

Dry reforming of propane over supported Re catalyst

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Abstract

Fourier-transformed infrared spectroscopy revealed that there is no strong interaction between propane and Re/Al₂O₃ catalyst at 250–300 K producing di-σ-bonded propylene or propylidyne. Whereas CO₂ is adsorbed mainly molecularly on supported Re reduced at 673 K, the presence of propane induces its dissociation even at 300 K resulting in the formation of adsorbed CO absorbing at ~2041 cm⁻¹. In addition, the co-adsorption of the two compounds 5% Re/Al₂O₃ at 373–573 K leads to the formation of formate species. Re/Al₂O₃ catalyzes the dehydrogenation and cracking of propane at 773–923 K. The selectivity of propylene formation is 43–74%. The addition of CO₂ to propane dramatically affected the reaction pathway, and, instead of the dehydrogenation process, the formation of H₂ and CO with a ratio of 0.56–0.61 became the dominant route. The highest conversion values were measured for the Re/Al₂O₃ reduced at 673 K. The steady-state conversion of propane also depended on the composition of the reacting gas mixture: it was ~50% at C₃H₈/CO₂ (1/3) and ~80% at C₃H₈/CO₂ (1/6). The deposition of carbon was observed, the extent of which can be lowered with increasing CO₂ content of the reacting mixture. From the kinetic studies it was inferred that the CO₂ is involved in the rate-determining step of the dry reforming of propane. As propylene was not detected or was detected only in traces, it was assumed that the hydrocarbon fragments formed in the activation of propane reacted quickly with adsorbed oxygen and CO₂. A possible mechanism for the dry reforming of propane on Re catalysts is proposed.

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1. Introduction

In the last decade more attention has been paid to the production of synthesis gas by the CO₂–CH₄ reaction [1]. From the first comparative study it was found that on the basis of the turnover frequency measured on noble metals, Ru and Rh are the most active catalysts [2]. An interesting and important feature of Rh is that only a very limited amount of carbon is deposited on its surface during the reaction, which was explained by the direct reaction of CH₃, the primary dissociation product of methane, with CO₂ [3]. This idea was confirmed by the study of the reaction of ad-

sorbed CH₃ with gaseous CO₂ by the combined technique of infrared spectroscopy and mass spectrometry [4]. Subsequent works disclosed several details of the CH₄ + CO₂ reaction over Rh catalyst [5–10] and showed that in contrast to the first detailed kinetic study [3], the nature of the support markedly influences the catalytic performance of the Rh. In the last couple of years, the work in this area has been extended to the CO₂ reforming of other hydrocarbons, mainly ethane and propane [11–20]. Based on the specific activity, Ru and Rh were also found to be the most active among Pt metals in the C₃H₈ + CO₂ reaction [18]. In a kinetic study on Ru/Al₂O₃ Ross et al. [17] observed zero-order rate dependence in propane and a fractional dependence in CO₂. Same kinetic features were established on Rh/Al₂O₃ [19]. In addition, it was observed that the propane dehydrogenates over Rh, and propylene reacts rapidly with CO₂ [19]. Very recently Mirodatos et al. [20] investigated propane reform-

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ing by carbon dioxide on 1.9% Ni/Mg(Al)O hydrotalcite-derived catalyst at 873 K. This material exhibited limited initial deactivation and high stability.

Recently, our interest turned to Re catalyst, which exhibited a unique property among the metals. With its combination of ZSM-5, it catalyzed the aromatisation of methane [21–23], ethane [24], propane, and *n*-butane [25]. Interestingly, there was relatively little carbon deposition during the reactions of these hydrocarbons, which made it worthwhile to test its catalytic performance in the dry reforming of propane. The behavior of rhenium supported on alumina has been examined for the partial oxidation and dry reforming of methane at different temperatures [26]. At 1050 K the conversion of methane was greater than 85%. Carbon deposition was not detected even after an extended reaction time [26].

2. Experimental

2.1. Materials

The catalysts were prepared by impregnation of Al₂O₃ support (Degussa P110Cl, 100 m²/g) with (NH₄)₂ReO₄ · 4H₂O salt to yield a nominal 2 or 5 wt% metal. Some FTIR measurements have also been made for SiO₂ support (Cab-O-Sil, 200 m²/g). The pretreatment of the catalyst consisted of the following steps: calcination of the sample in air at 773 K for 4 h and reduction at 673 K for 1 h with a pure H₂ stream (flow rate 20 ml/min). An exception was when the effect of the reduction temperature was examined. The gases used were initially of commercial purity. CO₂ was further purified by fractional distillation. Ar (99.95%) was deoxygenated with and oxytrap. The other impurities were adsorbed on a 5A molecular sieve at the temperature of liquid air. Re/Al₂O₃ catalysts have been characterized by XPS measurements. We found that the sample reduced at 673 K contained higher valence Re (~Re⁴) in a few percent.

2.2. Methods

Kinetic measurements were carried out in a fixed-bed continuous-flow reactor made from a 7-mm I.D. quartz tube. The amount of catalyst used was 0.3 g. The total gas flow rate was 60 ml/min. Inert gas was used as a diluent to determine the partial order of the reaction. In the case of C₃H₈ decomposition the carrier gas was Ar containing 12.5% propane. The decomposition of CO₂ was studied in the same way. The CO₂ content was 10%. When the dissociation of CO₂ was followed by pulse experiment, one CO₂ pulse contained 20.45 μmol of CO₂. In the study of the C₃H₈ + CO₂ reaction we used a stoichiometric (1:3) gas mixture. The propane content was again 12.5%. The exit gases were analyzed by gas chromatography (Hewlett-Packard 5890) on Porapak Q + S columns. For IR measurements self-supporting wafers (30 × 10 mm, 10 mg/cm²) were used. Infrared spectra were recorded with a Biorad

Fourier transform IR spectrometer (Digilab; Div. FTS 155) with a resolution of 4 cm⁻¹. Typically 128 scans were collected. All subtractions of the spectra were made without the use of a scaling factor ($f = 1.0000$). All IR spectra were taken at room temperature. The amount of carbon-containing compounds deposited on the catalyst during the reaction was determined by temperature-programmed reaction (TPR). The sample was cooled in flowing argon and then heated in a pure H₂ stream (20 ml/min). The heating rate was 6.0 K/min. The hydrocarbons formed were measured by gas chromatography.

3. Results

3.1. Adsorption of C₃H₈ and CO₂

The interaction between propane and Re catalyst was first investigated at 173–300 K. FTIR spectra obtained for 5% Re/Al₂O₃ ($T_R = 673$ K) are shown in Fig. 1. Note that the gas-phase spectrum has been subtracted from each spectrum. At 173–193 K absorption bands appeared at 2964, 2940 (shoulder), 2903, 2874, 1469, 1455 cm⁻¹, and several weak bands appeared between 1386 and 1335 cm⁻¹. A further increase in the temperature led to the attenuation of all of these bands, but it did not result in appreciable spectral changes. After evacuation at 300 K very weak bands remained at almost the same positions as at lower temperatures. Absorption bands were observed; their possible assignments are listed in Table 1. Note that in the case of pure alumina no absorption band could be detected at or above 253 K at all.

Adsorption of CO₂ on 5% Re/Al₂O₃ at 300 K produced strong bands in the FTIR spectrum at 2334, 1646, 1481, 1444, and 1230 cm⁻¹ (Fig. 2A). The first one belongs to the vibration of weakly adsorbed CO₂, the others to that of carbonate species bonded to alumina. No CO band appeared in the spectra of the sample reduced at 673 K. It was observed only on the catalysts reduced at high temperatures, 973–1073 K. The spectrum remained practically the same when the adsorption temperature was increased to 573 K in the presence of CO₂.

After the co-adsorption of the gas mixture on 5% Re/Al₂O₃ at 300 K the dominant spectral features were those observed during the CO₂ adsorption alone. New bands were also seen at 2041 and 1936–1945 cm⁻¹ (Fig. 2A). At 473–573 K weak bands could also be identified at 1594 and 1396 cm⁻¹. Some experiments have been also carried out with 5% Re/SiO₂. Adsorption of CO₂ alone at 300 K gave no spectral features. Co-adsorption of the C₃H₈/CO₂ (1:1) gas mixture on this sample at 300 K yielded a broad absorption at 2035 cm⁻¹ and another one at 1870 cm⁻¹ at 573 K. We detected no peaks in the low-frequency range. As we tentatively assume that the 1594 and 1396 cm⁻¹ bands observed for 5% Re/Al₂O₃ are associated with formate species, adsorption of HCOOH was performed on Re samples and on the supports alone. Spectra obtained are

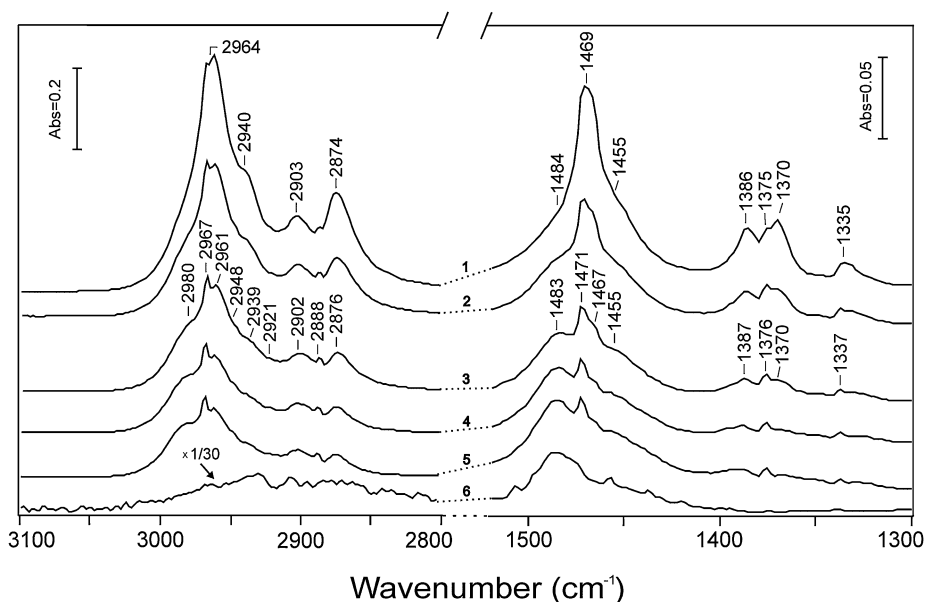


Fig. 1. FTIR spectra of 5% Re/Al₂O₃ ($T_R = 673$ K) following the adsorption of propane (1 Torr): (1) 193; (2) 213; (3) 233; (4) 253; (5) 273; (6) 300 K after evacuation.

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

Assignment	Propane on						
	Gas [27]	Rh/SiO ₂ at 173 K [25]	5% Re/Al ₂ O ₃ at 193–273 K (present work)	Pt/SiO ₂ at 300 K [28,29]	Surface species	Rh/SiO ₂ at 300 K [25]	Surface species
$\nu_{as}(\text{CH}_3)$	2977	2960	2964	2960	(II)	2964	(II)
$\nu_{as}(\text{CH}_2)$	2973			2920	(II, III)	2926	(II, III)
$\nu_s(\text{CH}_3)$	2962	2940	2940			2898	(II, III)
$\nu_{as}(\text{CH}_2)/\nu_{as}(\text{CH}_3)$	2968	2904	2903	2895	(III)	2877	(I)
$\nu_s(\text{CH}_2)/\nu_{as}(\text{CH}_3)$	2887	2876	2874	2870	(II, III)	2868, 2831	(II, III)
$\delta_{as}(\text{CH}_3)$	1476	1466	1469			1490	(II, III)
$\delta_{as}(\text{CH}_2)$	1472						
$\delta_{as}(\text{CH}_3)$	1464			1450	(III)	1450	(II, III)
$\delta(\text{CH}_2)$	1462	1448	1458	1410	(II, III)	1404	(III)
$\delta_s(\text{CH}_3)$	1392	1387	1386	1365	(II, III)	1382	(II, III)
$\delta_s(\text{CH}_2)$	1378	1371	1375	1355	(I, II)	1354	(III)
$\omega(\text{CH}_2)$	1338	1335	1335			1338	

Note: I π -bonded propylene; II di- σ -bonded-propylene; III propylidyne.

shown in Fig. 2B. Intense absorption features at 1594–1596 and 1393–1379 cm^{-1} appeared on pure and Re-containing alumina, but not at all on 5% Re/SiO₂. In this case we found only one band at 1734 cm^{-1} , which is very likely due to the molecularly adsorbed HCOOH.

3.2. Decomposition of propane

The decomposition of propane was investigated in greater detail on 2% Re/Al₂O₃. At 923 K, the initial conversion (at 5 min) was 17–18%, which decreased with time on stream. The initial fast decay was followed by a slower deactivation process. The main product was propylene; it formed with 43–74% selectivity at 923 K and varied with the progress of the reaction. The other major products were ethylene ($S \approx$

18–27%), methane ($S \approx 18$ –17%), and benzene ($S \approx 5$ –8%). These values are shown in Fig. 3A. The reactivity and the amount of carbonaceous products deposited during the reaction have been determined by TPR measurements. The main product was methane; it gave two peaks at 853 and 973 K. Other hydrocarbons were produced only in negligible amounts. Results are plotted in Fig. 3B. From the integration of the curve, the amount of carbon deposited was calculated; this is given in Table 2.

3.3. Decomposition of CO₂

The decomposition of CO₂ was first followed by pulse experiments. One CO₂ pulse contained 20.45 μmol of CO₂. As seen in Fig. 4A, the formation of gaseous CO over 5%

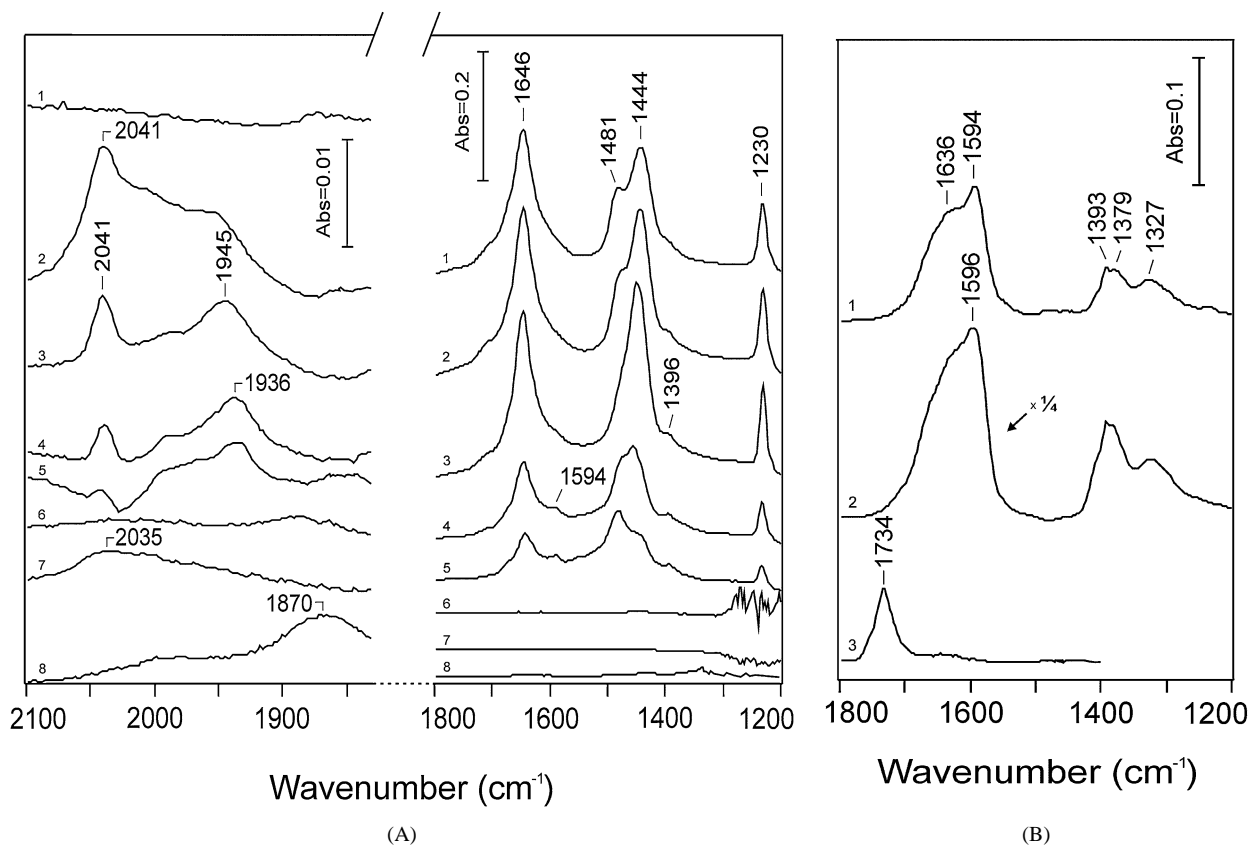


Fig. 2. (A) FTIR spectra of 5% Re/Al₂O₃ and 5% Re/SiO₂ ($T_R = 673$ K) following the adsorption of CO₂ (25 Torr) and C₃H₈ + CO₂ (1:1) gas mixture (50 Torr) at different temperatures. Re/Al₂O₃; (1) CO₂, 300 K; (2) C₃H₈ + CO₂, 300 K; (3) 373 K; (4) 473 K; (5) 573 K, Re/SiO₂; (6) CO₂, 300 K; (7) C₃H₈ + CO₂, 300 K; (8) 573 K. (B) FTIR spectra of different samples following the adsorption of HCOOH (0.1 Torr) and subsequent evacuation at 300 K. (1) 5% Re/Al₂O₃; (2) Al₂O₃; (3) 5% Re/SiO₂.

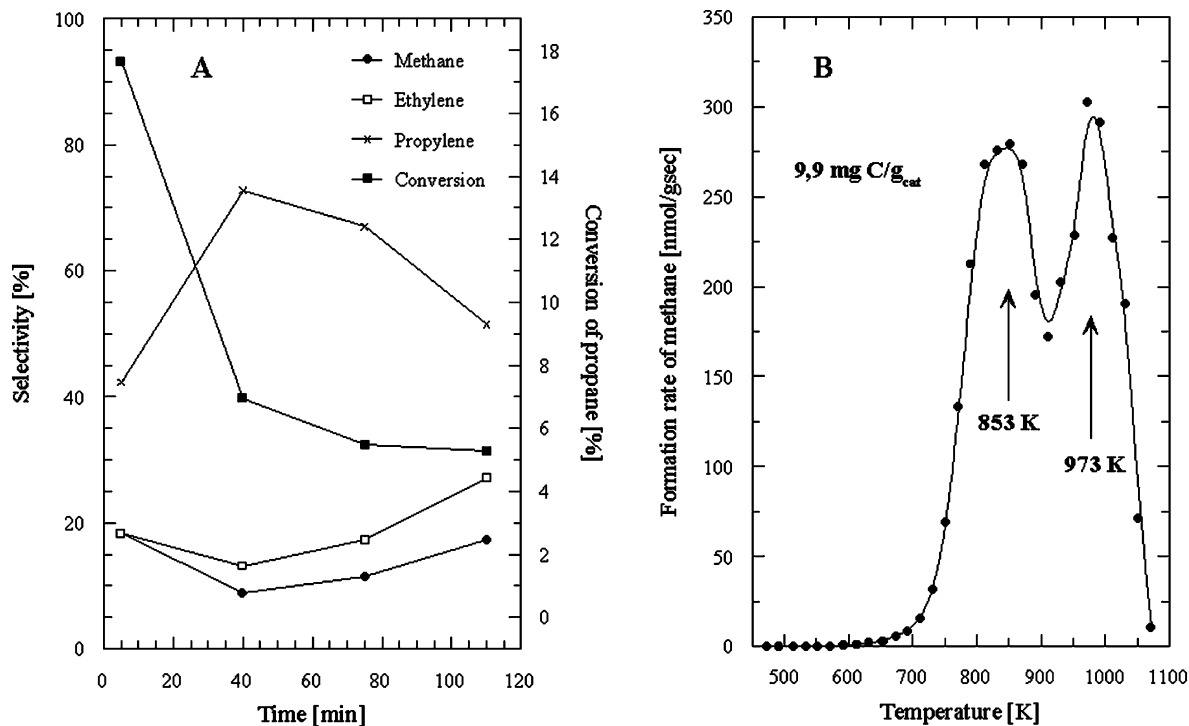


Fig. 3. (A) Conversion of propane and selectivities of different products formed in the decomposition of propane on 2% Re/Al₂O₃ ($T_R = 673$ K) at 923 K. (B) TPR curves for the reaction of surface carbon formed in the decomposition of propane at 923 K in 105 min on 2% Re/Al₂O₃.

Table 2
Characteristic data for the $C_3H_8 + CO_2$ reaction over 2% Re/ Al_2O_3 at 923 K

C_3H_8/CO_2 ratio	T_R (K)	Conversion of propane (%)		H_2/CO ratio		C_S (mg/gcat)
		Initial (5 min)	Steady state	Initial (5 min)	Steady state	
1:3	673	67.4	50.1 ^a	0.49	0.46 ^a	1.34
1:3	673	81.2	50.6 ^b	0.49	0.47 ^b	–
1:6	673	90.2	80.7 ^c	0.43	0.43 ^c	–
1:3	1073	40	32.4 ^a	0.56	0.44 ^a	–

^a Data were obtained at steady state ~110 min of reaction.

^b After 14 h of reaction.

^c After 20 h of reaction.

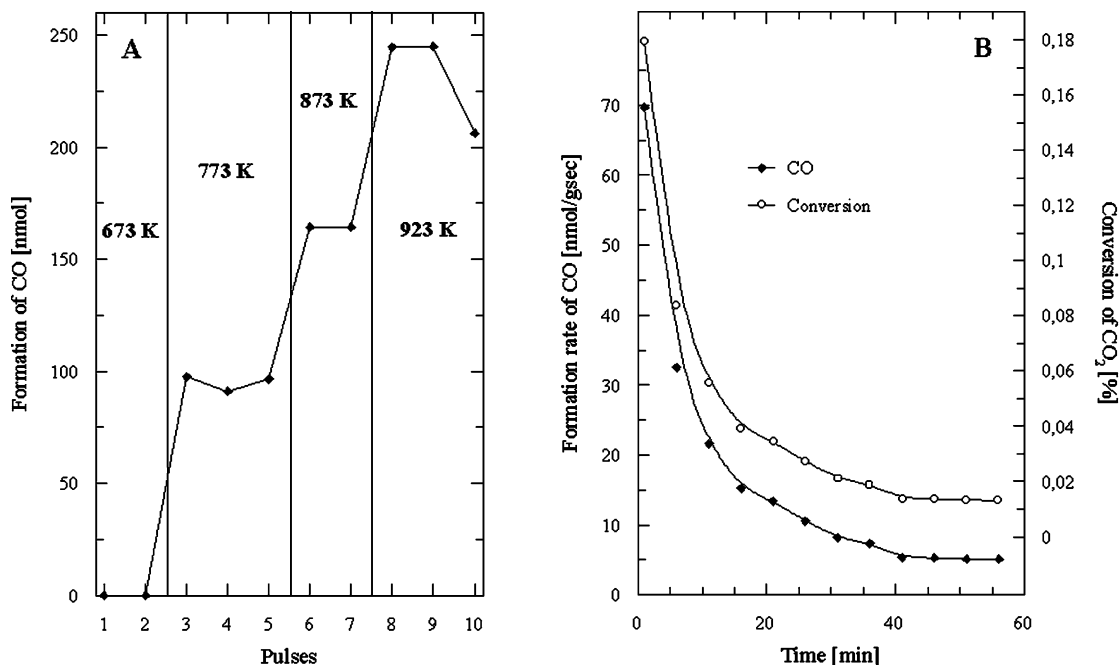


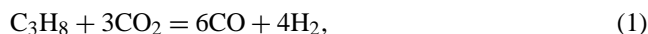
Fig. 4. Formation of CO in the decomposition of CO_2 on 5% Re/ Al_2O_3 ($T_R = 673$ K) in pulse experiments (A) and in a flow of CO_2 (10%) + Ar gas mixture (B). One pulse contained 20.45 μmol CO_2 . The conversion of CO_2 was calculated from the amount of CO formed.

Re/ Al_2O_3 was observed even at 773 K. At 923 K, at the temperature of the $C_3H_8 + CO_2$ reaction, the extent of dissociation of CO_2 became larger. An attempt was made to follow the decomposition of CO_2 in a flow system under the same conditions as applied in the $C_3H_8 + CO_2$ reaction. We found only a limited formation of gaseous CO at 923 K; the initial conversion of CO_2 was about 0.11%, which gradually decayed with time on stream (Fig. 4B). The calculation of the CO_2 conversion was based on the amount of CO formed.

3.4. Reaction of propane with CO_2

The addition of a small amount of CO_2 to propane exerted a dramatic influence on its decomposition over 2% Re/ Al_2O_3 at 923 K (Fig. 5). The rate of the formation of propylene decreased markedly, whereas that of hydrogen increased and CO was also evolved. At $C_3H_8/CO_2 = 1:1$ composition, the rate of propylene production was only ~10% of that measured in the absence of CO_2 . With a further increase in CO_2 content the conversion of propane and the production

of H_2 and CO gradually increased, whereas that of propylene decreased almost to zero. The formation of ethylene also ceased, whereas that of methane increased slightly. As a result, some variation occurred in the ratios of H_2/CO and CH_4/CO (Fig. 5). For a stoichiometric composition of reacting gas mixture, $C_3H_8/CO_2 = 1:3$, corresponding to the equation



the H_2/CO ratio was 0.61–0.52, and the initial conversion of propane was 53%, which decayed slowly. The conversion of CO_2 showed the same trend. A much higher conversion, ~90%, of C_3H_8 was achieved in the presence of a large excess of CO_2 ($C_3H_8/CO_2 = 1:6$).

With regard to the effect of reduction temperature of 2% Re/ Al_2O_3 , we found that the maximum conversions of the reactions were attained at $T_R = 673$ K (Fig. 6). The effect of temperature on the reaction measured on this sample is displayed in Fig. 7A. Lowering the reaction temperature led to a decrease in the H_2/CO ratio, and at 773 K it was

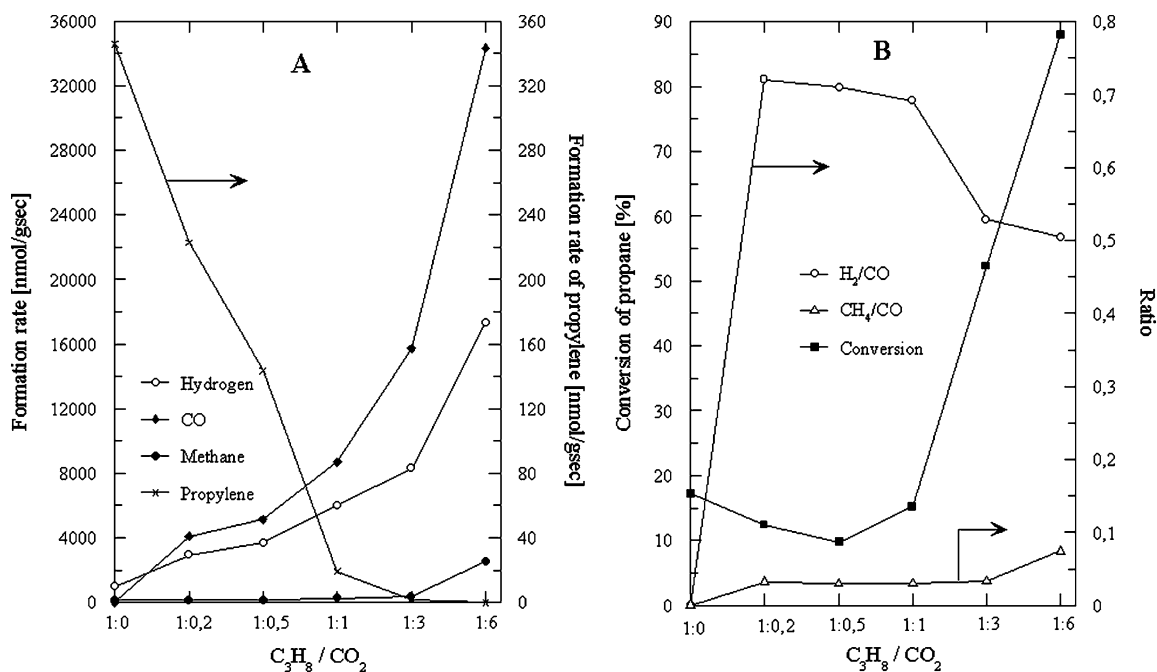


Fig. 5. Effects C_3H_8/CO_2 ratio (A) on the rate of formation of various products, (B) on their ratios and the initial conversion of C_3H_8 over 2% Re/Al_2O_3 at 923 K. Values measured at 110 min of reaction.

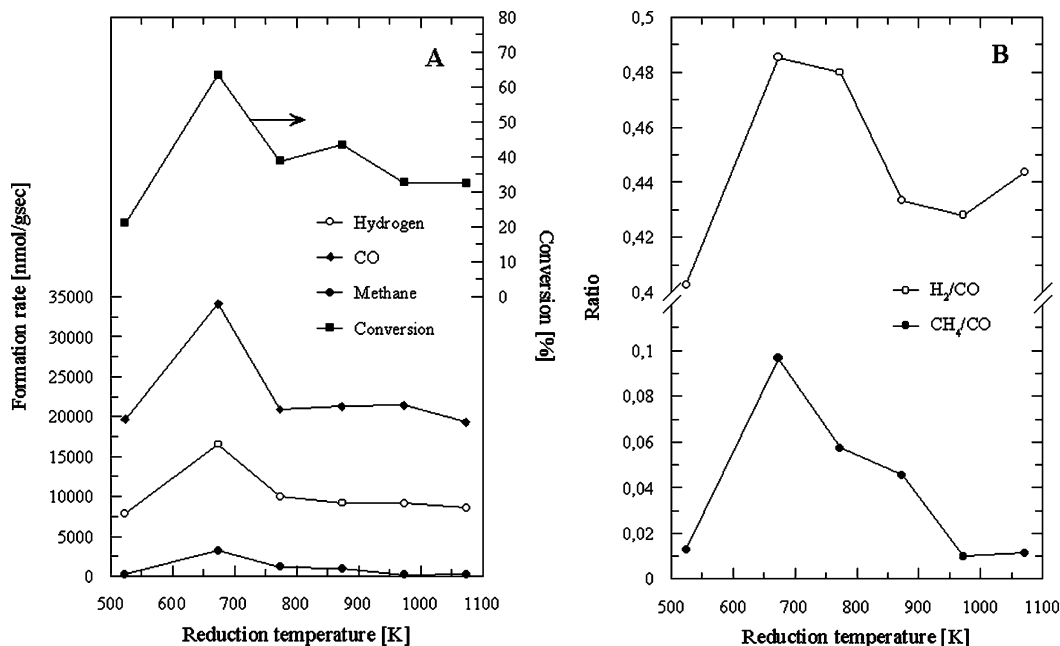


Fig. 6. Effects of the reduction temperature of 2% Re/Al_2O_3 on the reaction of $C_3H_8 + CO_2$.

only 0.18. When the measurements over 2% Re/Al_2O_3 were extended to longer periods, an initial decay occurred in the conversion for $C_3H_8/CO_2 = 1:3$, but it was $\sim 50\%$ even after 14 h. However, the high conversion, $\sim 80\%$, determined for the reaction of the gas composition at $C_3H_8/CO_2 = 1:6$ was preserved and stabilized even after an extended time, ~ 20 h. The H_2/CO ratio varied between 0.45 and 0.50. This is shown in Fig. 7B. From a study of the variation in flow rate we found that a higher flow rate resulted in decay in

the conversion, and a slight decrease in both the H_2/CO and CH_4/CO ratios.

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 CO_2 was held constant at 285.0 Torr, while that of C_3H_8 was varied. In the other case, the partial pressure of C_3H_8 was kept constant at 95.0 Torr, and that of CO_2 was changed. The order of the reaction was zero in C_3H_8 , and it was frac-

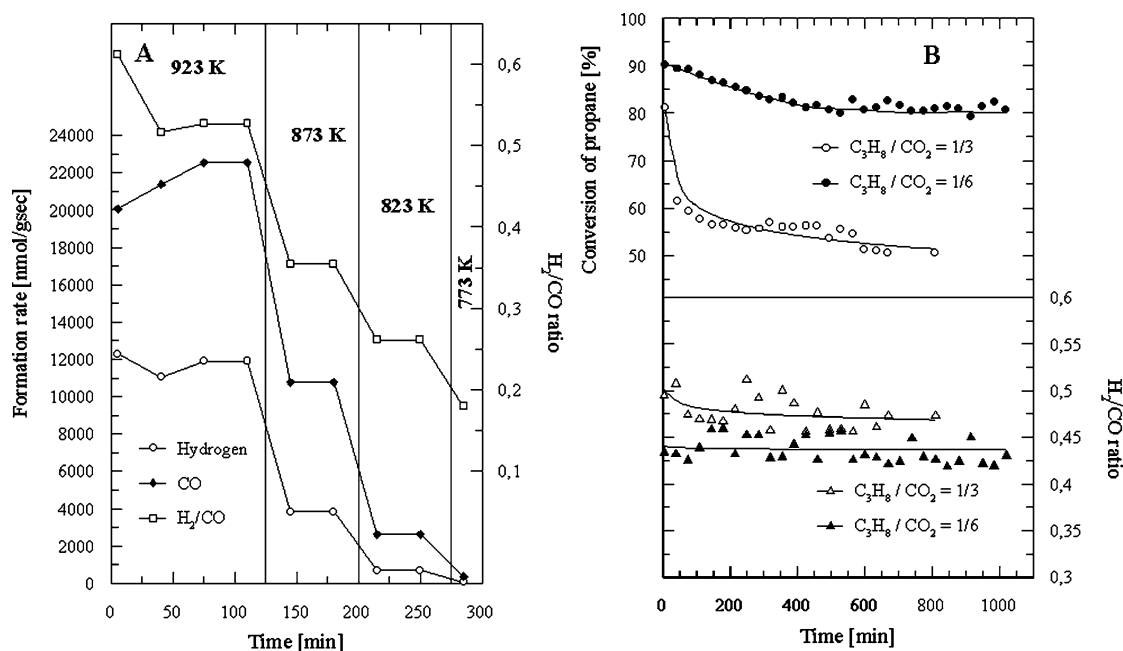


Fig. 7. (A) Rate of formation of H₂, CO and the H₂/CO ratio at different temperatures (B) the conversion of C₃H₈ over 2% Re/Al₂O₃ ($T_R = 673$ K) in time on stream at 923 K at two C₃H₈ + CO₂ compositions.

tional (0.6) with respect to CO₂ on the Re/Al₂O₃. From the Arrhenius plots, we obtained 84 kJ/mol for the activation energy of the dry reforming of propane, indicating that the process is limited by the diffusion.

The amount of carbon that remained on the catalyst after the reaction has been determined by the TPR method in the same way as after the decomposition of propane. We obtained less carbon with only one with a lower peak temperature, 825 K. Characteristic data for the at C₃H₈ + CO₂ reaction are listed in Table 2.

4. Discussion

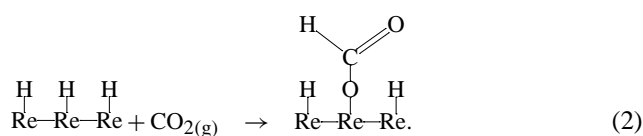
4.1. Interaction of propane and CO₂ with supported Re

The interaction of propane with supported Re has been studied by IR spectroscopy. Considering the characteristic vibrations of propane and some related compounds shown in Table 1, we can conclude that the absorption bands observed after the adsorption of C₃H₈ on 5% Re/Al₂O₃ at 173–193 K correspond very well to the different vibrations of propane [27]. Raising the temperature caused only very little change in the position of the bands and did not produce new spectral features, as was found for Pt metals [28,29] and on Mo₂C [30,31]. This indicates that the interaction of propane with Re is not so strong in the low temperature range. In the present case we did not find convincing evidence for the appearance of di- σ -bonded propylene or propylidyne.

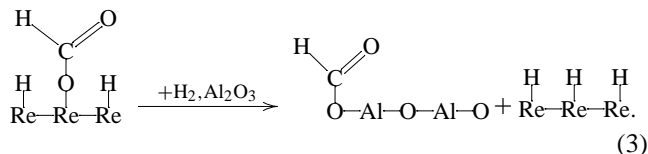
As disclosed by vibrational spectroscopic measurements, the nature of the adsorption of CO₂ on metals sensitively depends on the reduction temperature of the catalyst and on

the support [32]. This was particularly observed in a detailed study of the adsorption of CO₂ on supported Re [33]. In the present study the dissociation of CO₂ on Re catalysts reduced at 673 K was not detected by FTIR spectroscopy.

The addition of CO₂ to propane influenced only slightly its transformation described above. As a result of the surface interaction of the two compounds, however, new absorption bands were detected on Re/Al₂O₃ at 2041 and 1945 cm⁻¹, even at 300–373 K (Fig. 2A). The former belongs to the linearly bonded and the second one to the bridge bonded CO [34–37]. This suggests that propane, or probably the hydrogen formed in its surface decomposition, promotes the dissociation of CO₂ over Re. In addition, weak absorption features at 1594 and 1396 cm⁻¹ were also developed at 373–473 K, which was missing in the case of Re/SiO₂ (Fig. 2). These absorption bands were produced with much higher intensities by the co-adsorption of H₂ + CO₂ over alumina-supported Re. Taking into account the vibration characteristics of molecularly and dissociatively adsorbed HCOOH [38–40], the 1594 cm⁻¹ band can be attributed to the asymmetric and the 1396 cm⁻¹ band to the symmetric stretch of formate species. This assumption was confirmed by the adsorption of HCOOH on Re/Al₂O₃ catalysts, which produced spectral features at the same frequencies (Fig. 2B). A formate group is very likely produced in the surface interaction of adsorbed hydrogen formed in the dissociation of C₃H₈ and CO₂



The fact that neither the co-adsorption of $C_3H_8 + CO_2$ nor the adsorption of $HCOOH$ on Re/SiO_2 gave formate (Figs. 2A and 2B) suggests that it is formed on the Re, but after its formation it spills over the alumina, where it is strongly bonded:



The absence of formate on Re/SiO_2 is consistent with the former findings that this surface complex does not exist on a silica surface [41–44].

4.2. Dehydrogenation of propane

The decomposition of propane on Re/Al_2O_3 was easily measurable at and above 873 K (Fig. 3A). The main product is propylene, indicating that the dehydrogenation reaction



is the dominant process. The selectivity of propylene formation was 43–74% at 923 K. Methane and ethane were also produced, very likely as a result of the cracking of propylene. During the decomposition of propane a very unreactive carbon layer was deposited on the catalysts, which could be dehydrogenated only above 650 K (Fig. 3B). Its low reactivity suggests that the carbon is mainly in the form of graphite.

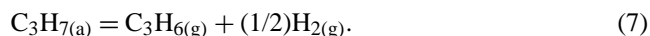
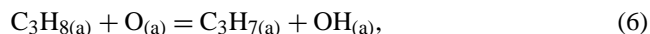
4.3. Reaction of propane with CO_2

With regard to the mechanism of the dry reforming of C_3H_8 over Ru/Al_2O_3 , Ross et al. [16] assumed the fast and complete decomposition of C_3H_8 to carbon and its subsequent reaction with adsorbed O and OH formed in the dissociation of CO_2 . The mechanism proposed by Olafsen et al. [20] was based on that of methane dry reforming, which involves the complete decomposition of methane on the very active nickel. The results of the present study, however, showed that in the absence of CO_2 the main process is the dehydrogenation of propane to propene. Addition of even a small amount of CO_2 to propane, however, opened a new route of the reaction, namely the formation of $H_2 + CO$ (Eq. (1)). At higher CO_2 content ($C_3H_8/CO_2 = 1:3$) the dehydrogenation of propane completely ceased, and its dry reforming became dominant. This suggests that the adsorbed O originating in the dissociation of CO_2 ,



changed the direction of the reaction. Taking into account the low-temperature FTIR spectroscopic results, we assume that the dissociation of CO_2 is promoted by hydrogen or C_xH_y fragments of the C_3H_8 decomposition, which is also facilitated by adsorbed O. Because formate is located on the support, we do not think that it plays any role in the dry

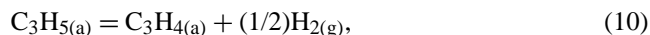
reforming of propane. Accordingly, we can count with the occurrence of the following elementary steps:



Because propene is missing from the reaction products, we may speculate that the C_3H_7 radical decomposes to carbon and hydrogen:



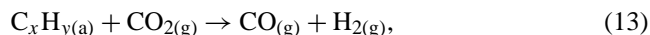
or the C_3H_6 formed in Eq. (7) is activated by adsorbed O atoms to give further reactive species:



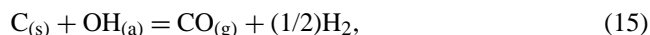
which react with adsorbed O on one hand to give CO and decompose to hydrogen and carbon on the other hand:



These processes are probably responsible for the addition of a sufficient amount of CO_2 to propane and the disappearance of propene from the reaction products. In addition to the above elementary steps, a direct reaction of one of the hydrocarbon fragments and CO_2 ,



may also occur. Experiments with CH_3 produced by the pyrolysis of azomethane showed that adsorbed CH_3 on Rh reacts readily with gaseous CO_2 [4]. We cannot exclude the possibility that, similarly to the case of dry reforming of methane, surface carbon formed in the complete decomposition of hydrocarbon fragments reacts with adsorbed O or OH:



to yield CO and H_2 .

Taking into account the rates of the decomposition of propane and CO_2 on Re catalyst and the reaction orders, we come to the conclusion that CO_2 is involved in the rate-determining step of the dry reforming of propane.

5. Conclusions

- (i) Propane interacts weakly with supported Re at 253–300 K.
- (ii) The co-adsorption of propane + CO_2 at 373–573 K led to the formation of adsorbed CO and formate species.
- (iii) At 873–923 K the decomposition of propane sets in, yielding propylene with a selectivity of 43–74%.
- (iv) The presence of CO_2 changed the reaction pathway of propane, and the formation of CO and H_2 came into prominence.
- (v) Re/Al_2O_3 reduced at 673 K exhibited a high catalytic influence on the dry reforming of propane.

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References

- [1] M.C.J. Bradford, M.A. Vannice, *Catal. Rev.* 41 (1999) 1.
- [2] F. Solymosi, Gy. Kutsán, A. Erdőhelyi, *Catal. Lett.* 11 (1991) 149.
- [3] A. Erdőhelyi, J. Cserényi, F. Solymosi, *J. Catal.* 141 (1993) 287.
- [4] J. Raskó, F. Solymosi, *Catal. Lett.* 54 (1998) 49.
- [5] E. Mark, W.F. Maier, *J. Catal.* 164 (1996) 122.
- [6] Z.L. Zhang, V.A. Tspouriari, A.M. Efstathiou, X.E. Verykios, *J. Catal.* 158 (1996) 51, 64.
- [7] R.N. Bhat, W.M.H. Sachtler, *Appl. Catal. A* 150 (1997) 279.
- [8] J. Nakamura, K. Aikawa, K. Sato, T. Uchijima, *Catal. Lett.* 25 (1998) 265.
- [9] P. Ferreira-Aparicio, A. Guerrero-Ruiz, I. Rodriguez-Ramos, *Appl. Catal. A* 170 (1998) 177.
- [10] M. Sigl, M.C.J. Bradford, H. Knözinger, M.A. Vannice, *Top. Catal.* 8 (1999) 211.
- [11] I.R. Rostrup-Nielsen, *J. Catal.* 33 (1974) 184.
- [12] F. Rossner, O. Klepel, A. Hagen, *Stud. Surf. Sci. Catal.* 107 (1997) 517.
- [13] Y. Liu, J. Xue, X. Liu, R. Hou, S. Li, *Stud. Surf. Sci. Catal.* 119 (1998) 593.
- [14] F. Solymosi, R. Németh, *Catal. Lett.* 62 (1989) 197.
- [15] F. Solymosi, A. Szőke, L. Óvári, *J. Catal.* 186 (1999) 269.
- [16] F. Solymosi, A. Szőke, L. Egri, *Top. Catal.* 8 (1999) 249.
- [17] D. Sutton, J.F. Moisan, J.R.H. Ross, *Catal. Lett.* 75 (2001) 175.
- [18] F. Solymosi, P. Tolmacsov, *Catal. Lett.* 83 (2002) 183.
- [19] F. Solymosi, P. Tolmacsov, K. Kedves, *J. Catal.* 216 (2003) 377.
- [20] A. Olafsen, Å. Slagtern, I.M. Dahl, U. Olsbye, Y. Schuurman, C. Mirodatos, *J. Catal.* 229 (2005) 163.
- [21] S. Liu, Q. Dong, R. Ohnishi, M. Ichikawa, *J. Chem. Soc. Chem. Commun.* (1997) 1445.
- [22] S. Liu, L. Wang, Q. Dong, R. Ohnishi, M. Ichikawa, *Stud. Surf. Sci. Catal.* 109 (1997) 241.
- [23] L. Wang, R. Ohnishi, M. Ichikawa, *J. Catal.* 190 (2000) 276.
- [24] F. Solymosi, P. Tolmacsov, *Catal. Lett.* 93 (2004) 7.
- [25] P. Tolmacsov, A. Széchenyi, F. Solymosi, *Stud. Surf. Sci. Catal.* 147 (2004) 559.
- [26] J.B. Claridge, M.L.H. Green, S.C. Tsang, *Catal. Today* 21 (1994) 455.
- [27] A.A. Efremov, A.A. Davydov, *Kinet. Katal.* 21 (1980) 488.
- [28] M.A. Chesters, C. De La Cruz, P. Gardner, E.M. McCash, P. Pudney, G. Shahid, N. Sheppard, *J. Chem. Soc. Faraday Trans.* 86 (1990) 2757.
- [29] N. Sheppard, C. De La Cruz, *Adv. Catal.* 42 (1998) 181.
- [30] F. Solymosi, R. Németh, L. Óvári, L. Egri, *J. Catal.* 195 (2000) 316.
- [31] F. Solymosi, R. Németh, A. Oszkó, *Stud. Surf. Sci. Catal.* 136 (2001) 339.
- [32] F. Solymosi, *J. Mol. Catal.* 65 (1991) 337.
- [33] F. Solymosi, T. Süli Zakar, *J. Mol. Catal.*, in press.
- [34] J.B. Peri, *J. Catal.* 52 (1978) 144.
- [35] C. Bolivar, H. Charcosset, R. Frety, M. Primet, L. Tournayen, *J. Catal.* 45 (1976) 163.
- [36] M. Komiyama, T. Okamoto, Y. Ogino, *J. Chem. Soc. Chem. Commun.* (1984) 618.
- [37] F. Solymosi, T. Bánsági, *J. Phys. Chem.* 96 (1992) 1349.
- [38] L.H. Little, *Infrared Spectra of Adsorbed Species*, Academic Press, London, 1966.
- [39] M.L. Hair, *Infrared Spectroscopy in Surface Chemistry*, Dekker, New York, 1967.
- [40] R.P. Eischen, W.A. Pliskin, *Proc. 2nd Int. Congr. Catalysis*, Editions Technip, Paris, 1961.
- [41] B. Imelik, J. Francosi-Rossetti, P. Sigli, *J. Chem. Phys.* 56 (1959) 1048.
- [42] K. Hirota, K. Fueki, K. Shindo, Y. Nakai, *Bull. Chem. Soc. Jpn.* 32 (1959) 1261.
- [43] F. Solymosi, A. Erdőhelyi, T. Bánsági, *J. Chem. Soc. Faraday Trans.* 1 77 (1981) 2645.
- [44] F. Solymosi, A. Erdőhelyi, *J. Catal.* 91 (1985) 327.