

Utilization of Carbon Dioxide to Combustible Materials using Co-Mo Catalyst over Alumina Bed**¹Abdolreza Karbul, ²Mohammad Ali Takassi, ²Abulfazl Gharibi Kharaji, ¹Mohammad Sadegh Sekhavatjou**¹*Department of Environmental Engineering, Science and research branch, Islamic Azad University, Khouzestan, Ahvaz, Iran 6198144475*²*Department of Science, Faculty of Petroleum, Petroleum University of Technology, Ahwaz, Iran 6198144471*

Abdolreza Karbul, Mohammad Ali Takassi, Abulfazl Gharibi Kharaji, Mohammad Sadegh Sekhavatjou: Utilization of Carbon Dioxide to Combustible Materials using Co-Mo Catalyst over Alumina Bed

ABSTRACT

Power plants using fossil fuels emit a great amount of CO₂, CO, steam and the like to the air annually. The emissions from power plants' chimneys are converted to dry gas upon water separation in a refrigeration process. CO₂ and CO are converted to combustible gas through combining with hydrogen in a catalysis process. In this article, first, Co-Mo catalyst was prepared over Alumina bed using sedimentation technique. Then, CO₂ and CO hydrogenation was examined in an autoclave reactor using the catalyst. In the hydrogenation of CO₂ - at pressure (12bar) and CO₂/ H₂ (1:3) at 700 °C and in half an hour - CO₂ (%85) was converted to CO (%75) and Methane (%10).

Key words: hydrogenation, Co.Mo catalyst, autoclave reactor, combustion**Introduction**

Increasing amount of CO₂ emissions in the air, fossil fuels consumption growth and their resources decrease, as well as low efficiency of alternative energies are among the main factors concerning CO₂ utilization as a global challenge [1]. A wide range of studies has been conducted regarding reforming of CO₂ to chemical and combustible materials [2-4]. CO₂ is a thermodynamically stable and passive compound. So, high energy catalysts are required in CO₂ chemical reactions. The reactions of CO₂ are also conducted through electrochemical [5-7] and photochemical [8-9] processes. Although CO₂ is not so chemically active, studying its molecular structure shows the spectrum of reactions feasible by CO₂. It is a linear molecule. Oxygen atoms present a low basic (Lewis) quality in CO₂, whereas its C atom is an electrophile (electron-absorbent). As a result, most CO₂ reactions are of nucleophilic (nucleus-absorbent) types in which chemical nucleus-absorbent groups (chemical agents able to give electron) attach themselves to C atom. CO₂ is easily combined with water, alkyl oxides and amines to produce carbonic acid and carbamic acid. It can also form organic metals (organometallic) complexes with nucleus-absorbent groups existing on solid surface of

some metals. So there are many methods for activating it; however, since it is thermodynamically stable, the energy level required for the reactions must be supplied which is complicated and expensive. Some of the materials activating CO₂ reaction are: hydrogen [10-12], alcohols [13-14], amines [15-16], acetals [17-18], epoxides [19-20], alkanes [21-22], alkenes [23-24], ethers [25-26], esters [27-28], organometallic compounds [29-30], etc.

A variety of chemical materials are produced from the combination of CO₂ and other materials in the above reactions some of which include: formic acid, formic acid esters, formamide, methanol, dimethylether, urea, urea resins, combustible materials (gas and liquid hydrocarbons), hydrogen, alkenes carbonates (solvent), B-oxynaftoic acid (raw material for paint), salicylic acid and its derivatives having pharmaceutical applications and still used as food preservatives and the like.

CO₂ chemical reactions are conducted in two types of solvents; supercritical CO₂ and other solvents. Catalysts used in CO₂ reactions are divided into two groups:

Homogenous catalysts and heterogeneous catalysts; the latter have some superiorities such as sustainability, separation, reusability, feasibility, yet the number of products produced here is limited.

Corresponding Author

Mohammad Ali Takassi, Department of Science, Faculty of Petroleum, Petroleum University of Technology, Ahwaz, Iran 6198144471
E-mail: takassi@put.ac.ir

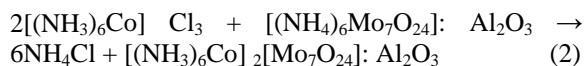
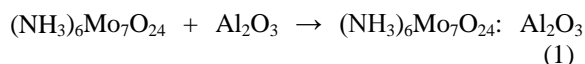
Most of the products resulting from CO₂ reactions employ homogenous catalysts.

In this article, CO₂ hydrogenation is studied using Co/Mo catalyst over the alumina bed.

Arranging Lab Activities and its Steps:

Preparing Catalyst:

0.1M (NH₃)₆Mo₇O₂₄ hexaammoniumheptamolybdate (Merck) is dissolved in 1L distilled water, the solution is white. 11g Alumina (aluminum oxide – mesh 135) is added to the solution for every 3g hexaammoniumheptamolybdate. The solution is stirred by a mechanical stirrer for 10h so that Mo₇O₂₄⁶⁻ ions seat on aluminum oxides particles. Now, 0.2M (NH₃)₆CoCl₃ (hexaammoniumcobalt trichloride) complex (Merck) the which is dark orange to red is dissolved in adequate amount of distilled water. Then the cobalt complex was added drop-wise to the chemisorbed/alumina slurry. Stirring continued for 5 more hours. Consistent pink formation on aluminum oxide particles and colorless solution indicate the completion of the reaction. The estate of the reaction below is explained in Equations 1 and 2.



[(NH₃)₆Co]₂Mo₇O₂₄ complex looks light pink over Alumina particles. The complex is washed by distilled water so that the other compounds formed during the reaction are extracted.

The precatalyst was insoluble and unreactive in water at 273-373 °K. The pre-catalyst was gently dried in an oven. The formation of the pink [(NH₃)₆Co]₂Mo₇O₂₄ : Al₂O₃ precatalyst was demonstrated by both the developed color of the alumina as well as by potassium bromide disc infrared spectroscopy which indicated the presence of (NH₃)₆Co³⁺ ion by NH₃ spreading modes and the Mo=O units of Mo₇O₂₄⁶⁻ ion by strong Mo=O stretching absorption. . The partial reduction of cobalt/molybdate pre-catalyst was performed in a batch reactor with hydrogen gas at pressure of 40 bars and Temperature of 873°K for 5 hours. During reduction, the color of the pre-catalyst changed from pale pink to dark black.

Catalyst Characterization:

The powder x-ray diffraction of unreduced Co-Mo/alumina was obtained using PW1840 powder X-ray diffractometer with Cu tube anode operated at 40 kV and 30 mA with step size 0.02 from 10° to 90°.

XRD patterns of unreduced Co-Mo/alumina showed the specific peaks of Al₂O₃. The promoter Co-Mo was ray amorphous. Cobalt/molybdenum promoter with impregnation method affected only slightly the textural properties of alumina. XRD pattern of reduced Co-Mo/alumina catalyst only one peak of MoO₂ at 2θ = 53.6 and other peaks of MoO₂ which appear in the same position as Al₂O₃ that include peaks at 2θ = 25.8°, 37.4°, 57.6°, 66.6°, 84.7°. The lines corresponding to cobalt are not observed, probably because of its very low proportion. The specific surface area of the Co/Mo catalyst powder sample (73.13m²/g) was determined by nitrogen adsorption in accordance to the BET method, with Quanta Chrome Quantasorb.

Reactor:

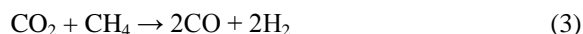
The catalyst was examined in a one liter autoclave reactor was made of 316 stainless steel. The reactor is equipped with an electric thermal device and accurate electric control system as well as a magnetic mixer. It can be operated up to 150bar and 1100°k.

Preparing Combustible Gas:

To synthesize combustible gas from CO₂ and H₂ reaction, we place a certain amount of the catalyst in the reactor first, and then reach the reactor to a certain temperature. In the end, we inject CO₂ and H₂ gases into the reactor in a ratio of 1:3 and a total pressure of 12bar, and turned on the magnetic mixer. After a certain time, we pass the reaction products through a condenser so that the steam inside and or other probable products turn into liquid. We collect gas products in a special container and gas chromatography is used for separation and determination of the amount of existing materials.

Results and Discussion

Annually, 8 trillion of tons CO₂ are emitted by industrial plants, power plants, automobiles and the like into the air. In the last few years, at least two environment-friendly power plants are established in the U.S. where the emissions of the chimneys are converted into combustible gas after a series of operations feasible to be used again as fuel in the plants. The process is highly valuable which prevents CO₂ from being released in the air. The process of converting power plants chimneys emissions is conducted in different methods two of which are described here. First, emitted gas is converted to a relatively dry gas after water separation which combines with suitable methane catalysts [31] in high-temperature reactor and produces H₂ and CO gases. The reaction is showed by Equation [3].



The mixture of H_2 and CO is a combustible gas which can burn by O_2 in torches and produce heat. The combustion of these gases is shown by Equations 4 and 5:



In the second method, CO_2 combines with H_2 at the presence of the catalyst to produce CO and water; after steam separation - and the CO then can combine with H_2 and convert into methane. The mixture of methane and CO is a combustible gas. Respective reactions are shown in Equations 5 and 6:



To enhance thermal value of the above combustible gas, we can combine it with hydrogen in a reactor, in the presence of a suitable catalyst, almost its total CO content will be converted into methane.

$Co-Mo$ catalyst activity over Al_2O_3 bed for CO_2 hydrogenation was examined at a pressure of 12bar and at a temperature of $600^\circ C$ in a $CO_2:H_2$ ratio 1:3.

In 20min, CO_2 (%63) is converted into CO and less than %1 methane is produced, as well. After 10h, CO_2 (over %87) is converted into CO (%72) and methane (%15). Water is the coproduct of the reverse water gas shift reaction. Figure (1) displays the state of CO_2 conversion into CO and methane.

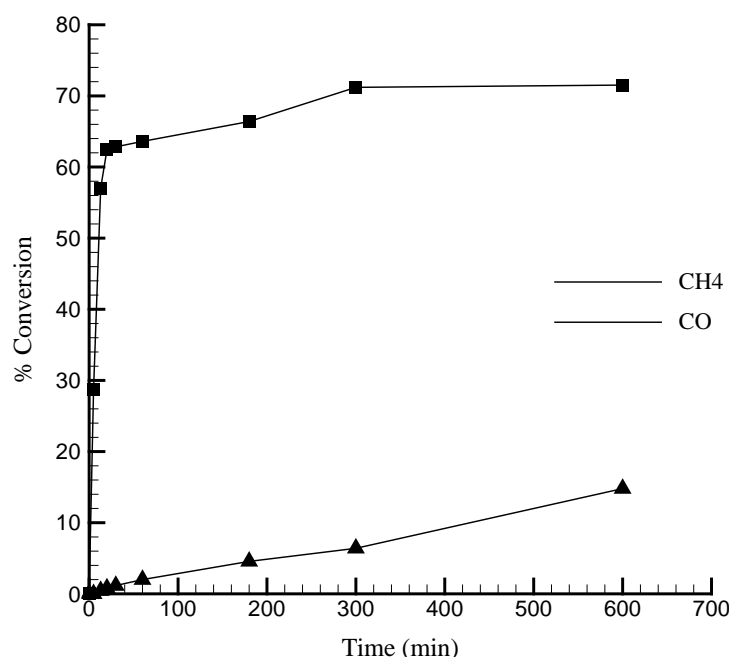


Fig. 1: the percentage of CO_2 hydrogenation reaction products (in pressure 12bar and temperature $600^\circ C$, and $CO_2:H_2$ ratio 1:3).

The effect of temperature on $CO_2:H_2$ reaction was studied in the presence of the above catalyst. $573^\circ K$ is the minimum temperature in which the catalyst is active (threshold temperature). In half an hour reaction time and at a temperature of $573^\circ K$,

CO_2 (about %6) is converted into CO , but at a temperature of $973^\circ K$ and the same span, CO (%72) and methane (%5) are produced. The effect of temperature on CO_2 hydrogenation is illustrated in figure 2.

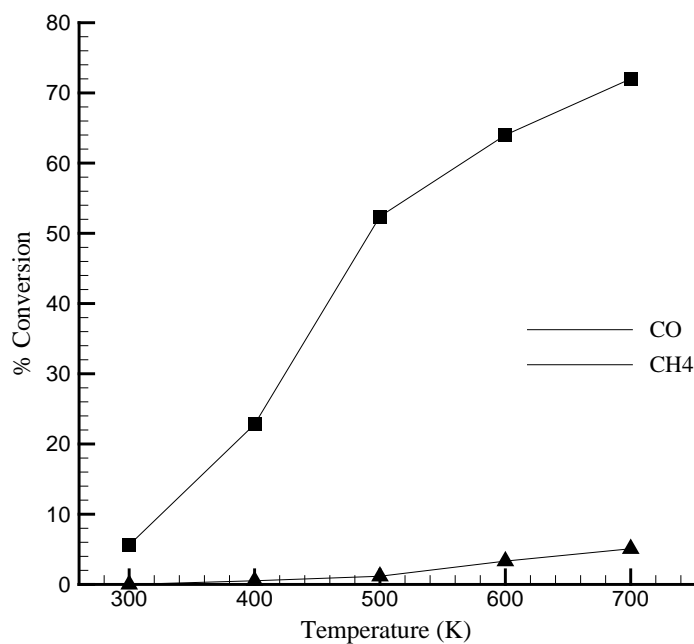


Fig. 2: the effect of temperature on CO₂ hydrogenation (in 30min and 12bar with CO₂:H₂ ratio 1:3).

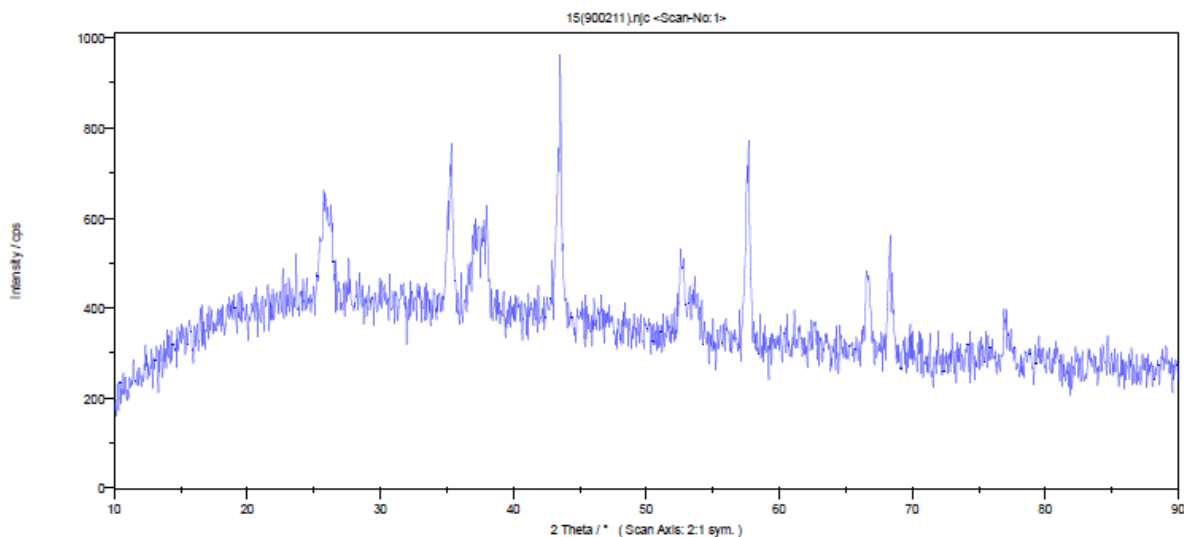


Fig. 3: XRD spectrum of reduced alumina supported cobalt/molybdenum catalyst

No	d_Fit(A1)	∠ _{Peak}	∠ _{Coop}	Limit _{low}	Limit _{high}	I _{net}	FWHM	I _{rel}	2θ	Scan No
1	3.4442	26.8488	26.8886	25.1500	28.8000	231.01	1.0002	41	26.8488	1
2	2.6388	36.3248	36.3183	34.8500	36.7000	348.70	0.4848	82	36.3248	1
3	2.4033	37.3878	37.2041	36.5500	37.8000	203.87	0.6978	38	37.3878	1
4	2.3880	38.0004	37.9922	37.4500	38.2500	218.51	0.2188	38	38.0004	1
6	2.0788	43.6401	43.6278	42.8500	43.8000	681.18	0.3888	100	43.6401	1
7	1.7378	62.8244	62.7018	62.3000	63.1500	181.77	0.3881	34	62.8244	1
8	1.7078	63.8204	63.8679	63.3000	64.0500	111.98	0.6216	20	63.8204	1
8	1.6978	67.8407	67.8428	67.2000	68.0000	408.83	0.3828	73	67.8407	1
9	1.4028	68.8242	68.8486	68.2000	67.0500	192.48	0.4008	34	68.8242	1
10	1.3715	68.3388	68.3482	68.0000	68.7500	281.72	0.2788	47	68.3388	1
11	1.2382	78.8400	78.8401	78.7500	77.6500	108.18	0.3102	18	78.8400	1
12	1.1435	84.7000	84.7087	84.8000	84.8000	73.36	0.1272	13	84.7000	1

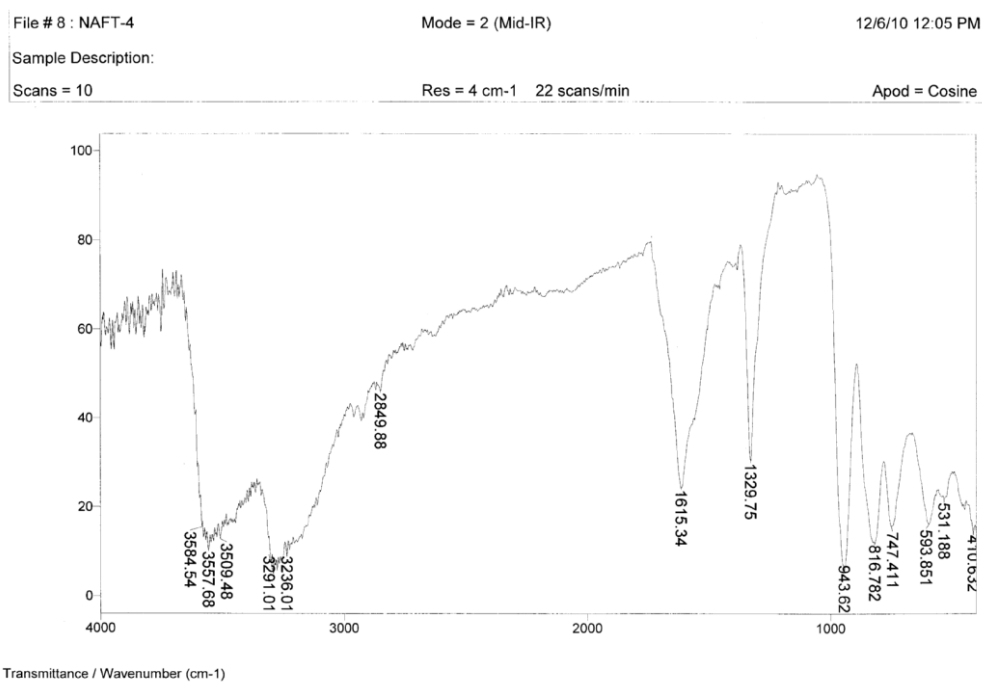


Fig. 4: FTIR spectrum of alumina supported dihexaammoniumcobaltheptamolybdate $[(\text{NH}_3)_6\text{Co}]_2\text{Mo}_7\text{O}_{24} : \text{Al}_2\text{O}_3$.

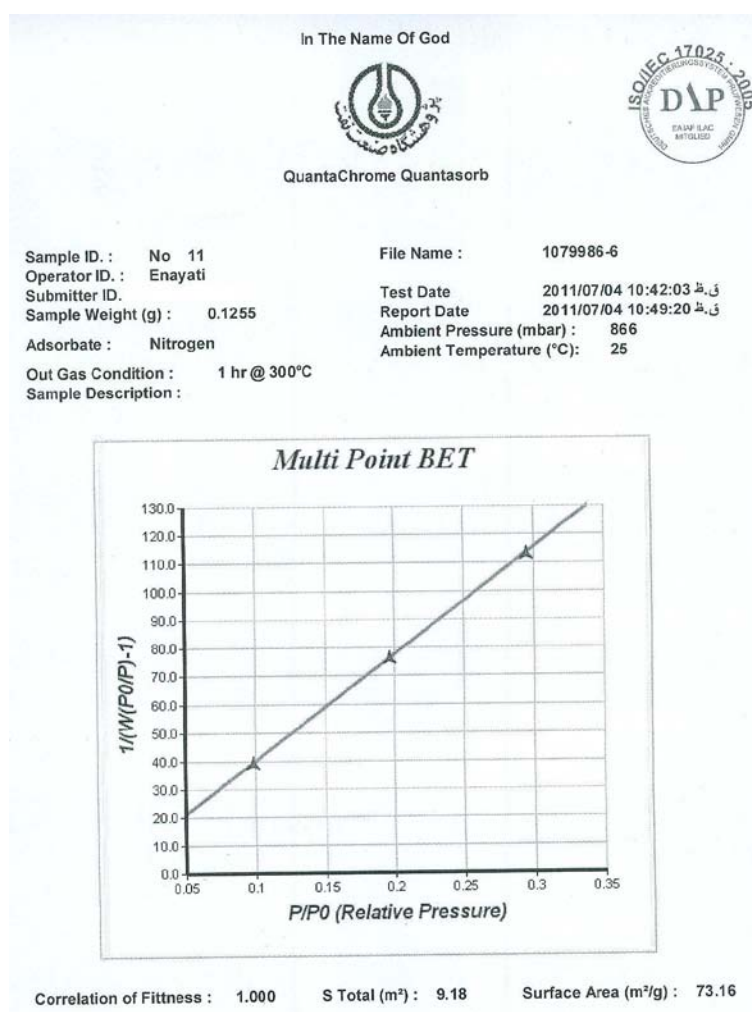


Fig. 5: BET graph of alumina supported cobalt/molybdenum catalyst

Previous experimental studies of our group demonstrated that CO (%80) is converted into methane in CO hydrogenation and in presence of Co-Mo catalyst over Alumina bed (in 30min, 35bar, 573°k and CO:H₂ = 1:4). So, it is concluded that Co-Mo catalyst over Alumina bed is suitable for converting CO₂ into CO and methane. Accordingly, power plants chimneys emissions or the similar plants releasing great volumes of CO₂ can be again converted into combustible gases by separating the steam and placing them in reactors with appropriate catalysts to be combined with H₂ and, by so doing, we can prevent the CO₂ emissions into the air.

Conclusion:

The reverse water gas shift and hydrocarbon reforming reactions in which carbon dioxide converts to carbon monoxide. Carbon monoxide is a major chemical feed stock. The above mentioned reactions can be used to recycle CO₂ produced by major fossil fuels consuming plants such as power plants. Today few power plants in USA recycle the CO₂. Let's hope in near future by worldwide reduction in fossil fuel consumption and the improvement of the other sources of energy we are able to prevent the global environment devastation.

Acknowledgement

We would like to acknowledge The Petroleum University of Technology for financial support of this research.

References

- Song, C., 2006. "Global challenges and strategies for control, conversion and utilization of CO₂ for sustainable development involving energy, catalysis, adsorption and chemical processing" *Catalysis Today*, 115(1-4): 2-32.
- Fan, M-S., Z.A. Abdullah, S. Bhatia, 2010. "Utilization of greenhouse gases through carbon dioxide reforming of methane over Ni-Co/MgO-ZrO₂: Preparation, characterization and activity studies." *Appl. Cat. B*: 100(1-2): 365-377.
- Omae, I., 2006. "Aspects of carbon dioxide Utilization" *Catalysis Today*, 115: 33-52.
- Centi, G., S. Perathoner, 2009. "Opportunities and prospects in the chemical recycling of carbon dioxide to fuels." *Catalysis Today*, 148(3-4): 191-205.
- Gangeri, M., S. Perathoner, S. Caudo, G. Centi, J. Amadou, D. Bégin, C. Pham-Huu, M.J. Ledoux, J-P. Tessonnier, D.S. Su, R. Schlögl, 2009. "Fe and Pt carbon nanotubes for the electrocatalytic conversion of carbon dioxide to oxygenates" *Catalysis Today*, 143(1-2): 57-63.
- Cheung, K-C., P. Guo, M-H. So, L.Y. Suk Lee, K-P. Ho, W-L. Wong, K.H. Lee, W-T. Wong, Z-Y. Zhou, K.Y. Wong, 2009. "Electrocatalytic reduction of carbon dioxide by a polymeric film of rhenium tricarbonyl dipyridylamine." *J. Organometallic Chemistry*, 694(17): 2842-2845.
- Kaneco, S., N-H. Hiei, Y. Xing, H. Katsumata, H. Ohnishi, T. Suzuki, K. Ohta, 2002. "Electrochemical conversion of carbon dioxide to methane in aqueous NaHCO₃ solution at less than 273 K." *Electrochimica Acta*, 48(1): 51-55.
- Lo, C-C., C-H. Hung, C-S. Yuan, J-F. Wu, 2007. "Photoreduction of carbon dioxide with H₂ and H₂O over TiO₂ and ZrO₂ in a circulated photocatalytic reactor" *Solar Energy Materials a Solar Cells*, 91(19): 1765-1774.
- Premkumar, J., R. Ramaraj, 1997. "Photocatalytic reduction of carbon dioxide to formic acid at porphyrin and phthalocyanine adsorbed Nafion membranes." *J. Photochem. Photobio. A*: 110(1): 53-58.
- Xu, Q., D. He, M. Fujiwara, M. Tanaka, Y. Souma, H. Yamanaka, 1998. "Hydrogenation of carbon dioxide over Fe-Cu-Na/zeolite composite catalysts: Na migration via solid-solid reaction and its effects on the catalytic activity." *J. Mol. Cat. A*: 136(2): 161-168.
- Fujiwara, M., H. Ando, M. Tanaka, Y. Souma, 1995. "Hydrogenation of carbon dioxide over Cu---Znchromate/zeolite composite catalyst: The effects of reaction behavior of alkenes on hydrocarbon synthesis." *Applied Catalysis A*: 130 (1) pp. 105-116.
- Ando, H., M. Fujiwara, Y. Matsumura, M. Tanaka, Y. Souma, 1999. "Catalytic hydrogenation of carbon dioxide over LaNi₅ activated during the reaction." *J. Mol. Cat. A*: 144(1): 117-122.
- Liao, S., Y. Hou, S. Li, X. Chen, W. Wu, 2010. "High-pressure phase equilibria for the binary system carbon dioxide + benzyl alcohol" *J. Supercritical Fluids*, 55(1): 32-36.
- Yoshiyuki Sasaki, Y., 1986. "Reaction of carbon dioxide with propargyl alcohol catalyzed by a combination of Ru₃(CO)₁₂ and Et₃N." *Tetrahedron Let.*, 27(14): 1573-1574.
- Aresta, M., A. Dibenedetto, E. Quaranta, M. Boscolo, R. Larsson, 2001. "The kinetics and mechanism of the reaction between carbon dioxide and a series of amines: Observation and interpretation of an isokinetic effect." *J. Mol. Cat. A*: 174(1-2): 7-13.
- Davies, P.R., J.M. Keel, 2000. "The reaction of carbon dioxide with amines at a Cu surface" *Surface Science*, 469(2-3): 204-213.
- WANG, Z., H. JIANG, C. QI, Y. SHEN, S. YANG, Y. ZENG, 2007. "PdCl₂/PSPhenol Co-catalyzed Acetalization of Methyl Acrylate

- with Methanol in Supercritical Carbon Dioxide” *Chinese J. Cat.* 28(7): 607-610.
18. Abdulla, R.F., R.S. Brinkmeyer, 1979. “The chemistry of formamide acetals” *Tetrahedron*, 35(14): 1675-1735
 19. Jing, H., T. Chang, L. Jin, M. Wu, W. Qiu, 2007. “Ruthenium Salen/phenyltrimethylammonium tribromide catalyzed coupling reaction of carbon dioxide and epoxides.” *Cat. Commun.*, 8(11): 1630-1634.
 20. Darensbourg, D.J., M.W. Holtcamp, 1996. “Catalysts for the reactions of epoxides and carbon dioxide.” *Coordination Chemistry Reviews*, 153: 155-174.
 21. Kotze, F.J., C.A. Strydom, du A. Plessis, T.L. Dlamini, 2010. “Fast and ultra-fast laser pulse induced reactions between carbon dioxide and methane.” *J. Nat. Gas Chem.*, 19(2): 198-202.
 22. Chen, H-W., C-Y. Wang, C-H. Yu, L.T. Tseng, P-H. Liao, 2004. “Carbon dioxide reforming of methane reaction catalyzed by stable nickel copper catalysts.” *Catalysis Today*, 97(2-3): 173-180.
 23. Kontkanen, M-L., L. Oresmaa, M.A. Moreno, J. Jänis, E. Laurila, M. Haukka, 2009. “One-dimensional metal atom chain [Ru(CO)₄]_n as a catalyst precursor—Hydroformylation of 1-hexene using carbon dioxide as a reactant” *Appl. Cat. A*: 365(1): 130-134.
 24. Döhring, A., P.W. Jolly, 1980. “The palladium catalyzed reaction of carbon dioxide with allene.” *Tetrahedron Let.*, 21(32): 3021-3024.
 25. Ju, M-H-Y., M-D. Manju, K-H. Kim, S-W. Park, D-W. Par, 2008. “Catalytic performance of quaternary ammonium salts in the reaction of butyl glycidyl ether and carbon dioxide” *J. Ind. and Eng. Chem.*, 14(2): 157-160.
 26. Park, D-W., N-Y. Mun, K-H. Kim, I. Kim, S-W. Park, 2006. “Addition of carbon dioxide to allyl glycidyl ether using ionic liquids catalysts” *Catalysis Today*, 115(1-4): 130-133.
 27. Liu, K-J., Y. Huang, 2010. “Lipase-catalyzed production of a bioactive terpene ester in supercritical carbon dioxide.” *J. Bio. Tech.*, 146(4): 215-220.
 28. Behr, A., U. Kanne, 1986. “Palladium- and rhodium-catalyzed synthesis of esters by reaction of butadiene, carbon dioxide and oxiranes” *J. Organometallic Chem.*, 309(1-2): 215-223.
 29. Deng, M.Z., Y.T. Tang, W.H. Xu, 1984. “Reaction of carbon dioxide with trialkylalkynyl borates—a novel method for the synthesis of stereospecific α,β -unsaturated acids.” *Tetrahedron Letters*, 25(17): 1797-1800.
 30. Ramin, M., van N. Vegten, J-D. Grunwaldt, A. Baiker, 2006. “Simple preparation routes towards novel Zn-based catalysts for the solvent less synthesis of propylene carbonate using dense carbon dioxide.” *Journal of Molecular Catalysis A*: 258(1-2): 165-171.
 31. Ross, J.R.H., 2005. “Natural gas reforming and CO₂ mitigation” *Catalysis Today*, 100: 151-158.