30 ppm).

The plot of the logarithm of the activity in butadiene hydrogenation versus the logarithm of the butadiene partial pressure (at 60, 75 and 90°C) provides an apparent reaction order with respect to butadiene of 0.2, i.e., close to zero (Figure 3C).

Figure 6 shows that propene conversion is not affected by the presence or the absence of butadiene. Since vice versa propene concentration has not a strong influence on hydrogenation of butadiene, one can conclude that the reactions of hydrogenation of butadiene and of alkenes are barely related to each other.

C. Activation energy of the reaction of butadiene hydrogenation

For a series of Au/Al_2O_3 and Au/TiO_2 catalysts prepared by DPU and activated either in air or in hydrogen at 300, 400 or 500°C, so as to obtain

various average gold particle size between 2 and 5 nm (see Table 3 in ref. (1)), the apparent activation energy for butadiene hydrogenation measured between 45 and 90°C is around $50 \pm 2 \text{ kJ}\cdot\text{mol}^{-1}$, and does not depend on the particle size and the nature of the support.

Note that the apparent activation energy for propene hydrogenation in the temperature range of 240–300°C was not measured because it would have been meaningless to compare it with that of butadiene hydrogenation calculated at much lower temperature.

Discussion

A. Kinetics and reaction mechanism

Our results show that the two reactions of selective hydrogenation of butadiene and hydrogenation of alkenes operate in two different ranges of temperature, the first one below 170°C and the second one above this temperature. The reaction rate equations for the hydrogenation of butadiene and that of propene can be expressed as follows:

$$V_{\text{butadiene}} = k [\text{butadiene}]^{0.2} \cdot [\text{H}_2]^{0.7} \cdot [\text{propene}]^{-0.4} \quad (\text{Equation A})$$

$$V_{\text{propene}} = k' [\text{propene}]^0 \cdot [\text{H}_2]^1 \cdot [\text{butadiene}]^0 \quad (\text{Equation B})$$

In the classical mechanism of Polanyi-Horiuti (10) that usually applies for hydrogenation of hydrocarbons on metallic catalytic sites, the elementary steps are the following:



In the case of gold catalysts, it has been proposed by Zanella et al. (11) on the basis of results of selective hydrogenation of crotonaldehyde performed at 120°C and by Bus et al. (12) on the basis of a study on hydrogen chemisorption, performed between 25 and 250°C, that Step 1 of dissociative adsorption of hydrogen is the rate limiting step for hydrogenation. Bus et al. (12) reported that supported gold particles exhibit unique properties, i.e., the increasing capacity of hydrogen dissociation and of hydrogen uptake as temperature increases because hydrogen dissociation over gold nanoparticles is activated, as also suggested by Lin and Vannice (13). This behaviour is opposite to that of group VIII metals such as platinum, for which the amount of adsorbed hydrogen decreases with temperature, because the equilibrium shifts toward molecular hydrogen recombination in the gas phase, in agreement with thermodynamics. On supported gold nanoparticles, according to Bus et al. (12), H₂ adsorption is limited by kinetic factors at moderate temperature, between 298 and 373 K.

As a consequence, we can propose that in the range of low temperature of the reaction of butadiene hydrogenation, the hydrogen dissociation and the amount of adsorbed hydrogen are limited, so that Step 1 is an equilibrated reaction. At higher temperature, in the range of temperature of propene hydrogenation, hydrogen dissociation is more favoured and Reaction 1 is shifted toward the formation of adsorbed atomic H.

In the hypothesis that Reaction 1 is equilibrated (Mechanism I), i.e., hydrogen coverage is low, according to ref. (14), one can calculate that the overall reaction rate is equal to: $v = K [\text{H}_2]^{1/2}$ with

$K = k_4 \sqrt{K_1} [L] / [L]$, where [L] is the number of adsorption sites and [*] is the number of free sites, and the reaction orders with respect to hydrogen and alkenes or alkadienes are 0.5 and 0, respectively.

In the hypothesis that Reaction 1 is non-equilibrated and shifted towards the right hand side (Mechanism II), which means that hydrogen dissociation is favoured compared to molecular hydrogen desorption, and that the gold coverage by atomic hydrogen is higher than in Mechanism I, one can calculate that the overall reaction rate is equal to: $v = K' [\text{H}_2]$ with $K' = k_4 [L] / [L]^2$. The reaction orders with respect to hydrogen and alkenes or alkadienes are 1 and 0, respectively.

Concerning the rate expression of butadiene hydrogenation established between 60 and 90°C (Equation A), the reaction order with respect to butadiene is close to zero. In terms of adsorption, this means that the gold surface is covered by butadiene, but this does not mean that propene cannot adsorb. Indeed, Figure 4 shows that the presence of propene slightly inhibits the reaction, and the reaction order with respect to propene was found slightly negative. The value of 0.7 for the reaction order with respect to hydrogen indicates that the amount of adsorbed hydrogen is low. This is consistent with the fact that as mentioned above, at moderate temperature hydrogen dissociation is not favoured. This result also indicates that H₂ dissociation is the limiting step of the reaction of hydrogenation, as already proposed (3,11,12). The value of 0.7 is intermediate between that of Mechanisms I and II, indicating that Step 1 of dissociative adsorption of hydrogen is not equilibrated but slightly shifted towards H₂ dissociation.

Concerning the rate expression of propene hydrogenation established between 240 and 300°C (Equation B), the reaction order with respect to propene is close to zero when the concentration of propene is in large excess. Indeed, for concentrations of 20 and 30%, it has no influence on the conversion of propene into propane. One can note from Figure 4 that when the propene concentration is lower (10%), an effect on the propene conversion starts to be visible. In this range of temperature, the gold surface is saturated by propene and butadiene does not compete with propene (Figure 5). The reaction order with respect to hydrogen, which is equal to one (see Results Section B.1), indicates that the reaction of hydrogen dissociation is not equilibrated and is also the limiting step of the reaction of hydrogenation.

The higher order with respect to hydrogen for propene hydrogenation between 240 and 300°C (1) than for butadiene hydrogenation (0.7) in lower temperature range, indicates a higher gold coverage by atomic hydrogen at higher temperature, and means that the reaction of dissociative adsorption of hydrogen is more displaced towards atomic H adsorption. Again, this result is consistent with the results of Bus et al. (12) reported above.

The apparent reaction orders deduced from the dependence of rate on partial pressure in the gas phase and apparent activation energy for butadiene hydrogenation evaluated in this study (50 ± 0.2 kJ.mol⁻¹) are consistent with the few results of the literature on selective hydrogenation over gold catalysts. Buchanan et al. (2) found that selective hydrogenation of butadiene at 200°C over Au/Al₂O₃ was first order in hydrogen and zeroth order in butadiene with an activation energy of 36 kJ.mol⁻¹ between 170 and 260°C. Note that the study was performed on catalysts deactivated after 8 to 10 cycles of hydrogenation, and at much higher temperature than ours, probably also because of large gold particles present in these catalysts prepared by impregnation. Jia et al. (5) reported a value of 34 ± 1 kJ.mol⁻¹ for the apparent activation energy for acetylene hydrogenation (98% hydrogen) between 65 and 120°C over Au/Al₂O₃ (3.8 nm in size) and reaction order of 0.1 ± 0.1 in acetylene and 0.4 ± 0.1 in hydrogen. Naito et al. (3) found values between 0.85 and 1 for the order of reaction with respect to H₂ for propene hydrogenation over Au/SiO₂ at 150°C, in low pressure conditions and performed with a recirculation system (2.6 kPa of propene and 40 kPa of hydrogen). We can however wonder whether such kind of comparison is valid since kinetic results depend on reaction conditions. For instance, for palladium catalysts, Deganello et al. (15) reported that for the reaction of selective hydrogenation of acetylene in the presence of ethene, the apparent activation energies measured for H₂/C₂H₂ ratios of 130, 45 and 2 between 10 and 60°C, were equal to 36, 58 and 65 kJ.mol⁻¹ respectively.

B. Comparison with Pd catalysts

Gold catalysts are much less active than palladium but much more selective. This was also found for other selective reactions, such as selective hydrogenation of unsaturated aldehydes (11,16) or nitro-chloroaromatics into amines (17).

For both types of catalysts, the reaction order is close to 1 with respect to hydrogen and negative or

close to zero with respect to acetylene or butadiene for palladium (18) and for gold (19, 20). The values of the reaction orders indicate that for both metals, the surface is saturated by hydrocarbons, which adsorb more strongly on palladium than on gold (21), and the step of dissociative adsorption of hydrogen is disfavoured. However, the dissociation of H₂ is much easier on palladium than on gold, since it takes place on any surface atoms whereas for gold, it only occurs on low coordination sites; this point has been already discussed in our former paper (1). As mentioned above, gold is also very peculiar since it exhibits increasing capacity of hydrogen dissociation and uptake when temperature increases (12).

The reason for the high selectivity to alkenes over gold catalysts is different from that for palladium. For gold, the two reactions of hydrogenation of butadiene and propene are rather independent from each other, and occur in two different ranges of temperature (Figure 1). The presence of propene has only a limited influence on the reaction of butadiene hydrogenation (Figure 4), and the presence of butadiene has no influence on that of propene hydrogenation (Figure 6). Acetylene and ethene hydrogenations over Au/Al₂O₃ were also found to occur in different ranges of temperature, from 40 to 250°C for acetylene to ethene and above 300°C for ethene to ethane, whereas over Pd catalysts, they take place in the same range of temperature (5).

The selectivity of palladium catalysts results from a competition of adsorption between dienes (or alkynes) and alkenes on catalytic sites. Because of the stronger adsorption energy of the most unsaturated molecules (21-25) and in spite of the fact that the rate of hydrogenation of alkenes is higher than that of alkadienes (or alkynes) (5), butadiene adsorption inhibits alkene hydrogenation, thus palladium catalysts are selective (more subtle details can be found in the two recent reviews of Borodzinski and Bond (18, 26)). This remains true as long as dienes (or alkynes) are present in the gas mixture. When their concentration becomes very low, either because the impurity level in the feed gas is temporarily low, or because conversion is close to 100%, alkenes start to adsorb, and to hydrogenate with a higher rate than that of dienes (alkynes), resulting in drastic drops in selectivity (9).

Dienes (alkynes) and alkenes also adsorb differently on gold catalysts. Jia et al. (5) showed that 0.92 molecule of acetylene per surface atom of gold can adsorb at 0°C on Au/Al₂O₃ catalyst and only

0.05 molecule of ethene, i.e., with a ratio of about 20 between the two molecules. Segura et al. (21) reported different adsorption energies of propyne and propene on unsupported Au₁₉ cluster, -0.42 and -0.01 eV, respectively, but comparable barriers of the first hydrogenation step of propyne and propene (0.49 and 0.63 eV, respectively). They explained that only propyne can be hydrogenated since propene cannot adsorb. Regarding this last point, preliminary DFT calculations performed by D. Loffreda (27) did not reach exactly to the same conclusion: he also found that butadiene adsorbs more strongly on Au₁₃ cluster supported on ceria than propene (150 kJ.mol⁻¹ versus 116 kJ.mol⁻¹), but that propene adsorbs as well. To explain the difference of reactivity between palladium and gold catalysts, i.e., that for gold, butadiene and propene hydrogenation occur in two separate ranges of temperature, and are barely influenced by the presence of each other, one can propose that the activation energies for the two reactions are very different, i.e., the activation energy for propene hydrogenation would be much higher than that for butadiene hydrogenation, which is not consistent either with Segura's calculation results reported above. As mentioned above (Results Section C), we could not calculate the apparent activation energy for propene and butadiene hydrogenations in the same temperature range, thus this remains a hypothesis.

Conclusion

The study of the kinetics and mechanism of reaction of selective hydrogenation of butadiene in the presence of excess of propene over supported gold catalysts showed that the two reactions of hydrogenation of butadiene and propene operate in two different ranges of temperature, so one can consider that they hardly influence each other. The reaction of alkene hydrogenation is not an easy reaction over gold catalysts, and it is necessary to reach a higher temperature than that of butadiene to initiate the reaction. The selectivity to butenes does not result from a competition of adsorption between butadiene and alkenes as in the case of palladium, but it is probably related to different activation energies for the two reactions; it is much higher for alkenes than for butadiene hydrogenation. For this reason, gold catalysts are very selective in hydrogenation of butadiene.

Gold particles are not very active for hydrogen dissociation, which is the rate limiting step of the reaction. This low hydrogen dissociation capacity

can be considered as responsible for the low activity of gold. Although the activity is much lower than that of palladium-based catalysts used in industry for that process, their outstanding selectivity at 100% conversion (of alkadiene) makes gold catalysts very promising as "finition" catalysts, i.e., as catalysts able to remove the ultimate ppm of alkenes that palladium cannot selectively hydrogenate. For such a use, high activity is not crucial.

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