

TITLE OF THE INVENTION**METHOD OF PREPARING ALKYL CARBOXYLIC ACIDS BY
CARBOXYLATION OF LOWER ALKANES METHANE**

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BACKGROUND OF THE INVENTIONField of the Invention

The present invention relates to a method of preparing acetic and higher carbon number aliphatic acids directly by carboxylation of lower molecular weight alkanes such as methane using a solid, heterogeneous catalyst without the intermediate formation of synthesis gas, e.g., $\text{CH}_4 + \text{CO}_2 \rightarrow \text{CH}_3\text{COOH}$.

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Description of the Background

Organic acids are widely used as intermediates and as solvents in chemical processing. One of the most widely used of these acids is acetic acid, which is a high-value, high-volume chemical currently produced at the rate of 6×10^6 tons/yr. worldwide. Acetic acid is widely used as a raw material in the production of vinyl acetate, acetic anhydride, and cellulose acetate, and as an industrial and pharmaceutical solvent.

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Although prior art exists for the indirect conversion of methane and other alkanes to acids, no prior art is known to exist for the direct synthesis of acetic acid from methane or other lower molecular weight alkanes on solid catalysts. U.S. 5,659,077 describes a method for production of acetic acid by subjecting a feed mixture consisting of (a) methane gas and (b) gaseous oxygen, air, or a mixture thereof to partial oxidation without production of synthesis gas in a reaction zone at elevated temperature and pressure to form a reaction mixture containing methanol, carbon monoxide, carbon dioxide, methane, and water vapor. At least a portion of the water vapor is removed from the reaction mixture, and the remaining partial oxidation reaction mixture is fed, together with additional methanol from an external source, through a carbonylation reaction zone at elevated temperature and pressure to form a reaction product containing acetic acid and/or methyl acetate and methanol. The additional

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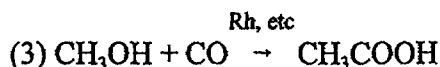
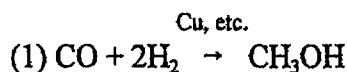
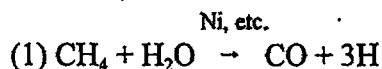
methanol is added in an amount such that the additional methanol together with the methanol produced by partial oxidation is sufficient to convert substantially all of the carbon monoxide produced by partial oxidation. Excess methane and carbon dioxide are recycled from the carbonylation reaction zone back to the partial oxidation reaction zone, and methanol in the carbonylation reaction product is recycled back to the carbonylation reaction zone and acetic acid and/or methyl acetate is recovered as product. This process, in effect, produces acetic acid by the partial oxidation of methane to methanol, followed by carboxylation to acetic acid. Unlike the present invention, oxygen is required and methanol is produced as a separable intermediate product. Methanol is then carbonylated to form acetic acid, in manner similar in principle to conventional commercial technology.

U.S. 5,510,525 describes a process for direct oxidative carbonylation of lower alkanes to acids having one greater carbon atom. The process requires both CO and oxygen as reactants and uses a homogeneous metal salt catalyst system promoted by halide ions and/or a metal (with oxygen as the oxidant) in an aqueous medium. Although the process converts methane to acetic acid, again as in U.S. 5,659,077, oxygen is used and carbonylation is required as a separate step. Neither U.S. 5,659,077, nor U.S. 5,590,525 contemplate the use of CO₂ and both absolutely require oxygen to react with methane. Additionally, U.S. 5,510,525 requires an aqueous homogeneous catalyst system, unlike the solid heterogeneous catalyst of the present invention.

U.S. 5,393,922 describes a process for direct catalytic oxidation of hydrocarbons, particularly C₁ - C₆ alkanes and single ring aromatics to acids by hydrogen peroxide (or dihydrogen and dioxygen) under mild temperature conditions (70 - 200°C) using liquid phase metal or metal salt catalysts. This process is similar to that of U.S. 5,510,525, where an aqueous metal salt catalyst system is used, and the presence of CO and dioxygen is required. Acetic acid is formed only from ethane, and methane reacts to form formic acid. U.S. 5,393,922 thus contemplates no formation of a carbon-carbon bond, e.g., no formation of acetic or higher acids from methane and is therefore unlike the present invention in which a given carbon number alkane, such as methane, reacts with CO₂ to form a higher carbon number aliphatic acid.

As an example of the current commercial technology used to produce aliphatic acids

from alkanes, acetic acid is widely produced from methane in a series of independent steps in which a separate catalyst and reactor is typically used in each step:



In step (1), methane is typically converted to synthesis gas, a mixture of CO and hydrogen using a nickel-based catalyst. This synthesis gas can also be produced by gasification of coal or other carbonaceous material using widely known conventional technology. Synthesis gas, in turn, is used to produce a number of chemicals, including methanol as shown in step (2), typically using a Cu-based catalyst. Finally, methanol is reacted with CO in a carbonylation step using a homogeneous Rh-based catalyst. This three-step process currently fulfills about 98% of the acetic acid market. Syngas generation alone typically accounts for at least 60% of the overall production cost of acetic acid. Obviating this step is clearly desirable to reduce the cost of synthesizing aliphatic acids such as acetic acid.

In step (3), this conventional process relies on the reaction of methanol and CO to form acetic acid using an expensive Rh catalyst dissolved in the liquid phase, often using iodine-based promoters. The economics of the process depends on successful recovery and recycle of the catalyst. As an example of the importance of developing a solid, heterogeneous catalyst, the cost of the separation unit can be more than 110 percent of the cost of the reaction unit. Also, Rh-based catalysts are expensive, and I-based promoters (mostly CH_3I) are toxic and corrosive, requiring expensive metallurgy, thus resulting in higher costs.

In theory, acetic acid might be made using a two-step reaction sequence where syngas is first converted into methanol, and methanol is then carbonylated into acetic acid in the vapor phase using heterogeneous catalysts. Although vapor phase methanol carbonylation has been a subject of intense lab-scale research for the past several years, no

catalyst has been reported to be of industrial interest. The catalysts for vapor phase reactions have included RhCl_3 supported by silica, alumina, and $\text{SiO}_2\text{-Al}_2\text{O}_3$. Ni is also reported to be an active catalyst for this reaction (Fujimoto et al., 1987). Further, nickel supported on activated carbon (AC) has been investigated for this reaction and tin has been studied as a promoter (Liu and Chiu, 1994a, 1994b). Although the catalyst was active, significant deactivation was observed via reduction of Ni to an inactive form and reduction of Ni by the AC support to form Ni carbide.

Thus, to date no industrially practical heterogeneous catalyst has been developed for the vapor phase carbonylation of methanol. Even if such a heterogeneous catalyst were developed, the overall process for the conversion of methane to acetic acid would still be indirect, requiring steps (1) and (2) above. Thus, there is a clear need for a process based on a solid heterogeneous catalyst for the direct reaction of lower alkanes (like methane) with CO_2 to form aliphatic acids such as acetic acid. This also provides an environmentally benign route to acetic acid based on inexpensive feedstocks.

Another conceptual route for the synthesis of acetic acid entails the reaction of methane, CO, and small amounts of oxygen. This type of oxidative conversion to carboxylic acids has been reported for a number of lower alkanes, such as methane and ethane homogeneous catalysts (Nishiguchi et al., 1992; Kurioka et al., 1995; Lin et al., 1997; Sen and Lin, 1996). For example, the reaction of CH_4 (20 atm), CO (15 atm), in the presence of $\text{Pd}(\text{OAc})_2$, $\text{Cu}(\text{OAc})_2$ (0.05 mmol, ea), and $\text{K}_2\text{S}_2\text{O}_8$ (9 mmol) in trifluoroacetic acid (TFA) (5 mL) at 80°C gives acetic acid in high yields. The results are summarized in Table 1. However, the reaction times are 20 to 40 h. Further, homogeneous catalysts such as $\text{Cu}(\text{OAc})_2$, $\text{Pd}(\text{OAc})_2$, and $\text{K}_2\text{S}_2\text{O}_8$ are required and are used in a reaction medium (such as trifluoroacetic acid, TFA). The use of a homogeneous reaction medium where the product (acetic acid) is soluble in the reaction mixture requires the use of cost-intensive and energy-intensive separations, which increase the cost and complexity of the overall process design.

TABLE 1. Acetic Acid Synthesis From CH₄ and CO^a

Run	K ₂ S ₂ O ₈ /mmol	Time (h)	AcOH Yield (%) ^b
1	--	20	240
2	--	40	410
3	--	20 ^c	--
4	9 ^d	20	120

^a CH₄ (20 atm), CO (15 atm), O₂ (15 atm), Pd(OAc)₂ = Cu(OAc)₂ = 0.05 mmol, TFA (5 mL), 80°C.

^b Yield based on Pd metal content.

^c No catalyst used.

^d No oxygen used.

Although the results demonstrate the possibility of this route, reaction times of 20 to 40 h make these catalysts commercially impractical. In addition, this differs from the present invention which uses solid, heterogeneous catalysts.

Direct conversion of methane to acetic acid using oxygen as an oxidant, with no added CO, has also been studied by other researchers (Lin et al., 1997; Lin and Sen, 1994; Sen and Lin, 1996). Oxidative carbonylation of methane to selectively produce acetic acid was carried out at 95°C in a glass-lined stainless steel (SS) bomb. CH₄ at 800 psi (54 atm), CO at 150 psi (10 atm), and oxygen at 50 psi (3.6 atm) were added to the bomb which contained RhCl₃, HCl, and HI, and 5 mL of D₂O as the solvent. No methanol was formed in the reaction products after 420 h, only acetic acid was recovered along with trace quantities of formic acid, as determined by nuclear magnetic resonance (NMR) spectroscopy. The results clearly suggest that CO and O₂ can be used to carboxylate CH₄ but, again, require homogeneous catalysts. The use of heterogeneous catalysts to activate methane has not been demonstrated experimentally.

In related work, the reaction of an adsorbed methyl group with CO₂ to form an acetate was suggested as a possibility (Bowker, 1992) because the reverse reaction (i.e., the

decomposition of an acetate into a methyl group) was observed over Rh(110) (Bowker and Li, 1991). Formation of an acetate from dissociative adsorption of CH_3I and CO_2 over Ni(110) catalysts has also been demonstrated using high resolution electron energy loss spectroscopy (HREELS) (Wambach and Freund, 1994), although the formation of acetate was not clearly confirmed. The fact that heterogeneous catalysts can activate methane and form acetic acid has not been demonstrated prior to the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates an integrated CO_2 recovery and reuse scheme.

Figure 2 illustrates conceptual economics of an integrated gasification combined cycle (IGCC) - acetic acid (AA) co-production scheme.

Figure 3 illustrates FTIR spectra over a 5% Pd/C catalyst after exposure to acetic acid under variable temperatures.

Figure 4 illustrates an FTIR spectra evidencing formation of acetate with 5% Pd/C under variable temperatures.

SUMMARY OF THE INVENTION

Accordingly, the present invention provides a process for the preparation of lower alkane acids by carboxylation of $\text{C}_1\text{-C}_{12}$ alkanes by utilizing CO_2 and these alkanes to directly produce acids of one higher carbon number using heterogeneous (solid) catalysts.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention provides a process for synthesis of acids such as acetic acid via carboxylation of alkanes such as methane. As noted above, the conventional route practiced industrially for synthesis of acetic acid is an indirect route in which methane or other carbon source(s) are first reformed into syngas, a mixture of hydrogen and carbon monoxide (CO), CO is then hydrogenated to methanol, and methanol is carbonylated with CO to produce acetic acid using homogeneous catalysts. Some of the benefits of the direct route to acetic acid provided by the present invention are as follows.

First, the energy- and cost-intensive methane reforming step is not necessary. This step can contribute at least 60 percent to the overall production costs of acetic acid.

Second, the rhodium-based homogeneous catalysts currently used in methanol carbonylation (MC) are replaced by a heterogeneous catalyst, making separation of the product simpler and less expensive. Thus, no intermediate methanol is required to be formed, and no carbonylation is required.

Third, the MC step, using toxic, corrosive, and potentially hazardous iodine-based promoters like methyl iodide, is replaced.

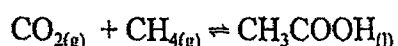
Fourth, the direct route of this invention reduces emissions of the greenhouse gases, CO₂, and, in the case of acetic acid, also utilizes the greenhouse gas methane.

Fifth, the solid, heterogeneous catalysts of the present invention are much more amenable to high throughput industrial processes, and product separation is simple and relatively inexpensive.

Sixth, a principle environmental advantage of the present invention is the reduced risk and secondary pollution produced as compared to the current technology. At least 55 percent of the worldwide acetic acid production uses the methanol carbonylation (MC) technology, which uses expensive Rh catalysts, employs toxic I-based promoters, and involves cost-intensive separations. The occupational and potential environmental hazards of the compounds provide a second clear environmental incentive to develop benign manufacturing processes for acetic acid.

In accordance with the present invention, solid heterogeneous catalysts are used for the direct synthesis of alkyl carboxylic acids such as acetic acid from CO₂ and alkanes, such as methane.

One reaction of interest is shown:



$$\Delta H^\circ = -16.2 \text{ kJ/mol CO}_2$$

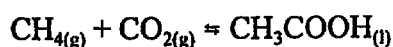
$$\Delta G^\circ = +55.7 \text{ kJ/mol CO}_2$$

The ΔG°_{298} for this reaction is +55.7 kJ/mol CO₂, corresponding to an equilibrium conversion of CO₂ and CH₄ and equilibrium yield of acetic acid that are extremely low.

Despite the is equilibrium limitation, the reaction can be carried out at non-equilibrium conditions to maximize the yield of acetic acid.

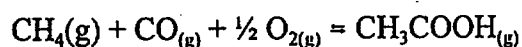
An alternative way to synthesize acetic acid from methane would be to use carbon monoxide and oxygen as oxidants, instead of or in addition to CO₂. The ΔG°_{298} from the reaction, among methane, carbon monoxide, and oxygen to form acetic acid is in fact negative, at -212.2 kJ/mol, i.e., this reaction is thermodynamically favorable. Of course, the reactor design and catalyst choice can be used to maximize the yield of acetic acid. The calculations for ΔG°_{298K} for these two alternate routes to acetic are summarized:

1. Synthesis of acetic acid from CH₄ and CO₂:



$$\begin{aligned}\Delta G^\circ_{298K} &= (G^\circ_f)\text{CH}_3\text{COOH} - (G^\circ_f)\text{CH}_4 - (G^\circ_f)\text{CO}_2 \\ &= +55.7 \text{ kJ/mol.}\end{aligned}$$

2. Synthesis of acetic acid from CH₄, CO, and O₂:



$$\begin{aligned}\Delta G^\circ_{298K} &= (G^\circ_f)\text{CH}_3\text{COOH} - (G^\circ_f)\text{CH}_4 - (G^\circ_f)\text{CO} - \frac{1}{2} (G^\circ_f)\text{O}_2 \\ &= -212.2 \text{ kJ/mol.}\end{aligned}$$

Such a large negative free energy of reaction for 2 above corresponds to a thermodynamically favorable reaction, with very high equilibrium conversions. Several non-limitative examples herein below illustrate how the present invention may be utilized in the production of acetic acid.

Example 1: CO₂ Removal from Power Plants. One way in which this process can, in principle, be used is to recover CO₂ from conventional coal-fired power plants, is shown in Figure 1. The total CO₂ emissions in the United States in 1998 were approximately 4,400 metric tones (Mt), with about 1,700 Mt CO₂ coming from the power plants. The removal of CO₂ on a large scale from industrial power plants is practiced industrially; there are currently two large coal-based power plants where CO₂ is recovered in large quantities. One is ABB Lummus Crest's Shady Point, Oklahoma, operation where CO₂ is recovered in large quantities. The cost of CO₂ production from such plants is estimated to be in the range of

\$20 to \$30/ton CO₂. This provides a useful application of the present invention to removal of CO₂ from this type of combustion source.

5 Example 2: Conceptual Economics of CO₂ Removal. Some preliminary cost estimates shown in Figure 2 for CO₂ removal scheme indicate that the process is economically viable, provided CO₂/CH₄ reaction can quantitatively form acetic acid, in good yields with extremely high selectivities. The conceptual economics of CO₂ reuse from an integrated gasification combined cycle (IGCC) power plant for acetic acid production is shown in Figure 2. The economics assumes a carbon tax of CO₂ emissions of \$50/ton of CO₂ emitted. Although preliminary, these costs show the possibility of a commercially practical
10 process.

Example 3: CO₂ Removal from Natural Gas Streams. CO₂ is also generated as a byproduct in natural gas processing operations, with raw natural gas containing up to 20 to 30 percent CO₂. Such a gas can be used directly as a feedstock for the reaction envisaged in the present invention, reducing its cost, simplifying the process design, and providing a
15 direct gas-to-liquids process of the type needed for remote gas field operations.

 As noted above, the present invention utilizes heterogeneous catalysts, particularly Group 8-11 transition metal catalysts, in a direct carboxylation of alkanes such as methane to form acids of one higher carbon number such as acetic acid. These heterogeneous transition metal catalysts may be prepared according to known preparatory procedures, including
20 impregnation, incipient wetness and co-precipitation.

 Generally, the transition metal catalyst contains one or more transition metals from the Periodic Table, however, of particular note are Group 8-11 transition metals, such as Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag and Au. These transition metal catalysts may be supported on an inert or acidic/basic support, such as carbon, silica, alumina or even
25 diatomaceous earth. Generally, one or more transition metals are used in an amount of 0.5 to 20% relative to the support. For example, 5% Pd/AC may be noted.

 Generally, the reaction temperature may be from about 100°C to about 500°C. While ambient pressures may be used, pressures of CO₂ and CH₄ of from about 0.5 to about 200 atmospheres can also be used with higher equilibrium conversions at higher pressures.

However, it is preferable to use a pressure of CO₂ and CH₄ of from about 10 to 150 atmospheres.

Additionally, while any relative amounts of lower alkane and CO₂ may be used, in general, approximately equimolar amounts of each are used. By "equimolar" is meant a molar ratio range of from 0.1 to 10 of CH₄/CO₂. Generally, the amount of catalyst used is that typically used as a catalyst, and as is used for these known catalysts in other reactions. Generally, from about 10⁻⁶ moles to about 0.5 moles per mole of each reactant is used. Preferably, the amount used is 0.1 mole or less of catalyst per mole of reactant.

The present inventors carried out various experiments demonstrating the formation of the acetate group of acetic acid from a mixture of CO₂ and CH₄. The following examples are provided solely for purposes of illustration and are not intended to be limitative.

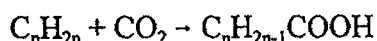
Example 5

Acetic acid was absorbed on a 5 % Pd/AC catalyst to identify the infra-red adsorption bands corresponding to acetic acid on 5 % Pd/C as follows. The adsorption of acetic acid was carried out at 25°C over a 5 percent Pd/C catalyst, in a high temperature environmental chamber (HTEC). The catalyst was mixed with KBr powder (transparent to IR radiation), and loaded onto the sample cup in a HTEC. Helium was bubbled through an acetic acid impinger (maintained at 25°C using a circulating coolant) and adsorbed on the catalyst at standard temperature and pressure (STP) mL/min for 60 min. The spectra were collected under flow-through conditions and under sealed conditions and ratioed to the background (Figure 3). Subsequent temperature programmed desorption (TPD) of chemisorbed species was carried out at 50°/min to 320°C, and spectra were collected at each temperature, after the spectra reached stable levels (after ca. 30 min).

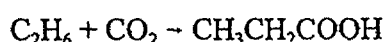
Then, CO₂/CH₄ were preadsorbed on the same catalyst and TPD-diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was carried out and the appearance/disappearance of spectral bands was matched with pure acetic acid spectral data on an identical catalyst (5% Pd/C)-KBr admixture.

In this case, the adsorption was carried out for 60 min and subsequent desorption was performed at 50°/min up to 420°C (Figure 4). The purpose of this experiment was to determine whether a 5% (5% Pd/C) 95% KBr admixture catalyzes the CO₂/CH₄ reaction to acetic acid. The spectra at 25°C under flow-through (spectrum a) and sealed (spectrum b) conditions are identical. At 25°C characteristic bands at 3,729, 3,010, 2,362, and 1,301 cm⁻¹ are observed. The bands at 3,010 and 1,301 cm⁻¹ can be assigned to gas-phase methane (Zhang et al., 1996) and a pronounced band at 2,362 cm⁻¹ is due to CO₂. A small shoulder band at 2,371 cm⁻¹ visible in the adsorption spectra (spectra a, b) in Figure 4 is due to naturally occurring ¹³CO₂. (Burkett et al., 1990). The spectrum at 120°C (spectrum c) is similar to adsorption spectra, suggesting that no reaction has occurred among the adsorbates. However, at higher temperatures of 220 to 420°C (spectra d to f), small but distinct peaks in the 1,790 to 1,740 cm⁻¹ region corresponding to characteristic carbonyl carboxylate linkages are observed leading to the first evidence for synthesis of a carbonyl species. Further, small bands at 1,513 and 1,565 cm⁻¹ can be assigned to an acetate (CH₃COO) species (Viswanathan et al., 1990). These studies clearly evidence, for the first time, the synthesis of acetic acid from CO₂ and CH₄ on a heterogeneous catalyst.

In another aspect of the present invention, higher carboxylic acids may be prepared from higher alkanes in accordance with the following scheme:



Specific examples of this reaction are the reactions of the use of ethane and propane, respectively, with CO₂:



In order to effect this reaction, the same conditions and heterogeneous catalysts are used as described above. Generally, in the formulae above, n has a value of from 1 to about 12, however, it is preferred that n have a value of from 1 to 8. This reaction may be used with CO₂ and any of methane, ethane, propane, butane, pentane, hexane, heptane, octane,

nonane, decane, undecane and/or dodecane. Of course, one may use any of the n-, sec-, tert- or iso- isomers of these alkanes.

Having described the present invention, it will now be apparent that many changes and modifications may be made to the above-described embodiments without departing from
5 the scope of the present invention.

WHAT IS CLAIMED IS:

1. A method of producing acetic acid directly by carboxylation of methane, which comprises reacting carbon dioxide and methane in the presence of a heterogeneous catalyst.
2. The method of Claim 1, which is conducted in the presence of oxygen and carbon
5 monoxide.
3. The method of Claim 1, which is conducted without oxygen.
4. The method of Claim 1, wherein said carbon dioxide is obtained by recovery from a power plant based on the combustion or gasification of coal or other carbonaceous materials.
- 10 5. The method of Claim 1, wherein said carbon dioxide is obtained as a byproduct in a natural gas processing operation.
6. The method of Claim 1, wherein said heterogenous catalyst is a transition metal catalyst.
7. The method of Claim 6, wherein said transition metal catalyst comprises a
15 transition metal selected from the group consisting of Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, and Au.
8. The method of Claim 7, wherein said transition metal catalyst is a bimetallic or multi-metallic system.
9. The method of Claim 1, wherein said heterogeneous catalyst is on a support which
20 is inert, acidic or basic.



10. The method of Claim 9, wherein said catalyst support is selected from the group consisting of activated carbon, alumina, silica, silica/alumina, hydrotalcites, metal oxides of group 2, and/or mixed metal oxides of Group 13-14 elements.

5 11. The method of Claim 7, wherein said transition metal catalyst is a 5% Pd/C catalyst system containing up to 20% Pd.

12. The method of Claim 1, which is effected at a temperature in excess of 100°C.

13. The method of Claim 1, which comprises:

a) contacting a gaseous mixture of methane and carbon dioxide in contact with said heterogenous catalyst; and

10 b) reacting said methane and carbon dioxide at elevated temperature in the pressure of said heterogeneous catalyst.

14. The method of Claim 12, wherein step b) is effected at a temperature of at least 100°C.

15. The method of Claim 1, which is conducted in a single reaction step.

15 16. The method of Claim 1, which effects C-C bond formation.

17. The method of Claim 1, which avoids carbonylation of methanol.

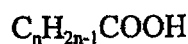
18. The method of Claim 1, which avoids syngas generation.

19. The method of Claim 1, which avoids iodine-based promoters.



20. The method of Claim 1, which is incorporated in an integrated gasification combined cycle - acetic acid co-production process.

21. A method of producing a lower alkyl carboxylic acids of the formula:



5 wherein n is an integer 1 to 12, which process comprises reacting carbon dioxide and an alkane of the formula C_nH_{2n} , wherein n is as defined above, in the presence of a heterogeneous catalyst.

22. The method of Claim 21, wherein n is an integer of 1 to 8.

10 23. The method of Claim 21, which proceeds directly by carboxylation of said alkane.

24. The method of Claim 21, wherein said alkane is ethane.

25. The method of Claim 21, wherein said alkane is propane.

26. The method of Claim 21, which is effected at a temperature in excess of about 100°C.

15 27. The method of Claim 21, which effects C-C bond formation.

28. The method of Claim 21, which is conducted in a single reaction step.

29. The method of Claim 21, wherein said heterogeneous catalyst is a transition metal catalyst.



30. The method process of Claim 21, wherein said heterogeneous catalyst comprises a transition metal selected from the group consisting of Group 8-11 metals: Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, and Au.