Dehydrogenation of propane with CO_2 – a new green process for propene and synthesis gas production

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Dehydrogenation of propane in the presence of CO_2 was considered as an alternative to commercial dehydrogenation pathway of obtaining propene and the new sources of synthesis gas. Based on thermodynamic calculations and a catalytic tests it was shown that by controlling CO_2 concentration in the feed the molar ratio of H_2/CO (synthesis gas) in the products mixture can be regulated. Several different pathways of DHP-CO_2 process integration with commercialized chemical processes utilized synthesis gas were proposed

Keywords: Dehydrogenation with CO_2, propene, synthesis gas, integrated processes.

INTRODUCTION

Propane dehydrogenation with CO_2 (DHP-CO_2) has been recently investigated as an alternative to traditional dehydrogenation of propane (DHP) that is currently applied as one of the methods of propene production. In the new process with CO_2 the yield of propene is higher than in the traditional ones. This promoting effect of CO_2 is due to its participation in the following reaction (2–4):

$$C_3H_8 \leftrightarrows C_3H_6 + H_2 \tag{1}$$

$$CO_2 + H_2 \leftrightarrows CO + H_2O \tag{2}$$

$$CO_2 + C_3H_8 \leftrightarrows C_3H_6 + CO + H_2O \tag{3}$$

$$CO_2 + C \leftrightarrows 2CO \tag{4}$$

It is generally accepted that one of the most important roles of CO_2 in the DH-CO_2 is consumption of hydrogen that is produced in the thermodynamically limited DHP reaction. Coupling of DHP (reaction 1) with the reverse water-gas shift RWGS (reaction 2) enhances the yield of propene. Such promoting effect of CO_2 was postulated not only in the case of DHP-CO_2 but also in dehydrogenation of other hydrocarbons such as, ethane, butanes and ethylbenzene over different oxide-based catalysts[1–6]. It was also postulated that CO_2 may participate in the oxidative dehydrogenation of propane (reaction 3) that is an additional way of propene formation as well as in coke gasification (reaction 4) that enhances the catalyst stability.

From the above it is clear that the additional useful (from chemical point of view) product of DHP-CO_2 is CO that is formed in reactions 2–4. This compound separately or together with H_2 produced in reaction 1 (CO + H_2 – synthesis gas) has many applications.

The goal of the present work was to discuss the possibilities of the application of the primary products of propane dehydrogenation with CO_2 other than propene, based on thermodynamic considerations and catalytic tests. We have proposed several pathways for the utilization of synthesis gas produced in the DHP-CO_2 process.

EXPERIMENTAL

The thermodynamic data of the substances were taken from the database Chemcad II Version 2.60. The calculation of the equilibrium yield of propene and molar ratio of CO/H_2 were done as reported previously[7].

Two kinds of oxides were used as supports; γ-Al_2O_3 (BET surface 155 $m^2 \cdot g^{-1}$, Aldrich) and SiO_2 (BET surface 304 $m^2 \cdot g^{-1}$, POCH Poland). The Cr-O/SiO_2 and Cr-O/Al_2O_3 catalysts were prepared by the impregnation technique from an aqueous solution of $Cr(NO_3)_3$ (POCH, Poland). The solutions were mixed with the supports (SiO_2, γ-Al_2O_3), followed by evaporation under constant stirring and calcined at 923 K for 3 h in air. The intended content of Cr in the both catalysts was 3.4 wt.%.

The interaction of CO_2 with the surface of the supports and catalysts was probed by FTIR spectroscopy. Before the experiments the samples (prepared as self-supporting discs, 10 mg) were placed in IR cell and then activated in vacuum (10^{-3} Pa) at 873 K for 60 min. Then after the sample was cooled and dry CO_2 adsorption was carried out at room temperature. The FTIR spectra were recorded at 298 K after evacuation of CO_2 from the cell for 30 min at 298 K (10^{-3} Pa) on Equinox 55 Bruker spectrometer with a MCT detector (resolution 2 cm^{-1}).

The dehydrogenation of propane in the presence and absence of CO_2 was carried out in the flow-type quartz reactor packed with 500 mg catalyst (grain size 0.2–0.3 mm). The feed was a mixture of propane (Linde, 99.95%), carbon dioxide (Linde, 99.9993%) and helium (Linde, 99.999%). The partial pressure of propane was kept constant (14.5 kPa), and the partial pressure of carbon dioxide was changed by diluting CO_2 with He. In all the cases the total flow rate was 30 $cm^3 \cdot min^{-1}$. The catalysts were first preheated in a stream of helium at 873 K and then the reaction was started at this temperature. The reactants and products were analyzed on-line using two gas chromatographs. One of them was equipped with a glass column (3mx3mm) packed with Porapak Q and a flame ionization detector. It was used to analyze the hydrocarbons C_1-C_3. The second chromatograph was equipped with a stainless steel column (3mx3mm) packed with Carboxen 1000 and, a thermal conductivity detector (for CO, H_2 and CO_2 analyses). Propane conversion, hydrocarbons yields and propene selectivity were calculated as reported previously[8].

Under reaction conditions applied in this work the conversion of propane in the process without catalysts was below 1%.

RESULTS AND DISCUSSION:

Thermodynamic considerations

The results of thermodynamic considerations reported in literature indicate that in the dehydrogenation with CO_2 the yield of propene is higher than in the simple dehydrogenation that is a widely commercialized process for propene production. Calculations of equilibrium conversion for propane dehydrogenation alone (DHP) and for propane dehydrogenation coupling with the RWGS (DHP-RWGS) indicate that the equilibrium yield of propene is much higher in the presence of CO_2 than in its absence[1]. In other words, by using CO_2 as a coregent similar propene yield as in the traditional processes can be obtained at lower temperature. The effect of the temperature and molar ratio of CO_2/C_3H_8 substrates on the equilibrium yield of propene is presented in Table 1.

Table 1. Variation of equilibrium yield of propene with temperature and initial molar ratio of $CO_2:C_3H_8$ (feed gas composition)[a]

| T (K) | Initial molar ratio of $CO_2:C_3H_8$ | | | |
| | 5:1 | 1:1 | 0.5:1 | 0.2:1 |
	Equilibrium yield of propene			
673	0.26	0.09	0.07	0.06
723	0.47	0.18	0.15	0.12
773	0.72	0.32	0.27	0.23
823	0.88	0.51	0.44	0.38
873	0.96	0.70	0.63	0.57
923	0.99	0.84	0.79	0.74
973	0.99	0.93	0.89	0.86

[a] Total pressure = 1 Atm. In the simplified model selectivity to propene is 100%, thus the equilibrium yield of propene is equal to equilibrium propane conversion.

From this table it is clear that the equilibrium yield of propene increases with the increase either of the initial molar ratio of CO_2/C_3H_8 or the temperature. Furthermore, the data reported in Table 2 indicates that by changing the temperature and the feed gas compositions (ratio of CO_2/C_3H_8) not only the yield of propene can be controlled but also the molar ratio of other useful primary products, i.e. CO/H_2 (synthesis gas).

Under the investigated conditions the CO/H_2 ratio varies in a wide range between 4.0 to 0.2. Some of these

Table 2. Variation of equilibrium molar ratio of CO/H_2 with temperature and initial molar ratio of $CO_2:C_3H_8$ (feed gas composition)[a]

| T (K) | Initial molar ratio of $CO_2:C_3H_8$ | | | |
| | 5:1 | 1:1 | 0.5:1 | 0.2:1 |
	Equilibrium ratio of CO/H_2			
673	2.9	1.5	1.1	0.7
723	2.6	1.3	0.9	0.5
773	2.5	1.1	0.7	0.4
823	2.5	0.9	0.6	0.3
873	2.8	0.9	0.5	0.3
923	3.2	0.9	0.5	0.2
973	4.0	0.9	0.5	0.2

[a] Total pressure = 1 Atm.

ratios are suitable for the chemical processes in which synthesis gas is the substrate. The general description (reaction conditions, synthesis gas composition, ect.) of the most important industrial processes in which the synthesis gas as the substrate was used is reported on in Table 3. It can be generally seen that in all these processes the synthesis gas with relatively low molar ratios of CO/H_2 (1–0.5) is applied. The thermodynamic considerations reported in Table 2 indicate that in the DHP-CO_2 such values can be obtained only when the initial ratios of CO_2/C_3H_8 are equal 1:1 or lower. Using the feed gas rich in CO_2 ($CO_2/C_3H_8 > 1$) leads to obtaining the synthesis gas with a higher CO/H_2 ratios which have to be corrected before being used in any mentioned processes.

The thermodynamic considerations indicate that the temperature has much smaller effect on the equilibrium molar ratio of CO/H_2. Moreover, the effect of temperature on the CO/H_2 value varies with the initial composition of feed gas. At initial molar ratio of $CO_2:C_3H_8$ between 1:1 to 0.2:1 the values of CO/H_2 decrease slightly as temperature increase from 673 to 973 K, while when the initial ratio of $CO_2:C_3H_8$ is 5:1, the CO/H_2 ratio drops gradually between 673–773 K and then increases above 823 K.

Catalytic tests

Our previous catalytic experiments and literature results reveal that the catalysts which are active and selective in the nonoxidative dehydrogenation of light alkanes exhibit also good catalytic performance in the dehydrogenation with CO_2. Therefore, it is not suppressing that chromium oxide-based materials are considered as a one of the most promising catalysts for DHP-CO_2.

Table 4 summarized the results obtained over selected chromium oxide-based catalysts in the dehydrogenation of propane in the presence of CO_2 at 823 K and 873 K. Over the investigated catalysts propane conversion and propene yield increase with the increase of reaction temperature, while the selectivity to propene drops as the reaction temperature increases. In addition to the primary products (propene, CO, H_2 and H_2O-not analyzed) several others by-products, such as methane, ethane and ethene are produced. These byproducts are formed with quite similar selectivities over Cr-O/SiO_2 catalysts both in the presence and absence of CO_2 while over Cr-O/Al_2O_3 the selectivities to methane and ethene are much higher in the processes carried out with CO_2.

Over both catalysts, in the investigated narrow range of temperature, the ratios of CO/H_2 are changed slightly. As we reported in our previous works concerning SBA-1[9] and MCM-41[7] supported chromium oxide systems the CO/H_2 values (or H_2/CO) vary much significantly in a wider range of temperature, i.e. 673–923 K. However, from a practical point of view, the range 823–873 K is more suitable. Below 823 K the conversion of propane is insignificant and a large amount of unreacted substrates has to be separated and recycled, whereas above 873 K the side reactions leading to fast catalyst deactivation and low selectivity to primary product are accelerated.

Figures 1a and b display the variation of the yield of propene and molar ratio of CO/H_2 with feed gas composition over Cr-O/Al_2O_3 and Cr-O/SiO_2 catalysts. It is

Table 3. General description of selected processes used synthesis gas.

Process		Primary reactions	Temperature (K)	Pressure (MPa)	Catalyst	Feed composition	Products composition (wt. %)
Methanol synthesis	High-pressure method	$CO + 2H_2 = CH_3OH$	613÷673	30÷32	$Zn\text{-}Cr\text{-}O$	$H_2:CO \approx 2:1$ 8÷15% inert components (N_2, Ar, CH_4)	CH_3OH (~95%), vestigial amounts of: C_2H_5OH, DME
Methanol synthesis	Low-pressure method	$CO + 2H_2 = CH_3OH$ $CO_2 + 3H_2 = CH_3OH + H_2O$	473÷533	5÷10	$Cu\text{-}Zn\text{-}O/Al_2O_3$	$H_2:(CO+CO_2) = (2÷2,2):1$	
OXO synthesis	Ruhrchemie Process	$RCH_2{=}CH_2 + CO + H_2 = RCH_2CH_2CHO$ (n- i iso-)	413÷453	20÷35	$HCo(CO)_4$		Aldehydes (80%), Alcohols (10%)
OXO synthesis	Shell Process	$RCH_2{=}CH_2 + CO + 2H_2 = RCH_2CH_2CH_2OH$ (n- i iso-)	433÷473	5÷10	$HCo(CO)_3 P(n\text{-}C_4H_9)_3$	$H_2:CO = (1÷1,2):1$	Alcohols (80%), Paraffins (15%)
OXO synthesis	Union Carbide Process		353÷393	1,5÷2,5	$HRh(CO)_2 P(Ph_3)_3$		Aldehydes (96%), Paraffins (2%)
Fischer-Tropsch synthesis	Low-pressure method	$2nH_2 + nCO = CnH_{2n} + nH_2O$ $(2n{+}1)H_2 + nCO = C_nH_{2n}{+}2 + nH_2O$	463÷603	0,5÷2,7	Fe or Co (+Ti, Rh, Cu, Zn, V, K)		Hydrocarbons (alkanes and alkenes)
Fischer-Tropsch synthesis	High-pressure method	$2nH_2 + nCO = C_2H_{2n+1}OH + (n{-}1)H_2O$ $(2n{-}1)H_2 + nCO = C_nH_{2n}O + (n{-}1)H_2O$	453÷523	30÷45	Ru, Co	$H_2:CO = (1,5÷3):1$	Alcohols, aldehydes, carboxylic acids, esters

clear that over both investigated materials CO_2 exerts an opposite effect on propene yield (Fig.1a) and a similar effect on the molar ratio of CO/H_2 (Fig.1b). Over the Cr-O/Al$_2$O$_3$ catalyst that is commercially applied in propane dehydrogenation (e.g. in CATOFIN® Process) even a small amount of CO_2 in the feed leads to a dramatic decrease of propene yield. In contrast, over Cr-O/SiO$_2$ carbon dioxide exerts a promoting effect on the yield of propene. With the increasing molar ratio of $CO_2:C_3H_8$ the yield of propene increases gradually. However, the

Table 4. A comparison of catalytic performances of chromium oxide-based catalysts at different temperatures[a]

Catalyst	Feed gas	T (K)	Conversion of C_3H_8 (%)	Selectivity (%)				Yield of C_3H_6 (%)	CO/H_2 (mol/mol)
				C_3H_6	CH_4	C_2H_4	C_2H_6		
Cr-O/SiO$_2$	CO$_2$:C$_3$H$_8$	823	17.2	94.4	2.5	2.4	0.8	16.3	1.5
		873	27.7	90.8	3.2	4.5	1.5	25.2	1.4
	He:C$_3$H$_8$	823	12.7	92.1	2.7	3.3	1.8	11.7	<0.1
Cr-O/Al$_2$O$_3$	CO$_2$:C$_3$H$_8$	823	12.9	88.3	7.8	3.8	0.0	11.4	4.2
		873	29.7	80.7	10.0	8.2	1.1	24.0	3.8
	He:C$_3$H$_8$	823	14.0	95.8	2.9	1.3	0.0	13.4	<0.1

[a] Reaction conditions: Molar ratio of CO$_2$:C$_3$H$_8$ = 5:1 and He:C$_3$H$_8$ = 5:1; Total flow rate = 30 cm^3·min^{-1}; Catalyst weight = 500 mg; Results after 10 min-on-stream.
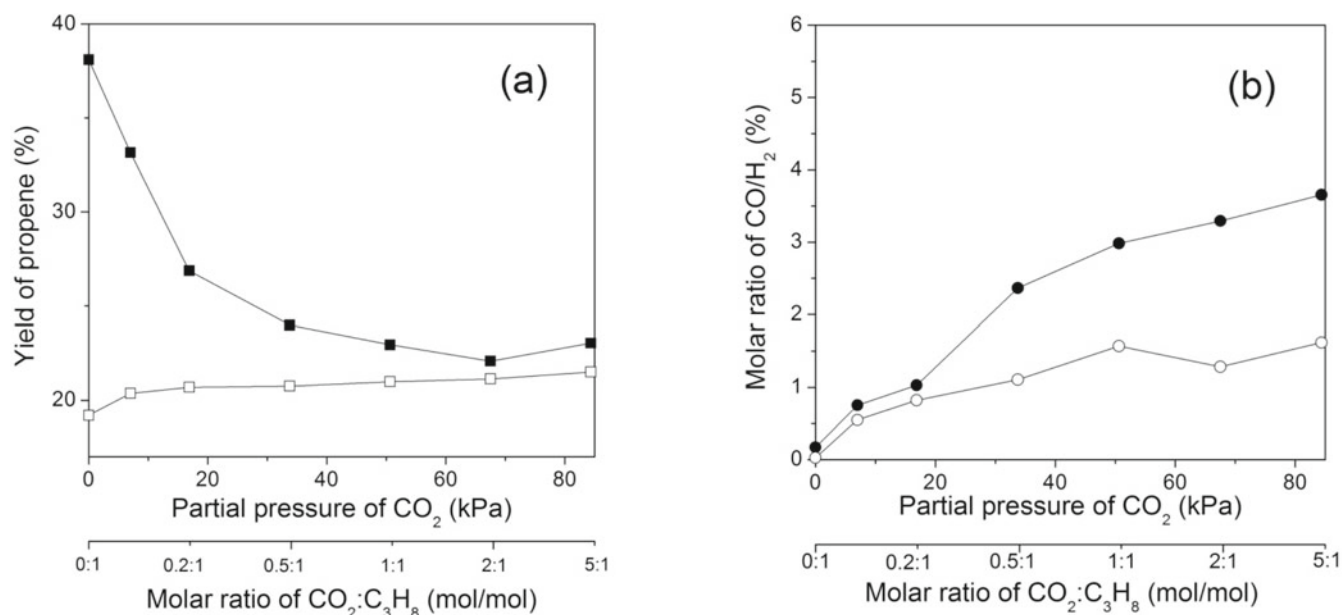
Figure 1. Variation of propene yield (a) and molar ratio of CO/H$_2$ (b) with the molar ratio of CO$_2$:C$_3$H$_8$ in the feed over Cr-O/Al$_2$O$_3$ (solid symbols) and Cr-O/SiO$_2$ (empty symbols) catalysts. Reaction conditions: Temperature 873 K; Total flow rate of feed gas=30 cm3·min^{-1}; Catalyst weight = 500 mg; Reaction time 10 min

positive effect of CO$_2$ observed over Cr-O/SiO$_2$ is much smaller than the negative effect exerted on the catalytic performances of Cr-O/Al$_2$O$_3$.

Such great differences in the effects of CO$_2$ are probably caused by the difference in supports nature. Figure 2 a and b show the IR spectra obtained after the adsorption of CO$_2$ on γ-Al$_2$O$_3$, SiO$_2$, Cr-O/Al$_2$O$_3$ and Cr-O/SiO$_2$ activated at 873 K. No new spectral features developed following the deposition of chromium oxide on the supports. In the case of Cr-O/Al$_2$O$_3$ and γ-Al$_2$O$_3$ strong bands appeared at 1646, 1474, 1443, 1233 and 2345 cm^{-1}. These bands were assigned to two families of adsorbed species: (i) carbonate-like species characterized by ν_{CO} bands at 1646, 1474, 1443 cm^{-1} and by a band δ_{OH} at 1233 cm^{-1} (Fig.2a) and (ii) linear form of cation-coordinated CO$_2$ species characterized by strong band at 2345 cm^{-1} (Fig.2b)[10,11]. The linear species are formed by the interaction of CO$_2$ with Lewis acid sites, whereas carbonate-like species by the interaction with basic hydroxyl groups or with acid-base sites[10]. The appearance of the band at 1233 cm^{-1} confirmed formation of HOCO$_2^-$ species, which are formed by the interaction of CO$_2$ with basic OH groups persisting after activation at 873 K. Similar experiments on SiO$_2$ and Cr-O/SiO$_2$ catalyst produced very weak adsorption bends at 1620, 2340 and 2364 cm^{-1}, which clearly indicates that, the

basicity and Lewis acidity of these materials are much weaker than those of Cr-O/Al$_2$O$_3$ and γ-Al$_2$O$_3$. These results coincide well with general observation that oxides of semi-metal elements, like SiO$_2$, show weak basicity and Lewis acidity, while ionic oxides, like γ-Al$_2$O$_3$, show medium basicity and strong Lewis acidity[12].

The FTIR studies lead us to suggest that the unfavorable effect of CO$_2$ observed in the dehydrogenation of propane on the Cr-O/Al$_2$O$_3$ catalyst is caused by the nature of γ-Al$_2$O$_3$. Adsorption of CO$_2$ on γ-Al$_2$O$_3$ may certainly reduce the possibility of propane adsorption on the surface of Cr-O/Al$_2$O$_3$ catalyst, leading to reduced propane conversion. A similar explanation for the inhibiting effect of CO$_2$ was proposed by Xu et al.[13].

CONCLUSIONS

The process of propane dehydrogenation in the presence of CO$_2$ can be considered not only as an alternative to traditional dehydrogenation of propane pathway of propene production but also as a new resourses of synthesis gas. The thermodynamic calculations for the simplified model and the catalytic tests indicate that the synthesis gas composition (molar ratio of CO/H$_2$) can be controlled easily by changing the molar ratio of CO$_2$:C$_3$H$_8$ in the feed. Moreover, the catalytic experiments indicate that the effect of CO$_2$ on the yield of
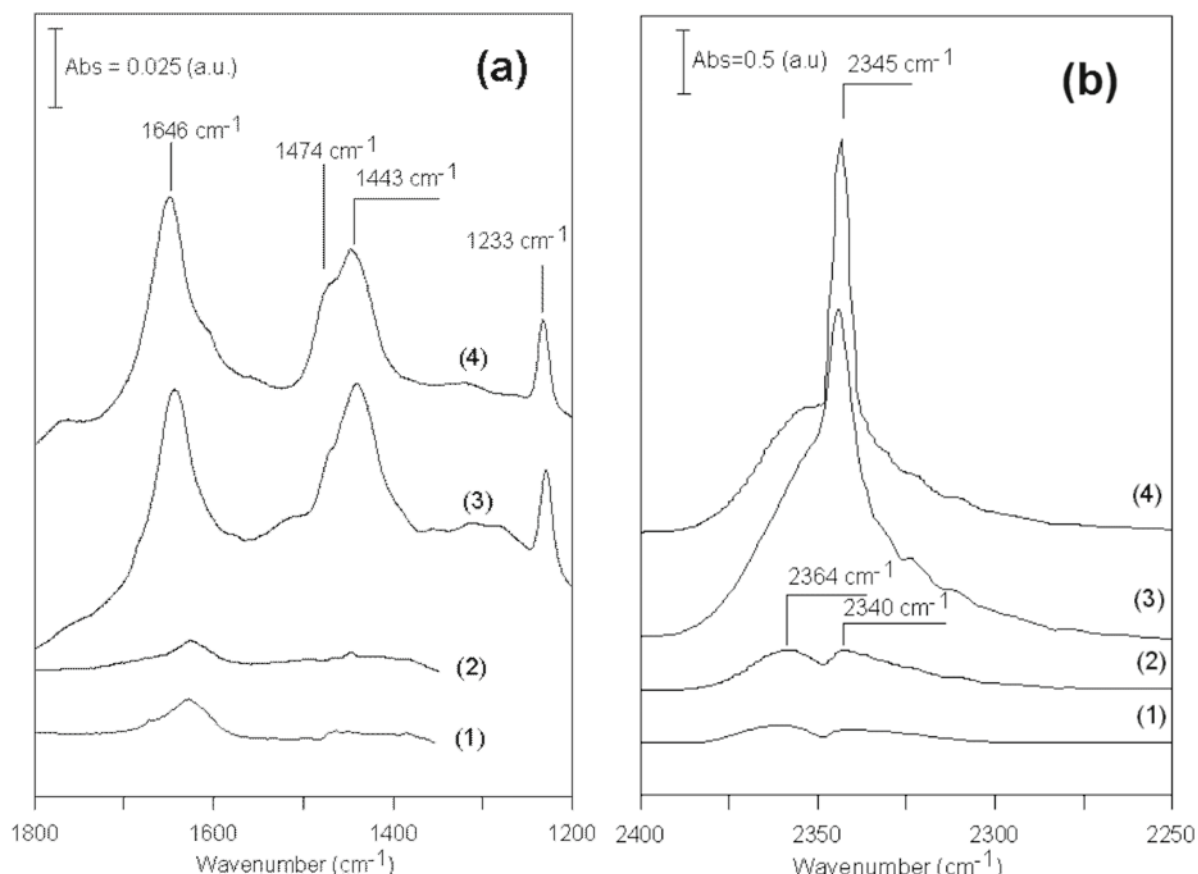
Figure 2. FTIR spectra of CO_2 adsorbed on supports and catalysts activated at 873 K. Designations: (1) Cr-O/SiO_2, (2) SiO_2, (3) Cr-O/Al_2O_3 and (4) Al_2O_3
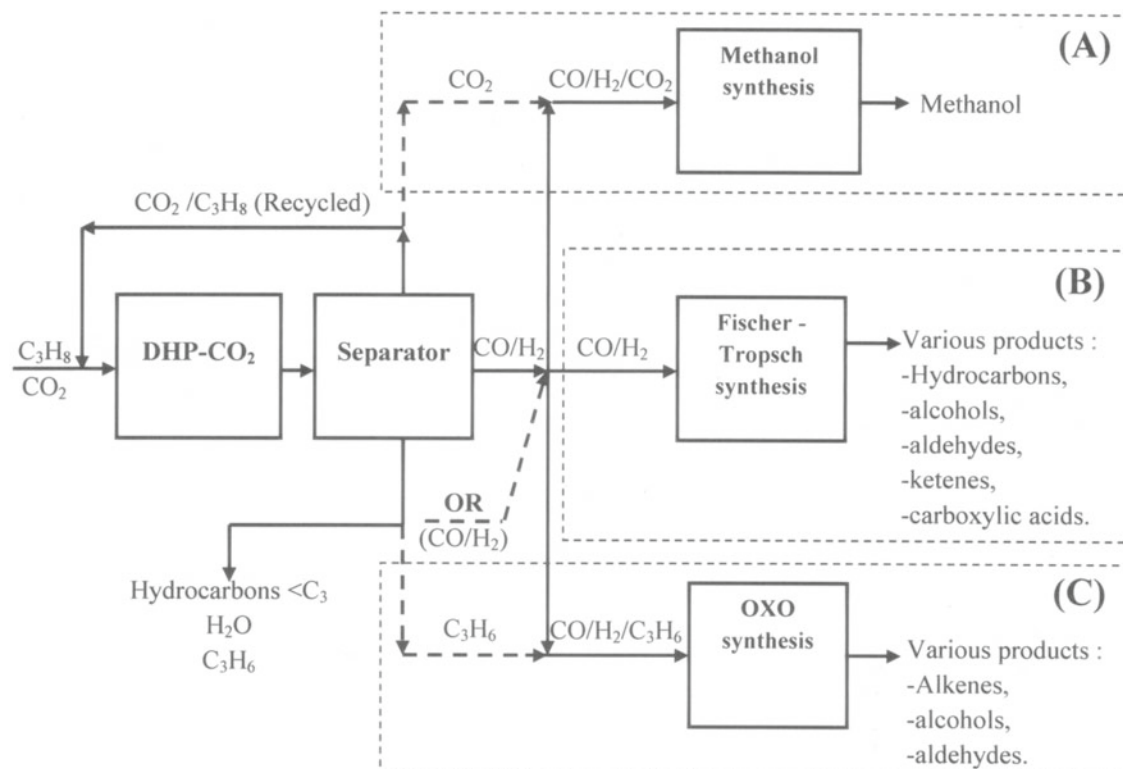

Figure 3. Pathways of DHP-CO_2 process integration with the various commercially available processes utilize synthesis gas and propene/carbon dioxide as substrates. Designations: OR- Synthesis gas from others recourses needed for CO/H_2 ratio correction in the feed; Installations of (A) methanol, (B) Fisher-Tropsch and (C) OXO synthesis

propene and CO/H_2 molar ratio depends strongly on the catalyst nature. The low ratio of CO/H_2 suitable for a direct application of synthesis gas in chemical processes

can be obtained over Cr-O/SiO_2 catalyst using feed gas with low CO_2 concentration.

Figure 3 summarized the pathways of DHP-CO_2 integration with some of the widely applied processes

using synthesis gas and propene/carbon dioxide as the substrates. The reaction mixture from DHP-CO_2 process after partial separation and correction of CO/H_2 ratio from other resources (OR) can be directed on one of the three installations, for example on methanol (A), Fischer-Tropsch (B) or OXO (C) synthesis. This schemata does not exhaust all the possibilities, it only illustrates the ways of DHP-CO_2 process integration with some of the widely applied chemical process utilized synthesis gas.

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