

CO₂ reforming of propane over supported Rh

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Abstract

The adsorption, decomposition, and reaction of propane with CO₂ have been investigated on Rh catalysts, deposited on various supports. The strong interaction of propane with Rh was noticed above 273 K. By means of Fourier transform infrared spectroscopy, π -bonded propylene, di- σ -bonded propylene, and propylidyne have been identified. Propane underwent dehydrogenation and cracking on supported Rh at 824–923 K. Propylene formed with a selectivity of 50–60%. The other major products were ethylene and methane. The deposition of carbonaceous species was also observed, the hydrogenation of which occurred only above 700–750 K, with a peak temperature of 900–950 K. The amount of carbon was more than one order of magnitude higher than that of surface Rh atoms, suggesting its diffusion from the Rh onto the support. The presence of CO₂ basically altered the reaction pathway of propane, and the formation of H₂ and CO with a ratio of 0.42–0.59 came into prominence. Propylene was detected only in traces. This led to the assumption that propylene reacted quickly with CO₂ over Rh after its formation. This idea was confirmed by separate study of the reaction of propylene with CO₂. Taking into account the rates of decomposition of propane and CO₂ on Rh catalysts, as well as the reaction orders, we came to the conclusion that the CO₂ is involved in the rate-determining step of the dry reforming of propane. The highest specific rates for the production of H₂ and CO were measured for Rh/TiO₂; this was explained by the extended dissociation of CO₂ due to the electronic interaction between Rh and TiO₂.

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1. Introduction

Supported Rh is one of the most active catalysts for the dry reforming of methane to produce synthesis gas [1,2]. Its advantage is that it limits the carbon deposition that causes the significant deterioration of other catalysts. This was explained by the reaction of CO₂ and CH_x fragments formed in the dissociation of methane [2]. Experiments showed that this process is faster than the reaction between CO₂ and surface carbon formed at high temperature over Rh [3]. Subsequent studies confirmed the high activity of Rh and revealed several features of this catalytic reaction [4–9]. Later it was also observed that the presence of ethane in the CH₄ + CO₂ gas mixture caused the enhancement of carbon deposition and thereby the deactivation of the catalyst [10]. Detailed kinetic study on the C₂H₆ + CO₂ reaction disclosed that the deposition of surface carbon and the deactivation of the catalyst can be prevented by larger amounts of CO₂ [10].

In the present work the study of the catalytic performance of the Rh catalyst has been extended to the dry reforming of propane. Particular attention is paid to the C deposition and to the effects of supports. A literature search for the CO₂ reforming of propane yielded only a few works. Sutton et al. [11] examined the kinetics and the mechanism of this process over Ru/Al₂O₃, whereas we performed a comparative study on the catalytic efficiencies of alumina-supported Pt metals [12]. The latter clearly indicated that Ru and Rh are outstanding catalysts for this process. The reaction of propane with CO₂ was also investigated on supported Mo₂C catalysts, but the aim of the work was to promote the production of propylene [13].

2. Experimental

The catalysts were prepared by impregnating the supports with RhCl₃ · 3H₂O salt to yield a nominal 1 wt% metal. The following supports were used: Al₂O₃ (Degussa P110Cl), 100 m²/g; SiO₂ (Cab-O-Sil), 200 m²/g; MgO (DAB6), 170 m²/g; TiO₂ (Degussa P25), 50 m²/g. The catalyst samples were oxidized at 523 K for 30 min and reduced at 773 K

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for 60 min. The dispersion of Rh was determined by H_2 adsorption at 300 K. The gases used were initially of commercial purity. CO_2 was further purified by fractional distillation. Ar (99.95%) was deoxygenated with an oxytrap. The other impurities were adsorbed on a 5-Å molecular sieve at the temperature of liquid air. In the case of C_3H_8 decomposition the carrier gas was Ar which contained 12.5% propane. In the study of $C_3H_8 + CO_2$ reaction we used a stoichiometric (1 : 3) gas mixture. The propane content was again 12.5%. Kinetic measurements were carried out in a fixed bed continuous-flow reactor made from a 0.7-mm i.d. quartz tube. The amount of catalyst used was 0.3 g. The reaction between C_3H_6 and CO_2 has been studied in the same way. For IR measurements self-supporting wafers (31×10 mm, 10 mg/cm^2) were used. The flow rate of the reactant gases was 60 ml/min. Inert gas was used as a diluent to determine the partial order of the reaction. The exit gases were analyzed by gas chromatograph (Hewlett–Packard 5890) on a Porapak QS column. Infrared spectra were recorded with a Biorad Fourier transform IR spectrometer (Digilab. Div. FTS 7) with a resolution of 4 cm^{-1} . Typically 128 scans were collected. All subtractions of the spectra were taken without the use of a scaling factor ($f = 1.0000$). The supplementary method used was temperature-programmed reaction (TPR). The heating rate was 6.0 K/min .

3. Results

3.1. Interaction of propane with Rh catalyst

The interaction between propane and Rh catalyst was first investigated at 173–300 K. For this study the more inert SiO_2 support was chosen. In order to obtain more intense absorption bands 10 wt% Rh was used. The solid sample was cooled in 1.33 mbar of propane to a selected temperature and the IR spectrum was recorded after 10 min. FTIR spectra obtained are shown in Fig. 1A. Note that the gas-phase spectrum has been subtracted from each spectrum. At 173–193 K absorption bands appeared at 2960, 2940 (shoulder), 2904, 2876, 1649, 1466, and 1448 cm^{-1} and several weak bands between 1335 and 1387 cm^{-1} . Further increase in the temperature led to the attenuation of all these bands. At 253 K a slight shift occurred in the positions of these bands and new features clearly developed or intensified at 2930, 1452, 1353, and 1333 cm^{-1} . At 273 K, the only change was the enhancement of the bands at 1353 cm^{-1} . After evacuation at 300 K for 10 min absorption bands remained at 2964, 2925, 2898, 2866, 2832, 1638, 1450, 1424, 1402, 1381, 1353, and 1333 cm^{-1} .

In the next experimental series the reduced sample was exposed to 1.33 mbar of C_3H_8 at 300 K for 10 min, and then the adsorbed layer was annealed under continuous evacuation at different temperatures for 10 min. Spectra are displayed in Fig. 1B. At 300 K we observed practically the same bands as in the previous measurement. A dramatic

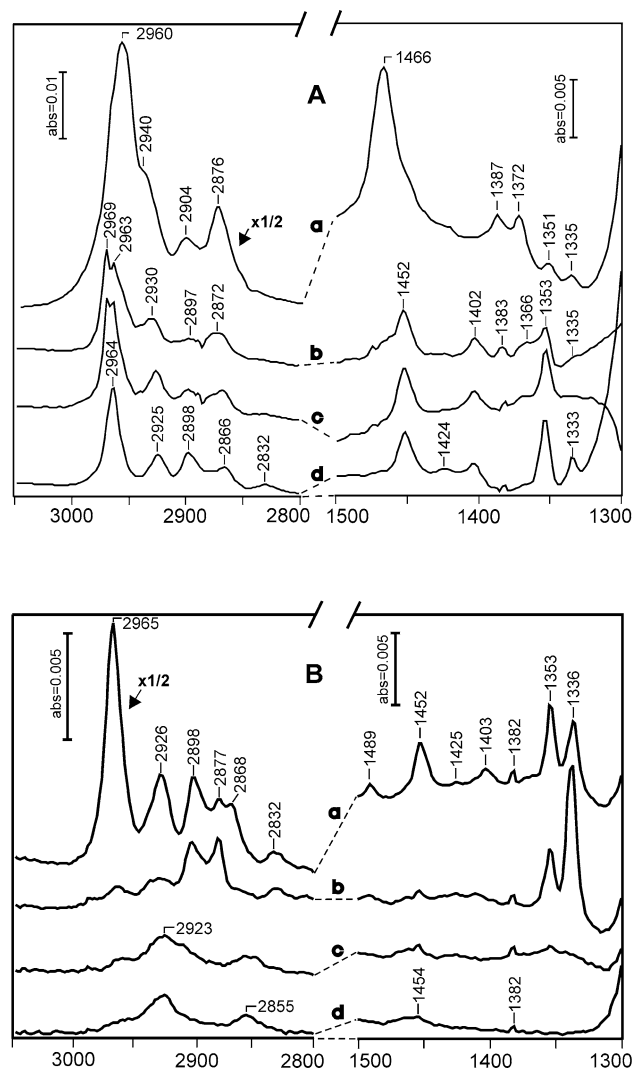


Fig. 1. IR spectra of Rh/ SiO_2 following the adsorption of propane. For (A): 1 Torr propane at 173 K (a), at 253 K (b), at 300 K (c), and after evacuation at 300 K (d). For (B): 1 Torr propane at 300 K and evacuation at 300 K (a), at 360 K (b), at 423 K (c), and at 523 K (d).

attenuation of the bands at 2965 and 2927 cm^{-1} occurred at 360 K, where the low-frequency bands also became very weak. The next significant change was observed at 423–473 K, when only the spectral features at 2923, 2854, 1462, and 1455 cm^{-1} remained; they were eliminated only above 573 K. Absorption bands observed and their possible assignments are shown in Table 1. Note that in the case of pure silica no absorption band could be detected at and above 253 K at all. The above characteristics were observed for 1% Rh/ SiO_2 , too, but the bands were much weaker.

The same IR spectroscopic measurements have been carried out in the presence of CO_2 . We found practically identical spectral features with slight variations in the positions and intensities of the absorption bands.

Table 1
Characteristic vibrations and their assignments observed for gaseous and adsorbed propane

Assignment	Propane on						
	Gas [14]	Mo ₂ C/SiO ₂ at 173 K [17]	Rh/SiO ₂ at 173 K	Pt/SiO ₂ at 300 K (surface species) [15,16]	Rh/SiO ₂ at 253 K (surface species)	Rh/SiO ₂ at 300 K (surface species)	Rh/SiO ₂ at 423 K (surface species)
$\nu_{\text{as}}(\text{CH}_3)$	2977	2963	2960	2960 (II)	2969 (I)	2964 (II)	2960 (III)
$\nu_{\text{as}}(\text{CH}_2)$	2973			2920 (II,III)	2963 (III)	2926 (II,III)	
$\nu_{\text{s}}(\text{CH}_3)$	2962	2939	2940		2930 (II,III)	2898 (II,III)	2923 (II,III)
$\nu_{\text{as}}(\text{CH}_2)/\nu_{\text{as}}(\text{CH}_3)$	2968	2904	2904	2895 (III)	2870 (II)	2877 (I)	
$\nu_{\text{s}}(\text{CH}_2)/\nu_{\text{as}}(\text{CH}_3)$	2887	2877	2876	2870 (II,III)		2868, 2831 (II,III)	2854 (II,III)
$\delta_{\text{as}}(\text{CH}_3)$	1476	1467	1466			1490 (II,III)	
$\delta_{\text{as}}(\text{CH}_2)$	1472						1462 (III)
$\delta_{\text{as}}(\text{CH}_3)$	1464			1450 (III)	1452 (II)	1450 (II,III)	1455 (II)
$\delta(\text{CH}_2)$	1462	1450	1448	1410 (II,III)	1402 (III)	1404 (III)	
$\delta_{\text{s}}(\text{CH}_3)$	1392	1388	1387	1365 (II,III)	1383 (II,III)	1382 (II,III)	1383 (II,III)
$\delta_{\text{s}}(\text{CH}_2)$	1378	1371	1371	1355 (I,II)	1353 (III)	1354 (III)	1354 (III)
$\omega(\text{CH}_2)$	1338	1334	1335			1338	

(I) π -bonded propylene; (II) di- σ -bonded-propylene; (III) propylidyne.

3.2. Decomposition of propane

The decomposition of propane was investigated in a greater detail on Rh/Al₂O₃. A well measurable reaction occurred at 823–923 K. The initial fast decay was followed by a slower deactivation process. The main product is propylene; it formed with 56–58% selectivity at 923 K, which slightly increased with lowering the temperature. The other major products were ethylene ($s \approx 20\%$), methane ($s \approx 10$ –12%), and benzene ($s \approx 5$ –8%). The decomposition of propane and the formation of various products over Rh/Al₂O₃ are shown in Fig. 2A.

In order to see whether the deposition of some carbonaceous species occurred during the reaction, the used Rh/Al₂O₃ has been heated in H₂ flow and the products formed were analyzed from time to time. The formation of methane was observed above 750 K, other hydrocarbons were produced only in negligible amounts. Results are plotted in Fig. 2B. The peak temperature is 960 K. From the integration of the curve the amount of carbon deposited was calculated (Table 2). It was more than one order of magnitude higher than that of surface Rh atoms.

The reaction of propane gave practically the same products over Rh/SiO₂. In the case of Rh/MgO and Rh/TiO₂ the formation of benzene was not detected. Data for the ef-

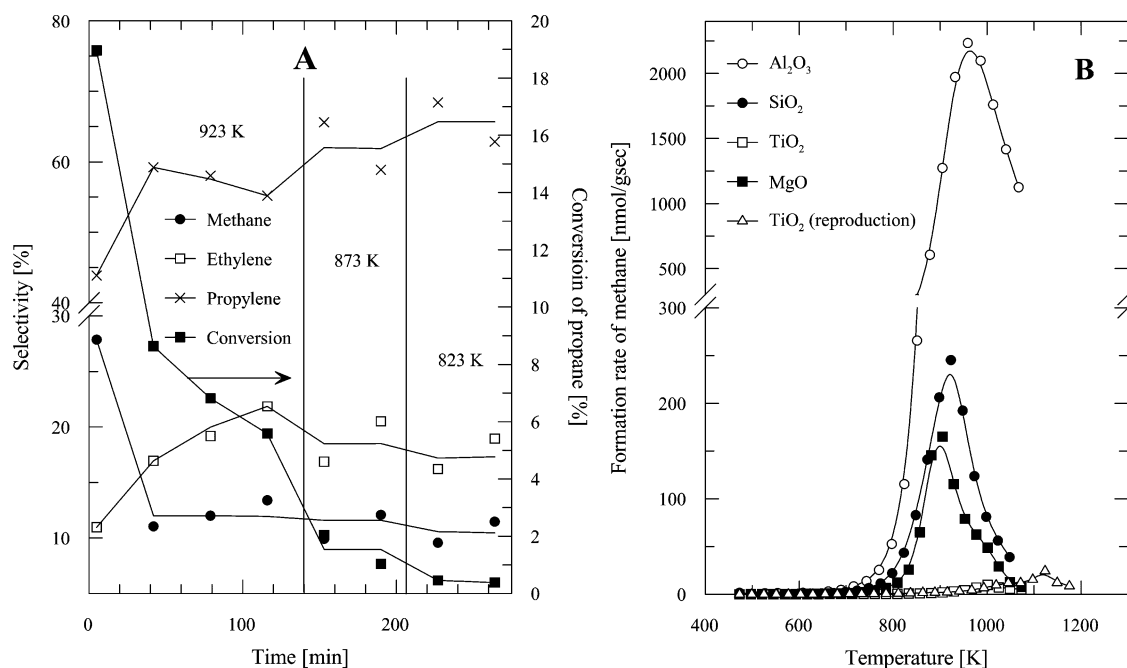


Fig. 2. (A) Conversion of propane and selectivities of different products formed in the decomposition of propane on Rh/Al₂O₃ at different temperatures. (B) TPR curves for the reaction of surface carbon formed in the decomposition of propane at 923 K in 120 min on oxide-supported Rh.

Table 2
Characteristic data for the decomposition of C₃H₈ over supported Rh catalyst at 923 K^a

Metals <i>D</i> (%)	Conversion of propane (%)	<i>N</i> _{C₃H₈} (s ⁻¹)	<i>N</i> _{C₃H₆} (s ⁻¹)	Selectivity (%)			<i>C</i> _S (nmol)
				C ₃ H ₆	C ₂ H ₄	CH ₄	
Al ₂ O ₃ (31.0)	5.58	0.025	0.0082	55.18	21.85	13.40	–
	5.01	0.022	0.0067	48.17	30.67	17.19	8.94 × 10 ⁵
SiO ₂ (11.0)	1.70	0.021	0.0059	55.40	27.59	13.39	–
	1.89	0.023	0.0060	59.09	24.32	11.20	8.95 × 10 ⁴
TiO ₂ (2.0)	1.65	0.104	0.0116	31.2	45.82	21.94	–
	1.31	0.083	0.019	50.06	33.61	15.71	3.36 × 10 ³
MgO (15.0)	2.47	0.022	0.0003	49.22	33.57	16.28	–
	1.22	0.011	0.0006	60.03	26.74	12.71	5.63 × 10 ⁴

*N*_{C₃H₈} and *N*_{C₃H₆} are rates related to the number of Rh atoms.

^a Data were obtained at 120 min of reaction.

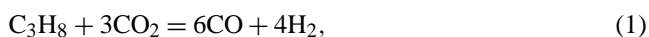
fects of the support on the decomposition of propane on Rh is collected in Table 2. TPR measurements were also carried out after the reaction. TPR spectra are also displayed in Fig. 2B. The reactivity of carbon exhibited only a slight variation with the support. The quantity of carbon formed was the highest for Rh/Al₂O₃ and the lowest for Rh/TiO₂.

3.3. Decomposition of CO₂

In harmony with the previous FTIR spectroscopic measurements the dissociation of CO₂ proceeds on the most active Rh/Al₂O₃ catalyst at and above 473 K as indicated by the appearance of an absorption band at 2010 cm⁻¹ due to adsorbed CO [2]. In the reacting gas mixture this absorption band appeared already at 373–423 K. The decomposition of CO₂ has also been studied in a flow system under the same conditions as appeared in the C₃H₈ + CO₂ reaction. We found only very limited formation of gaseous CO at 923 K; the conversion of CO₂ was below 0.5%.

3.4. Reaction of propane with CO₂

The addition of a small amount of CO₂ (2.5% of C₃H₈) to propane exerted a dramatic influence on its decomposition over Rh/Al₂O₃ at 923 K (Fig. 3). The rate of the formation of propylene markedly decreased, whereas that of hydrogen increased. CO and a small amount of methane were also formed. With increased CO₂ content the conversion of propane and the production of H₂ and CO gradually increased, while that of propylene abruptly decreased to trace amounts. A decrease was measured in the ratio of H₂/CO and a slight increase in the CH₄/CO ratio. Using a stoichiometric composition of reacting gas mixture corresponding to the equation



the initial conversion of propane was 80–85%, which decayed only to 63% after 2 h. The H₂/CO ratio was 0.50–0.55. The CH₄/CO ratio was around 0.11–0.13. These results are plotted in Fig. 4. When the measurements over Rh/Al₂O₃ were extended to 24 h, we found only very slight

changes in the data determined in 120–150 min. Lowering the reaction temperature caused a slight increase in the H₂/CO ratio and a decrease of the relative rate of CH₄ production occurred. Doubling the flow rate of the reacting gas mixture led to an increase of the H₂/CO ratio from 0.53 to 0.56 and to a decrease of the CH₄/CO ratio from 0.13 to 0.09.

The amount of carbon remaining on the catalyst after the reaction has been determined by TPR in the same way as after the decomposition of propane. We obtained much less carbon with a lower peak temperature, 825 K.

The kinetic orders were calculated from the logarithmic plots of the various rates versus the volume percentage of the reactants. In one experimental series the partial pressure of CO₂ was held constant at 285.0 Torr, while that of C₃H₈ was varied. In the other case, the partial pressure of C₃H₈ was kept constant at 95.0 Torr, and that of CO₂ was changed. The order of the reaction was zero in C₃H₈ and it was fractional (0.4–0.45) with respect to CO₂. From the Arrhenius plots the activation energies were calculated. For the formation of H₂ and CO, we obtained 87.4 and 92.2 kJ/mol, respectively.

3.5. Effects of support

Kinetic measurements were repeated for Rh deposited on various supports. Some characteristic data are plotted in Fig. 5. The rate of consumption of C₃H₈ and the H₂/CO ratios varied with the support but the general features remained the same. Reaction rates were less than those measured for Rh/Al₂O₃, which decreased in the order Rh/TiO₂, Rh/MgO, and Rh/SiO₂. The H₂/CO ratio was the highest, 0.53–0.64, for Rh/TiO₂. It was only 0.42 for Rh/SiO₂. The formation of methane was not detected. As in the case of Rh/Al₂O₃, less carbon was deposited on the catalysts than in the decomposition of propane. The peak temperature of hydrogenation fell in the range 860–940 K. The most important data are collected in Table 3.

3.6. Reactions of propylene with CO₂

As we can count with the transitory formation of propylene during the dry reforming of propane, it was important to

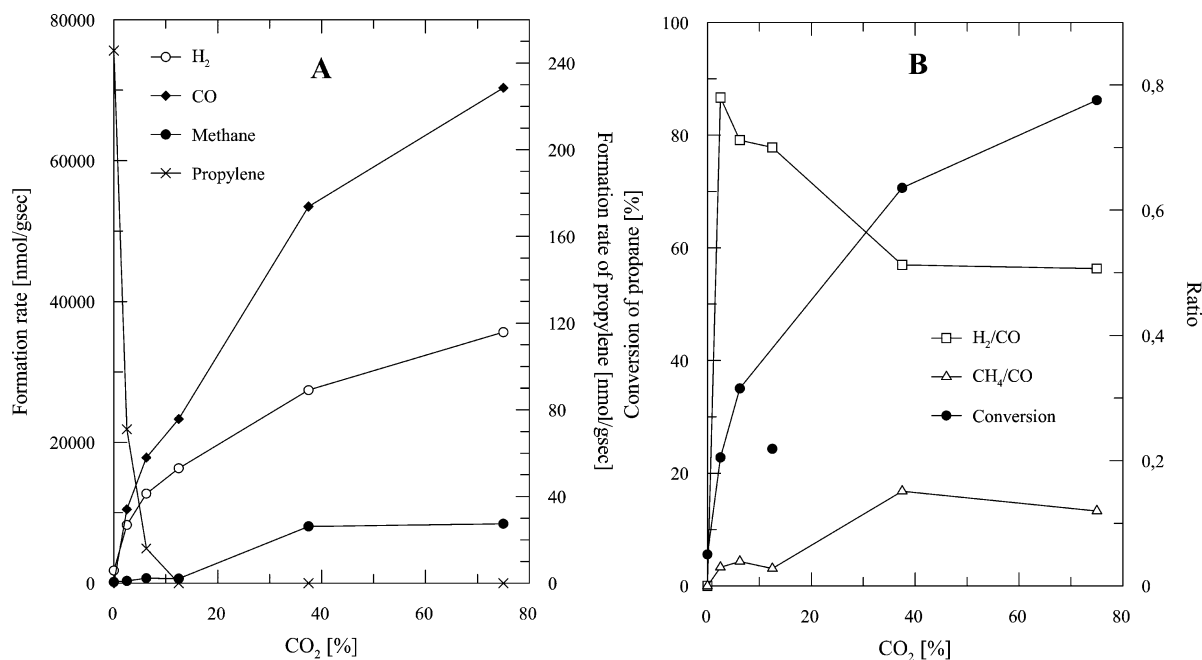


Fig. 3. Effects of CO₂ content (A) on the rate of formation of various products and (B) on the conversion of C₃H₈ and on the ratios of products of the C₃H₈ + CO₂ reaction over Rh/Al₂O₃ at 923 K. Values measured at 120 min of reaction.

know more about its reactions under the same experimental conditions. In the absence of CO₂, the cracking of propylene proceeded at a very high rate at 923–773 K, producing a large amount of carbon, which leads to a fast decay in the rate of propylene decomposition. In the presence of CO₂ (C₃H₆/CO₂ = 1/3), the product distribution dramatically changed, and CO and H₂ became the main products. Starting the reaction at 773 K, the initial rates of the for-

mation of H₂ and CO were higher than those determined for C₃H₈ + CO₂, but due to the carbon deposition the rates measured after 120 min were somewhat lower (Fig. 6). The activity order of the Rh samples followed that determined for the C₃H₈ + CO₂ reaction. The reactivity of carbon towards H₂ was practically the same as that of the carbon produced by the C₃H₈ + CO₂ reaction. The peak temperatures fell in the temperature range 900–950 K. The amount of carbon mea-

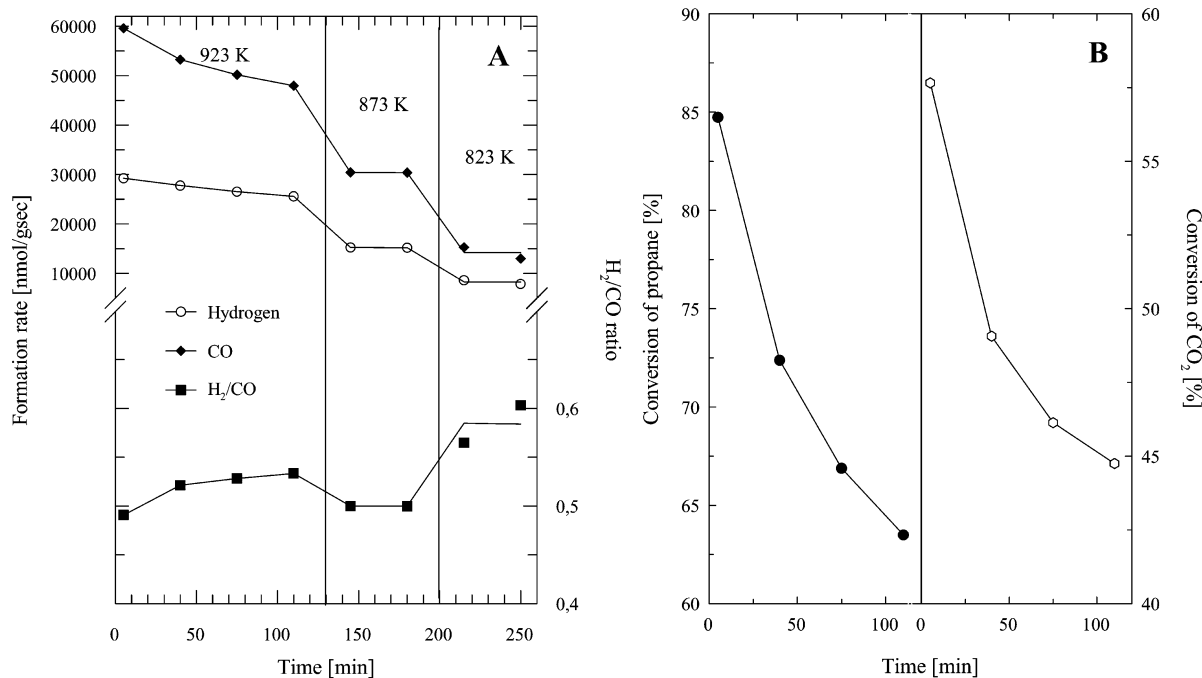


Fig. 4. (A) Rate of formation of H₂ and CO and (B) the conversion of C₃H₈ and CO₂ in the C₃H₈ + CO₂ reaction over Rh/Al₂O₃ in time on stream at 923 K.

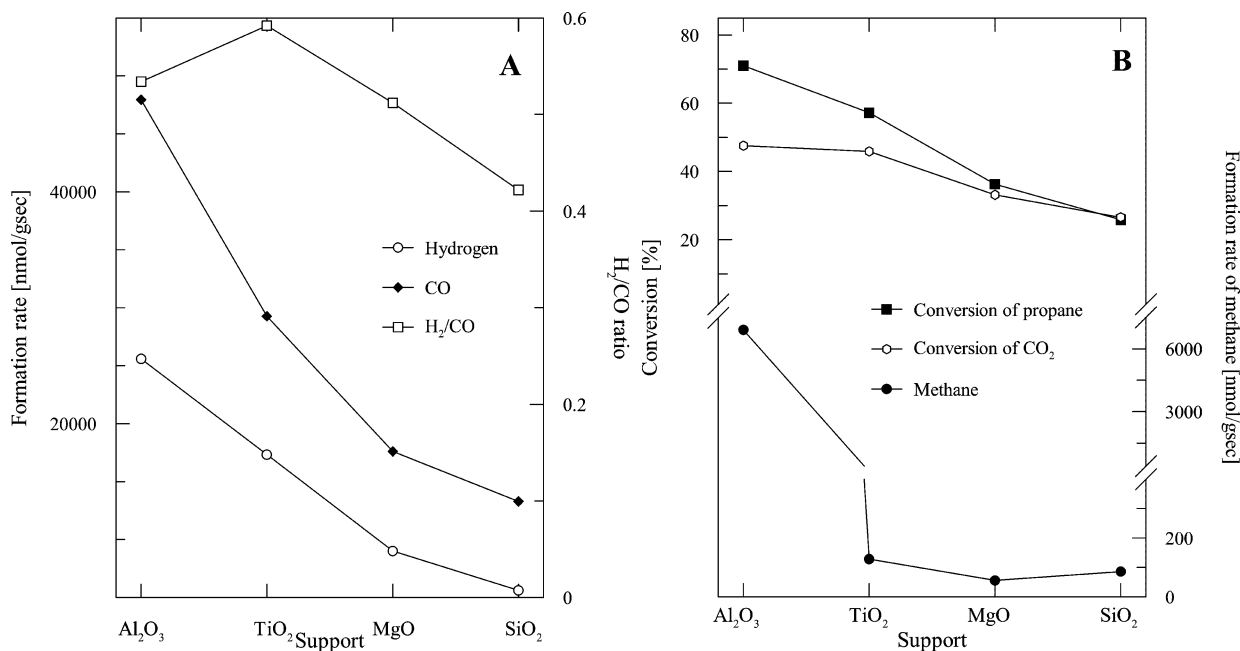


Fig. 5. Effects of support on the characteristic data of $C_3H_8 + CO_2$ reaction over Rh at 923 K. Values measured at 120 min of reaction. The dispersion of Rh on different supports is as follows: 31% (Rh/ Al_2O_3), 11% (Rh/ SiO_2), 2.0% (Rh/ TiO_2), and 15% (Rh/ MgO).

sured decreased in the order Rh/ Al_2O_3 , Rh/ MgO , Rh/ SiO_2 . Over Rh/ TiO_2 we found only a small amount of carbon, which reacted with H_2 above 800 K. When the C_3H_8/CO_2 ratio was decreased from 1/3 to 1/6 the initial rate of formation of H_2 was doubled and decreased more slowly. The amount of carbon formed in 120 min was also less.

4. Discussion

Although the complexity of the reaction and the occurrence of several secondary processes make it difficult to determine the mechanism of the $C_3H_8 + CO_2$ reaction, some conclusions can be drawn on the basis of our supplementary studies on the interaction of CO_2 and C_xH_y with metal surfaces [8–17].

4.1. Interaction of propane with supported Rh

The interaction of propane with Rh/ SiO_2 has been studied by IR spectroscopy. Considering the characteristic vibra-

tions of propane and some related compounds (Table 1), we can conclude that the absorption bands observed following the adsorption of C_3H_8 onto Rh/ SiO_2 at 173–193 K correspond very well to the different vibrations of propane [14]. At 253–273 K, a marked attenuation of these bands occurred as a result of the desorption of propane. The spectral features that remained or developed at 2930, 2830, 1429, 1411, and 1374 cm^{-1} suggest that a fraction of propane interacted strongly with Rh (Fig. 1A). This is clearly indicated when propane was brought into contact with the catalyst at 300–360 K. Taking into account the IR spectra of adsorbed propylene and propylidyne [13,15–17], some of these absorption bands are attributed to di- σ -propylene formed in the dehydrogenation of propane, and some to the vibrations of propylidyne, which is produced in the further dehydrogenation of di- σ -propylene (Table 1). These surface species were also detected following the adsorption of propane on Pt/ SiO_2 [15,16] and on Mo_2C/SiO_2 [13,17].

Table 3
Characteristic data for $C_3H_8 + CO_2$ reaction over supported Rh catalyst at 923 K^a

Support <i>D</i> (%)	Conversion of propane (%)	Conversion of CO_2 (%)	N_{H_2} (s^{-1})	N_{CO} (s^{-1})	H_2/CO ratio	C_S (nmol)
Al_2O_3 (31.0)	63.50	44.75	0.849	1.592	0.54	6.60×10^4
SiO_2 (11.0)	25.83	26.56	0.525	1.243	0.42	4.18×10^4
TiO_2 (2.0)	42.75	45.86	8.920	15.060	0.59	2.24×10^4
(20) ^b			0.892	1.506		
MgO (15.0)	26.02	33.14	0.618	1.207	0.51	1.01×10^4

N_{H_2} and N_{CO} are rates related to the number of Rh atoms.

^a Data were obtained at 120 min of reaction.

^b In this case the dispersion of Rh was multiplied by a factor of 10.

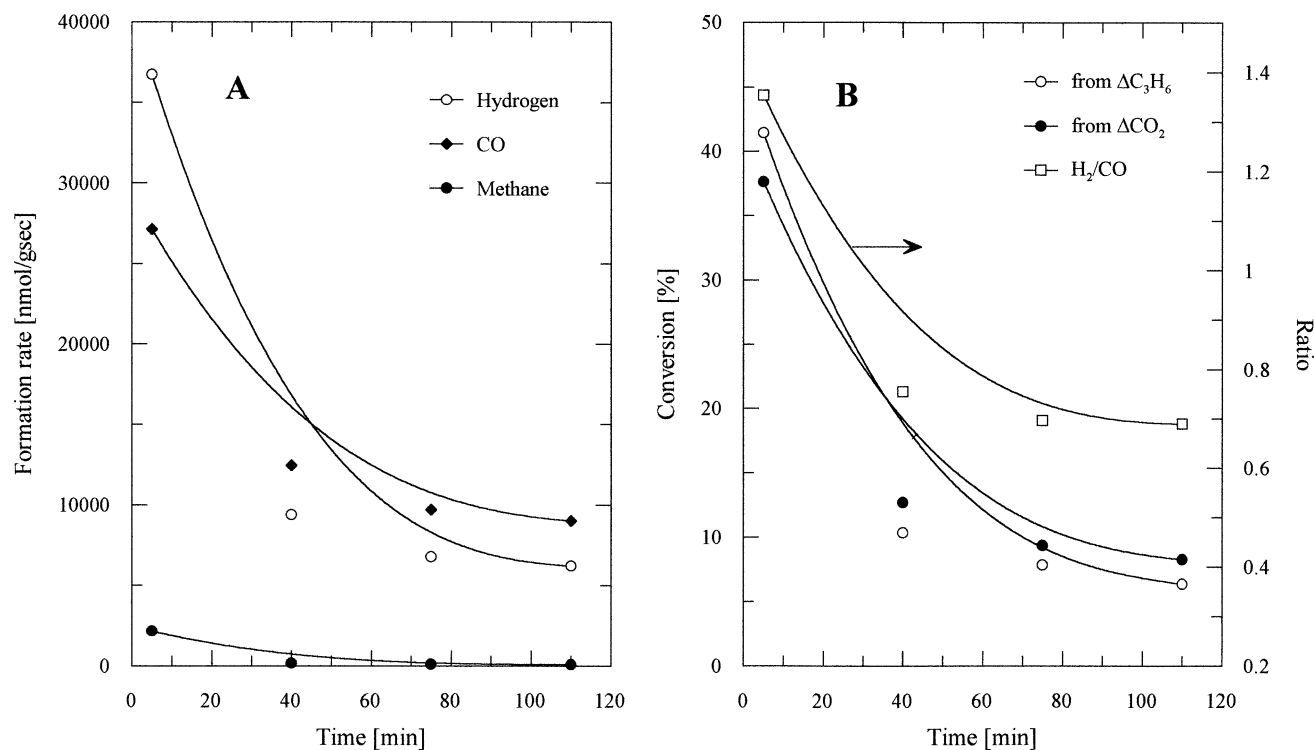


Fig. 6. (A) Rate of formation of H₂ and CO and (B) the conversion of C₃H₆ and CO₂ in the C₃H₆ + CO₂ reaction over Rh/Al₂O₃ at 773 K.

4.2. Decomposition and dehydrogenation of propane

In the decomposition of propane the dehydrogenation reaction



is the dominant process, in contrast to the reaction of methane, which decomposes to carbon and hydrogen on the same Rh catalysts [2]. Ethane was also produced in minor amounts. This is very likely the result of the coupling of CH₃, the primary dissociation product of methane. If we assume the same initial step in the interaction of propane with metals, then we expect the transitory formation of propyl species, C₃H₇,



which dehydrogenates further to propylene,



On the single-crystal surfaces of Pt metals under UHV conditions, C₃H₇ species underwent dehydrogenation and hydrogenation, but its coupling into C₆ compounds was not observed [18,19]. It occurred, however, over Cu(110) [20], Ag(111) [21], Au(111) [22], and to a limited extent, on Mo₂C/Mo(100) [23] surfaces. The last, with the combination of ZSM-5, is able to convert methane into aromatics [24–28]. Under the present experimental conditions, the cracking of C₃H_{7(a)}} and C₃H_{6(a)}}, resulting in the formation of a very unreactive carbon layer, also proceeded. Its low reactivity suggests that the carbon is mainly in the form

of graphite. Taking into account the amount of carbon deposited and the dispersion of Rh we can come to the conclusion that the larger part of the carbon locates on the support. It is an interesting result that we detected the formation of C₆ compounds on some supported Rh catalysts. Accordingly, under the present experimental conditions the reductive coupling of C₃H₇ into C₆ compounds also took place.

From the calculation of the specific activities (turnover number) of various catalysts in the dehydrogenation of propane we obtained only slight deviations for different samples (Table 2). An exception is Rh/TiO₂, which exhibits the highest activity. This value, however, can be considered with caution due to the very low dispersion of the Rh. As the support alone exerts no or very little activity we have to assume that the activation and the reaction of propane occur on the Rh or at the Rh/support interface. The large amount of surface carbon measured, however, suggests that the majority carbonaceous species formed in the cracking of the reaction intermediates diffuses from the Rh onto the support. The formation of surface carbon seems to be in strong correlation with the conversion of propane (Table 2).

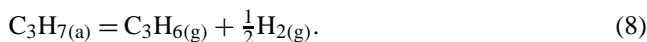
4.3. Reaction of propane with CO₂

The presence of CO₂ dramatically influenced the reaction pathway of C₃H₈, and, instead of dehydrogenation and cracking, the formation of H₂ and CO came into prominence. Although the presence of CO₂ significantly reduced the amount of carbon deposited, it could not prevent its formation. This very unreactive carbon is probably responsible

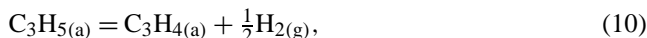
for the deactivation of the catalyst. Note that the formation of carbon in the $C_3H_8 + CO_2$ reaction has been observed on all alumina-supported Pt metals [12]. However, it was not reported by Sutton et al. [11] for Ru/Al_2O_3 . As in the dry reforming of methane we assume that the adsorbed species of each reactant strongly influence the reactivity of the other. Accordingly, (i) the dissociation of CO_2 ,



is promoted by C_xH_y fragments of the decomposition of C_3H_8 , and (ii) the dissociation of C_3H_8 is facilitated by adsorbed O formed in the decomposition of CO_2 . In the latter case we may count with a new route for the formation of C_3H_7 and C_3H_6



This is, however, not sufficient to explain changes in the product distribution. The results suggest that in the presence of adsorbed O atoms the reaction does not stop at the formation of propylene. The latter compound may also be activated by adsorbed O atoms to give further reactive species,

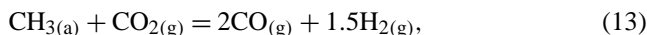


which react with adsorbed O on one hand and decompose to hydrogen and carbon on the other hand,



Control measurements showed that the propylene + CO_2 reaction proceeds at a high rate on supported Rh to give CO and H_2 . That is probably the reason that when a sufficient amount of CO_2 is added to propane, propylene disappears from the reaction products. Taking into account the rates of decomposition of propane and CO_2 on Rh catalyst, as well as the reaction orders, we come to the conclusion that CO_2 is involved in the rate-determining step of the dry reforming of propane.

In our previous study of the dry reforming of methane over Rh and Pd catalysts we found that the carbon species formed or treated at high temperature is very unreactive toward CO_2 [2,29]. Therefore the lack of deposition of a significant amount of carbon, which also leads to deactivation, was explained by the direct reaction of CH_3 or CH_2 with CO_2 ,



which does not involve the formation of any kind of carbon. Experiments with CH_3 produced by the pyrolysis of azomethane confirmed this assumption, as adsorbed CH_3 reacted readily with gaseous CO_2 [3]. We may assume

that the reaction of C_xH_y fragments with CO_2 proceeds to certain extent in the present case, too.

From the study of the effects of supports we obtained that the reaction of propane took place at the highest rate over Rh/Al_2O_3 catalyst (Table 3). On the basis of the turnover numbers, the Rh/TiO_2 shows the highest activity. This, however, is partly due to the very low dispersion of that sample due to the decoration effect occurred at the reduction of the Rh/TiO_2 at 773 K. Nevertheless, Rh/TiO_2 is still the most active catalyst, if we multiply the dispersion of Rh by a factor of 10 (Table 3). Note that the Rh/TiO_2 exhibited the highest activity towards the dissociation of CO_2 and CO, which was explained by the electronic interaction between Rh and the *n*-type TiO_2 resulting in an extended electron transfer from the Rh into the π orbital of CO_2 and CO [30,31].

5. Conclusions

- (i) Propane interacted with supported Rh to give propylene and propylidyne even at 253–300 K.
- (ii) The dehydrogenation of propane to propylene occurred with selectivities of 40–55% over supported Rh catalysts. Carbon species deposited was very unreactive toward H_2 : the peak temperature of its dehydrogenation fell in the range of 900–950 K.
- (iii) In the presence of CO_2 the reaction pathway of propane is changed, and the formation of CO and H_2 came into prominence.
- (iv) It was shown that propylene, the product of the dehydrogenation of propane, reacted rapidly with CO_2 to give CO and H_2 . As regards the dry reforming of propane, the highest specific rates were measured for Rh/TiO_2 .

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