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Integrating low-temperature methanol synthesis and CO_2 sequestration technologies: application to IGCC plants

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Abstract

Coupling a low-temperature once-through methanol synthesis process with CO_2 separation technology would provide an option for integrated gasification combined cycle (IGCC) power plants to address the CO_2 mitigation issue and also create the capability to utilize methanol as a peak-shaving fuel. Data are presented that show that several nickel complexes activated by alkoxide bases catalyze facile synthesis of methanol from synthesis gas (primarily a mixture of CO and H_2) in homogeneous liquid phase under mild conditions of temperature ($<150\,^{\circ}C$) and pressure (<5 MPa). Under these mild conditions, batch-mode productivity of up to 20 g mol MeOH/l cat. h is achieved and more importantly, per pass gas conversion and methanol selectivity exceed 90 and 95%, respectively. The overall synthesis gas to methanol process has built-in waste-minimization and minimum by-product formation features and thus achieves CO_2 mitigation. The potential of this low-temperature methanol synthesis approach is considered in light of the recent advances in CO_2 sequestration technologies. A successful development of this technology may also provide an atom-economical pathway to transport remote natural gas in the form of methanol, a liquid energy-carrier.

Keywords: CO_2 sequestration; Reverse water-gas-shift; Methanol synthesis; CO hydrogenation; Homogeneous catalysis

1. Introduction

There is now sufficient scientific evidence to suggest that CO_2, a greenhouse gas, is primarily responsible for global warming. This realization is leading researchers to develop multiple options to sequester CO_2 [1–3]. Irrespective of the CO_2 sequestration method under development, the overall schemes under consideration involves two steps: (1) CO_2 capture and separation from an emitting source and (2) transport of the separated CO_2 to the chosen location, for example, ocean, aquifers, coal mines, for burial. But irrespective of the ultimate sequestration scheme selection, the CO_2 capture and separation step remains expensive [4], and several projects are underway to develop a technology that will lead to a decrease in the cost of this step [2].

Power plants are one of the largest stationary sources of CO_2 emissions. It is logical that several studies are targeting these sources to couple CO_2 sequestration technologies [3]. The IGCC concept has been developed to increase the efficiency of coal-based power plants thereby reducing CO_2 emissions [3]. An advanced IGCC concept would further increase the plant efficiency by co-production of electricity and methanol, an easily storable peak-shaving liquid fuel [5]. In the advanced IGCC concept, methanol is first produced from gasified coal in a once-through process followed by generation of electric power from the converted synthesis gas [5]. The

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challenge to implement this concept is to develop a high throughput once-through methanol synthesis process.

Two approaches are described in this paper that are the subject of an ongoing effort at Brookhaven National Laboratory (BNL) in developing CO_2 mitigation and sequestration technologies. The first approach, the main emphasis of this paper, describes the latest development in once-through methanol synthesis technology [6]. Methanol is an ultra-clean fuel, a versatile feedstock and a convenient high-density H_2-energy carrier (12.5 wt.%), that is also favored as a liquid energy-carrier in the economical transport of remote natural gas [6,7]. An atom-economical catalytic methanol synthesis process, based on synthesis gas derived from natural gas or coal, is of continuing interest at BNL. Our earlier work showed that a “single-site” catalyst operates in liquid phase to convert premixed CO/H_2 (1/2 ratio) synthesis gas to achieve high (>90%) per pass carbon conversion with high reaction rates (9 g mol MeOH/l cat. h) and methanol specificity (>99%) rivaling enzyme-driven reactions [7]. The BNL approach to methanol synthesis thus has CO_2 mitigation as a built-in component. However, reaction rates are adversely affected by the presence of CO_2 in synthesis gas during methanol synthesis with the BNL system. This limitation necessitates a CO_2 clean-up step when utilizing synthesis gas that typically contains CO_2 irrespective of the initial source [6]. Therefore, we have studied ways to address the CO_2 issue with respect to the BNL system. The second approach that combines CO_2 capture from power plants followed by its efficient recycle via conversion into methanol is considered. Preliminary results are presented on catalyst screening for direct CO_2 hydrogenation to methanol. A successful development of either of these approaches would provide an option for an advanced methanol synthesis process in integrated gasification combined cycle (IGCC) applications.

2. Experimental

The procedures described in this section pertain to experiments that were carried out to: (1) further develop the low-temperature catalytic methanol synthesis from balanced synthesis gas process ($H_2/CO = 2/1$) and (2) screen catalysts that will allow direct and efficient CO_2 hydrogenation into methanol.

2.1. Materials

Potassium methoxide (>95% purity), nickel tetracarbonyl (>99% purity), and complexes or salts of Cu, Pt, Co, Ru, Mo were purchased from Alfa and used as received. Ni powder (∼3 μm size, >99% purity), nickel chloride hexahydrate ($NiCl_2\cdot6H_2O$), triphenylphosphine (PPh_3), bis(acetylacetonato) nickel ($Ni(acac)_2$), methanol, tri(ethyleneglycol) dimethyl ether (triglyme), and tetrahydrofuran (THF) were purchased from Aldrich. Methanol was distilled in 400 ml batches with Mg turnings and iodine under argon. Pure CO, H_2, CO_2 and syngas mixture (34% CO, 66% H_2) were purchased from Scott specialty gases. Syngas mixtures were calibrated to check stoichiometries certified by the manufacturer.

2.2. Synthesis of Ni complexes

Anhydrous $NiCl_2$ was prepared by heating the hydrated salt in a vacuum oven at 110 °C for 24 h. Ni powder, $Ni(acac)_2$ and $Ni(CO)_4$[1] were used as received. $Ni(CO)_4$ was stored in a fume-hood. The PPh_3 complex of nickel was prepared by modification of the literature method [8]. PPh_3 (10 mmol) was refluxed in 50 ml hexane to yield a colorless solution. After cooling, 10 mmol $Ni(CO)_4$ was slowly added to the phosphine solution. The resulting slurry was filtered and the filtrate was reduced to dryness to yield a green solid (yield based on starting $Ni(CO)_4$ was 62%). Based on the infrared (IR) data, the bands at 2060 and 1990 cm^{-1} (two CO ligands *trans* to each other and one *trans* to PPh_3) the complex was assigned the formula $Ni(PPh_3)(CO)_3$. The solid was air-stable.

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[1] Specific mention here is the procedure utilized to work with Ni catalysts. $Ni(CO)_4$ is extremely toxic: the OSHA limit is set at 1 ppb for an 8 h daily exposure. Therefore, the batch unit was placed in a well-ventilated fume-hood. A customized procedure has been developed to handle this material. Even in runs with other Ni complexes that have a potential to form $Ni(CO)_4$ under the reaction conditions, precaution was taken to ensure the safety of all personnel.

2.3. Catalyst evaluation in batch mode

A commercially available AE Zipperclave stirred batch unit was modified at BNL and used in these studies. The unit consisted of a 0.55 l pressure vessel fitted with a Dispersimax six-blade impeller, and a removable metal ring inserted into the vessel to break up any vortices that might form during stirring. The unit had the following provisions: (1) heating/cooling through a Parr temperature controller and (2) several inlet and outlet ports for sampling of gases and liquids. The maximum working pressure was 20 MPa at 350 °C. A dual channel Omega chart recorder was attached to the unit to monitor any change in temperature and pressure during a reaction. For catalyst evaluation studies, a typical run involved loading of the selected metal catalyst, any additive, and solvent into the pressure vessel. The vessel was pressurized with feed gas containing H_2, CO and or CO_2 and heated to a desired temperature, and the pressure drop was followed as a function of time on the chart recorder. Gas and liquid samples were taken at the start, during and after the run. All samples were analyzed on gas chromatographs.

2.4. IR studies

The IR spectra of the gas phase above the solution after a typical methanol synthesis run were recorded on a Perkin-Elmer (PE) 1330 IR spectrophotometer. A customized 1-inch path length IR cell was filled with the gas sample to 0.13 MPa (slightly above the atmospheric pressure) from the pressure vessel of the batch unit. A signature peak at 2058 cm^{-1} for $Ni(CO)_4$ was monitored to detect its presence in runs in which any Ni-based catalyst was used. The presence of $Ni(CO)_4$ in the gas phase established that $Ni(CO)_4$ was present in solution that formed during the methanol synthesis run.

2.5. Ultraviolet–visible (UV/VIS) studies

For colored solutions, UV/VIS spectra were recorded on a PE Lambda 4B spectrophotometer. After mixing the Ni complex and potassium methoxide (KOMe) in a desired solvent mixture in the batch unit, the spectrum was recorded. The spectrum of the solution after the methanol synthesis run was also recorded.

Ni was quantified by the colorimetric method. In this procedure, a 5 ml gas sample was taken from the gas phase above the reaction solution in the batch unit and mixed with 1 ml of 6 M nitric acid to instantaneously convert any $Ni(CO)_4$ or Ni salt to nickel nitrate. Bromine water (1 ml) was added followed by aqueous ammonia until the solution was basic. The solution was diluted to 9 ml with water and 1 ml dimethylglyoxime (dmg) (1% solution in ethanol) was added. A pink color indicated the formation of the Ni-dmg complex. The visible spectrum of the pink solution was recorded in a 1 cm cell. The Ni-dmg complex was characterized by a band at $\lambda = 445$ nm.

3. Results and discussion

Two approaches are presented to develop technologies that would be suitable for integration with the IGCC plants. These are: (1) development of a low-temperature once-through methanol synthesis process that, due to its high throughput, has a built-in CO_2 mitigation feature and (2) the CO_2 capture and utilization concept in which the captured CO_2 is recycled by its conversion into methanol. These two approaches are discussed below.

3.1. Approach 1: low-temperature CO hydrogenation to methanol with Ni complexes

The conversion of syngas into methanol is temperature dependent due to the exothermic nature and the reversibility of Reaction 1

$$CO + 2H_2 \Leftrightarrow CH_3OH_{(l)}, \quad \Delta H^{\circ}_{R} = -128.6\,\mathrm{kJ\,mol^{-1}} \tag{1}$$

Commercial synthesis of methanol utilizes supported Cu/ZnO catalyst that is effective at 250 °C and 5 MPa [6]. The thermodynamic data plotted as the temperature–pressure (*T*–*P*) curves in Fig. 1 show that under the commercial operating conditions, the theoretical CO conversion is limited to ~20% [9,10]. Fig. 2 shows the recycle ratios required to achieve >90% CO with the commercial catalyst [10]. Fig. 2 also shows that gas recycling poses a problem with an accumulation of inerts in the recycled gas. The data of Figs. 1 and 2 were the guiding factors that led

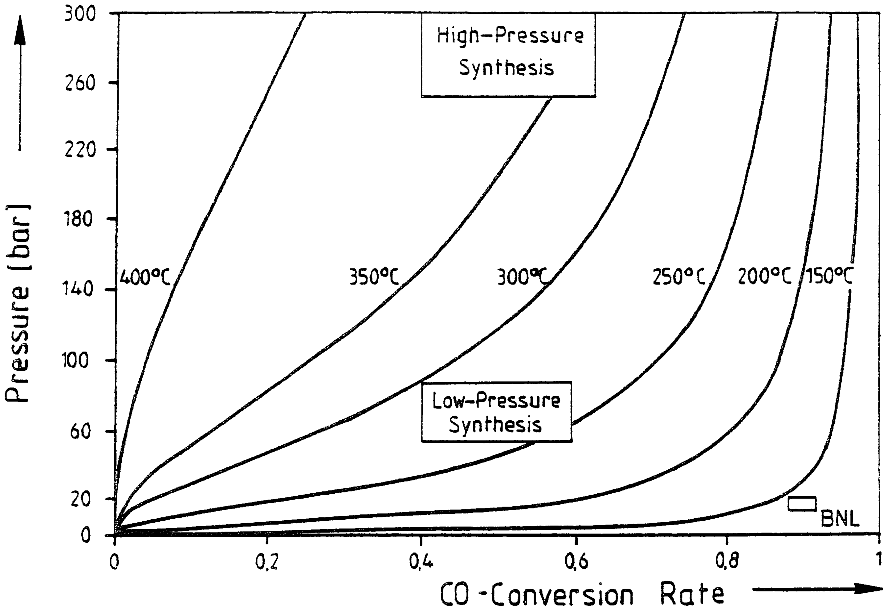

Fig. 1. Thermodynamic equilibrium curves for the conversion of CO to methanol with balanced synthesis gas ($H_2/CO = 2$) [8].

to the formulation of the low-temperature Ni catalyst. The *T–P* curves in Fig. 1 show favorable conversions (>80%) at temperatures below 150 °C and at reasonably low pressure (<5 MPa). This is the subject of the ongoing effort at BNL to design a low-temperature methanol synthesis process [11]. The low-temperature methanol synthesis catalyst is formed by mixing a Ni complex, an alkoxide base in a methanol/glyme solvent mixture [11]. Typically, a homogeneous solution results upon mixing these components. When this solution is heated in a reaction vessel to 50–130 °C under 2–5 MPa synthesis gas (H_2/CO ∼2/1), an active catalyst is generated and synthesis gas is rapidly consumed to yield methanol according to Reaction 1. The kinetic data with the Ni/alkoxide/methanol/triglyme catalyst system where Ni is $Ni(CO)_4$ and alkoxide is potassium methoxide is a subject of a recent publication [12]. The unique features of the BNL methanol synthesis catalyst system are:

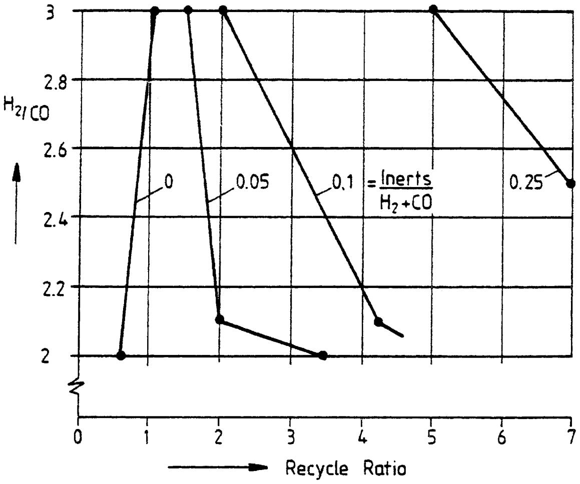

Fig. 2. Recycle ratios required in commercial methanol synthesis process to achieve CO conversion of 96% (250 °C, 6 MPa) with CO_2-free synthesis gas [8].

- A low-temperature operation ($T < 150$ °C) thermodynamically allows very high (>90%) syngas conversion per pass thus eliminating the need for gas recycle.
- A liquid medium allows theoretically maximum gas conversion due to an excellent isothermal operation.
- A low-pressure operation (∼2–3 MPa) during methanol synthesis and the inertness of the catalyst to N_2 allow methanol synthesis to take place with

N_2-containing syngas [6,7]. This feature allows partial oxidation of natural gas with air thus eliminating the need for an O_2-separation plant during syngas production.
- The main solvent for the process is the product (MeOH) itself. But glymes are utilized as cosolvents to enhance reaction rates.
- The catalyst is highly selective (>95%) and highly active for methanol synthesis.
- The homogeneous catalyst formulation renders itself amenable to the mechanistic study for process optimization.

In an effort to further develop the low-temperature methanol synthesis technology, the process uncertainties are being addressed. One of the critical issues relates to $Ni(CO)_4$ that is previously used as a catalyst precursor to catalyze the low-temperature methanol synthesis reaction [7,11,12]. A replacement for toxic $Ni(CO)_4$ is necessary to avoid cumbersome handling of the reaction solutions during methanol synthesis. Table 1 lists runs that were carried out with potential alternative catalyst formulations to replace toxic $Ni(CO)_4$ as the catalyst precursor. The data compare the methanol synthesis rate and selectivity data of the evaluated Ni compounds. The mmol/min values in the rate column in Table 1 refer to the total number of millimole of syngas consumed that was averaged over the total reaction time. Since in all the runs, balanced syngas ($H_2/CO = 1.95/1$), as required in Eq. (1), was utilized, the methanol synthesis rates can be deduced simply from dividing the rate numbers by 3. These numbers are a good approximation since methanol selectivity is high as shown in the product selectivity column in Table 1. For example, in the reference Run 1 with $Ni(CO)_4$ at the catalyst precursor, methanol is synthesized at a rate of 0.018 mol/min. A total of 0.5 mol methanol and 0.004 mol methyl formate (MF) was synthesized during the run. These data demonstrated that the process was truly catalytic (82 cycles in Ni and over 4 cycles in base). Similar numbers were obtained with other catalyst entries in Table 1 except for runs 4, 6 and 7. The rate was further enhanced in Run 2 when triglyme solvent was replaced with THF. Run 3 data were obtained with $NiCl_2$, one of the least expensive, air-stable and easy-to-handle salts of Ni. The $NiCl_2$/KOMe system showed remarkable activity for methanol synthesis essentially doubling the rate as compared to that obtained with $Ni(CO)_4$/KOMe system (Run 3 versus Run 1). It was reported in an earlier publication [11] that the presence of both the $Ni(CO)_4$ and the alkoxide base (KOMe) was necessary to generate an effective catalyst. This earlier finding is confirmed in Run 4 in which it was observed that the absence of KOMe rendered $NiCl_2$ ineffective for methanol synthesis.

Table 1
Catalytic activity of various Ni complexes for methanol synthesis[a]

Run	Catalyst	Rate (mmol/min)	Product selectivity (%)		
			MeOH	MF	DME
1	$Ni(CO)_4$	54	>99	<1	Trace
2[b]	$Ni(CO)_4$	66	95.7	4	0.3
3	$NiCl_2$	98	99.2	0.2	0.6
4[c]	$NiCl_2$	–	–	–	–
5	$Ni(acac)_2$	72	98	1.4	0.6
6	$Ni(PPh_3)(CO)_3$	1.2	64	36	–
7	Ni	–	–	–	–

[a] 0.5 l AE Zipperclave batch reactor, solvent: 90% triglyme–10% MeOH = 120 ml, [Ni] = 0.05 M, KOMe = 1.0 M, syngas: 66% H_2–34% CO, $T = 120\,^{\circ}C$, $P_I = 700$ psig.

[b] Triglyme was replaced with THF.

[c] No KOMe was added.

The success of the $NiCl_2$/KOMe system led to the evaluation of other Ni complexes for methanol synthesis. $Ni(acac)_2$ was found to be an effective catalyst that yielded a reaction rate of 72 mmol/min (Run 5). However, the triphenylphosphine-CO complex of Ni ($Ni(PPh_3)(CO)_3$) showed minimal catalytic activity for methanol synthesis (Run 6). In this case, 50 mmol H_2 and 110 mmol CO were consumed in 2.3 h. The liquid analysis showed that 20 mmol MeOH and 10 mmol MF had formed during the entire run. The entry in Run 7 shows that the Ni/KOMe system where Ni represents a commercial Ni powder (~3 μm) was essentially inactive.

The data in Table 1 clearly indicate that simple Ni salts and complexes are suitable replacements for toxic $Ni(CO)_4$ and show facile synthesis of methanol under low-temperature conditions. These data also show that per pass syngas conversion in these runs varied between 96 and 98% and batch-mode productivity of up to 20 g mol MeOH/l cat. h was obtained. These data have also been confirmed under continuous-flow conditions. For example, a preliminary run under continuous gas-flow conditions with 5% N_2 in syngas at 130 °C and 4 MPa total pressure yielded a reaction rate of 8.9 g mol MeOH/l cat. h. This compares well with the commercial catalyst that yields an equivalent rate of 6 g mol MeOH/l cat. h at 250 °C and ~5 MPa with syngas containing no N_2 [6].

$Ni(CO)_4$ shows a sharp signature absorption band at 2058 cm^{-1} in the IR region. This band serves as a sensitive qualitative test to detect this species even in the gas phase. The recorded IR spectra of the final gas phases of the $Ni(CO)_4$/KOMe (Run 1) and $NiCl_2$/KOMe (Run 4) catalyzed reactions after methanol synthesis are shown in Fig. 3a and b, respectively. The run with $Ni(acac)_2$ showed an IR band similar to that observed with $NiCl_2$. But with $Ni(PPh_3)(CO)_3$, no $Ni(CO)_4$ was detected in the gas phase. For all the Ni systems evaluated, the peak intensity of the $Ni(CO)_4$ peak in the final gas phase followed the order: $Ni(CO)_4 > NiCl_2 \sim Ni(acac)_2 \gg Ni(PPh_3)(CO)_3$. These results suggest that when starting with $NiCl_2$ or $Ni(acac)_2$, $Ni(CO)_4$ forms during methanol synthesis though it is suppressed. In addition to the IR band at 2058 cm^{-1} for $Ni(CO)_4$, other recorded IR bands shown in Fig. 3a and b were assigned as follows: 2171 and 2119 cm^{-1} for CO and 1730 cm^{-1} for MF.

The gas-phase $Ni(CO)_4$, observed in the IR spectrum, was quantified in each run by developing a colorimetric analysis procedure (see Section 2) that involved formation of the pink Ni-dmg complex. Two absorption bands at 536 and 454 nm in the visible region are characteristics of the Ni-dmg complex. For example, the band at 536 nm was used to calculate the gas-phase concentration of 0.0046 mmol in Run 4. This corresponds to 0.08% of the total $NiCl_2$ that was initially added in this run. These numbers are useful in the quantification of Ni partitioning in the liquid and gas phases of the reactor.

The Ni complexes listed in Table 1 are appropriately considered as “catalyst precursors”. The “active” catalyst species is formed when the Ni/KOMe catalyst is pressurized with synthesis gas under reaction conditions. A preliminary spectroscopic study is underway to identify the “active” catalyst species. For example, the visible spectra of solutions related to Run 1 in Table 1 are shown in Fig. 4. The intense red solution formed by mixing a colorless solution of $Ni(CO)_4$ (0.05 M) with a yellow solution of KOMe (1.0 M) in 90% triglyme–10% MeOH at room temperature under N_2 shows two absorption bands at 503 and 376 nm (Fig. 4a) with absorption coefficient (ε) values of 345 and 308 $M^{-1}\,cm^{-1}$ respectively. The formation of an intense red solution by reacting $Ni(CO)_4$ with KOH in methanol at room temperature under N_2 has been reported previously [13]. In this reaction [13], the intense red hue was associated with the presence of dodecacarbonylhexanickelate(2−) anion that was in equilibrium with the dodecacarbonylpentanickelate(2−) anion at an ambient temperature and under 0.1 MPa CO pressure (Eqs. (2) and (3))

$$Ni(CO)_4 \underset{N_2}{\overset{KOH/MeOH}{\rightarrow}} [Ni_6(CO)_{12}]^{2-} \tag{2}$$

$$[Ni_6(CO)_{12}]^{2-} + 4CO \Leftrightarrow [Ni_5(CO)_{12}]^{2-} + Ni(CO)_4 \tag{3}$$

In Eq. (3), the reverse reaction that involves redox condensation is also facile [14]. It is likely that the species present in the intense red solutions of the $Ni(CO)_4$/KOMe system are very similar to the Ni_5 and the Ni_6 anionic species shown in Eq. (3). The intense red solution that turned yellow after methanol synthesis under synthesis gas (H_2/CO ~2/1) showed no absorption bands (Fig. 4b). Detailed measurements are underway to further understand the nature of these species and their relevance to methanol synthesis. These together with the IR data are being utilized to design a robust catalyst system for high throughput once-through low-temperature methanol synthesis.

In Fig. 5, relative rates of all the Ni complexes that were evaluated in 90% triglyme–10% MeOH solvent mixture are compared. These data were extracted from the rate of syngas consumption column in Table 1. These data show that facile methanol synthesis is achieved with Ni-based catalysts at low temperatures with the $NiCl_2$/KOMe catalyst system showing the highest activity. The low-temperature approach to once-through methanol synthesis process, due to its high throughput, has a built-in CO_2 mitigation feature. The high methanol productivity and >90% gas conversion per pass avoids the expensive and cumbersome gas recycle step (Fig. 2), a requirement in the commercial process, that makes it ideally suited for integration with the IGCC power plants. Under this scenario, a slip-stream of synthesis gas would be converted to methanol that will be stored as a peak-shaving fuel. However, the synthesis gas

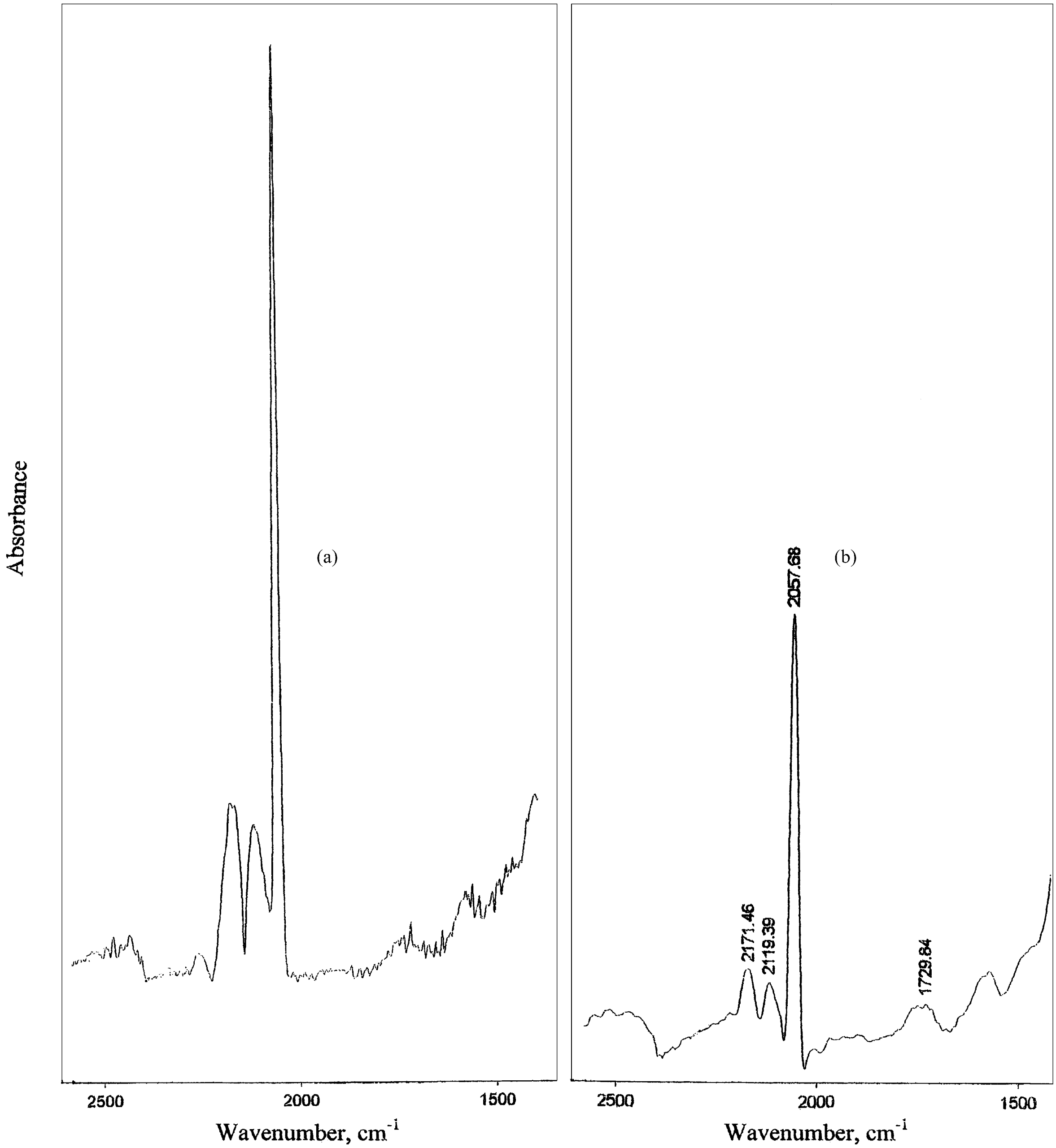

Fig. 3. Room temperature IR spectra of the final gas phase after methanol synthesis. (a) $Ni(CO)_4$/KOMe system (Run 1) and (b) $NiCl_2$/KOMe system (Run 4). Run conditions are given in Table 1.

feedstock for methanol synthesis invariably contains a few percent CO_2 and therefore, the sensitivity of the low-temperature methanol synthesis catalyst to CO_2 needs to be addressed. This process limitation could be overcome by integration with the CO_2 capture and removal step that may be based on a future low-cost efficient membrane technology for removal of CO_2 from synthesis gas [3].

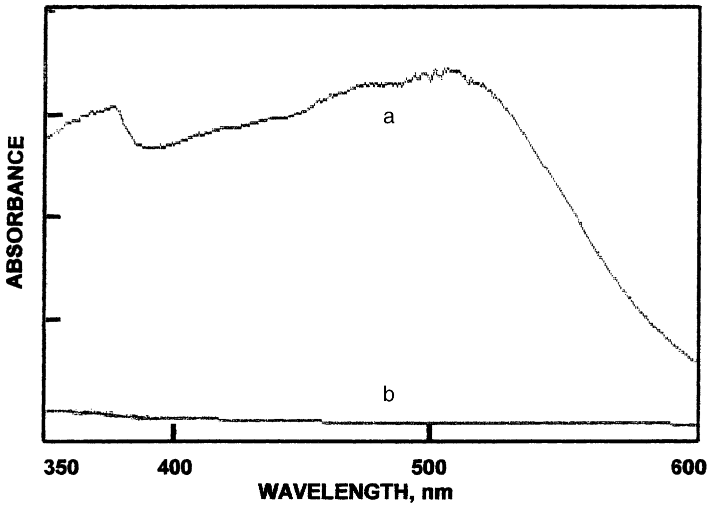

Fig. 4. Room temperature visible spectra of solutions from Run 1 in Table 1 for the $Ni(CO)_4$/KOMe system: (a) initial solution of $Ni(CO)_4$ and KOMe under N_2 and (b) final solution under syngas after methanol synthesis.

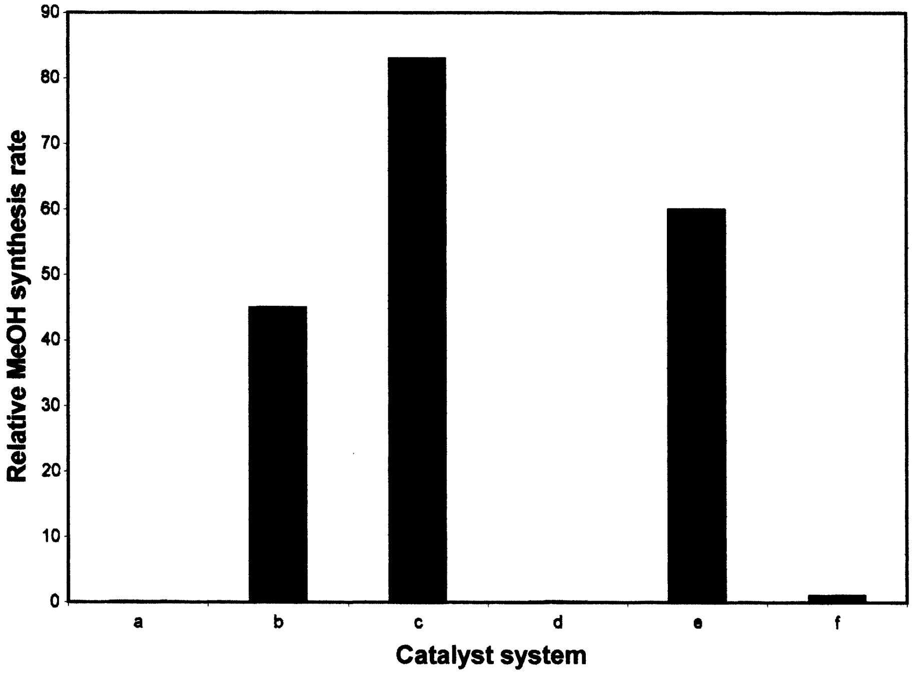

Fig. 5. Relative rates of methanol synthesis catalyzed by Ni complexes: (a) commercial Ni (~3 μm size), (b) $Ni(CO)_4$/KOMe, (c) $NiCl_2$/KOMe, (d) $NiCl_2$, (e) $Ni(acac)_2$/KOMe, (f) $Ni(PPh_3)(CO)_3$/KOMe. Run conditions are shown in Table 1.

3.2. Approach 2: CO_2 capture and utilization

One of the CO_2 sequestration schemes involves the reaction of CO_2 with an amine solvent to form a CO_2·amine adduct in an exothermic step followed by heating the formed adduct in a stripper up to 150 °C to release the absorbed CO_2 and recycle the amine solvent [4] (Eqs. (4) and (5))

$$\text{AA (alkanolamine)} + CO_2 \rightarrow AA \cdot CO_2 \tag{4}$$

$$AA \cdot CO_2 \rightarrow AA + CO_2 \tag{5}$$

An approach that involves replacement of the stripping step (Reaction 5) with a once-through methanol synthesis reactor is presented. This is relevant to the ongoing low-temperature methanol synthesis work, discussed above, that utilizes a very basic medium (alkoxide) to achieve high per pass syngas conversion at $T < 150\,^\circ C$. The challenge here is to utilize an appropriate AA as a solvent to replace the alkoxide base in the low-temperature methanol synthesis process that will make the CO_2 capture and the CO_2 utilization steps compatible. This will allow CO_2 processing under mild conditions of temperature and pressure.

The thermodynamic T and P curves for direct CO_2 hydrogenation conversion into methanol are shown in Fig. 6. It is apparent that even at a low temperature of 125 °C, ~30 MPa pressure is required to achieve >80% CO_2 conversion. Therefore, simply lowering the reaction temperature is not enough to compensate for the high pressure required to achieve a high conversion during CO_2 hydrogenation. The strategy here is to combine the reverse water-gas-shift (R-WGS) reaction to yield CO that can be converted to methanol via the low-temperature methanol synthesis process discussed in Approach 1 (Reaction 1) for which the thermodynamics allows lower T and P conditions (Fig. 1). With the AA·CO_2 adduct, the R-WGS is shown in Eq. (6)

$$AA \cdot CO_2 + H_2 \rightarrow CO + H_2O + AA \tag{6}$$

This requires the development of a catalyst system that can promote both Reactions 6 and 1. This approach is being investigated and catalysts that are known to efficiently catalyze the R-WGS reaction have been selected. The challenge then is to design a catalyst system that can also effectively hydrogenate CO into methanol under mild conditions with high productivity and product selectivity. Since the Ni complexes are specific to affect CO hydrogenation into methanol but are sensitive to CO_2, metals other than Ni have been evaluated. Preliminary screening results of a few potential catalyst systems that can catalyze Reaction 1 are shown in Table 2. The evaluated metal catalysts

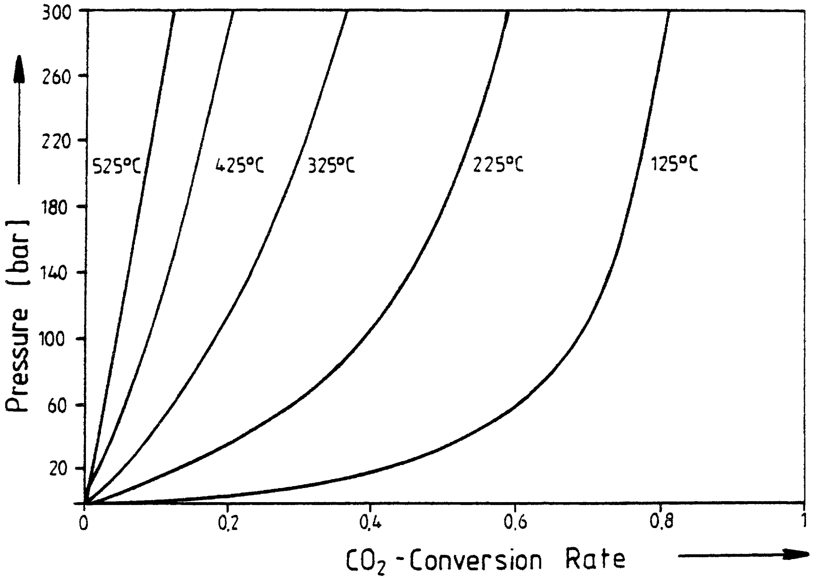

Fig. 6. Thermodynamic equilibrium curves for the conversion of CO_2 into methanol with balanced synthesis gas ($H_2/CO_2 = 3$) [8].

Table 2
Catalytic hydrogenation screening runs[a]

Catalyst	T (°C)	Gas consumed (mmol)	Rate (mmol/min)
CuL_x	130	230	1.2
PtL_x	150	190	2.0
CoL_x	130	–	0
RuL_x	160	185	1.2
MoL_x	150	201	0.7

[a] 0.5 l AE Zipperclave batch unit, catalyst: 1 mmol, base: potassium methoxide = 100 mmol, solvent: TEA or glycol = 120 ml; syngas: $H_2/CO \sim 2$, $P_I = 5$ MPa at room temperature. L is a coordinating ligand: methoxide, chloride, and carbonyl.

are not bulk/naked metals but well-defined complexes that contain ligands of the type, methoxide, chloride or carbonyl. The data in Table 2 show that: (1) except Co, all evaluated metal catalysts exhibited their ability to process syngas, and (2) the operating conditions are desirable to achieve high per pass conversion. The gas consumption rate data show the highest syngas consumption rate of 2.0 mmol/min that is about a factor of 50 slower than those obtained with the Ni catalyst system, shown in Table 1. Work to formulate a high selectivity and high productivity catalyst system is continuing. In this case, an ideal catalyst system will process both CO and CO_2 with productivity numbers similar to those successfully achieved with the Ni system for CO hydrogenation.

4. Conclusions

In this paper, it is demonstrated that efficient methanol synthesis can be achieved with a variety of Ni salts and complexes that are effective at low temperatures of $<150\,^{\circ}C$, the temperature regime in which >90% CO conversion is thermodynamically allowed. The Ni-based catalysts are ideal for processing balanced synthesis gas ($H_2/CO = 2/1$). But this scheme also requires CO_2 removal from synthesis gas prior to entering the methanol synthesis reactor [11]. The CO_2 clean-up from synthesis gas that utilizes the commercial AAs CO_2 removal technology [3,4] has been considered but adds up to ∼10% to the methanol process cost [15]. We are monitoring the ongoing work in various laboratories that is targeting cost reduction of the CO_2 capture and removal step [3,4]. The methanol synthesis technology, based on the low-temperature approach, has unique features that may allow a compact methanol synthesis plant design for integration with an IGCC plant. Such a technology may also allow economical processing of natural gas by its conversion into methanol, a liquid energy carrier.

Preliminary results are also presented to integrate CO_2 capture and subsequent recycle via methanol synthesis. If successfully developed, it may allow efficient co-processing of both CO and CO_2 in synthesis gas. A combination of high gas conversion per pass and low temperature/low pressure operation would allow integration with the IGCC power plants where methanol could be used as a peak-shaving fuel.

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