Ethane and Propane Hydrogenolysis on Ru Catalysts

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The hydrogenolysis of ethane and propane has been investigated on ruthenium catalysts and a detailed kinetic study is reported.

Activation energies ranging from 70 to 170 kJ mol⁻¹, positive orders of reaction with respect to the hydrocarbon and negative orders with respect to hydrogen were generally found. No direct correlation between the catalytic activity and the metal particle size seems to exist. However, the apparent activation energies and pre-exponential factors increased with increasing ruthenium dispersion. This agrees with the concept that hydrogenolysis reactions are structure-sensitive reactions.

Hydrogenolysis reactions of hydrocarbons on metal catalysts have been studied extensively. It is generally accepted that the hydrogenolysis of ethane and propane is a structure-sensitive reaction. Different reaction mechanisms and intermediates have been proposed and extensive reviews exist in the literature.^{1, 2}

The demanding nature of these reactions makes them useful for probing catalytically active surface sites, especially in the case of bimetallic systems consisting of both an active and an inactive metal component. A typical example is a combination of a Group VIII metal, which is active for the hydrogenolysis, and an inactive Group IB metal.

This approach has been used previously to investigate bimetallic Ru–Au catalysts.^{3, 4} Striking differences in the behaviour of the catalysts were observed in terms of surface composition, bimetallic cluster formation and catalytic activity, by using either SiO₂ or MgO as support. It was also found that monometallic Ru/SiO₂ behaved differently compared with Ru/MgO.³⁻⁵ Therefore it seemed important to perform an extensive investigation on several ruthenium catalysts with the objective of exploring whether parameters such as metal–support interactions, preparation method and metal dispersion can influence the hydrogenolysis activity of ruthenium.

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EXPERIMENTAL

Supported ruthenium was prepared according to the following methods.

(a) The support was impregnated (by the incipient wetness method for all supports except MgO, which was soaked in an excess volume of liquid) with a solution of $\operatorname{RuCl}_3 \cdot \operatorname{H}_2O$ (Rudi-Pont reagent grade) followed by drying at 110 °C for 4 h. The catalysts were then reduced in flowing hydrogen at 400 °C for 2 h.

(b) A solution of $Ru [(CH_3 - CO)_2 CH]_3$ in toluene was heated with the support under reflux for 2 h. The toluene was removed by filtering and the catalyst precursor was washed with toluene until the washings were clear. The red solid obtained was dried under vacuum at 110 °C and reduced in flowing H₂ at 400 °C for 2 h.

(c) $Ru_3(CO)_{12}$ in toluene was treated with the support as in method (b). The resulting greyish-brown solid was dried at 110 °C under vacuum and reduced in flowing H₂ at 400 °C for 2 h.

The supports were commercial SiO₂ (surface area 680 m² g), Al₂O₃ (surface area 160 m² g⁻¹) and MgO (surface area 15 m² g⁻¹). The MgO–CaO support (surface area 94 m² g⁻¹) was prepared by coprecipitation of MgCl₂ and CaCl₂ by (NH₄)₂ CO₃, followed by decomposition at 600 °C. The unsupported ruthenium was a commercial Ru sponge (Baker).

A summary of the Ru catalysts studied is reported in table 1. More details concerning the physico-chemical characterization of the samples $3.0 \text{ wt} \% \text{ Ru/SiO}_2$, $2.9 \text{ wt} \% \text{ Ru/Al}_2\text{O}_3$ and $3.1 \text{ wt} \% \text{ Ru/SiO}_2\text{-Al}_2\text{O}_3$ have been previously reported.⁶ The characterization of the samples 4.44 wt % Ru/MgO and $3.86 \text{ wt} \% \text{ Ru/SiO}_2$ are reported in ref. (3) and (7).

Ru (wt %)	support	particle size (chemisorption)/Å	Ru exposed (%)	preparation method
3.86	SiO ₂	34	26	a
3.00	SiO ₂	22	43	а
2.9	$Al_2 \tilde{O}_3$	34	26	а
1.16	Al_2O_3	14	66	b
0.69	Al_2O_3	13	72	С
3.1	SiO ₂ –Al ₂ O ₃	28	33	а
4.44	MgO	129	7.1	а
5.38	MgO	16	60	С
4.13	CaO-MgO	21	44	С
100		1000	0.09	

TABLE	1 -PREPARATION	AND CHA	RACTERIZATION	OF 9	SUPPORTED	Rıı	CATAL VSTS
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 O_2 chemisorption experiments to determine the percentage of Ru exposed on the surface were performed at room temperature in a flow system using the pulse technique with a thermal conductivity detector.

The surface area of the unsupported Ru sample was determined by H₂ chemisorption at room temperature in a static system. The stoichiometries of chemisorption used were: $Ru/O = \frac{1}{2}$ and Ru/H = 1.

The rate of ethane and propane hydrogenolysis was followed in a flow system employing a tubular reactor at atmospheric pressure using helium as diluent. Prepurified hydrogen was passed through Pd asbestos (400 °C) and a molecular sieve trap at liquid-nitrogen temperature. Ultra-high purity He was passed through an oxytrap (Alltech) at room temperature followed by a molecular sieve trap at liquid-nitrogen temperature. Ethane and propane (CP grade) were used without further purification. The reactor, of Pyrex glass, was filled with 50-500 mg of catalyst diluted with 0.3 g of ground Pyrex glass. The reactant mixture was fed to the reactor after passing a preheating section. The reactants and products were analysed by a gas chromatograph (HP model 5750 with flame detector) connected directly to the flow system and employing a column filled with silica gel (100-120 mesh).

Since preliminary runs showed a decrease of activity with time the following procedure was used to measure the initial rates. The reactant gases were passed over the catalyst for 2 min prior to sampling the products for analysis. The hydrocarbon and helium were then cut out and the hydrogen flow continued for 15 min prior to another reaction period. After 4 or 5 runs the catalyst was treated at 350 °C in flowing H₂ for 15 min and cooled at the reaction temperature in H₂ before another series of experiments was undertaken.

Reaction rates were determined at a partial pressure of hydrocarbon between 1 and 10 kPa and of hydrogen between 10 and 50 kPa. The temperature was varied between 120 and 260 °C. Within the range of flow rates investigated the reaction rates were found to be independent of the gas flow rate, indicating the absence of external mass transfer limitations. Absence of diffusional limitations within the catalyst pellets was verified by calculations based on the criteria developed by Weisz.⁸ The conversion was kept low (< 5%) throughout the experiments in order to operate under differential conditions.

RESULTS

PROPANE HYDROGENOLYSIS

Rates, V, were calculated from the expression:

$$V$$
/molecule s⁻¹ (Ru surface atom)⁻¹ = (F/A_s) α

where F is the feed rate of propane or ethane, A_s is the number of Ru surface atoms (by chemisorption) and α is the fraction of consumed hydrocarbon.

The catalyst pretreatment, before kinetic measurements, included an *in situ* reduction in flowing hydrogen at 400 °C for 2 h.

Under our experimental conditions, the propane hydrogenolysis led to a products ratio $CH_4/C_2H_6 > 1$. This indicates that two reactions took place:

$$C_3H_8 + 2H_2 \rightarrow 3CH_4 \tag{1}$$

$$C_3H_8 + H_2 \rightarrow CH_4 + C_2H_6. \tag{2}$$

The selectivity to C_2H_6 was calculated by the expression:

$$S = \frac{V_{\rm p2}}{V_{\rm p1} + V_{\rm p2}} = \frac{V_{\rm p2}}{V_{\rm p}} \tag{3}$$

where V_{p1} and V_{p2} are the rates of propane hydrogenolysis according to reactions (1) and (2), respectively.

The influence of temperature on the reaction rates was studied at a partial pressure of H₂ of 20.0 kPa and of propane of 3.0 kPa. The plot of log V against 1/T of all but two samples (namely, 4.44 wt % Ru/MgO and unsupported Ru) gave a straight line for V_{p1} , V_{p2} and V_p (V_p is the rate of the total disappearance of propane). A typical plot is reported in fig. 1. From the slope of this and other similar plots

A typical plot is reported in fig. 1. From the slope of this and other similar plots the apparent activation energies have been calculated and are reported in table 2. The activation energy of reaction (1) is always higher than that of reaction (2), resulting in a general decrease in the selectivity S with temperature. Samples 4.44 wt % Ru/MgO and unsupported Ru behaved in a quite different manner. Fig. 2 and 3 show the effect of the temperature on the reaction rates for these two samples. For the total disappearance of propane an activation energy of 75 and 88 kJ mol⁻¹ was found on 4.44 wt % Ru/MgO and unsupported Ru, respectively. These values are significantly lower than those for the other samples. Furthermore, at temperatures > 145-150 °C



Fig. 1.—Arrhenius plot for propane hydrogenolysis on the 3.86 wt % Ru/SiO₂ sample. $p_{H_2} = 20.0$ kPa, $p_{C_3H_3} = 3.0$ kPa; \Box , V_{p1} ; \triangle , V_{p2} ; \bigcirc , V_p .



FIG. 2.—Arrhenius plot for propane hydrogenolysis on the 4.44 wt % Ru/MgO sample. $p_{H_1} = 20.0$ kPa, $p_{C_3H_8} = 3.0$ kPa; \Box , V_{p1} ; \bigcirc , V_{p2} ; \triangle , V_p .

the amount of ethane formed on 4.44 wt % Ru/MgO and on unsupported Ru levelled off.

The rates of reaction and the selectivity for all catalysts are compared at 160 $^{\circ}$ C in table 2.

The SiO_2 -supported samples had, in terms of the overall reaction rate, V_p , the

Ru (wt %)	support	Ru exposed (%)	reaction ^a	E /kJ mol ⁻¹	temperature range/°C	V at 160 °C /molecule s ⁻¹ (Ru surface atom) ⁻¹	S at 160 °C (%)
3.86	SiO	26	1	196	119-157	2.8×10^{-2}	87
	2		2	109		18.9×10^{-2}	
			Т	113		21.7×10^{-2}	
3.00	SiO,	43	1	167	131-148	2.1×10^{-2}	93
	4		2	125		25.9×10^{-2}	
			Т	125		28.0×10^{-2}	
1.16	Al ₂ O ₃	66	1	184	173-229	1.3×10^{-4}	96
	2 0		2	130		3.3×10^{-3}	
			Т	142		3.4×10^{-3}	
0.69	Al ₂ O ₃	72	1	201	150-188	1.0×10^{-4}	99
	2 0		2	134		4.4×10^{-3}	
			Т	134		4.5×10^{-3}	
2.90	Al ₂ O ₃	26	1	159	126-180	5.3×10^{-4}	85
	• •		2	105		3.1×10^{-3}	
			Т	104		3.6×10^{-3}	
3.10	SiO ₂ -Al ₂ O ₂	33	1	188	151-212	1.4×10^{-5}	99
			2	109		1.5×10^{-3}	
			Т	109		1.5×10^{-3}	
4.13	CaO-MgO	44	1	180	153-195	1.1×10^{-3}	88
	-		2	130		8.2×10^{-3}	
			Т	142		9.3×10^{-3}	
4.44	MgO	7.1	1		145-200	3.3×10^{-3}	38
	-		2			$2.0 imes 10^{-3}$	
			Т	75		5.3×10^{-3}	
100		0.09	1		120-200	5.2×10^{-3}	47
			2			4.5×10^{-3}	
			Т	88		9.7×10^{-3}	

TABLE 2.—ACTIVATION ENERGY, E_a , CATALYTIC ACTIVITY, V, and selectivity, S, for the hydrogenolysis of propane on supported Ru catalysts

^{*a*} T = reaction (1) + reaction (2).

highest activities followed by unsupported ruthenium, ruthenium supported on CaO-MgO, MgO and Al_2O_3 and finally by SiO_2/Al_2O_3 , which was the least active. Under the experimental conditions used, C_2H_6 was the main product in the

hydrogenolysis of propane, with the exception of 4.44 wt % Ru/MgO and unsupported Ru, on which the selectivity dropped to a value < 50% at 160 °C.

After determining the influence of temperature, a value of T intermediate in the range examined was used to study the effect of propane and hydrogen partial pressure on the reaction rates. The dependence of the rates of reaction on the partial pressure of the reactants can be expressed in the form of a simple power rate low:

$$V = k p_{\rm H}^m p_{\rm P}^n. \tag{4}$$

Kinetic orders n and m, calculated from the slopes of the curves of log V against log p, are reported in table 3.

On 4.44 wt % Ru/MgO and unsupported Ru the reaction orders were measured at different temperatures and the results are collected in table 4.

Ru (wt %)	support	reaction ^a	reaction order in H_2^b	reaction order in propane ^c	T/°C
3.86	SiO ₂	1	-2.5	0.40	143
	-	2	-1.3	0.67	
		Т	-1.3	0.65	
3.00	SiO ₂	1	-2.9	0.42	131
	-	2	-1.5	0.49	
		Т	-1.6	0.49	
1.16	Al ₂ O ₃	1	-1.7	0.50	191
		2	-0.7	0.68	
		Т	-0.9	0.65	
0.69	Al_2O_3	1	-2.9	0.48	179
		2	-1.8	0.62	
		Т	-1.8	0.61	
2.90	Al_2O_3	1	-2.4	0.57	145
		2	-1.2	0.88	
		Т	-1.3	0.88	
3.10	SiO ₂ -Al ₂ O ₃	1	-1.9	0.54	184
		2	-1.5	0.69	
		Т	-1.5	0.69	
4.13	CaO–MgO	1	-2.7	0.81	169
		2	-1.4	0.91	
		Т	-1.6	0.89	
4.44	MgO	1	-1.74	0.74	154
		2	+0.05	1.12	
		Т	-0.82	0.92	
100		1	-2.2	0.76	154
		2	0	0.79	
		Т	-0.79	0.80	

TABLE 3.—PRESSURE DEPENDENCE EXPONENTS FOR THE HYDROGENOLYSIS OF PROPANE

^a T = reaction (1) + reaction (2). ^b Propane partial pressure = 3.0 kPa. ^c Hydrogen partial pressure = 20.0 kPa.

ETHANE HYDROGENOLYSIS

The reaction of ethane and hydrogen produced methane, according to

$$C_2H_6 + H_2 \rightarrow 2 CH_4. \tag{5}$$

The temperature dependence of the reaction rates was studied under conditions identical to those used for the hydrogenolysis of propane (H_2 partial pressure = 20 kPa, ethane partial pressure = 3 kPa).

Fig. 4 shows the temperature dependence of the reaction rates on the different ruthenium catalysts. Table 5 summarizes the apparent activation energies and the activities measured at 160 °C for ethane hydrogenolysis on the Ru catalysts. The SiO₂-supported samples had the highest activities, followed by the ruthenium sponge, ruthenium supported on MgO, CaO-MgO, Al₂O₃ and finally SiO₂-Al₂O₃-supported ruthenium, which was clearly the least active. Once again both the unsupported Ru and 4.44 wt % Ru/MgO had a lower apparent activation energy than the other samples.

The orders of reaction with respect to both hydrogen and ethane are reported in

Ru (wt %)	support	reaction ^a	reaction order in H_2^b	reaction order in propane ^c	T/⁰C
4.44	MgO	1	-1.74	0.74	154
	Ū.	2	+0.05	1.12	
		Т	-0.82	0.92	
		1	-1.25	0.96	172
		2	+0.40	1.10	
		Т	-0.80	0.99	
		1	-0.68	0.94	194
		2	+0.45	1.10	
		Т	-0.57	0.97	
100		1	-2.90	0.81	134
		2	-0.75	0.98	
		Т	-1.15	0.96	
		1	-2.20	0.76	154
		2	0	0.79	
		Т	-0.79	0.80	
		1	-1.30	0.95	177
		2	+0.41	0.90	
		Т	-0.77	0.94	

Table 4.—Pressure dependence exponents for the hydrogenolysis of propane on 4.44 wt %~Ru/MgO and unsupported ruthenium at different temperatures

^a T = reaction (1) + reaction (2). ^b Propane partial pressure = 3.0 kPa. ^c Hydrogen partial pressure = 20.0 kPa.



FIG. 3.—Arrhenius plot for propane hydrogenolysis on unsupported Ru. $p_{H_2} = 20.0$ kPa, $p_{C_3H_8} = 3.0$ kPa; \Box , V_{p1} ; \bigcirc , V_{p2} ; \triangle , V_p .



FIG. 4.—Arrhenius plot for ethane hydrogenolysis on Ru catalysts. $p_{H_2} = 20.0 \text{ kPa}$, $p_{C_2H_4} = 3.0 \text{ kPa}$. 3.86 wt % Ru/SiO₂, \bigcirc ; 3.0 wt % Ru/SiO₂, \bigoplus ; unsupported Ru, \diamond ; 1.16 wt % Ru/Al₂O₃, \blacksquare ; 4.44 wt % Ru/MgO, \triangle ; 0.69 wt % Ru/Al₂O₃, \boxtimes ; 4.13 wt % Ru/CaO–MgO, \blacksquare ; 2.9 wt % Ru/Al₂O₃, \oplus ; 5.38 wt % Ru/MgO, \blacksquare ; 3.1 wt % Ru/SiO₂-Al₂O₃, \square .

Ru (wt %)	support	Ru exposed (%)	Ea /kJ mol ⁻¹	temperature range/°C	Vat 160 °C /molecule s ⁻¹ (Ru surface atom) ⁻¹	reaction order in H_2^a	reaction order in ethane ^b	T/°C°
3.86	SiO,	26	125	160-191	2.7×10^{-3}	-2.21	0.66	160
3.00	SiO ₂	43	142	161-196	1.2×10^{-3}	-1.92	1.00	186
1.16	$Al_2\bar{O}_3$	66	155	183-214	1.6×10^{-4}	-2.37	0.85	206
0.69	Al ₂ O ₃	72	142	179-213	9.8×10^{-5}	-1.45	0.82	190
2.90	Al ₂ O ₃	26	130	184-217	2.3×10^{-4}	-1.12	1.04	203
3.10	SiO ₂ -Al ₂ O ₃	33	138	179-247	9.0×10^{-6}	-1.45	0.88	242
4.13	CaO-MgO	44	167	159-200	6.1×10^{-5}	-1.55	0.88	180
4.44	MgO	17.1	88	161-225	3.9×10^{-4}	-0.73	0.98	189
5.38	MgO	60	171	169-200	7.7×10^{-5}	-1.93	0.84	185
100		0.09	88	192-243	8.3×10^{-4}	-1.10	1.03	188

TABLE 5.—KINETIC PARAMETERS FOR THE HYDROGENOLYSIS OF ETHANE ON RU CATALYSTS

^{*a*} Ethane partial pressure = 3.0 kPa. ^{*b*} Hydrogen partial pressure = 20.0 kPa. ^{*c*} Temperature used in determining the order of reaction.

table 5. The order of reaction with respect to ethane was always positive and close to unity. The hydrogen orders were always negative, ranging from -2.4 to -0.7. This latter value applied for the 4.44 wt % Ru/MgO sample.

The catalytic activity measured on our Ru/SiO_2 catalysts is in excellent agreement with that reported by Sinfelt under similar reaction conditions.⁹



FIG. 5.—Activation energy for overall propane hydrogenolysis as a function of ruthenium dispersion.



FIG. 6.—Activation energy for ethane hydrogenolysis as a function of ruthenium dispersion.

DISCUSSION

From the results obtained for ruthenium samples it appears that the same overall behaviour applies for the hydrogenolysis of ethane and propane. Activation energies ranging from 70 to 170 kJ mol⁻¹, positive orders with respect to the hydrocarbon and negative orders with respect to hydrogen were generally found. Furthermore, tables 2 and 5 show that for both reactions the catalytic activity per Ru surface atom measured at 160 °C is higher on Ru/SiO₂ than on all the other catalysts, with Ru/SiO₂-Al₂O₃ being the least active sample. However, due to the large variation in the apparent activation energies and orders of reaction, any ranking of activity is only meaningful for a certain reaction condition. Changing hydrogen partial pressures



FIG. 7.—Plot of pre-exponential factors against activation energies for hydrogenolysis of ethane.

and/or temperature can lead to a different picture. No direct correlation between the catalytic activity and dispersion of Ru seems to exist. This raises the possibility that an interaction between the metal and the support modifies the catalytic properties of Ru. However, there seems to be a trend for the apparent activation energies to increase with increasing dispersion (fig. 5 and 6). Similar changes in activation energies for the hydrogenolysis reaction have been observed previously. Calculating the fraction of metal atoms on the surface of a Ni catalyst supported on silica from the data reported by Taylor *et al.*,¹⁰ it can be seen that an increase in the Ni dispersion corresponds to an increase in activation energy.

In fig. 7 the apparent activation energy, E_{a} , for ethane hydrogenolysis is plotted as a function of $\ln A$, where A is the pre-exponential factor in the equation:

$$V_{\rm E} = A \exp\left(-E_{\rm a}/RT\right) P_{\rm H}^m P_{\rm E}^n \tag{6}$$

where $V_{\rm E}$ is the rate of ethane hydrogenolysis.

With increasing activation energy a corresponding increase in $\ln A$ is found. The lowest activation energy and $\ln A$ values were found on the samples with the lowest dispersion.

Note that the values of A used for the plot were estimated by assuming that the reaction orders do not depend upon temperature. This assumption was experimentally verified for the order of the reaction with respect to ethane. However, the order of reaction with respect to hydrogen generally assumed a smaller negative value with increasing temperature. For example, on the 4.44 wt% Ru/MgO an order of -0.9 was found at 160 °C, while a value of -0.73 was found at 189 °C; similarly on 3.0 wt% Ru/SiO₂ the order changed from -2.2 at 161 °C to -1.92 at 186 °C. For ethane hydrogenolysis such an effect has been reported previously.^{11,12}

A plot similar to fig. 7, showing a linear relationship between $\ln A$ and E, has been found in catalytic systems exhibiting a compensation effect and various interpretations have been given to explain the phenomenon.¹³⁻¹⁶ Most of the interpretations assume

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the existence of a heterogeneous surface with different distributions of sites B_i on which the activation energy for a particular reaction is E_i . For our Ru system, it could be suggested that the catalysts with lower dispersion and consequently higher metal coordination number mainly have sites with lower activation energy. By decreasing the metal particle size the relative amount of highly coordinated atoms decreases. The increase in the activation energy with increasing metal dispersion could be explained by assuming that the hydrogenolysis reaction on the smaller metal particles involves sites with low coordination number where the activation energy could be higher.

Note also that the chemisorption of ethane or propane is dissociative, requiring the accommodation of hydrogen atoms split-off from the hydrocarbon molecules on metal sites. It is possible that the extent of dissociative removal of H atoms from the hydrocarbon differs from one catalyst to another. From the experimentally determined reaction orders, one can estimate the hydrogen content of the adsorbed hydrocarbon intermediate.² According to this calculation the adsorbed species on the samples 4.44 wt % Ru/MgO and unsupported ruthenium seem to be less depleted of hydrogen than on the other samples. It cannot be ruled out that the less pronounced inhibiting effect of hydrogen and the lower activation energy found on 4.44 wt % Ru/MgO and on unsupported Ru is to some extent related to the smaller amount of atomic hydrogen resulting from the dissociative chemisorption of the hydrocarbon.

The question has been raised in the literature¹² as to whether the presence of chlorine contamination on the metal surface could lead to modifications of the hydrogenolysis activity. Generally, the use of $RuCl_3 \cdot H_2O$ as a precursor in the catalyst preparation leads to significant amounts of residual chlorine in the reduced samples. Some of our samples were prepared from precursors which did not contain chlorine. Nevertheless, they show the same catalytic pattern. Therefore, it is unlikely that the large activity differences observed in our samples are due to the presence of chlorine.

The results presented for the ruthenium catalysts show complex catalytic behaviour, caused by an intricate interplay of factors such as the nature of the support, the metal dispersion, the distribution of active sites, the ratio between hydrogen and hydrocarbon in the reactant mixture, the strength of adsorption and the extent of dissociative hydrocarbon adsorption. Among these factors, the metal particle size seems to play a central role in determining the catalytic characteristics. This agrees with the concept that hydrogenolysis reactions are structure-sensitive reactions. In particular, the apparent activation energies and pre-exponential factors show a clear trend, decreasing with increasing metal particle size.

We will now comment further on the selectivity observed in propane hydrogenolysis. The ratio CH_4/C_2H_6 in the reaction products was always > 1. This can be explained by the following overall scheme:



Under the experimental conditions used, the rate of hydrogenolysis of C_2H_6 is much lower than that of propane. Furthermore, the possibility that a consecutive reaction occurs is minimized by the low conversions used. Therefore, it seems reasonable to conclude that reaction (c) does not play an important role in our system. Thus,

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propane hydrogenolysis takes place mainly through two parallel reactions, namely (a) and (b). However as mentioned earlier, the two Ru samples with large particle size showed a much lower selectivity toward ethane formation than the other samples. For these two catalysts, an increase in temperature beyond 150 °C did not lead to a further increase in ethane formation, but resulted in a levelling off (fig. 2 and 3). Furthermore, these two catalysts showed an order of reaction with respect to hydrogen for reaction (2) close to 0 at a temperature of 154 °C. With increasing temperature, the order of reaction became positive reaching a value of ca. 0.5 at 180-190 °C (table 4). On all the other catalysts the hydrogen order remained negative. This indicates that a modified reaction mechanism contributes to the observed 'abnormal' product distribution on ruthenium catalysts with low dispersion. The mass transfer and diffusion limitation tests allow us to rule out physical effects as being responsible for the observed phenomena. Further studies will be necessary to clarify the modified reaction mechanism.

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