Support Effects in the Hydrogenolysis of Tetrahydrofuran on Platinum Catalysts

Karl Kreuzer and Reinhard Kramer

Institute of Physical Chemistry, University of Innsbruck, A-6020 Innsbruck, Austria

In the hydrogenolysis of tetrahydrofuran on supported platinum the primary product is *n*-butanol. On unsupported platinum the primary reaction proceeds distinctly slower than on supported platinum, and on these catalysts the activity increases in the order $Pt/SiO_2 < Pt/Al_2O_3 < Pt/TiO_2$. Thus it is deduced that for the C–O bond scission the presence of a support enhances the activity, with titania exhibiting an excellent ability to activate the C–O single bond. The primary product butanol undergoes two different secondary reactions, either by a hydrodeoxygenation to butane or by a decarbonylation to propane. The selectivity toward these products depends again on the supporting material, changing form about 0% deoxygenation by unsupported platinum to almost 100% deoxygenation by Pt/TiO_2. Again, the supported catalysts are more active in C–O bond scission and therefore more selective for butane formation. The product CO causes self-poisoning of the platinum surface. As a consequence, the reaction rate decreases soon after admission of the reaction mixture. Furthermore, upon CO poisoning the selectivity is shifted toward less butane formation. This indicates that CO inhibits preferentially the sites for C–O bond scission presumably situated at the platinum support phase boundary. © 1997 Academic Press

1. INTRODUCTION

In the hydrogenolysis of 2-methyltetrahydrofuran on platinum it is known that the ring opening occurs by the scission of one of the two C–O bonds, resulting in pentanol-(1) and pentanol-(2) as primary products (1, 2). In consecutive reactions both of these pentanols can be converted to pentane by a second C–O bond scission. In addition, butane can be formed by CO abstraction from pentanol-(1). Thus, the distribution of the final products pentane and butane depends not only on the selectivity of the primary reaction (which in turn is a function of metal dispersion and of the nature of the support) but also on the selectivity of the secondary reaction of pentanol-(1) to either pentane or butane, which is a function of reaction conditions such as temperature and hydrogen partial pressure.

In order to study the selectivity of the secondary reaction (hydrodeoxygenation versus decarbonylation) we investigated the hydrogenolysis of tetrahydrofuran (THF) on plat-inum catalysts. The primary product *n*-butanol reacts via two different pathways either to butane (and water) or to propane (and CO). One aim of this study was to investigate the effect of reaction temperature and of hydrogen pressure on the two pathways and to gain insight into the mechanism of the C–O scission and the CO abstraction reaction.

Since the hydrogenolysis of methyltetrahydrofuran was distinctly affected by the nature of the support, we also varied the composition of the catalysts, choosing a fixed set of reaction conditions, using either unsupported platinum (platinum black and in some experiments also a platinum foil) or platinum supported on alumina, silica, or titania as catalysts.

Of further interest was studying the effect of the product CO on catalyst activity and selectivity. Therefore, in some experiments the catalysts were prepoisoned by CO. The results of these experiments shed some light on the mechanism of CO removal and methane formation on platinum catalysts.

2. EXPERIMENTAL

2.1. Catalysts

Platinum black, the well-characterized standard catalysts EUROPT-1 (6.3% Pt/SiO_2) and EUROPT-3 (0.3% Pt/Al_2O_3) (3, 4), and two platinum catalysts prepared by impregnation of SiO_2 (Aerosil 130, Degussa) and of TiO_2 (P-25, Degussa), were used in the experiments. The catalysts were characterized by measuring the uptake of H_2 and CO at room temperature in a conventional volumetric adsorption apparatus. The H/Pt and CO/Pt values were obtained by extrapolating the saturation range of the adsorption isotherms to zero pressure (Table 1). The differences of these values for EUROPT-1 and EUROPT-3 are discussed elsewhere (3, 4), for Pt/TiO_2 the high CO/Pt ratio may be due to adsorption of CO on titania. The catalysts were also characterized by TEM inspection (Zeiss EM 10C). However, in case of EUROPT-3 we were not able to resolve any platinum particles in the micrographs. Thus, for the calculation of TOF values we took the H/Pt value as dispersion. For platinum black the dispersion was estimated by the rate

Catalyst	Support	%Pt	H/Pt	CO/Pt	TEM, mean diameter/Å
EUROPT-1	Sorbosil AQ U30	6.3	1.02	0.6	18
Pt/Aerosil	Aerosil 130	5	0.56	0.46	21
EUROPT-3	Alumina CK 300	0.3	1.24	ND	ND
Pt/TiO$_2$	TiO$_2$ P-25	2.5	0.84	1.21	16
Pt black	Unsupported	100	ND	ND	ND

Note. ND, not determined.

of benzene hydrogenation at 323 K measured *in situ* on this catalyst. This reaction is agreed to exhibit rather low or no structure sensitivity (5, 6). Hence we assumed the TOF value of 0.032 sec^{-1}, measured on EUROPT-1 under the same conditions, to also be valid for platinum black. This estimation resulted in a dispersion of 0.01% for platinum black, corresponding to a specific surface area of 0.03 m^2/g.

Before every reaction the catalysts were pretreated by heating in oxygen at 673 K followed by reduction in H$_2$ at 673 K. Only with platinum black the pretreatment temperature was 523 K to avoid excessive sintering. Reduction of Pt/TiO$_2$ at 523 K instead of 673 K did not lead to a distinct change in the catalytic performance.

2.2. Catalytic Measurements

The catalytic measurements were performed either in a tubular flow reactor or in a recirculation batch reactor.

In the tubular flow reactor the influence of hydrogen partial pressure and of the reaction temperature on the activity and selectivity was investigated. The partial pressure of THF, or *n*-butanol, was held constant by using two saturators arranged in series, both held at 273 K in a stirred ice-water bath. Thus the partial pressure of THF was 74 mbar; that of butanol was only 1.3 mbar. The partial pressure of H$_2$ was adjusted by changing the H$_2$/He composition in the gas flow. The gas lines downstream of the saturator were held at 373 K to prevent condensation of any components.

The recirculation batch reactor was used to study the effects of self-poisoning of the freshly regenerated catalyst during the first minutes of time-on-stream. In this reactor also the effect of the support on the catalytic performance was studied. Since the contact time in this reactor can be varied over a wide range, catalysts of different activity could be compared in the same temperature window. The pressure of the reactants was 50 mbar in case of THF and 5 mbar in case of butanol. H$_2$ (and in some experiments also He) was added to attain atmospheric pressure.

In both reactors in control experiments the amount of catalyst was changed systematically verifying that no diffusion limitation are affecting the kinetic data. For all experiments high-grade hydrogen, helium (each 99.999%), and

oxygen (99.99%) were used, all of Messer-Griesheim. Hydrogen was purified by passing through an oxygen removing purifier (Matheson), and helium was passed through an Anoxy-Cil-unit. Both gases were further freed from condensable contaminants by nitrogen traps. Oxygen was passed through a trap cooled with liquid/solid ethanol to remove water vapor. Carbon monoxide (99%) was used as delivered; in some experiments it was passed through a reduced copper catalyst held at 473 K, in order to remove possible traces of oxygen.

The effluent stream from both reactors was analysed by on-line gas chromatography using a capillary column (dimethylsilicone) and FID detection. In separate experiments a GC system equipped with a thermoconductivity detector was used to monitor the amount of CO in the products.

2.3. FTIR Measurements

In order to detect possible reaction intermediates the IR spectra of a Pt/Aerosil pellet (mass thickness 25 μg/cm^2) were monitored in transmission by a FTIR spectrometer (Perkin Elmer System 2000). The stainless-steel IR cell could be heated to 673 K and the reaction mixtures could be recirculated by a membrane pump thus providing the recording of IR spectra under reaction conditions.

3. RESULTS

3.1. Product Distribution as a Function of Time

The conversion versus time behavior observed in the recirculation batch reactor showed a fast deactivation of the freshly pretreated EUROPT-1 catalyst immediately after the first contact with the reactants (Fig. 1). After this short initial period a stationary reaction regime and a nearly linear conversion-time behavior was observed. The proportion of *n*-butanol changed in a manner typical for intermediate products: after reaching a maximum the partial pressure decreased slowly according to the now slower overall reaction. At 473 K propane and butane were formed with nearly the same selectivity, but at longer reaction times the product distribution was shifted to more propane and CO formation (Fig. 1). In this reactor the product CO remains in the reaction system, but is not found in the product analysis, presumably due to its adsorption on the catalyst. Furthermore, at temperatures lower than 473 K only traces of methane were formed during the reaction. Only at reaction temperatures higher than 473 K does the ratio of methane to propane approximate to unity.

3.2. Effect of Reaction Temperature

The effect of temperature on the activity and selectivity in the stationary reaction regime was studied in the tubular flow reactor. With EUROPT-1 as well as with Pt/Aerosil only at temperatures above 423 K were measurable conversions observed. At these low temperatures (and, of
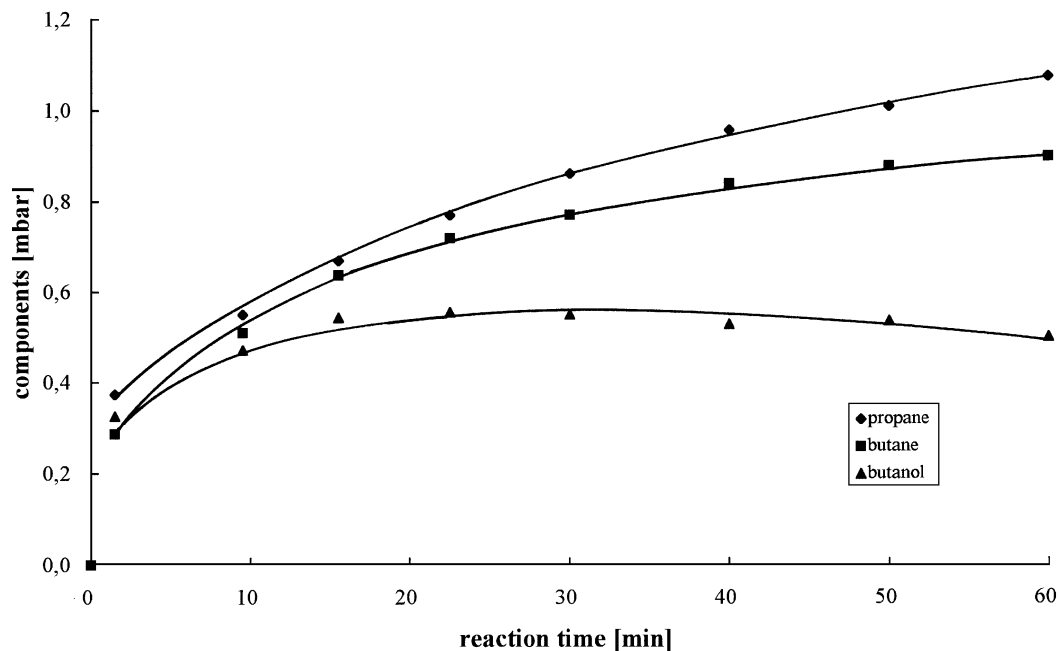
FIG. 1. Evolution of products on EUROPT-1 as a function of reaction time. Experiments performed in the recirculation reactor with 50 mbar THF and 950 H_2 at 473 K on 25 mg EUROPT-1.

course, low conversions) a high proportion of the primary product *n*-butanol was found in the reaction mixture (Fig. 2). In addition to the final products propane and butane traces of butyl ether were formed, presumably due to a side reaction of the intermediate product butanol. In the tubular flow reactor the product distribution was shifted to more butane formation compared to the recirculation batch reactor.
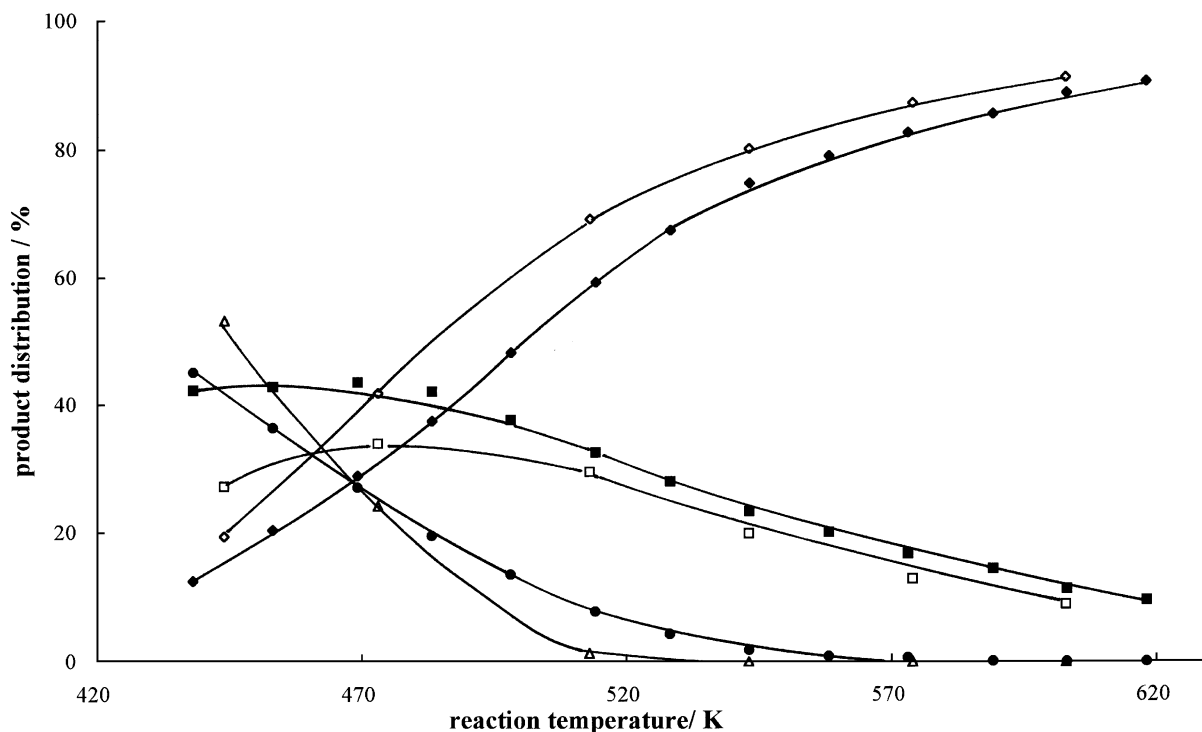

FIG. 2. Product distribution of the reaction (a) of THF and (b) of butanol with H_2 on EUROPT-1 as a function of reaction temperature. (a) Closed symbols: ◆, propane; ■, butane; ●, butanol. (b) Open symbols: ◇, propane; □, butane; △, butylether. (Space time of 1 sec, experiments performed in the tubular flow reactor).

With increasing temperature the rate of reaction increased according to Arrhenius' equation, corresponding to an activation energy of about 75 kJ/mol. As expected, due to the higher overall conversion, the proportion of the primary product *n*-butanol decreased with increasing reaction temperatures. More distinctly the product distribution was shifted toward more propane formation at the higher temperature (Fig. 2).

When butanol was used as a reactant, the proportion of propane and butane showed the same temperature dependence as with THF (Fig. 2). However, due to the higher partial pressure of butanol more butyl ether was formed, at least at low temperatures and therefore low conversions. Butyl ether behaved like an intermediate product, i.e., at longer reaction times it reacted to either butane or propane. In a control experiment performed in the recirculation batch reactor, butanal was used as reactant. At short reaction times the main product was butanol. The further reaction course was the same as with THF or butanol, i.e. after attainment of butanol/butanal equilibrium the butane/propane ratio was independent of the reactant used. However, during the initial time of butanal reaction a much higher propane proportion was observed than in a similar *n*-butanol experiment.

3.3. Effect of Hydrogen Partial Pressure

The influence of hydrogen partial pressure was studied with EUROPT-1 at a reaction temperature of 423 K. When the hydrogen partial pressure was decreased from 990 to 250 mbar the reaction rate increased by a factor of 1.5. Further reduction of the hydrogen partial pressure to 80 mbar caused a further 10% increase of activity. Thus the reaction order versus hydrogen is slightly negative.

Simultaneously, the product ratio of propane to butane was shifted to higher propane formation by a factor of 2 at 200 mbar hydrogen pressure and of 2.5 at 80 mbar hydrogen pressure, if compared to the ratio obtained with 950 mbar H_2.

3.4. Effect of CO Prepoisoning

Since CO most likely causes the deactivation during the first contact between the reaction mixture and the catalyst, we conducted reaction runs with CO-prepoisoned catalysts. For this purpose the freshly regenerated catalyst was recirculated with a mixture of CO in 1 bar of H_2. The amount of CO in this mixture was chosen equivalent to either 0.5, 1, or 2 monolayers precoverage of CO. In the last case in addition to the amount of CO adsorbed at the Pt surface the same amount of CO remained in the gas phase inside the reactor. The reactor was then isolated from the recirculation system, the reactants were premixed in the recirculation cycle and then admitted to the prepoisoned catalyst system. Figure 3 shows the conversion vs reaction time for these prepoisoning experiments at the relatively low temperature of 423 K. In this diagram, the conversion is related to the number of surface platinum atoms and we used therefore the term "turnover" for the ordinate axis. If the stationary conversion of the unpoisoned reaction (Fig. 3a)
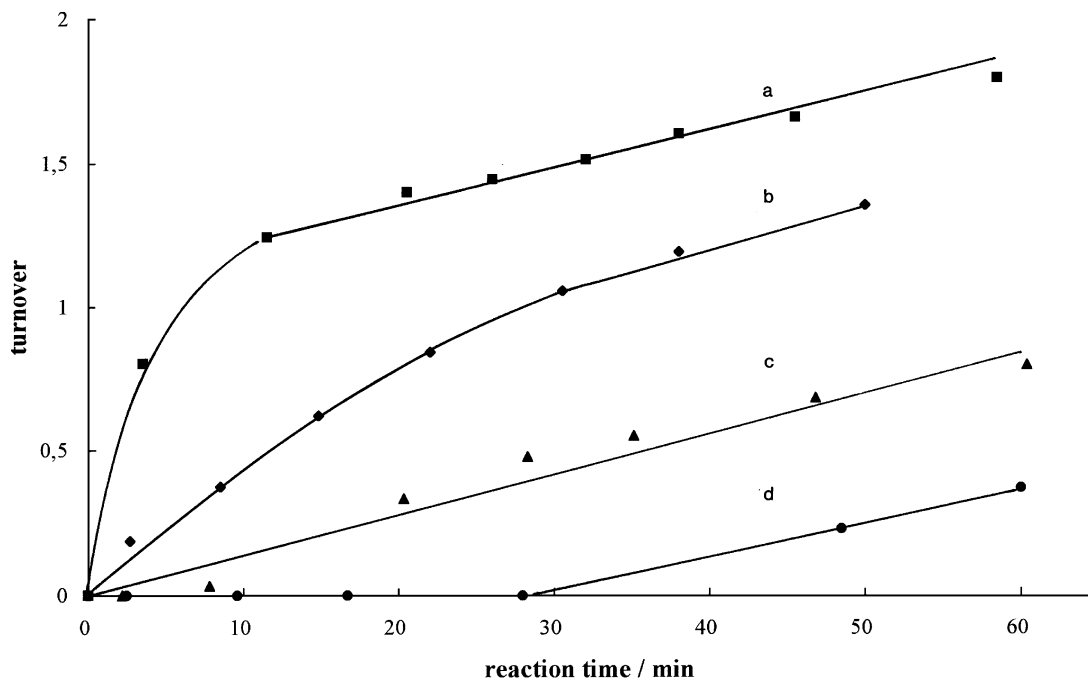

FIG. 3. Conversion correlated to the number of surface Pt atoms (turnover) at 423 K as a function of reaction time on EUROPT-1 after different dosages of CO: (a) freshly activated, and prepoisoned corresponding to (b) 0.5, (c) 1, and (d) 2 monolayers.

is extrapolated to zero reaction time, the intercept of about 1.2 THF molecules resembles the turnover during the initial period of the reaction. Thus in this period the surface of platinum reacts rather stoichiometrically than catalytically. Considering the selectivity of the reaction toward propane (and of course CO), the amount of CO formed in the initial high activity period is about 0.4 molecules per surface platinum atom.

When the catalyst was prepoisoned by half a monolayer of CO, the initial high activity period has disappeared resulting in a conversion time plot starting nearly linear from the origin. The slope of this plot is about the same as that of the stationary unpoisoned reaction. Additionally, due to the prepoisoning the proportion of propane on the final products at 423 K is shifted from about 35% for the unpoisoned reaction to about 40% for the poisoned reaction.

When the catalysts were prepoisoned by more than half a monolayer of CO the onset of product formation is delayed up to 30 min (with an amount of CO corresponding to two monolayers). During this time interval the catalyst obviously regains some of its activity, presumably by removal of CO from the platinum surface. However, analysis of the reactant gases proved that no methane is formed during this time interval. Finally, the steady-state activity with these catalysts was again nearly the same as that of the unpoisoned catalyst.

3.5. Effect of the Nature of the Support

The kind of the support used had a strong effect on the distribution of the final products. On unsupported platinum (platinum black or platinum foil) propane and butane were formed in a ratio of about 2:1 only in the initial period, when the catalyst was not yet poisoned by product CO. In the stationary reaction regime no butane formation could be detected at all, and the propane selectivity reached almost 100%.

On the EUROPT-1 catalyst both final products were formed. Again the butane selectivity was higher in the initial period of reaction than in the stationary reaction regime, where, on the other hand, the proportion of butane depended on reaction temperature, decreasing from 83% at 423 K to 60% at 473 K, 42% at 523 K, and 38% at 573 K (Table 2). Almost the same product distribution was obtained with the Aerosil-supported catalyst.

On the alumina-supported platinum (EUROPT-3) the butane proportion in the final products was slightly higher than on the silica supported catalyst, namely 86% at 423 K, 75% at 473 K, 69% at 523 K, and 62% at 573 K.

When titania was used as the support, the product distribution was distinctly shifted to almost selective butane formation. The selectivity of butane in the final products ranged from 99% at 423 K to 94% at 473 K and 87% at 523 K.

TABLE 2

Activity and Selectivity of the Hydrogenolysis of Tetrahydrofuran in the Stationary Reaction Regime

Catalyst	TOF*1000 (sec^{-1}) at 423 K	Percentage of butane on final products at			
		423 K	473 K	523 K	573 K
EUROPT-1	1	83	60	42	38
Pt/Aerosil	0.8	84	ND	ND	ND
EUROPT-3	2.5	86	75	69	62
Pt/TiO$_2$	5.7	99	94	87	ND
Pt black	0.02 at 453 K	ND	<1	<1	<1

Note. ND, not determined.

Since the catalysts lose a substantial part of their catalytic activity during the first minutes on stream, it is difficult to define a proper measure of activity. The TOF values given in Table 2 are calculated from the differential conversion in the stationary reaction regime, when the conversion was approximately 10%, and the number of exposed platinum atoms in the catalyst. On platinum black at 423 K the rate of reaction was too small for determining TOF values. Therefore, the rate at 453 K was given for comparison. As is seen from Table 2, the catalytic activity decreases in the order Pt/TiO$_2$ > Pt/Al$_2$O$_3$ > Pt/SiO$_2$ ≫ Pt black; i.e., the catalyst with higher activity also exhibits a higher selectivity for butane formation.

3.6. In Situ FTIR Spectroscopy

During cycling of a THF/H$_2$ mixture through the IR cell the formation of a C–O vibration peak was monitored in the IR spectra (Fig. 4). The onset of CO formation was at about 353 K; that is at a far lower temperature than the onset of reaction in the catalytic reactor. The first appearance of CO was characterized by a wavenumber of 2046 cm^{-1} that was shifted to higher wavenumbers upon higher CO coverage until a final wavenumber of 2064 cm^{-1} was reached, when the CO coverage attained a stationary value (at 373 and 383 K). This shift to higher wavenumbers with increasing CO coverage is due to increased dipole–dipole coupling in the more compressed CO layer (7, 8). The CO frequency at saturation is lower than the CO wavenumber observed from adsorption of pure CO. However, H$_2$ and THF are certainly also adsorbed on the platinum thereby diluting the CO layer and weakening the dipole–dipole interaction.

The integrated absorbance of the CO peak is shown in Fig. 5 as a function of time for different reaction temperatures. The initial rate of CO formation increases with increasing temperature corresponding to an activation energy of 110 kJ/mol.

At longer reaction times the CO peak area became constant. At the two higher reaction temperatures (373 and 383 K) the measured peak area was about the same; i.e., a
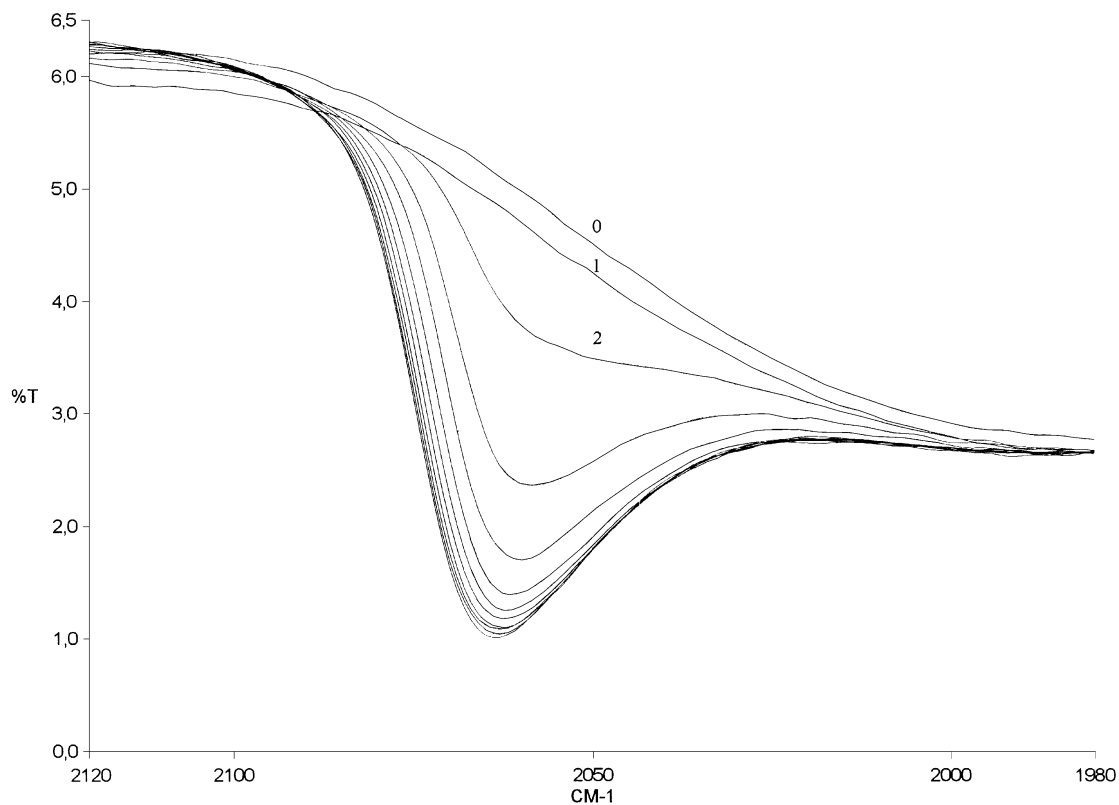
FIG. 4. IR spectra before (0 min) and after admission of THF in H_2 to Pt/Aerosil at 373 K after increasing contact times. Spectra were taken in a time interval of 1 min, the first two spectra after admission are indicated, the others follow the trend of that after 1 and 2 min after admission.
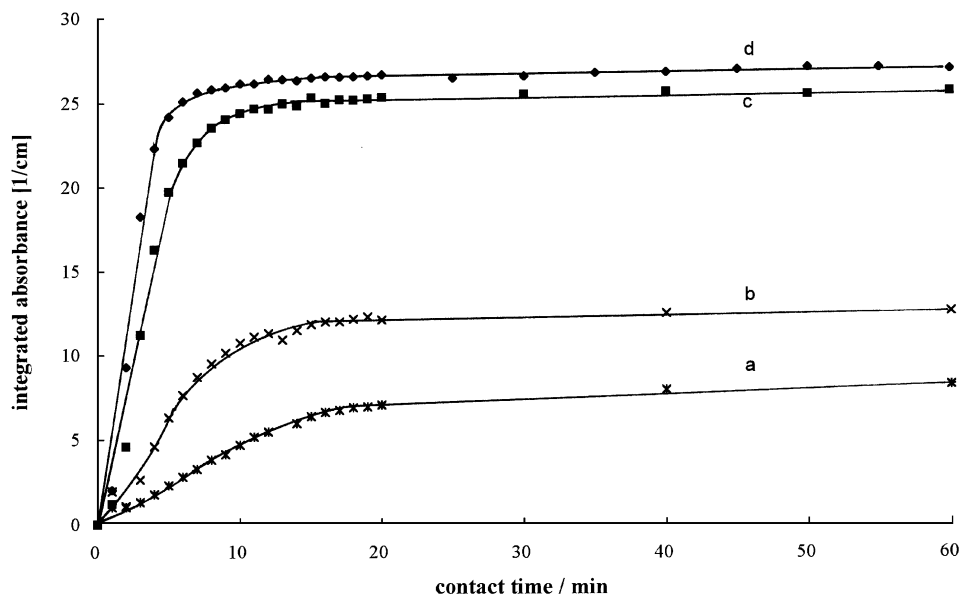

FIG. 5. Integrated absorbance of the CO peak obtained after admission of THF $+ H_2$ to Pt/Aerosil as a function of contact time at a temperature of (a) 353 K, (b) 363 K, (c) 373 K, and (d) 383 K.

CO coverage limit was reached at these temperatures (see Fig. 5).

The coverage necessary to inhibit the further reaction can be estimated from the stationary IR absorbance, when it is compared with that obtained for CO saturation adsorption. After saturation of the surface area with pure CO and evacuation of the gas phase the resulting integrated CO absorption is about twice that of the final CO absorbance obtained in the tetrahydrofuran hydrogenolysis experiments at 373 and 383 K.

The CO adsorption stoichiometry is reported to be $CO : Pt_s = 1 : 1$ for EUROPT-1 (9), when CO pressure is extrapolated to zero. Thus from the ratio of the integrated adsorbance the stationary CO coverage during THF hydrogenolysis at 373 and 383 K is roughly 0.5 monolayers. About the same CO coverage is found in the prepoisoning experiments to suppress the initial reaction regime of high activity.

On the other hand, at the lower reaction temperatures (353 and 363 K) the stationary CO coverage was lower than this threshold coverage (Fig. 5). At 353 and 363 K the stationary CO coverage was only about 32 and 47%, respectively, of that at 383 K, corresponding to CO coverages of 0.16 and 0.24 monolayers of CO, respectively. When after establishing the stationary CO coverage at 353 K (0.16 monolayers) the catalyst was heated to 363 K, the CO coverage increased to 0.24 monolayers, i.e., to the stationary value obtained in the 363 K run. Further heating to 373 K caused again an increase in the CO coverage up to the 0.5 monolayer coverage obtained at this temperature.

4. DISCUSSION

4.1. Reaction Mechanism

The primary reaction product of the hydrogenolysis of THF was *n*-butanol, but the secondary products butane and propane were formed immediately after admission of the educts to the reactor. However, CO was formed already at 353 K, as shown by FTIR measurements, proving that on the unpoisoned catalyst the reaction starts at far lower temperatures than on the working catalyst. The apparent activation energy for CO formation in this low temperature region is 110 kJ/mol, that is a much higher value than that obtained for the overall reaction in the stationary regime (75 kJ/mol). However, since the selectivity toward propane and CO increases with increasing temperature, the activation energy for CO formation has to be higher than that of the overall reaction.

The primary products butanol and butanal are equilibrated rapidly. When they are used as educts, they yield nearly the same distribution of final products as THF. However, during the initial period of reaction of butanal, when the proportion of butanal may exceed that of the equilibrium composition, a higher proportion of propane is ob-
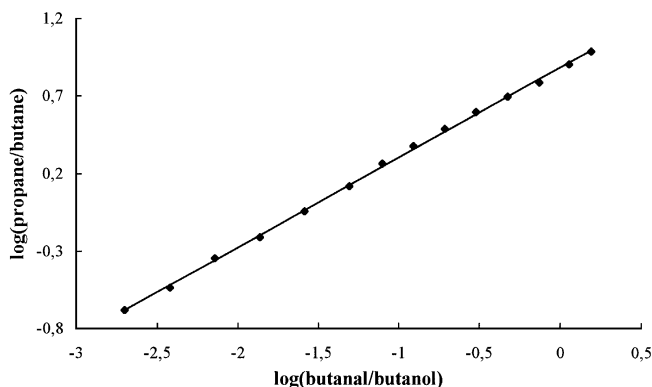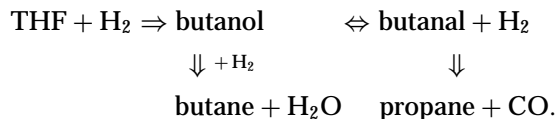

FIG. 6. Double log plot of the product ratio propane/butane, obtained on EUROPT-1 with a hydrogen pressure of 950 mbar and at a space time of 1 sec, versus the equilibrium composition ratio of butanal/butanol at the same temperature.

tained. This result indicates that butanal is a precursor for the decarbonylation to propane. This assumption is supported by the effect of the temperature and of the hydrogen pressure on the selectivity of the final products, since the equilibrium between butanal and butanol is shifted toward more butanal at the higher temperature and the lower hydrogen pressure.

To prove this assumption we plotted the propane/butane ratio obtained with EUROPT-1 against the equilibrium ratio butanal/butanol at the given hydrogen pressure and temperature in a double logarithmic plot (Fig. 6). The rather good linear correlation supports our assumption, the slope of 0.58 indicates, however, that the reaction orders versus butanol and butanal differ from each other. From these considerations the scheme of the reaction can be drawn as

$$THF + H_2 \Rightarrow butanol \quad \Leftrightarrow butanal + H_2$$
$$\Downarrow + H_2 \qquad\qquad \Downarrow$$
$$butane + H_2O \quad propane + CO.$$

In the stationary reaction regime the removal of CO from the surface is most likely the rate limiting step. The apparent activation energy obtained from the results of the flow reactor is 75 kJ/mol, at least for the silica supported catalysts. The integral heat of CO adsorption on Pt/SiO_2 is reported to be about 125 kJ/mol (10).

However, these results are not contradictory for the following reasons: (i) During the reaction the CO coverage is about one-half of a monolayer and the differential heat of adsorption at this coverage may be lower than the integral heat of adsorption. (ii) The presence of excess THF and hydrogen lowers the heat necessary to remove the CO from the surface due to their competitive adsorption. (iii) At higher temperatures the selectivity of THF hydrogenolysis is shifted to more propane due to the shift in the butanal/butanol ratio. Thus, at higher temperatures the

degree of poisoning by CO increases, which in turn retards the activity increase with increasing temperature and leads to a smaller apparent activation energy.

4.2. Support Effect on the THF Hydrogenolysis

For the initial reaction period on the fresh catalysts as well as for the stationary reaction regime the catalytic activity decreased in the series $Pt/TiO_2 > Pt/Al_2O_3 > Pt/SiO_2 \gg Pt$ black. The same sequence of catalytic activity was obtained by Vannice (11) for the CO hydrogenation. This indicates again that the rate-limiting step in the THF hydrogenolysis is the removal of CO from the working catalyst by reaction with H_2. However, in contrast to the methanation reaction of CO in the THF hydrogenolysis only small traces of methane were found in the gas phase, at least at reaction temperatures below 473 K. This is in accordance with the finding that the methanation of CO on platinum requires reaction temperatures higher than 473 K (12). At the lower temperatures the product CO is apparently removed from the platinum surface by a mechanism different from methanation, as will be discussed in the next paragraph.

The distribution of the products changes from a nearly selective propane formation on platinum black to an almost selective butane formation on titania supported platinum. Platinum supported by silica or alumina gives an intermediate product distribution. The high selectivity of Pt/TiO_2 catalysts toward butane formation may be caused by the high ability of adlineation sites on the Pt/TiO_2 interface to activate C–O bonds (13). On Pt/TiO_2 butanol is transformed from the butanol/butanal intermediate mixture at such a high rate that nearly no propane formation takes place. On the other hand, the absence of butane formation on platinum black together with the rather low overall activity indicates that the presence of a phase boundary platinum support is necessary for the C–O bond scission in the THF as well as in the butanol molecule. Therefore, we conclude that also on Pt/silica and Pt/alumina the C–O bond scission occurs at the phase boundary platinum/support, but with a lower rate than on Pt/TiO_2.

The higher CO selectivity obtained on the unsupported platinum causes an additional decrease of the overall activity due to CO poisoning. Furthermore, the lower methanation activity of this catalyst decreases again the rate of CO removal from the platinum surface, at least at temperatures above 473 K.

4.3. Effect of CO Poisoning on Selectivity

If the reaction is conducted below 423 K the product CO inhibits the further propagation of reaction. The CO coverage necessary for complete poisoning is about 0.5 monolayers at 373 and 383 K. The lower coverages obtained to inhibit reaction at 363 and 353 K are most likely due to additional competitive adsorption of THF at that low temperature.

Above 423 K the self poisoning by product CO causes a distinct loss in activity and a shift in selectivity toward more propane formation. CO prepoisoning of the catalysts shifts the selectivity in the same direction. The fact that in the recirculated batch reactor the products contain more propane, can also be explained by a higher CO content in the reaction gases because of its accumulation. Obviously, the product CO poisons the butanol deoxygenation more strongly than the butanal decarbonylation. This seems paradoxical, since CO is formed in the butanal decarbonylation and one should assume that CO inhibits mainly the sites where it is formed. However, in an earlier work (14) we could show that CO poisoning causes a shift in the selectivity of methylcyclopentane hydrogenolysis toward hexane formation. In turn, the hexane formation from methylcyclopentane is shown to occur selectively at the phase boundary platinum support (15). From this work it must be concluded that the adsorption of CO is stronger at the phase boundary sites and therefore causes a suppression of C–O bond scission in the present reaction. Hence, the effect of CO poisoning on the product distribution supports the assumption that the C–O bond scission occurs mainly on the phase boundary platinum support.

4.4. The Fate of Carbon Monoxide

The FTIR spectra taken under the same conditions as in the recirculation batch reactor demonstrate that on the unpoisoned Pt/SiO_2 catalyst CO is formed from THF already at temperatures far below those where measurable conversions are detected in the recirculation batch reactor. Since CO emerges in the reaction scheme as a final product, the formation of CO proves that on the unpoisoned catalyst the ringopening of THF as well as the decarbonylation of butanal proceeds even at 353 K, at least in the adsorbed phase.

The product CO formed at these low temperature inhibits the propagation of the reaction completely. Above 423 K the overall reaction can propagate and thus CO must be partially displaced from the surface. Nevertheless, up to 473 K no methane is found in the products. Moreover, after prepoisoning with excess CO the reaction starts after an induction period, the duration of which increases with the degree of CO prepoisoning. Also in this induction period no methane is found in the reaction mixture.

A reasonable sink for the product CO is the support surface. For platinum supported by titania as well as by alumina, a spillover of hydrogenated CO species from the platinum to the support has been reported by Falconer and co-workers (16, 17). The authors report that the formation of these CH_3O species starts at 385 K. This is in agreement with Robbins and Marucchi-Soos (18), who obtained a similar support-bonded species upon exposing the catalyst to a CO/H_2 mixture at 400 K. This temperature is very close to the onset temperature for the THF hydrogenolysis. The

formation of this CH_3O species occurs either on the platinum surface followed by a spillover to the support, or at first a spillover of CO and H occurs to the support where the reaction to the final product takes place. Obviously the adsorption capacity of the support surface is sufficient to accumulate the CO formed from a prepoisoning of the platinum surface equivalent to two monolayers coverage, or, in turn, the CO formed during one run in the recirculation system.

At temperatures above 473 K methane is found in the reaction products. At this temperature the CH_3O species starts to be hydrogenated by spilled over hydrogen. This result is in agreement with temperature-programmed reaction data (17, 18), who report the formation of methane at 490 K. Thus, above 473 K the product CO is transformed to methane and the mass balance in the reactor is again established.

5. CONCLUSIONS

In a primary reaction step of the hydrogenolysis of THF the five-membered ring is opened exclusively by breaking a C–O bond. The primary product butanol can undergo two different reaction pathways: (i) by a second C–O scission it is transformed to butane and water, or (ii) it reacts via butanal to propane and CO. On a given catalyst the product ratio butane to propane changes with temperature and hydrogen pressure in the same direction as does the equilibrium composition of butanol and butanal.

The support material has a strong effect on the reaction rate and on the selectivity. From the extremely low reaction rate found on platinum black we conclude, that for the C–O bond scission platinum sites adjacent to the support are necessary. From the support effect on the rate and on the selectivity it is deduced that the activity of the phase boundary for breaking the C–O bond increases in the series $Pt/SiO_2 < Pt/Al_2O_3 \ll Pt/TiO_2$. Particularly the platinum titania phase boundary forms excellent catalytic sites not only for the hydrogenation of CO, aldehydes and ketones (13),

but also for the scission of the single bond between carbon and oxygen.

Due to the production of CO the platinum surface is CO poisoned soon after the admission of the reaction mixture. In addition to the loss in activity, CO poisoning causes also a shift in the selectivity toward propane formation. The reason for this selectivity shift is the stronger adsorption of CO at the phase boundary than on the platinum surface, causing a stronger deactivation of the C–O bond scission sites compared with that of the CO abstraction sites.

From FTIR it is seen that the reaction starts already at 353 K, but is completely inhibited after the buildup of a distinct CO coverage. Above 423 K CO is removed from the platinum due to the formation of a hydrogenated CO species bound to the support and the reaction can further propagate. Finally, above 473 K CO is converted to methane and the mass balance of the reaction is established.

REFERENCES

1. Gennari, U., Kramer, R., and Gruber, H. L., *Appl. Catal.* **11**, 341 (1984).
2. Gennari, U., Kramer, R., and Gruber, H. L., *Appl. Catal.* **44**, 239 (1988).
3. Bond, G. C., and Wells, P. B., *Appl. Catal.* **18**, 221 (1985), and subsequent four papers.
4. Bond, G. C., *J. Mol. Catal.* **81**, 99 (1993).
5. Dorling, T. A., and Moss, R. L., *J. Catal.* **5**, 111 (1966).
6. Flores, A. F., Burwell, R. L., Jr., and Butt, J. B., *J. Chem. Soc. Faraday Trans.* **88**, 1191 (1992).
7. Eischens, R. P., and Pliskin, W. A., *Adv. Catal.* **10**, 1 (1958).
8. Stoop, F., Toolenaar, F. J. C. M., and Ponec, V., *J. Catal.* **73**, 50 (1982).
9. Wells, P. B., *Appl. Catal.* **18**, 259 (1985).
10. Sen, B., and Vannice, M. A., *J. Catal.* **130**, 9 (1991).
11. Vannice, M. A., *J. Mol. Catal.* **59**, 165 (1990).
12. Vannice, M. A., and Sudhakar, C., *J. Phys. Chem.* **88**, 2429 (1984).
13. Vannice, M. A., *Catal. Today* **12**, 255 (1992).
14. Kramer, R., Fischbacher, M., and Gruber, H. L., *Appl. Catal.* **42**, 337 (1988).
15. Kramer, R., and Zuegg, H., *J. Catal.* **80**, 446 (1983).
16. Mao, T. F., and Falconer, J. L., *J. Catal.* **123**, 443 (1990).
17. Flesner, R. L., and Falconer, J. L., *J. Catal.* **139**, 421 (1993).
18. Robbins, J. L., and Marucchi-Soos, E., *J. Phys. Chem.* **93**, 2885 (1989).