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Catalytic routes to transportation fuels utilizing natural gas hydrates

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Abstract

Gas hydrates hold >50% of earth's total combustible carbon. To make this vast but dilute (CH_4~3.9 wt%) energy source available, an economical three-step route is outlined. A major technological challenge is environmentally-benign mining of gas hydrates that releases "Aqueous CH_4" and makes it available at the surface (Step 1). Step 2 involves a cost-effective partial oxidation (POX) with air route that eliminates the O_2-separation plant (conventional POX with O_2) to produce synthesis gas. In Step 3, technologies that affect catalytic conversion of synthesis gas to Fischer–Tropsch (F–T) diesel, MeOH, and dimethylether (DME) transportation fuels are considered. The selection of MeOH and DME energy liquids is justified based on seven criteria: (1) low temperature; (2) low pressure; (3) high gas conversion per pass to eliminate recycle; (4) high space-time-yield; (5) high product selectivity; (6) robust catalyst; (7) overall high process efficiency. A Ni/Base catalyst system, presently undergoing pilot testing at Brookhaven National Laboratory (BNL), is described that by virtue of its homogeneous liquid phase operation selectively (>95%) produces methanol with unprecedented single pass conversion (>95%) at $T<150°C$ and $P=2–5$ MPa essentially satisfies these set-forth process requirements. A preliminary kinetic study on the original BNL catalyst system is presented and a limited kinetic rate expression is deduced.

Several areas for further research are identified that will allow economical production of MeOH or DME in the skid-mounted unit/flexible product option concept applicable to both on-land and off-shore gas hydrates. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

With the recent direct measurement of up to 35 gigatons of methane stored as hydrate and in sediments at >190 m below the sea floor off the south-eastern coast of the United States [1], and Japan's multi-million dollar commitment to recover methane from the sea surrounding Hokkaido, interest in gas hydrates as a fuel source is steadily growing. It is now known that clathrate hydrates of natural gas cover a vast expanse of earth being primarily found in perma-frost and deep waters and the estimated hydrates hold about 53% (10 000 gigatons) of earth's total combustible (organic) carbon. However, since gas hydrates are stable only under certain temperature (<20°C) and pressure (>2 MPa) conditions, the extraction and utilization of natural gas from hydrates poses a special challenge. Before natural gas can be recovered as an energy source, the structural features of gas hydrates

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must be considered. Methane clathrate hydrates are special type of inclusion compounds that form lattice like structures when host (water) molecules, link through their vertices via hydrogen-bonding and create a pentagonal dodecahedral cavity which allow gas molecules to slip into the host cavity. The encapsulated molecules with diameters in the 410–580 pm range are non-interactive with the hydrogen-bonding arrangement of the water molecules. The cubic unit cell has a 1200 pm side length with a cavity diameter between 780–920 pm. The cubic unit cell has two such cavities plus six tetrakaidecahedral which are formed as a result of the packing of the pentagonal dodecahedral. The subject of gas hydrate structures is covered in literature [2,3].

From the published data [3], it is inferred that natural gas hydrates contain 46 H_2O molecules per unit cell. On the basis of this composition, this translates into CH_4/H_2O mol ratio of 1/23. Excluding any additional contribution of H_2O from surroundings, $\sim$3.9 wt% CH_4 is expected at the point source. The economical recovery of this dilute CH_4 is a challenge since CH_4 release from the hydrate cavity involves breaking the H-bonded lattice. This scenario is created wherein CH_4 bubbles out of H_2O at the subsurface with changing temperature and pressure conditions. The released CH_4 is expected to be saturated with H_2O as this feedstock becomes available at the surface. For utilizing “Aqueous CH_4” (a term used for H_2O saturated CH_4), several options are available. Option 1 involves liquid/gas separation to allow CH_4 to be used directly as a gaseous fuel either as CNG or LNG for long distance transport. Here, the economics will depend on the cost of H_2O/CH_4 separation followed by pipeline option to transport this gas to customers. Option 2 envisions CH_4 conversion into liquid fuels to avoid pipeline transport of gas from permafrost or off-shore locations. Here, two scenarios needed to be considered. The first scenario involves “direct” conversion of CH_4 to liquids. Presently, this route is considered uneconomical though a few catalyzed reactions to produce $>C_1$ hydrocarbons, methanol or acetic acid, are reported [4]. In the other scenario, liquid fuels are produced via the “indirect route” where synthesis gas or syngas is first produced followed by catalytic conversion to products [5]. In case of gas hydrates, conversion of available “Aqueous CH_4” to syngas via commercial steam reforming technology appears a logical choice:

$$\underbrace{CH_4 + H_2O}_{\text{``aqueous methane''}} \xrightarrow{\text{steam reforming}} CO + 3H_2 \tag{1}$$

The ratio of CH_4/H_2O in the original feedstock can be adjusted to maximize the yield of syngas produced. Syngas produced primarily contains CO and H_2 but other components CO_2, CH_4, H_2O, etc. are also present. Components ($C_2H_6, C_3H_8, \ldots$) other than CH_4 that may be present in the original gas hydrates are also converted in reaction (1). Our selection of fuels synthesis from gas hydrate-derived syngas is based on the physical location of the plants under consideration. Gas hydrates to fuels technologies are envisioned for the following applications:

1. On-land skid-mounted units (e.g., for permafrost).
2. Off-shore on-ship “floating” units (e.g. for deep sea gas and for earthquake-prone land mass if proximity of nearby water body allows).

These constraints and environmental considerations dictate that the selected processes for synthesis of fuels are highly efficient and selective with minimum input of energy. This leads us to consider methanol (MeOH), Fischer–Tropsch (F–T) diesel and DME (dimethyl ether) as viable transportation liquid fuels from catalyzed conversion of natural gas hydrates (reactions (1)–(4)):

$$CO + 3H_2 \xrightarrow{\text{Cat 1}} CH_3OH_{(l)} + H_2 \tag{2}$$

$$xCO + yH_2 \xrightarrow{\text{Cat 2}} (\!-CH_2-\!)_n + pCO_2 + qH_2O \tag{3}$$

$$2CH_3OH \xrightarrow{\text{Cat 3}} H_3C{-}O{-}CH_3 \tag{4}$$

Reaction (2), (3) and (4) are exothermic in the forward direction. MeOH can be synthesized via a well-established commercial technology that utilizes a heterogeneous supported Cu/ZnO catalyst [6]. But high exothermicity and poor heat management thermodynamically limits per pass conversion of synthesis gas to methanol to <20% at the operating temperature of $\sim$250°C and 5 MPa pressure in the commercial process. In reaction (2), $H_2/CO=2/1$ stoichiometry is utilized to produce MeOH and given the feedstock composition of $H_2/CO=3/1$, this results in $MeOH/H_2$ coproduction in a 1/1 mol ratio. Reaction (4) considers DME synthesis via dehydration of 2 mol MeOH though both one-step as well as two-step synthesis of DME has been evaluated on a pilot scale using modified methanol catalyst and γ-Al_2O_3 catalysts, respectively [7]. Synthesis of diesel fuel via reaction (3) is now practiced commercially. At Brookhaven National Laboratory (BNL), a research program has been underway that involves application of the liquid phase low temperature (LPLT) concept, developed at BNL, to design homogeneous liquid phase or nanometer particle slurry-phase catalysts and allow process operation at lower temperatures to achieve high conversions per pass. A successful application of the LPLT concept resulted in the synthesis of a homogeneous catalyst system comprising of a nickel complex activated by an alkoxide base [8]. In a methanol/cosolvent mixed solvent, this novel catalyst system produces methanol from natural gas-derived synthesis gas at a lower temperature of <150°C and <5 MPa pressure with high selectivity (>95%) and high productivity and achieves >90% per pass syngas conversion thus eliminating the need for a gas recycle. In this paper, a kinetic study on this highly efficient catalyst system for synthesis of methanol is described. The utilization of a downstream process based on this catalyst system in the development of an overall scheme that will allow economical production of transportation fuels from gas hydrates is described.

2. Experimental

2.1. *Materials*

Potassium methoxide (>95% pure) and nickel tetracarbonyl (>99.9% pure) were purchased from Alfa and used as received. Methanol and *p*-dioxane were obtained from Aldrich and purified before use as follows. Methanol was distilled in 400 ml batches with magnesium turnings and iodine under dry argon. *p*-Dioxane was distilled in 400 ml batches after stirring with 1 g Na metal under argon. The removal of water from solvents was important to avoid methoxide based hydrolysis to methanol. Pure CO, H_2, and syngas mixture (66% H_2, 34% CO) were purchased from Scott Specialty Gases. Syngas mixtures were calibrated to reconfirm stoichiometries certified by the vendor.

2.2. *Apparatus*

A commercially available stainless steel Magne-Drive II Packless Zipperclave 0.5 l reactor manufactured by Autoclave Engineers (AE) was modified for use in this study. The reactor was equipped with a Dispersamax six-blade impeller mounted on a shaft driven by an AE variable speed motor. Ports were provided for loading nickel tetracarbonyl, reactant gases and sampling vapor and liquid phases. The temperature of the reactor was maintained with a Parr 4831 temperature controller, which controlled an external heating mantle and an internal air-cooling system. The pressure was monitored with a Setra 204 pressure transducer (accuracy to ± 1 psig). The transducer and temperature outputs were recorded using an Omega dual pen continuous chart recorder. The batch CSTR unit ratings were as follows: stirrer=0–2000 rpm, T=25–450°C, P=0.1–14 MPa.

2.3. *Run procedure and analysis*

Due to toxicity of nickel tetracarbonyl, all runs were performed under a well-ventilated fumehood.[1] A specified amount of $KOCH_3$ was weighed inside a Labconco glove box under N_2 and was brought out in a closed vial. The primary solvent mixture comprised of *p*-dioxane/methanol though tetrahydrofuran (THF), *t*-butanol and triglyme with or without added methanol were also used. After 100 ml of degased solvent was poured into the open reactor vessel, $KOCH_3$ in the vial was emptied in the solvent and the reactor was quickly sealed and purged several times with N_2. A known amount of nickel tetracarbonyl was then injected into the reactor through the catalyst injection port and the reactor was immediately pressurized with syngas to keep the solution under CO pressure. This ensured that no $Ni(CO)_4$ decomposition took place during this step. In a typical run, the reactor was pressurized to about 750 psig with syngas and the automatic temperature controller set at 120°C and the stirrer set at 1200 rpm

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[1] When working with $Ni(CO)_4$, a safety procedure should be developed. Since this material rapidly decomposes and gets oxidized to nickel oxide in a few seconds, it is the immediate vacinity that requires the utmost attention. A specific procedure was developed to deal with $Ni(CO)_4$ transfers to ensure that the personnel were fully protected.

were turned on.[2] The temperature and pressure in the reactor were recorded until the pressure decreased to about 100–150 psig in less than 30 min, at which time the reaction was quenched by replacing the heater with an ice-water bath. Once the reactor reached room temperature, the final pressure and temperature were recorded. Gas and liquid samples were taken for analysis and the final liquid volume was measured. For the kinetic study, methanol synthesis was carried-out under the following operating conditions: T=70–120°C, stirring rate=800–1800 rpm. The catalyst, methanol and base concentrations were manipulated to achieve the reaction time between 10–120 min.

Vapor phase samples were analyzed for H_2 and CO using Gow-Mac 550 gas chromatograph in the TCD mode that were connected to HP Model 3390A integrators for peaks quantification. To quantify CO, a (8 ft.×1/8 in.) molecular sieve column with He carrier was used while for H_2, a molecular sieve column (6 ft.×1/8 in.) with N_2 carrier was used. The GC measurements were reproducible to within ±2%. Liquid phase samples were analyzed using a Perkin-Elmer Model 8500 GC in the TCD mode and fitted with a chromosorb-102 (8 ft.×1/8 in.) column. A 2 μl sample was injected and the reproducibility was ±5%. A qualitative detection of $Ni(CO)_4$ in the vapor phase was achieved using a Perkin-Elmer Model 1330 infrared spectrophotometer. A 1 cm gas cell with KBr windows was evacuated and filled with the gas sample from the reactor. The IR spectrum was recorded between 4000 and 400 cm^{-1}. The broad peaks at 2170, 2120 cm^{-1} (free CO), 2060 cm^{-1} ($Ni(CO)_4$) and 1760 cm^{-1} (CH_3O_2CH) were monitored.

3. Results and discussion

3.1. Catalyst performance

Our earlier study [8] on the $Ni(CO)_4$/(AM)OMe system (where AM=alkali metal) included the effect of the nature of alkali metal on reaction rate. The reaction rate increased with increasing alkoxide ionization in solution that followed the order:

$$\mathrm{Li} < \mathrm{Na} < \mathrm{K} < \mathrm{Cs}$$

Taking into consideration reaction rates achieved (rate was at least five times faster with K than Na) and the price, K was the selected alkali metal for this kinetic study. When dissolved in a suitable solvent, the KOMe/$Ni(CO)_4$ catalyst system facilitates conversion of synthesis gas into methanol [8]. This transformation of CO and H_2 into methanol energy liquid is exothermic and favored at lower temperatures [9]:

$$\mathrm{CO}_{(g)} + 2\mathrm{H}_{2(g)} \overset{\mathrm{Ni/K^{-}OMe}}{\rightleftarrows} \mathrm{CH_3OH}_{(l)}$$

$$\Delta H^{\bullet}_{\mathrm{R}} = -128.6\,\mathrm{kJ\,mol^{-1}} \tag{5}$$

With this catalyst, reaction (5) proceeds at temperatures as low as 70°C that allows unprecedented high syngas conversion without sacrificing high selectivity and high reaction rates. Table 1 lists performance of this catalyst system in various solvents at 110°C. The listed batch rates represent average values obtained by dividing the total gas consumed by the corresponding reaction time. Though qualitative, these rate values are a good indicator to assess comparative performance of the catalyst. THF appears to be a good solvent medium but due to its volatility, *p*-dioxane and triglyme were preferred. Interestingly, methanol synthesis proceeded even in neat methanol solvent even at 6.0 M KOMe but at a slower reaction rate (Run 7, Table 1). Of particular interest is the fact that irrespective of the solvent, >90% syngas conversion was achieved in all runs listed in Table 1. Likewise, selectivity to methanol was typically >95%. The major by-product was methyl formate, a carbonylated product of methanol that is easily converted to methanol via Reaction (6):

$$\mathrm{CH_3OCHO} \overset{\mathrm{RO^-}}{\rightleftharpoons} \mathrm{CH_3OH} + \mathrm{CO} \tag{6}$$

where RO^- represent an alkoxide catalyst and both reverse and forward reactions are known to proceed in homogeneous liquid media [10]. The kinetics of the reverse reaction has been studied and the mechanism is proposed [10]:

$$\mathrm{RO:^-} + \mathrm{CO} \rightarrow \mathrm{ROCO^-} \tag{7}$$

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[2] With this experimental procedure, methanol synthesis reaction started well before the targeted reaction temperature as evidenced by syngas consumption. A reviewer has suggested an alternative where solvent/syngas could be initially heated and catalyst is added once isothermal conditions are attained. With experimental constraints associated with addition of $Ni(CO)_4$ at higher temperatures, more error is likely to be introduced. Therefore, the adopted procedure is more appropriate.

Table 1
Synthesis of methanol from synthesis gas catalyzed by the $Ni(CO)_4$/KOMe system[a]

Run no.	Solvent		KOMe (M)	Batch rate (g-mol MeOH/Kg Cat.h)	Gas conversion (%)	MeOH selectivity (%)
	MeOH (ml)	Cosolvent (ml)				
1	–	THF[b] (100)	1.0	570	96	99
2	–	*t*-Butanol (100)	2.0	34	91	90
3	50	*p*-Dioxane (50)	4.0	200	94	97
4	–	Triglyme[c] (100)	2.0	31	95	98
5	10	Triglyme[c] (90)	2.0	139	96	99
6	50	Triglyme[c] (50)	4.0	40	95	95
7	100	–	6.0	20	92	97

[a] Run conditions: $[Ni(CO)_4]=0.05$ M, total reaction solution=100 ml; syngas: $H_2/CO=66\%/34\%$, $T=110°C$, $P=5.0$ MPa.
[b] Tetrahydrofuran.
[c] 1,2-Bis(2-methoxyethoxy)ethane.

$$\mathrm{ROCO}^- + \mathrm{ROH} \rightarrow \mathrm{ROCHO} + \mathrm{RO:}^- \qquad (8)$$

$$\frac{-d[CO]}{\mathrm{d}t} = k[\mathrm{RO}]^p[\mathrm{CO}]^q_{\mathrm{liq}}[\mathrm{ROH}]^r$$

where $p=q=r=1$.

For NaOMe as the catalyst, the rate constant k was 7.40×10^{-3} $\mathrm{l^2\,mol^{-2}\,min^{-1}}$ at 60°C and 4 MPa with $E_{\mathrm{act}}=67.7$ kJ $\mathrm{mol^{-1}}$ (between 50–70°C). In the present system, though methyl formate was a minor product, the above methyl formate data are useful when formulating a kinetic model. Another minor (<1%) by-product detected in the present system was dimethyl ether (DME) but as discussed later, selective DME production is of interest here. No CH_4 was detected in the product stream. The data in Table 1 also confirmed the catalytic nature of the system with up to 1000 cycles in Ni and 100 cycles in base were calculated from the methanol produced. Given the potential of the described $Ni(CO)_4$/KOMe system, that by virtue of its high catalytic activity, allowed methanol synthesis to take place under thermodynamically favorable conditions, this system was subjected to further study.

3.2. Kinetic study

In *p*-dioxane, the rate was reasonable (Run 3, Table 1) and the $Ni(CO)_4$ /KOMe catalyst system in *p*-dioxane, with or without added methanol, was selected for a kinetic study. Batch runs were conducted to establish the effect of reaction parameters on reaction rate. The liquid phase concentrations of methanol, base, $Ni(CO)_4$, *p*-dioxane components, expressed in molar (M) term, were calculated by assuming: (1) no volume change on mixing i.e. ideal behavior and (2) negligible liquid density change from 25°C to reaction temperature. In selecting appropriate concentration range of the components for this study, the criteria used was to attain reaction rates that corresponded to 10–120 min for the pressure to drop from 5.0 MPa to about 0.7 MPa. The pressure and temperature profiles of a representative run are shown in Fig. 1. At [KOMe]=0.4 M, $[Ni(CO)_4]=0.05$ M, *p*-dioxane= 100 ml, $H_2/CO=66\%/34\%$, the initial 5.0 MPa reactor pressure maximized at 5.87 MPa at 104°C during heating before starting to drop. This drop in pressure represented syngas conversion to methanol. It is apparent that syngas started to get consumed at well below the intended temperature of 120°C. For rate constants calculations: (1) only the data at 120°C (±4°C) representing isothermal conditions were utilized; (2) Raoult's Law was used to calculate contributions of condensable (liquid) components that were typically <5% of the total gaseous phase in the reactor; (3) the Redlich-Kwong equation was used to model the vapor (gaseous) phase multi components. Another correction relates to the gas consumption that deviated from the $H_2/CO=2/1$ stoichiometry expected for methanol synthesis due to the $^-$OMe/CO reaction.[3] With these assumptions, partial pressures of CO and H_2 at a given time were individually calculated

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[3] The experimental data showed that more moles of CO disappeared due to a side reaction. The measured final H_2/CO ratio varied from 5/1 to 16/1 during these runs though the initial charge was $H_2/CO\sim2/1$.

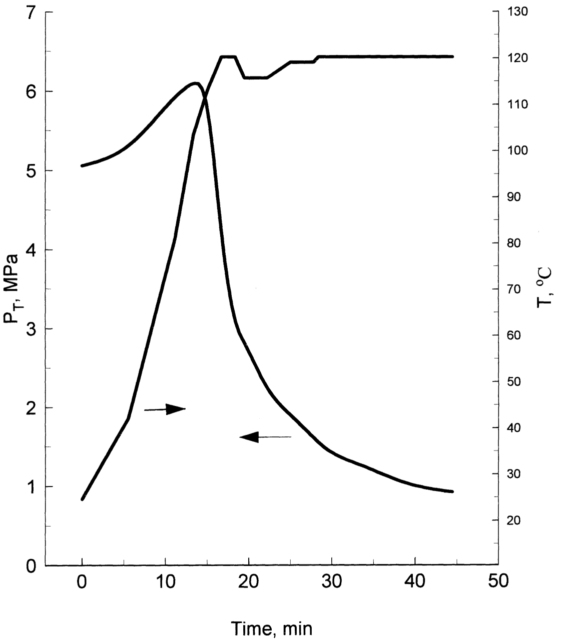

Fig. 1. Pressure and temperature profiles of a typical methanol synthesis batch run catalyzed by $Ni(CO)_4$ / KOMe catalyst system. Run conditions: *p*-dioxane=100 ml, [KOMe]=0.4 M, $[Ni(CO)_4]$= 0.05 M; syngas: H_2/CO=66%/34%, T=120°C, P_I=5.0 MPa at 25°C.

and are shown in Fig. 2 for the run data in Fig. 1. The reaction rate constant was calculated by correlating the rate of reaction with disappearance of CO:

$$\frac{-\mathrm{d}p_{\mathrm{CO}}}{\mathrm{d}t} = -kp_{\mathrm{CO}} \qquad (9)$$

or

$$\ln(p_{\mathrm{CO}}) = -kt + c \qquad (10)$$

where k=pseudo first-order rate constant and C is the constant of integration. Fig. 3 shows a linear plot (correlation coefficient=0.998) based on Eq. (10) and yielded k=0.083 min $^{-1}$ and c=6.26. A similar treatment of the H_2 data in Fig. 2 (correlation coefficient=0.991) yielded pseudo first-order rate constant of 0.035 min^{-1}.

The effect of other reaction components on rate was also investigated. Initially, the effect of stirring was established. Four runs ([MeOH]=20.0 M, [KOMe]= 4.0 M, $[Ni(CO)_4]$=0.05 M, H_2/CO=66%/34%), two at 120°C and two at 110°C yielded k values of 0.083, 0.048, 0.171 and 0.237 min^{-1} at 800, 1200, 1200 and

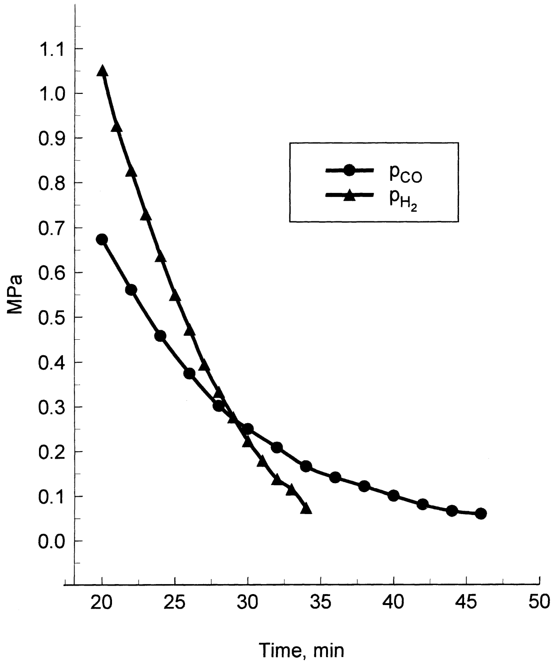

Fig. 2. Calculated individual p_{CO} and $p_{\mathrm{H_2}}$ pressure profiles. Data from Fig. 1.

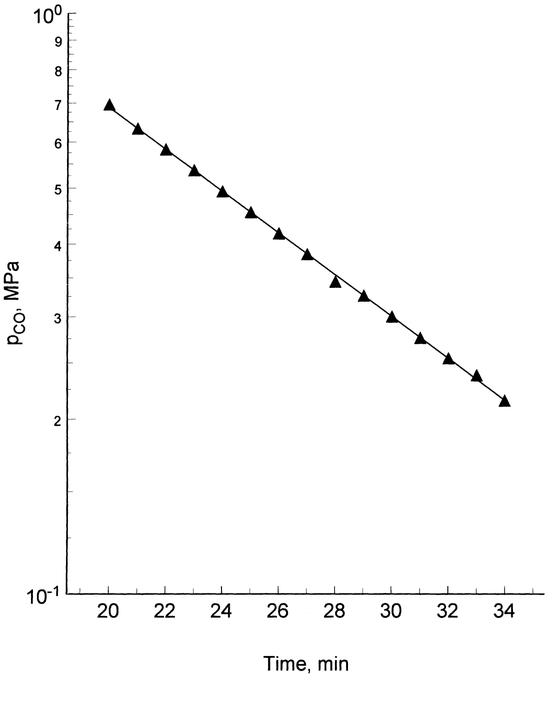

Fig. 3. A plot of $\ln p_{\mathrm{CO}}$ versus time for p_{CO} data from Fig. 2.

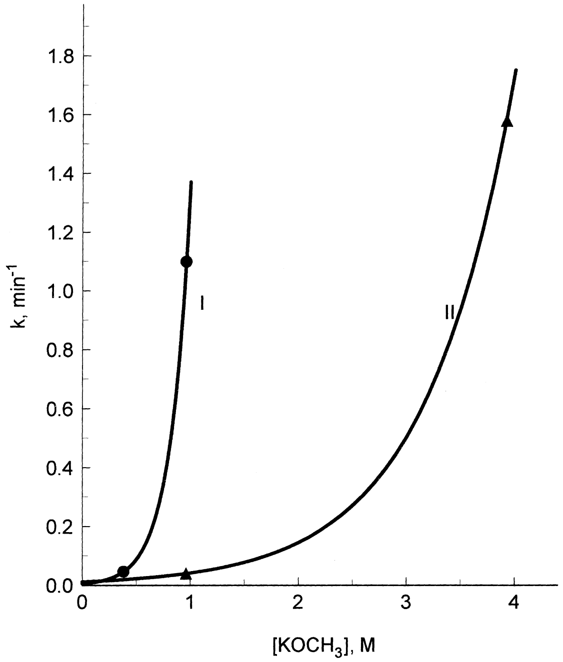

Fig. 4. Dependence of k on base concentration. Run conditions: T=120°C, $[Ni(CO)_4]$=0.05 M, H_2/CO=66%/34%. Curve I: p-dioxane=100 ml; Curve II: p-dioxane=75 ml, MeOH=25 ml.

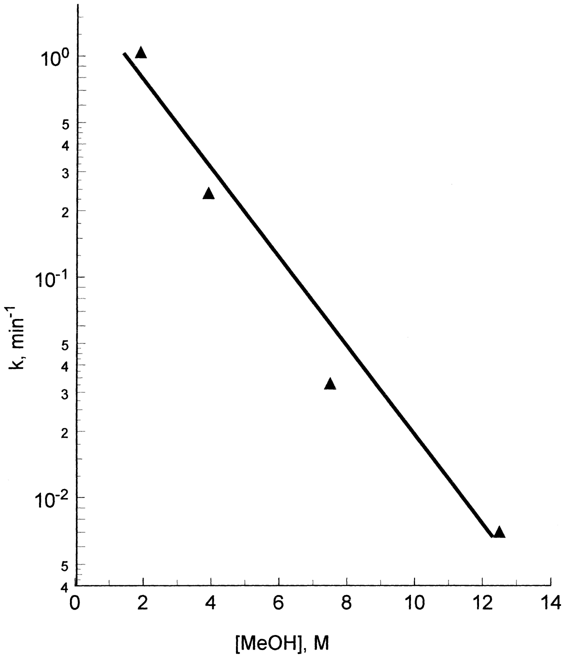

Fig. 5. A plot of MeOH concentration versus k. Run conditions: $[Ni(CO)_4]$=0.05 M, [KOMe]=1.0 M, p-dioxane=(100-MeOH) ml, H_2/CO =66%/34%, T=110°C.

1800 rpm, respectively, suggesting that mass transfer may not be rate controlling though more data are needed.[4] This led us to select 1200 rpm as the stirrer speed for the kinetic study. The effect of varying base concentration is shown in Fig. 4. From the data, a non-linear dependence of k on base concentration is evident. The data points on Curve II were obtained from runs containing 6.2 M initial [MeOH]. Interestingly, though the runs related to data points on Curve 1 were at lower base concentrations (0.4 and 1.0 M base) the rates were higher than those from data points on curve II (1.0 and 4.0 M base). It is concluded that increasing methanol concentration substantially lowered rates and this lowering was not offset by increased base concentration used. To understand this phenomenon, a set of runs were conducted at a fixed KOMe concentration of 1.0 M and [MeOH] was varied between 2.0 and 12.4 M. The data were analyzed and k was found to vary exponentially with MeOH and is modeled as follows:

$$k = k_1 \exp(-k_2[\mathrm{MeOH}]) \qquad (11)$$

where k_1 and k_2 are empirically determined constants. From Fig. 5, k_1 and k_2 were estimated to be 1.71 min^{-1} and 0.443 M^{-1}, respectively.

A set of runs were conducted to measure the rate dependence on temperatures of 116°C, 98°C, 87°C and 70°C. Fig. 6 shows the corresponding Arrhenius plot. From the slope, E_{act} was calculated to be 138.7 kJ mol^{-1} and A (pre-exponential factor) was 1.8×10^{13} min^{-1}.

Substitution of expression (11) for k into expression (9) yields:

$$\frac{-\mathrm{d}p_{\mathrm{CO}}}{\mathrm{d}t} = k_1 p_{\mathrm{CO}} \exp(-k_2[\mathrm{MeOH}]) \qquad (12)$$

where both k_1 and k_2 are independent of MeOH concentration and dependent on [KOMe]. This empirical expression is valid only in a limited range of concentrations described here. Also evident is the absence of the $[Ni(CO)_4]$ term. Due to its toxicity only a minimum amount of $Ni(CO)_4$ was used in the

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[4] A reviewer has suggested that the effect of gas–liquid mass transfer aspect should be revisited and has provided ([11]). The authors' intend to undertake this study to firmly establish the effect of stirrer speed on reaction rate

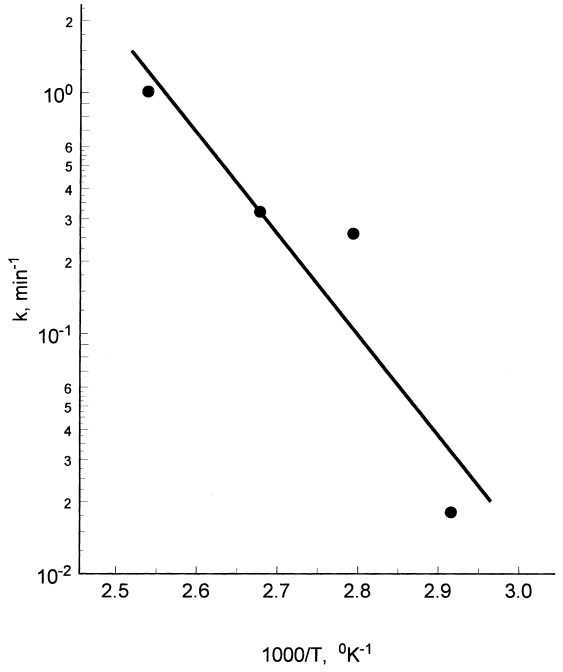

Fig. 6. An Arrhenius plot for methanol synthesis catalyzed by the $Ni(CO)_4$/KOMe system. Run conditions: $[Ni(CO)_4]=0.05$ M, [KOMe]=1.0 M, *p*-dioxane=100 ml, $H_2/CO=66\%/34\%$.

runs conducted. A preliminary study indicated that at 0.01 and 0.05 M [Ni], approximately the rate dependence was first-order. A more detailed rate dependence on Ni concentration study over a wide range of [Ni] is now underway.[5]

Though this rate expression is presently being refined to include all the reaction components, it was realized that a better understanding of the system was also needed to establish a true kinetic model. The subject catalyst system, being homogeneous in nature, would allow a thorough mechanistic understanding of the catalytic cycle that can help aid in establishing a true kinetic rate expression.

3.3. Mechanistic considerations

MeOH is a versatile molecule with multiple uses and its more economical synthesis has been a subject of intense research [12]. Of particular interest is synthesis of methanol at lower temperatures discussed here that is also being pursued by several other groups [13]. It is to be emphasized that the subject $Ni(CO)_4$/KOMe catalyst system is classified as a liquid phase homogeneous system in that the catalyst is truly dissolved in the solvent and methanol synthesis involves a liquid (catalyst)/gas (reactant gases) biphasic system [8]. The mechanistic study on a closely related catalyst system was reported in literature [13]. This study emphasized FTIR as a tool to discern the mechanism of the $Ni(CO)_4$/NaOMe system shown in Scheme 1. The proposed steps involve a nucleophilic attack of $^{-}$OMe on a coordinated CO of $Ni(CO)_4$ followed by production of methyl formate and $[HNi(CO)_3]^-$. Methyl formate is hydrogenated by this Ni anionic species to 2 mol of methanol via the intermediacy of formaldehyde and addition of CO regenerates $Ni(CO)_4$ complete the catalytic cycle. Though this proposed mechanism (Scheme 1) is plausible whether same intermediate species are involved during methanol synthesis catalyzed by the present $Ni(CO)_4$/KOMe system needs to be confirmed. More importantly, several crucial experiments that would establish the mechanism of the present system are also planned. By establishing these intermediate steps for the subject $Ni(CO)_4$/KOMe system will allow refinement of the kinetic model proposed above. A more detailed kinetic study has been carried-out and will be the subject of a forthcoming publication [14].

3.4. Relevance to transportation fuels

The above discussion specifically described the $Ni(CO)_4$/KOMe catalyst system for methanol synthesis. This system demonstrates a potential for highly efficient conversion of gas hydrates to methanol. Since DME is considered an environmentally-acceptable replacement for diesel [15], present interest in developing DME surpasses interest in methanol energy liquid. Synthesis of DME from methanol involves dehydration of 2 mol of methanol and is typically carried-out on γ-Al_2O_3 catalyst at $T>250°C$ [7]. Alternatively, this two-step synthesis can be carried-out in one-step i.e. direct syngas to DME conversion, at $\geq 250°C$ catalyzed by a hybrid methanol catalyst [6,7,15]. Yet, another transportation fuel option is to convert syngas to diesel via Fischer–Tropsch (F–T).

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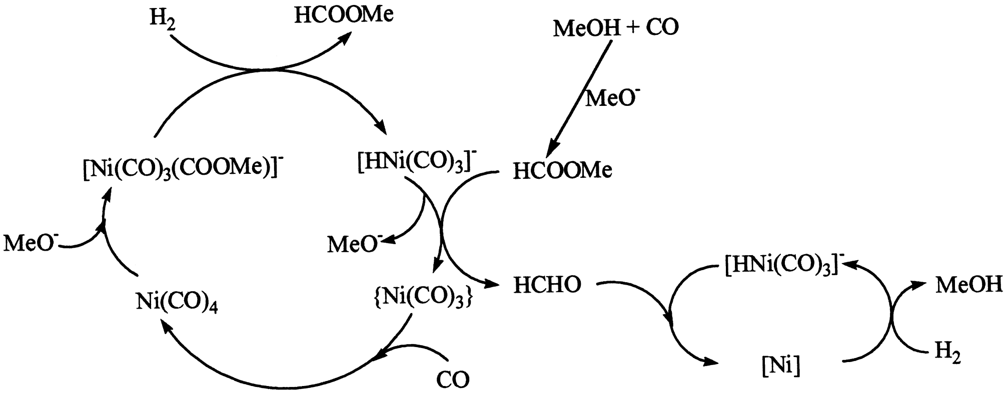
[5] In addition to its toxicity, the volatility of $Ni(CO)_4$ makes addition of precise amounts of this material rather difficult. A ±10% error is not uncommon. A strategy is now being developed to collect meaningful rate date for the Ni dependence parameter.



Scheme 1. Proposed mechanism of the $Ni(CO)_4$/NaOMe catalyzed methanol synthesis ([13]).

This shell process is now commercially operating in Indonesia. Therefore, both DME and F–T diesel are considered as suitable choice of fuels. For recovery and utilization of gas hydrates, small mobile processing units have distinct advantages. Thus, for the development of an economical process to utilize gas hydrates as an energy source, we consider the following criteria as necessary:

(1) *Low temperature operation*: This requirement relates both to thermodynamics and energy efficiency. Since all the reactions discussed here involving transformation of syngas to liquid fuels are exothermic, a lower temperature is thermodynamically desirable. As for energy efficiency, duty cycling and heat losses in small flexible units are greater than a constant running larger scale processing unit. There is also the energy requirement for raising the process stream to the operating temperature. For small units, these losses can exceed 25% of the energy value of the fuel. A low temperature operation is a requirement for developing an energy efficient system.

(2) *Low pressure operation*: The economy of a methanol synthesis process could be improved if syngas produced is utilized with minimum further compression. This is especially critical for air-blown natural gas partial oxidation (POX) where the total process pressure must be raised to compensate for ~40% N_2 in syngas feed. A recent paper [12] suggests an upper limit of the process pressure to be 2MPa.

(3) *High per pass gas conversion*: This requirement is essential for simplicity of a small plant due to elimination of the expensive gas recycles step. Such a system running at a lower pressure also matches conditions to allow POX with air (during syngas production) and subsequent carry-over of N_2 in the gas stream. But the use of partial oxidation of natural gas with air is feasible only for single pass conversion processes that avoid the problem of N_2 build-up in the synthesis loop.

(4) *High productivity*: High space-time yields (STY) are necessary in order to scale down the physical size of any process unit while maintaining high productivity.

(5) *High selectivity*: The generation of secondary products at a remote site raises separation, storage and disposal questions which adds complexity to the overall process.

(6) *Catalyst lifetime*: Catalyst replacement is costly and this is especially true at remote sites. Catalyst that is tolerant to H_2O, sulfur CO_2 and other trace impurities that may be present in the gas hydrate process stream is desirable to avoid cost associated with gas preclean-up.

(7) *High process efficiency*: Having all the above attributes gives the unit an overall high process efficiency. The bench mark for energy efficiency is between 70% and 80% which reflects the benchmark energy cost for liquefying natural gas. Since DME is a true diesel fuel (high cetane number), it would be preferred in the transportation energy sector over LNG if both were available at the same energy equivalent price.

As for a choice between DME and F–T diesel fuels, inherent problems are associated with the F–T process, namely: (1) low STY and (2) low product selectivity due to the chain growth mechanism that is

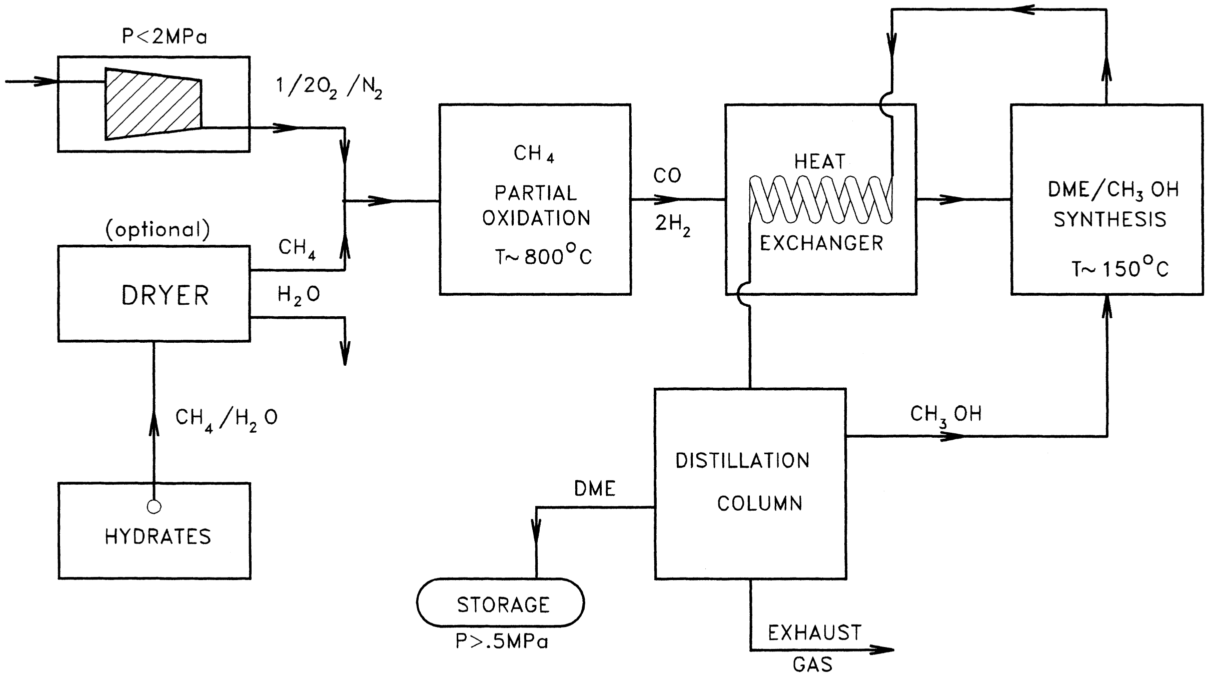


Fig. 7. A conceptual baseline scheme for economical conversion of gas hydrates into transportation fuels.

controlled by the Schulz-Flony distribution. This argument justifies the selection of DME as a promising candidate transportation fuel for further study. The preceeding discussion indicates that the unique features of the subject $Ni(CO)_4$ /KOMe system for methanol synthesis match closely with the set-forth criteria. These unique features were utilized to design a conceptual flow-sheet (Fig. 7) that illustrates a proposed process scheme for the remote production of DME/MeOH fuels from gas hydrates in a small flexible plant. Irrespective of the downstream process used, the gas hydrates to fuels study depicted in Fig. 7 will involve an overall three-step process.

Step 1. *Mining gas hydrates.* Essentially an unexplored area, mining gas hydrates will involve breaking the lattice structure to allow natural gas to evolve at the surface. Though the term "Aqueous CH_4" is introduced in this paper to describe natural gas hydrates, even including aerosoling of water vapor during gas escape, the water content of the escaping gas is expected to be minimal (note that the saturation vapor pressure of H_2O at 20°C is 17.5 mm Hg). The challenge is to capture essentially all of the escaping gas due to strong greenhouse effect of CH_4 (~20 times that of CO_2). Since the gas is enriched from 3.9 wt% CH_4 in H_2O at the point source to >95%, the gas drying step may not be necessary as long as the downstream catalyst is H_2O tolerant. This slightly wet gas becomes the feed stock.

Step 2. *Syngas generation.* The capital cost associated with this energy intensive step is 60–70%. Three well-established options are available for syngas production:

1. *Steam reforming.* At first glance, this option appears a natural fit due to excess H_2O water naturally present the following equation:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H = +226\,\text{kJ mol}^{-1} \tag{13}$$

   Due to endothermicity, this route is not preferred.
2. *Partial oxidation with O_2.* Commercially the most widely used route [16], this reaction is exothermic:

$$2CH_4 + O_2 \rightarrow 2CO + 4H_2 \quad \Delta H = -44\,\text{KJ mol}^{-1} \tag{14}$$

   The drawback is the expensive requirement for an O_2-separation plant.

3. *Partial oxidation with air.* Substituting air for O_2 yields the following equation:

$$2CH_4 + O_2/N_2 \rightarrow 2CO + 4H_2 + N_2 \qquad (15)$$

Here, the cost of O_2-separation plant is eliminated but this route is only feasible for a single pass (no gas recycle) conversion process that avoids the problem of N_2 build-up in the synthesis loop. At present, this route is the logical choice. The currently practiced technology requires the partial oxidation reactor to operate at 800°C and is not viewed as being low temperature. The lowering of the syngas reactor at lower temperatures is, therefore, a research topic. One of the identified problem of running the syngas production reactor at lower temperatures is coking (poisoning) of the catalyst via the Boudouard reaction that needs to be addressed:

$$2CO \rightarrow C + CO_2 \quad \Delta H = +170\,\mathrm{kJ\,mol^{-1}} \qquad (16)$$

Step 3. *Syngas to methanol/DME.* The thrust of this paper is the realization that a highly active catalyst that meets six of the above outlined criteria is available for application to make liquid fuels from gas hydrates. This methanol synthesis catalyst is a successful example of the basic LPLT concept that has been under development at BNL for several years. While improvements in the BNL low temperature catalyst continue, this catalyst can be modified to predominantly yield DME. Thus, the topic of further research relates to combining methanol synthesis directly with the dehydration step to produce DME at temperatures $\leq$200°C.

4. Future direction

For economical development of gas hydrates that are located in permafrost and deep sea locations, conversion of this resource into liquid fuels at the feed location is considered. Skid-mounted units that are flexible to allow synthesis of different fuel products are envisioned that, in a simplified scheme, will require highly efficient and selective processes with minimum input of energy. A criteria is established for processes to be considered under this scheme. Relevant to this, discussed here is an emerging low temperature methanol synthesis technology that is based on the LPLT concept, developed at BNL. A successful outcome of this concept is a homogeneously catalyzed liquid phase synthesis of MeOH in which >90% per pass gas conversion is routinely achieved at a thermodynamically favorable temperature <150°C. The catalyst achieves high reaction rates at low pressure of <5 MPa and yields MeOH with >95% selectivity with methyl formate (major) and dimethyl ether (minor) by-products. Methyl formate appears to form via carbonylation of methanol catalyzed by an alkoxide and DME is produced by dehydration of 2 mol of methanol. For methanol synthesis (the primary product), preliminary kinetic data are presented for the $Ni(CO)_4$/KOMe catalyst system in *p*-dioxane. The dependence of reaction rates on system components appear complex and an empirical kinetic expression is presented.

In this paper, an overall scheme for gas hydrates to liquid fuels is discussed. For this approach to be ready for future utilization, the critical topics for research are:

- A major technological challenge relates to mining gas hydrates with minimum loss of CH_4.
- The presently available POX with air technology needs to be modified to operate at lower temperatures. Development of other upcoming technologies (membrane, etc.) with targeted cost reduction of up to 30% are of interest.
- A single pass syngas conversion to MeOH or DME process that maintains high energy efficiency at lower temperatures.

The expertise at BNL is already addressing the downstream (syngas to liquids) aspect. The low temperature approach to methanol synthesis from syngas especially involving homogeneous catalysts appears extremely promising. For application to gas hydrates, several aspects are identified in the catalyst development area that require further research:

- The known toxicity of volatile $Ni(CO)_4$ makes it an undesirable catalyst precursor. Formulation of environmentally-benign non-$Ni(CO)_4$ catalyst precursors is ongoing and several substituted Ni complexes that are equally effective as catalysts for methanol synthesis have been synthesized [14].
- In pure methanol as a solvent, the reaction is relatively slow that directly translates into a lar-

ger/taller reactor to allow sufficient residence time. This aspect should be weighed against the cost of cosolvent/methanol product separation downstream if a cosolvent is utilized to attain faster rates as has been the case in the present study. Our present emphasis is on the development of a high performance catalyst that operates in an aqueous phase. If successfully developed, such a solvent system will address three aspects: (1) minimize cost of H_2O separation from "Aqueous CH_4" feed; (2) H_2O may also serve as a cosolvent; (3) the catalyst being soluble in the aqueous phase will facilitate catalyst/product separation to allow catalyst recycle in a continuous process.
- Minimize impact of CO_2 presence on catalyst activity.
- Develop a related high efficiency DME catalyst that operates at $\leq$200°C.

These three areas are already the subject of an ongoing effort in our group and promising approaches are being pursued [17]. Since DME is closely related to MeOH and is a minor product during MeOH synthesis with the subject highly active Ni system, a similar technology could be developed to synthesize this diesel-replacement fuel with high selectivity. Indeed, a slurry catalyst that converts MeOH into DME with high efficiency at <200°C appear promising [14]. If the targeted technological challenges are met, the skid-mounted/flexible unit concept would be applicable to both on-land and off-shore gas hydrate reserves and a vast source of clean energy will become available in the 21st century.

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