Ruthenium-Catalyzed Hydrogenation of Aqueous Sodium Bicarbonate

1980

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RUTHENIUM-CATALYZED HYDROGENATION OF AQUEOUS SODIUM BICARBONATE

BY

DUANE P. COVINO
B.S., Rensselaer Polytechnic Institute, 1974

RESEARCH REPORT

Submitted in partial fulfillment of the requirements for the degree of Master of Science: Industrial Chemistry in the Graduate Studies Program of the College of Natural Sciences at the University of Central Florida; Orlando, Florida

Winter Quarter
1980
ABSTRACT

This research report investigated the ruthenium-catalyzed hydrogenation of aqueous sodium bicarbonate. Subjects of the investigation included: the "blank" effect of the 316 stainless steel reactor in the batch mode; the catalytic activities at 150°C for unsupported ruthenium, including ruthenium purge and the metal produced from the in situ reduction of RuCl₃·1-3H₂O and Ru(IV)O₂·H₂O; the catalytic activities at 150°C for supported ruthenium including 4.05% w/w ruthenium on alumina, 5.25 and 20.85% w/w ruthenium on molecular sieve SK-41 (ammonium - substituted Y-type), 3.34 and 17.48% w/w ruthenium on SK-41 (prepared by the in situ reduction of the RuCl₃·1-3H₂O exchange sieve); orders of reaction rate with respect to hydrogen, bicarbonate, and catalyst at 150°C; activity as a function of temperature; and susceptibility to deactivation.

The reaction appears to be zero order in both hydrogen and bicarbonate and first order in catalyst at 150°C in the concentration ranges examined; saturation of an assumed limited number of active catalyst sites is assumed to cause the observed zero orders.

Conversion was negligible below 150°C, and optimum in the 150°C-200°C range, with product distribution at 150°C heavily favoring methane; e.g. 99% v/v.

The stainless steel reactor was found not to catalyze the reaction at 150°C during a two hour reaction. Catalytic activity for unsupported ruthenium paralleled metal surface area (as determined...
by BET adsorption), while the inverse was found to be true for sieve-supported metal; mass transfer impedance and electronic effects are assumed to be contributing factors. The reaction on alumina-supported ruthenium produced an undesirable white coating, composition as yet undetermined, which strongly adhered to the support and to the reactor walls.

Although the reaction investigated is even more exothermic than the Fischer-Tropsch production of methane, and the ruthenium catalyst was also found to be subject to deactivation, the reaction of interest may have an economic advantage over the Fischer-Tropsch synthesis, in that it is less expensive to decompose a bicarbonate species using hydration energy and then hydrogenate directly, than to thermally decompose the ore and hydrogenate the CO$_2$ produced.
ACKNOWLEDGEMENTS

The author wishes to thank his advisor, Dr. Chris Clausen, for his efforts and patience.

The author also wishes to thank the faculty and staff of the University of Central Florida Department of Chemistry, for their advice, their generosity, and their friendship.
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INTRODUCTION

CONSIDERATIONS IN THE HYDROGENATION OF INORGANIC CARBON SPECIES

Importance

Increased hydrocarbon production is of renewed importance for a variety of reasons, including the needs for chemical feedstocks and for high BTU fuel production. Oil supplies are dwindling, primarily as a result of political and economic considerations. The uncertainty over nuclear power has mandated continued consumption of crude oil in electric power generation. Coal liquefaction is being commercialized too slowly for political and economic reasons, and biomass conversion is still in its commercial infancy.

Suitable Carbon Species and Sources

Primarily, there are three suitable inorganic carbon species: carbon monoxide, carbon dioxide, and carbonate ores.

Carbon monoxide is prepared according to the following scheme:

\[ \text{coal} \xrightarrow{1300 \text{ K}} \text{coke} + \text{gas} + \text{tar} + \text{crude benzole} \]

\[ \text{coke(white hot)} + \text{H}_2\text{O(steam)} \rightarrow \text{CO} + \text{H}_2; \quad \Delta H = +31.1 \text{ kcal/mole} \]

The heat for this endothermic reaction is provided by a reaction which produces carbon dioxide:

\[ \text{coke(white hot)} + \text{O}_2 \rightarrow \text{CO}_2; \quad \Delta H = -93.2 \text{ kcal/mole} \]

In addition, sulfur and sulfur compounds, tars, phosphates, and other impurities which act as catalyst poisons are produced.
Carbon monoxide is also produced as a byproduct of the obsolete carbide route to acetylene:

\[
\text{CaO} + 3\text{C} \rightarrow \text{CaC}_2 + \text{CO}
\]

and is a byproduct of \( \text{CO}_2 \) hydrogenation, depending upon catalyst and conditions.

Carbon dioxide can be produced from the water-gas shift reaction,

\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2
\]

ore decomposition,

\[
2\text{NaHCO}_3 \xrightarrow{\Delta} \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2
\]

\[
\text{CaCO}_3 \xrightarrow{\Delta} \text{CaO} + \text{CO}_2
\]

and the fermentation of biomass, in addition to separation from air.

An often-neglected source of carbon is that bound in carbonate ores, such as calcite, limestone, dolomite, soda ash, trona, etc. These ores can be decomposed to metal oxides and carbon dioxide, or converted to bicarbonate by carbonic acid spray wash:

\[
\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{Ca(HCO}_3\text{)}_2
\]

It is the utilization of one of these ores in its bicarbonate form, sodium bicarbonate, that this report investigates.

**Thermodynamics and Mechanistic Considerations**

The hydrogenation of CO has been in commercial operation for
many years. In the hydrogenations of both CO and CO$_2$, which have been widely investigated, there are a variety of competing reactions$^1$:

1) $3\text{H}_2 + \text{CO} \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$

2) $2\text{H}_2 + 2\text{CO} \rightleftharpoons \text{CH}_4 + \text{CO}_2$

3) $4\text{H}_2 + \text{CO}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$ (Sabatier Reaction)

4) $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ (Shift Reaction)

5) $2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$ (Boudouard Reaction)

The reaction of interest in this study is:

6) $2\text{HCO}_3^- + 4\text{H}_2 \rightleftharpoons \text{CO}_3^{2-} + \text{CH}_4 + 3\text{H}_2\text{O}$

From the previous section, one sees that a choice exists; one can hydrogenate CO$_2$ from decomposition of either the carbonate or the bicarbonate species, or hydrogenate the bicarbonate species in solution.

The preceding reactions 1-5 are shown not only for comparison purposes (as the hydrogenations of carbon oxides), but for other, more subtle reasons, ones which relate to the mechanism for the reaction of interest, and which will now be developed.

If the hydrogenation of the bicarbonate form is, in actuality, the hydrogenation of carbon dioxide produced from a decomposition reaction, such as:

$$2\text{NaHCO}_3 \rightleftharpoons \text{CO}_2 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$$
then the only effects of conversion of the carbonate to the bicarbonate would be to increase the weight percent carbon (e.g. Ca(HCO$_3$)$_2$ is 15% w/w carbon, whereas CaCO$_3$ is 12% w/w) and perhaps the solubility (e.g. calcium bicarbonate is slightly soluble in water, whereas calcium carbonate is insoluble).

Reactions 1-5 will then enter into play, yielding unwanted, competing reactions, and decreased control of product distribution, as reactions 4 and 5 change the H$_2$/CO ratio. Carbon dioxide could be hydrogenated to alkanes in the Sabatier Reaction, or to CO in the reverse shift reaction. The CO can then either be hydrogenated to alkanes (reactions 1 and 2), or undergo an asymmetrical disproportionation reaction to produce carbon and CO$_2$ (reaction 5). The carbon produced can deposit and poison the catalyst, and the CO$_2$ can act to promote the reverse of the shift reaction, and also interfere with reactions 2 and 3. A detailed discussion of the complicated interplay between the reactions is beyond the scope of this study. However, one sees that reactions 1-3 are to be promoted, and reactions 4 and 5 are to be avoided during the production of the hydrocarbons.

From Figure 1, it is apparent that the relative influence of the carbon deposition reaction increases with temperature, dictating that a low temperature is thermodynamically favorable for avoiding that reaction. (Data for reaction 6 in both Figures 1 and 2 is from reference 2.) Additionally, from the same figure, one sees that operation at low temperature not only increases the ability to preferentially select among reactions 1-3, thus permitting slightly
Figure 1. Equilibrium constants as functions of temperature.

- \(3\text{H}_2 + \text{CO} \leftrightarrow \text{CH}_4 + \text{H}_2\text{O}\)
- \(2\text{H}_2 + 2\text{CO} \leftrightarrow \text{CH}_4 + \text{CO}_2\)
- \(4\text{H}_2 + \text{CO}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O}\)
- \(\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2\)
- \(2\text{CO} \leftrightarrow \text{C} + \text{CO}_2\)
greater product distribution control, but it also minimizes the influence of the shift reaction. This preference for low temperature is complicated by the large exothermicity of the alkane producing reactions, as is evidenced from Figure 2.1,2, with the obvious possibility of a "runaway" reaction; this not only increases the possibility of catalyst sintering, it favors the deposition of carbon. The engineering approaches to gas phase CO/CO₂ hydrogenation and the exothermic nature of the process are discussed in a later section.

In contrast to the multiplicity of difficulties encountered in gas phase CO/CO₂ hydrogenation, if the reaction mechanism proceeds through hydrogenation of a bicarbonate (or carbonate) species in solution, and therefore does not involve CO or CO₂ as intermediates, then reactions 1-5 can be avoided. Akbarnejad3, in his study of the liquid phase hydrogenation of carbon dioxide in aqueous solutions, concluded that the hydrogenation reaction occurs through a carbonate or bicarbonate mechanism in solution. This was reached on the basis of the observation that the conversion of CO₂ vs. molarity of an aqueous sodium hydroxide solution exhibited a maximum at the concentration of NaOH which yielded the maximum sodium bicarbonate concentration.

Thus, if one can find an economical system for the hydrogenation of the bicarbonate form of an ore, the numerous competing reactions characteristic of gas phase CO/CO₂ hydrogenations, with the concomitant engineering problems of reactor design, etc., can be avoided by
Figure 2. Temperature dependents of enthalpy of hydrogenation.

Legend: (1) CO + H₂O ↔ CO₂ + He
(2) 2CO ↔ CO₂ + C
(3) 4H₂ + CO₂ ↔ CH₄ + 2H₂O
(4) 3H₂ + CO ↔ CH₄ + H₂O
(5) 2H₂ + 2CO ↔ CH₄ + CO₂
(6) 2HCO₃⁻ + 4H₂ ↔ CH₄ + 3H₂O + CO₃^{2⁻}
the liquid phase hydrogenation of the bicarbonate species, either
mined directly, or produced from the carbonate.

One should be cognizant of the possibility that steady-state
concentrations of intermediates such as C, CO, and CO₂, can occur
from competing reactions, and this has been an influence upon
reactor design, as Mark Dry of SASOL reported on the hydrogenation
of CO₂ over iron catalysts. Selectivity to methane was not a
function of the partial pressure of CO₂ in a fixed-bed reactor,
whereas the converse was found to be true in fluidized-bed reactors,
with increasing P_{CO₂} decreasing the selectivity to methane. Although
relatively little work has been reported on CO₂ hydrogenation,
Anderson, Lee and Machiels have concluded that the hydrogenation of
CO₂ rather than CO decreases the generation of heat, and may have
other advantages.

Although this investigator was unable to find any reference to
reaction 6 as the subject of a detailed investigation, calculations
indicate that the reaction is even more exothermic beyond 75°C than
the CO/CO₂ hydrogenations, which places even greater strain upon
reactor design, feed compositions, and species allocations to satisfy
the mandate for improved heat transfer.

Commercial Production

Commercial hydrocarbon production from catalytic inorganic
carbon oxide hydrogenation began with the Ruhrchemie Process in 1913,
in which BASF reacted CO and H₂ on activated cobalt or osmium oxides
supported on asbestos to produce a variety of products, with methanol
the primary commercial product.

In 1923, Fischer and Tropsch produced an oily liquid called synthol by hydrogenation of CO over alkalized iron. The hydrogenation of CO with hydrogen has become known over the years as the Fischer-Tropsch Synthesis (FTS), with a wide variety of catalysts and reaction conditions being used, and the products available being dependent upon temperature, pressure, catalyst, residence time, etc., as shown in Table I.

Ruthenium, the catalyst in this study, as a carbon oxide hydrogenation catalyst, stands alone in its ability to produce high molecular weight waxes with a low oxygen content, and is a very active methanation catalyst, the most active of the Group VIII metals used. Additionally, in the Fischer-Tropsch Synthesis using ruthenium, no carriers or promoters have ever been found which could yield improvement. Although its high costs weigh heavily against its use, the fact that there were at least 20 units for gas purification by methanation in 1973 using ruthenium gives credence to its efficacy.

Ruthenium prepared by the reduction of the dioxide can operate at 195°C and 100 atm, giving constant activity and reproducible products for at least six months.

In the United States, the Carthage Hydracol Process at Brownsville, Texas was in operation from 1948 to 1957, being comprised of the following steps:

1) recovery of C₄ and higher hydrocarbons from natural gas
2) separation of high-purity oxygen from air
### TABLE I

Reactions of Carbon Monoxide and Hydrogen

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<tr>
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<th>Catalysts</th>
<th>Promoters</th>
<th>Temp. °C</th>
<th>Pressure, atm</th>
<th>Product</th>
</tr>
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<tbody>
<tr>
<td>A. Methane synthesis</td>
<td>Ni</td>
<td>ThO₂, MgO</td>
<td>250-500</td>
<td>1</td>
<td>Chiefly methane</td>
</tr>
<tr>
<td></td>
<td>Fe, Co, Ni</td>
<td>ThO₂, MgO</td>
<td>150-350</td>
<td>1-30</td>
<td>Paraffinic and olefinic hydrocarbons varying from methane to waxes, plus small to large quantities of oxygenated products</td>
</tr>
<tr>
<td>B. Fischer-Tropsch synthesis</td>
<td>Ru</td>
<td>K₂O</td>
<td>150-250</td>
<td>100-1,000</td>
<td>High-molecular-weight paraffinic hydrocarbons</td>
</tr>
<tr>
<td>C. Methanol synthesis</td>
<td>ZnO, Cu, Cr₂O₃, MnO</td>
<td></td>
<td>200-400</td>
<td>100-1,000</td>
<td>Methanol</td>
</tr>
<tr>
<td>D. Higher alcohol synthesis</td>
<td>same as in C</td>
<td>Alkali</td>
<td>300-450</td>
<td>100-400</td>
<td>Methanol and higher alcohols</td>
</tr>
<tr>
<td>E. Iso synthesis</td>
<td>ThO₂, ZnO + Al₂O₃</td>
<td>K₂O</td>
<td>400-500</td>
<td>100-1,000</td>
<td>Saturated branched hydrocarbons</td>
</tr>
<tr>
<td>F. Oxo synthesis*</td>
<td>Co, Fe</td>
<td></td>
<td>100-200</td>
<td>100-200</td>
<td>Oxygenated organic compounds</td>
</tr>
</tbody>
</table>

*This reaction involves hydrogen, carbon monoxide, and olefins
3) use of the CH$_4$ from natural gas to produce CO; (i.e.,

$$2\text{CH}_4 + 3\text{O}_2 \rightarrow 2\text{CO} + 4\text{H}_2\text{O}$$

4) $\text{H}_2 + \text{CO} \xrightarrow{\text{fluidized iron}}$ gasoline, etc.

5) separation of synthesis products

6) gas treatment to remove oxygenated compounds, etc.

**Engineering Approaches to CO Methanation**

As has been mentioned, the primary problem in carbon oxide hydrogenation is that of exothermicity, which can sinter catalysts, and favor undesirable competing reactions, such as the shift reaction or carbon deposition. Among the approaches used to avoid these problems are: equilibrium limitation, through-wall cooling, fluidized-bed catalysis, steam moderation, kinetic limitation, and slurry reaction.

Equilibrium reactors (Figure 3) are adiabatic, fixed-bed reactors in which sufficient product gas is recycled to control the temperature. These reactors are the basis for the CONOCO methanation process in Scotland, and the Lurgi-SASOL (South African Synthetic Oil, Ltd.) process.

In the through-wall cooled reactor (Figure 4), the heat of reaction is removed through walls of bundles of catalyst-filled tubes. Almost complete methanation can be achieved in one reactor rather than a series of reactors, but the potential for generating high local catalyst surface temperatures is also greater. This type of reactor is also used by SASOL.
Figure 3. Equilibrium-controlled adiabatic reactor
Figure 4. Throughwall-cooled reactor.
The fluidized-bed catalytic reactor (Figure 5)\textsuperscript{9} is based on a large catalyst circulation rate to absorb the heat of reaction. It has been used by SASOL (Kellog-designed) and Carthage Hydracol to produce liquid hydrocarbons, with the Carthage Hydracol version (Figure 6)\textsuperscript{9}, unlike SASOL (Figure 5), electing to have the catalyst remain in the reactor, rather than being withdrawn, circulated, and entrained. This process solves the heat transfer problem, which limited space-time yields in fixed-beds. It also permits higher synthesis temperatures, which permit higher conversions with cheaper catalysts, without producing excessive carbon or methane, along with permitting continuous operation, as the catalyst can be withdrawn and regenerated in a side stream\textsuperscript{8}.

The steam-moderated reactor seeks to limit conversion by adding steam to the feed gas, simultaneously providing elimination of the shift reaction and of carbon deposition. This increases byproduct steam recovery, and has as perhaps its primary advantage, significant capital savings, in that recycle gas compressors are unnecessary\textsuperscript{8}.

The kinetic limitation method avoids approach to equilibrium by using very high space velocities to produce an effluent gas far removed from equilibrium composition, thereby reducing conversion and the accompanying generation of heat\textsuperscript{8}.

Lastly, the slurry methanation system (Figure 7) uses a large circulating stream of catalyst in an oil-slurry to remove heat by internal cooling, external cooling of a portion of the slurry,
Figure 5. Fluidized bed reactor (SASOL).
Figure 6. Fluidized bed reactor (Carthage Hydracol).
Low BTU Feed Gas
15-20% CO
45-60% H₂

Figure 7. Slurry methanation system.
evaporation of some of the oil in the reactor, or a combination of these approaches\textsuperscript{10}.

An interesting long-range proposal for the hydrogenation of carbon oxides to produce motor fuel, etc., and one that makes use of the otherwise wasted energy of nuclear fission, is that of Thomas C. Breitner of Transor R & D, who advanced the following:

1) decomposition at approximately $900^\circ\text{C}$ of alkaline-earth carbonates using a High Temperature Gas Reactor (nuclear);

\[ \text{e.g. } \text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2 \]

2) thermal (non-electrolytic) catalyzed decomposition of water at temperatures ranging from $350^\circ\text{C}$ to $1350^\circ\text{C}$

3) reduction of $\text{CO}_2$ to $\text{CO}$ with the water-source hydrogen

4) FTS in a toroidal fluidized-bed reactor using a reduced 95% iron oxide - 5% cobalt oxide catalyst

5) sale of byproduct $\text{CaO}$ and oxygen

6) if desired, an increase from 12% to 15% in the weight percent carbon by converting the carbonate to the bicarbonate form via carbonic acid spray wash.

Using 54-60 atm and $300^\circ\text{C}$ it is purported that propylene and butylene will be the primary products, whose polymerization and subsequent reforming will produce 80-octane motor fuel\textsuperscript{11}.

The aforementioned proposed process is an example of the complicated and therefore expensive systems that can be avoided if the carbon oxide can be hydrogenated in solution in the bicarbonate form. Thus, one sees, that with regard to the hydrogenation of the
carbon oxides found in carbonate ores, a decision of critical import is whether to decompose the ore into a gaseous carbon oxide before admittance to the hydrogenation reactor, whether by thermal decomposition or by aqueous acidification followed by heating and CO₂ evolution, or to input the carbonates in a solution/slurry and hydrogenate them directly.
EXPERIMENTAL

Catalyst Preparation

All catalysts used were commercial grade. Ruthenium trichloride and ruthenium oxide were obtained from the Ventron Division of Alfa Products Corporation. The ruthenium sponge was a product of ROC/RIC (Research Organic/Inorganic Chemical Corporation).

Catalyst supports studied included SK-41 molecular sieve (ammonium-substituted zeolite Y), obtained from Alfa Products/Ventron Division, and 90/100 mesh Anasorb Activated Alumina from Analabs, Incorporated.

The ruthenium trichloride on SK-41 catalyst precursors were prepared by dissolution of the salt in a minimal amount of water, overnight mixing of the salt solution and molecular sieve, followed by vacuum filtration through a medium pore ceramic frit, with subsequent heating under reduced pressure in a vacuum dessicator at 120°C for two hours. The sample in which the molecular sieve was not predried was sent to Galbraith Laboratories for commercial ruthenium analysis, yielding 17.46% w/w Ru.

The ruthenium metal on SK-41 catalysts were prepared similarly, but were reduced in a Lindberg Hevi-duty oven. The powdered supported catalyst was loaded into ceramic boats, and transferred into a glass tube which was secured in the oven. Atmospheric oxygen was excluded from the reaction zone by suitable connections at the tube ends. After five minutes of a slow hydrogen bleed, the temperature program was initiated, consisting of: one hour to reach 100°C;
one hour to reach 200°C; one hour maintained at 200°C; one hour to reach 300°C; one hour to reach 400°C; one hour maintained at 400°C. Hydrogen bleed was continued until the furnace temperature returned to 25°C.

The 4.05% w/w Ru on alumina was prepared by the incipient wetness technique, using alumina predried under reduced pressure. The sample was then reduced as above.

**Catalyst Evaluation**

With exceptions as noted, catalyst/catalyst precursor evaluation trials were conducted in the stirred batch mode using the 300 ml Parr model 4561 Mini-Reactor.

After having determined the basic feasibility of the ruthenium catalyzed methanation of sodium bicarbonate at 150°C, the effect of the 316 stainless steel reactor surface was determined as a blank.

After the reactor was cleaned with steel wool, pipe cleaners, and deionized water to remove all traces of catalyst from the previous trial, and, having added a sufficient amount of catalyst/precursor to maintain a standard number of ruthenium atoms, the reactor was then charged by pipet with 50.00 ml of 1.00M sodium bicarbonate aqueous solution.

The reactor was then sealed, evacuated with a vacuum pump to remove nitrogen and oxygen, placed in the bomb heater, and connected to the hydrogen tank with the charging hose while the hose was passing a small flow of hydrogen; this rid the charging hose of atmospheric gases. The bomb was then heated to 150°C, while subject
to constant stirring to promote precursor dissolution.

Upon reaching 150°C, the reactor was charged with hydrogen to 300 psig for catalyst evaluation. For temperature effect trials the pressure was adjusted to keep a self-consistent $\text{H}_2/\text{HCO}_3^-$ ratio. Immediately after charging, timing was initiated. The exothermic reaction was prevented from reaching runaway conditions by the opposing actions of the slow stream of water passing through the cooling coils, and the proportional control temperature controller, which maintained the temperature within a ten degree dead band for a short time, after which the temperature was maintained within a five degree dead band, each band being centered upon 150°C, or the setpoint temperature, for temperature effect trials.

At the end of the preselected reaction times, stirring and heating were terminated, cooling water flow was increased, and the reactor removed from the heater and immersed in an ice-water bath, which reduced the bomb temperature to 50°C in approximately four minutes.

**Continuous Operation**

To the gaseous effluent port of the stirred tank reactor was connected an adjustable pressure-maintenance valve. The output from this valve was directed to a bubbler for instantaneous flow rate monitoring; flow rate in "bubbles/min" had been determined from calibration using a wet test meter. This is illustrated in Figure 8.

Upon reaching the desired 150°C temperature, the output valve was opened, and the reactor charged to 285 psig. The needle valve
Figure 8. Continuous operation.

- Pressure Gauge
- Stirring Spline
- Pressure-Maintenance Valve
- To Needle Valve and H₂ Tank
- To Wet Test Meter and Exhaust
- Bubbler
was adjusted to give an acceptable flow rate, a rate of approximately 5.6 ml per minute. Gas sampling occurred every few hours.

The number of moles of carbon converted was determined based upon the following assumptions: 1) that the flow rate of effluent remained fairly constant, an assumption which was verified from occasional observation; 2) that the total number of moles of effluent could be determined from this information; and 3) that methane remains the hydrocarbon produced in overwhelming preponderance (i.e., 99%).

By plotting percent methane vs. time and integrating, the moles methane produced could be calculated. As 100% methane (i.e., zero percent H₂) in the effluent corresponded to X graphical blocks (see Figure 9), if it was determined by integration that the methane production curve enclosed Y graphical blocks, then Y/X x no. mmoles effluent = no. mmoles CH₄.

**Sampling and Analysis**

Upon cooling to room temperature, the product gas was sampled using a Supelco glass sampling bulb, 250 ml which had Teflon stopcocks at each end and a sampling septum on the surface of the bulb bulk.

To minimize the possibility of shattered glass, the bulb was heavily taped and a Tygon tubing adapter with tubing was attached to one end, with a ballon securely taped to the adapter, as in Figure 10.

The assembly in Figure 10, with both stopcocks open was evacuated with a vacuum pump, the free end stopcock closed, and the
Figure 9. Mole percent methane vs. time for effluent from continuous reactor.
Figure 10. Sampling apparatus.
bulb inserted into a tight rubber sleeve on the reactor output gas valve. The free end stopcock was then opened, followed by the output gas valve. With bomb pressure reduced to approximately half and the balloon greatly inflated, the output gas valve was closed, followed by the bulb stopcocks, and the balloon/adapter assembly removed. The bottle was then sampled by withdrawing 50 μl, using a 100 μl gas-tight syringe (Supelco) from the sampling septum.

In addition to minimizing the glass fragmentation hazard, the balloon served a more subtle function. In letting the balloon expand, the gas sample expands to approximately atmospheric pressure (a "frictionless piston"), which minimizes the preferential, pressure-differential-caused, diffusion of hydrogen from the syringe during the few seconds from bulb sampling to gas chromatograph injection.

A Perkin-Elmer Sigma 1 gas chromatograph with automatic digital peak integration was used, with a 90/100 mesh, 8.5 foot carbosieve B column for analysis of hydrogen, nitrogen (indicative of leakage), methane, and carbon dioxide, with a 16 ml/min helium flow, and temperature program, with the temperature being maintained at 60°C for seven minutes, increasing to 110°C at the rate of 10°C/min. The thermal conductivity detectors were maintained at 150°C, and used the medium current setting, which corresponds to approximately 240 milliamps. Relative amounts of paraffin products were detected using the same chromatograph with a flame ionization detector, using a column in which the first ten foot section was comprised of 20% w/w sebaconitrile on acid-washed Anakron C22, and the final twenty foot
section consisting of 15% w/w bis-(2-methoxyethyl)-adipate on non-acid-washed chromasorb W, maintained at 25°C, with a 30 ml/min helium flow. The relative molar responses for the gases were obtained from literature sources, with the exception of that for hydrogen, which was determined experimentally\textsuperscript{12,13}.

Following completion of gas analysis, the liquid effluent was collected and diluted to 500.0 ml with bomb washings. The relative amounts of the two resulting carbon species, NaHCO\textsubscript{3} and Na\textsubscript{2}CO\textsubscript{3} were determined by titration of two separate aliquots with 0.1036N HCl, one sample to a bromocresol green endpoint, the other to a phenolphthalein endpoint (a pH meter was used to determine this endpoint to minimize subjective judgement), as referenced in literature sources\textsuperscript{14}.

Selection of Conditions

The selected temperature, 150°C, and pressure, 300 psig at 150°C, were chosen on the basis of related work by Akbarnejad\textsuperscript{3}, who determined that little conversion could be expected at temperatures below 150°C. Additional data in support of this premise are included in this report.

Surface Area Evaluation

Surface areas of some of the catalysts were determined using the standard B.E.T. technique. Physical adsorption with liquid nitrogen as the adsorbate was used to determine the surface areas of the ruthenium metal from the reduction of the tetravalent oxide and trichloride hydrates, which were desorbed prior to each determination.
by heating to 250°C, and maintaining the sample at that temperature for one hour, while under vacuum. Unspent ruthenium sponge was determined similarly.

Chemisorption with hydrogen was used on the unspent 5.2% w/w Ru on molecular sieve SK-41, with the surface area of the metal being determined by correcting for the adsorption of hydrogen on undoped sieve. Determination of the metal surface area permits determination of the average particle size, which permits speculation as to the location of the metal crystallites.
RESULTS AND DISCUSSION

Reproducibility

Having demonstrated the basic feasibility of the hydrogenation of aqueous sodium bicarbonate over ruthenium, and having determined that the 316 stainless steel reactor does not catalyze the reaction at 150°C after two hours, the reproducibility of the reaction data was determined using Ru(IV)O₂ trihydrate, 0.0768 grams; temperature, 150°C; carbon species, 50.00 ml of 1.00 M NaHCO₃; hydrogen charge, 300 psig at 150°C; reaction time, 2.0 hours. The mean of five trials was 10.22, with a standard deviation of 0.69 millimoles carbon converted to alkanes.

Order of Reaction

The data in Table II demonstrates that the reaction is zero order in bicarbonate concentration in the range of experimental conditions used.

<table>
<thead>
<tr>
<th>[NaHCO₃], M</th>
<th>Mmole Carbon Converted</th>
<th>% Product Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CH₄</td>
</tr>
<tr>
<td>1.0</td>
<td>8.78</td>
<td>99.12</td>
</tr>
<tr>
<td>0.7</td>
<td>8.68</td>
<td>99.31</td>
</tr>
<tr>
<td>0.4</td>
<td>8.53</td>
<td>99.56</td>
</tr>
</tbody>
</table>

Conditions were identical to those for the reproducibility study,
save for the fact that a reaction time of 1.5 hours was used.

Although there appears to be a relationship between the NaHCO₃ concentration and the conversion, the conversions are within three percent relative of each other, which, when coupled with the net extremely small magnitude of the standard deviation, and the fact that the bicarbonate concentration was varied over a 250% range, does not justify rejection of the null hypothesis that the reaction is zero order in [NaHCO₃], in the range of concentrations examined.

With regard to the order of reaction in hydrogen, again, the results do not lead to the acceptance of an hypothesis contrary to zero order in hydrogen in the concentration range examined.

**TABLE III**

Order of Reaction in Hydrogen

Conditions: temperature - 150°C
carbon species - 50.00 ml 1.00 M NaHCO₃
catalyst - 0.0768 g Ru(IV)O₂·3H₂O
time - 1.5 hours

<table>
<thead>
<tr>
<th>[H₂], psig</th>
<th>Mmole Carbon Converted</th>
<th>% Product Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CH₄</td>
</tr>
<tr>
<td>300</td>
<td>8.88</td>
<td>--</td>
</tr>
<tr>
<td>250</td>
<td>8.36</td>
<td>99.03</td>
</tr>
<tr>
<td>200</td>
<td>9.09</td>
<td>99.36</td>
</tr>
<tr>
<td>200</td>
<td>8.08</td>
<td>99.25</td>
</tr>
</tbody>
</table>

Additionally, although the conditions for determination of reaction orders in [NaHCO₃] and [H₂] drastically changed the H₂/C
ratio, no statistically significant trend in product distribution could be detected.

Order of reaction in catalyst concentration trials indicate that the reaction is first order in \([\text{Ru}]\). The results are presented in tabular form (Table IV), to illustrate the usually close correspondence between the extents of conversion as determined by the gaseous and liquid effluents analyses, and in graphical form, to illustrate the rationale for the first order fit (Figure 11).

**TABLE IV**

Order of Reaction in Ruthenium

<table>
<thead>
<tr>
<th>Conditions:</th>
<th>temperature - 150°C</th>
<th>carbon species - 50.00 ml of 0.500 M NaHCO₃</th>
<th>hydrogen charge - 250 psig</th>
<th>time - 1.5 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>grams Ru (as Ru(IV)O₂)</td>
<td>Mmoles Carbon Converted to Alkanes</td>
<td>Gas Basis</td>
<td>Titration Basis</td>
<td></td>
</tr>
<tr>
<td>0.0800</td>
<td>7.12</td>
<td>7.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0221</td>
<td>8.61</td>
<td>8.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0419</td>
<td>9.52</td>
<td>9.64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0824</td>
<td>10.8</td>
<td>10.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1037</td>
<td>11.1</td>
<td>11.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In Figure 11, the two data points corresponding to the trials with the largest amounts of catalyst were not plotted, as they approach equilibrium to the extent that they cannot be considered indicative of rate information. However, the extent of correlation of the three remaining data points to a first order fit (i.e.
Figure 11. Test for first order fit.
correlation coefficient 0.984) provides evidence for a first order fit.

As a test of a possible second order fit, Figure 12 has been constructed. If

\[
\left( \frac{-1}{[\text{Ru}]} \right)^2 \times \frac{d[\text{HCO}_3^-]}{dt}
\]

is fairly constant, then the equation approximates second order. Since the volumes and reaction times are constant, one can plot \((\text{moles Ru})^2\) vs. millimole carbon converted to test the second order fit. The resulting correlation coefficient of 0.939 mandates preference of the null hypothesis of first order, in contrast to the alternative hypothesis of second order.

The zeroth reaction order in hydrogen and bicarbonate ion can be interpreted by postulating that those reagents are in large excess of an assumed paucity of active sites on the catalyst; thus, a change in the concentrations of hydrogen and the bicarbonate ion yields an insignificant change in reaction rate.

Conversion As A Function Of Temperature

Looking at Table V, from 100 to 150°C, one sees that the reaction rate increases significantly, which is to be expected, based upon similar work by Akbarnejad\(^3\). The relatively small change in conversion from 150 to 200°C is likely caused by too long a reaction time, in that the reaction at the latter temperatures reached a significant extent of equilibrium (as the equilibrium constant generally decreases with temperature), and thus, yielded
Figure 12. Test for second order fit.
TABLE V

Conversion Data as a Function of Temperature

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Mmoles Carbon Converted to Alkanes</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.2</td>
</tr>
<tr>
<td>125</td>
<td>3.0</td>
</tr>
<tr>
<td>150</td>
<td>10.2</td>
</tr>
<tr>
<td>175</td>
<td>11.1</td>
</tr>
<tr>
<td>200</td>
<td>10.6</td>
</tr>
</tbody>
</table>

results more indicative of equilibrium than of rate.

The possibility existed that the inferior performance at 100 and 125°C was caused by too slow a rate of reduction of the precursor ruthenium oxide to the catalyst metal. As a test of this possibility, the procedure was repeated at 125°C using the metal reduction product from the oxide. The conversion of carbon was within 10% relative of the conversion using the precursor. As the rate of reduction of the oxide to the metal will increase with temperature, it was therefore unnecessary to pre-reduce the oxide for trials at greater temperatures.

Catalyst/Precursor Evaluation

Figure 13 depicts results typical of the catalyst/precursors used indicating a fairly linear rate of conversion until equilibrium
Legend: ▲ conversion
○ activity

Conditions: RuIV O2•3H2O
0.0768 gr.
150°C
is approached.

As a criterion to determine if the data is more representative of rate than of equilibrium, one need only perform a least-squares fit involving the conversion point in question with all earlier time points, and observe the intercept; if the intercept (i.e., conversion at zero reaction time) is reasonably close to zero percent conversion (e.g., ±1.5%), then equilibrium is not a significant factor, and the result is more representative of rate than of equilibrium.

Relative catalyst/precursor activities are plotted in Figures 14 and 15. One sees that the ruthenium trichloride hydrate, the ruthenium trichloride hydrate supported on molecular sieve SK-41 at 17.48% w/w, and the ruthenium(IV) oxide hydrate are superior to the remaining catalyst and catalyst/support combinations.

**Unsupported Ruthenium**

One sees from Figures 14 and 15 that the catalytic activities of the ruthenium metal from the reductions of the trichloride hydrate and tetravalent oxide hydrate are comparable, and much superior to the metal sponge. Table VI indicates the surface areas of the reduced, desorbed metal (with the exception of the sponge, where the unused metal was investigated).

The correlation between surface area and catalytic activity for the non-supported catalysts is far too striking to be coincidental.
Figure 14. Unsupported ruthenium.

Legend:
- RuCl$_3$.H$_2$O
- Ru$^{IV}$O$_2$.3H$_2$O
- Ru Sponge
Figure 15. Supported ruthenium.

Legend:
- 17.48% w/w Ru as RuCl$_3$·1·3H$_2$O on SK-41
- 20.85% w/w Ru on SK-41
- 3.34% w/w Ru as RuCl$_3$·1·3H$_2$O on SK-41
- 5.2% w/w Ru on SK-41
TABLE VI

Surface Areas of Unsupported Ruthenium/Ruthenium Precursors

<table>
<thead>
<tr>
<th>Catalyst/Precursor</th>
<th>Surface Area cm$^2$ g Ru$^{-1}$, x 10$^5$</th>
<th>Particle Size, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuCl$_3$·1-3 H$_2$O</td>
<td>6.33</td>
<td>80</td>
</tr>
<tr>
<td>Ru(IV)O$_2$·3H$_2$O</td>
<td>6.01, 6.28</td>
<td>80</td>
</tr>
<tr>
<td>Ru sponge</td>
<td>2.96</td>
<td>160</td>
</tr>
</tbody>
</table>

Supported Ruthenium

Ruthenium on Alumina

Ruthenium on alumina was found to be highly unfavorable as a catalyst/support combination for this reaction at 150°C. Although this supported catalyst gave somewhat larger amounts of n-butane, and also some n-pentane, the results were not reproducible. Additionally, the catalyst was found to be covered with a white, waxy substance, composition as yet undetermined, which failed to melt at 400°C, and which was insoluble in benzene, heptane, mixed heptanes, xylenes, methylene chloride, and acetone. It was, however, soluble in 10% v/v HCl, indicating an inorganic species.

Also, the coated catalyst/support adhered so firmly to the reactor walls that removal required a hammer and chisel; both the very existence of this coating and the difficulties associated with its removal mandate against selection of this catalyst/support combination. In comparison, D. L. King of Amoco Oil, using a
fixed-bed, continuous reactor found ruthenium on alumina to be quite useful to the reaction between hydrogen and carbon monoxide (2:1) at only 4 atm, with significant yields of propane (c. 15%) and butanes (c. 33%) at 175°c.

Ruthenium on Molecular Sieve SK-41

Results for the zeolite molecular sieve supported metal are apparently puzzling in that the 17.48% w/w metal/support is found to be on a par with that of the metal obtained from the trichloride and tetravalent oxide hydrates, and both the heavily loaded supports are far superior to the lightly loaded supports. One would predict that the lower weight percent loadings would be superior, in that greater dispersions would be promoted, yielding small particles, and larger surface areas.

Although no sample of the heavier loaded sieves remain for determination of surface area and crystallite location, the 5.2% w/w combination is undoubtedly indicative of the 3.34% w/w metal (as trichloride), showing a surface area of 50 x 10^5 cm^2 g-metal^-1, with a 10Å particle size. The average particle sizes for the heavily loaded sieves are undoubtedly larger than for the smaller loadings, with much, if not most, of the crystallites located on the surface of the sieve. This is in contrast to the lightly loaded supports, where the 10Å particle size indicates that a sizeable fraction of the crystallites is in the cavities.

A variety of hypotheses can be advanced for the apparent anomaly, including impedance to mass transfer, and unfavorable
alteration of the electronic environment of the metal by the abundant oxygen atoms. Geometric effects may also be operational, to include multicentered adsorption cite requirements, and the possibility that the crystal face distribution of the metal formed upon reduction may be a function of the electronic environment of the ion at the time of its reduction.

From Table VII, one may examine the possibility of impedance to mass transfer.

**TABLE VII**

<table>
<thead>
<tr>
<th>Molecular Dimensions of Reactants and Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic Diameter, Å</td>
</tr>
<tr>
<td>$H_2$</td>
</tr>
<tr>
<td>$H_2O$</td>
</tr>
<tr>
<td>CO</td>
</tr>
<tr>
<td>CO$_2$</td>
</tr>
<tr>
<td>CH$_4$</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
</tr>
</tbody>
</table>

Zeolite Y: free aperture, hydrated or dehydrated: 7.4Å
kinetic diameter 8.1Å
cavity diameter 13Å

Additionally, if one uses a trigonal planar (about carbon) structure for $HCO_3^-$, then one has a species of length 4.5Å, width, 4.3Å, and thickness (approximating by $CO_2$) 3.7Å, a fair-sized ion, however, this
species should be able to pass through the aperture unhindered.

The above data, coupled with the fact that a Y-type zeolite can adsorb a molecule as large as tri-n-butyl amine, should yield the conclusion that each reagent/product species can pass through the aperture into the cavity. However, as the net equation:

\[ 2\text{HCO}_3^- + 4\text{H}_2 \rightarrow \text{CO}_3^{2-} + \text{CH}_4 + 3\text{H}_2\text{O} \]

for this reaction involves a considerable number of species, mass transfer is undoubtedly a factor in the relatively poor performance of the lightly loaded supports (in which the crystallites are predominantly in the cages), as product species must diffuse out of the cages to permit additionally reagent species to enter.

Although dimensional data from van der Waals radii can yield information on size, admittance through the aperture is also a function of electronic factors; kinetic (collision) diameter, (i.e., the intermolecular distance of closest approach for two molecules colliding with zero kinetic energy) information is lacking for both the carbonate and bicarbonate species. Unlike the species in the previous table, the carbon-bearing reagent is not a neutral molecule, but is a charged species; indeed, repulsion between that ion and the electron-rich oxygen atoms of the sieve may also impede mass transfer.

If mass transfer is a factor in the relatively poor performance of the lightly loaded supports, then that performance can be explained. The greater the loading, the greater the particle size, and the greater the fraction of particles that remain outside the cavities,
on the surface of the sieve, where access to the metal does not require mass transfer through a gauntlet of electron-rich oxygen atoms.

Alternatively, a purely electronic effect apart from mass transfer may be in operation. The support may interact electronically with the metal, affecting its electron density, which will influence the strength with which species are adsorbed. It will also influence the strength of a given bond in an adsorbed molecule, although the effect of a particular support is a function of the metal. For example, whereas palladium methanation activity is relatively insensitive to extent of dispersion, it is acutely sensitive to the nature of the support, with acid (electron withdrawing) supports such as a Y-type zeolite yielding high activity. In contrast, the methanation activity of nickel is relatively insensitive to support nature or extent of dispersion.

In this case, if the electron-withdrawing oxygen atoms of the zeolite interact with the supported metal by leaving it with a slight positive charge, then the attraction for the negative basic reagent ion may be of such strength that a complex is formed between the metal and the ion, a complex which may be unreactive. It would not be out of the realm of probability to postulate that the white coating on Ru/Al₂O₃ is a complex between the acidic catalyst/support and a basic ion.

Thus, if impedance to mass transfer and/or unfavorable electronic interaction by the oxygen atoms contribute to decreasing
catalytic activity, one would expect the heavily loaded supports to be more efficacious; the larger the loading, the larger the fraction of metal atoms that reside on the surface of the sieve, where the oxygen effect is less than in the cavities, because the oxygen-ruthenium intimacy is much less. A study of D. L. King of the hydrogenation of CO on ruthenium supported on silica, alumina, chromia-alumina, and thoria showed a clear correlation between increasing activity and increasing metal crystallite size, results which are in agreement with those of Dalla Betta, Piken and Shelef.

Geometric effects may also be postulated, especially if the adsorption of the bicarbonate ion is involved in the rate-determining step. One possibility is that absorption of not only the central carbon atom but also the adsorption of each of the three oxygen atoms (assuming the four atoms to lie in a plane) upon separate metal atoms is necessary, perhaps to permit some minimum residence time on the metal. Alternatively, adsorption of the central carbon atom by more than one metal atom at a time may be necessary, as has been postulated by Araki and Ponec for dissociation of carbon monoxide. If either of these hypotheses are operative, then interatomic distances on a particular metal, in addition to the curvature of the crystallite (truncates polyhedron) would be important. To elaborate, the smaller the particle diameter (i.e., the greater the curvature), the less will be the extent to which any group of neighboring metal atoms will lie in a plane, thus decreasing the probability of adsorption.
Another possibility is that the crystal face distribution produced by hydrogenation of the metal ion is a function of its electronic environment at the time of reduction. Some catalyst systems for hydrogenation show greatly enhanced activity using a metal sample with a disproportionately large percentage of crystal planes with specific Miller indices, in contrast to using a sample comprised of a random distribution of crystal faces. Singh and Grenga have shown that in the Fischer-Tropsch synthesis, in which dissociative adsorption of carbon monoxide is necessary, CO is catalytically dissociated at steps near the low index poles of a single crystal of ruthenium. Indeed, the very fact that specific crystal planes can be preferentially produced warrants further investigation of this hypothesis.

Deactivation

Catalyst poisoning was investigated indirectly from the continuous operation, the results of which are displayed in Figure 16. An induction period (ostensibly caused by insufficient residence time of the hydrogen to reduce the catalyst precursor to catalyst) is followed by a period of accelerating rate. This is then followed by the asymptotic decrease in effluent methane, as the rate of production has fallen below the rate of removal of the product methane.

After approximately 50 hours of operation, approximately 5% of the bicarbonate remained unconverted, suggesting either a change in reaction order at extremely low concentrations of bicarbonate ion,
Figure 16. Continuous stirred tank reactor.

Conditions: Temp. - 150° C
Pressure - 285 psig
Cat. - RuO₂·3H₂O : .0802 g
Flow Rate - ~6ml/min
Charge - 50.00 ml
1.00 M NaHCO₃
catalyst deactivation, or both.

As batch scale reaction with the recovered catalyst indicated little conversion, with only 0.1% methane in the product gas, one is led to conclude that catalyst deactivation is operative. If the loss in activity is due to a surface carbonaceous deposit, then the results are understandable in light of the fact that of any of the Group VIII metals, the metals used in methanation, ruthenium has the greatest hydrogenolysis activity, with hydrogenolysis normally producing a carbonaceous residue²⁰.
CONCLUSIONS

The following conclusions are in order:

1. In the range of experimental conditions investigated, the reaction is zero order in hydrogen and bicarbonate ion, and is first order in ruthenium concentration. The zero order results are presumed to be caused by a large excess of hydrogen and bicarbonate ion, which overwhelms presumably few active catalyst sites.

2. Conversion is negligible below 150°C, and is optimum in the 150-200°C range.

3. Product distribution at 150°C heavily favored methane, and was insensitive to varying ratios of reagents. The saturation of the presumably few active catalyst sites is assumed to be a contributing factor.

4. As no carbon monoxide or carbon dioxide was detected, no evidence exists to support the hypothesis that the reaction proceeds through CO or CO$_2$ intermediates. This is of some significance in that the problems endemic to CO/CO$_2$ hydrogenation might be avoided if the mechanism of the bicarbonate hydrogenation is unique.

5. Catalytic activity for unsupported ruthenium in this reaction parallels metal surface area, while the inverse appears to be true for ruthenium supported on molecular sieve SK-41; mass transfer impedance and electronic effects are presumed to be contributing factors. The fact that the catalytic activity of ruthenium was not improved by using this faujasite-type zeolite as
a support suggests that zeolites be rejected as ruthenium supports for this reaction, as the aperture size in this particular sieve is of the order of the largest sizes known.

(6) The catalyst is, as in the Fischer-Tropsch synthesis, susceptible to deactivation.

(7) Although the reaction investigated in this study is even more exothermic than the hydrogenations of CO and CO$_2$, the liquid phase hydrogenation of sodium bicarbonate may have an advantage over the aforementioned hydrogenations. This advantage lies in the fact that it is less expensive to decompose (into sodium and bicarbonate ion) the ore using hydration energy and hydrogenate the bicarbonate directly than to thermally decompose the ore into CO$_2$ and then hydrogenate.
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