

Periodic Dosing of Methanol Synthesis Over a Copper Zinc
Mixed Oxide Catalyst

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INTRODUCTION

Transient operations of reactor systems have been used for many years in kinetic studies as a means of elucidating kinetic mechanisms. In the last two decades, however, interest has grown in using intentional transient operation as a means of improving the performance of chemical reactors. The requirement of maintaining a uniform level of production at unsteady state can be achieved through cyclic operations in which one of the variables in the reaction system is periodically shifted between two values. When viewed on a larger time scale than that of the periodic shifts, the system exhibits uniform production. Figure 1 illustrates how periodic operation may be performed. In the LHS of the diagram the normal steady state operation is shown. A feed of fixed composition is fed to the reactor and once steady state has been achieved, one expects a constant stream of product to flow from this unit, as illustrated in the upper LHS. In the cyclic mode, however, the partial pressure or concentration of both the reactants making up the feed are changed periodically between two levels (in the simplest case). Before a new steady state is achieved after this switch, a second switch is made back to the original levels. The operation is characterized by a period t . It can be seen from the diagram that it is not necessary for the length of time at the two different concentrations to be the same. This can be changed as well so that the system may be exposed to a short period in which there is a high concentration of one component and a much longer period in which that same component is at a much lower level. This introduces a new variable referred to as the cycle split. Additional variables are, of course, the amplitudes of the individual changes. The result of periodic changes in composition, as illustrated in the diagram, is a constantly varying product composition at the exit of the reactor. This variation occurs around a mean value which we will refer to hereafter as the time-average product concentration, and from this value we can obtain a time-average reaction rate.

There is a growing body of literature suggesting that this mode of operation can cause substantial improvements in catalyst activity (Unni et al., 1973; Asfour et al., 1983; Jain et al., 1982; Jain et al., 1980; Wilson and Rinker, 1981; Kenny and Cutlip, 1976; Lynch, 1982). For CO oxidation of platinum, the system most extensively explored, Lynch (1982) suggests that periodic operation is exploiting the existence of multiple steady states at low CO₂/oxygen ratios in the feed.

Apart from those reactions which exhibit multiple steady states, the explanation frequently advanced for the improvement found with cyclic operation is that redox reactions are involved in which periodic operation involves changes in the coordination of metal atoms in the surface oxide structures which can interact with the bulk of the system through diffusional processes. This gives rise to a storage phenomena in the bulk of the catalyst that is not attainable in steady state operation. The stored reactant becomes available through pulsing.

Methanol synthesis over the copper zinc oxide system appears as an interesting candidate for this new mode of reactor operation because it probably proceeds via a redox mechanism. The use of cyclic operation can be implemented in two ways. The first of these is to periodically change the hydrogen to carbon monoxide ratio in the feed just as has been done in most of the other studies given above. The use of carbon dioxide dosing of this system suggests an alternate mode which might be explored. It has been found with the copper-zinc oxide-alumina system, which forms the basis for many of the commercial methanol synthesis catalysts, that the catalyst undergoes slow deactivation unless a low concentration of carbon dioxide is maintained in the feed. In place of maintaining CO_2 at a constant level, it can be pulsed in the feed.

In an earlier paper (Nappi et al., 1984) we examined the performance of a reactor operating under cyclic variations of the hydrogen-to-CO ratio in the feed. Even though nonlinear transient behaviour was observed, periodic forcing of this system failed to improve the yield to methanol. Indeed, the main effect was to roughly double the production rate of methane in the system. We speculated that the surprising lack of improvement was due to rather small changes in the reducing power of the feed gas in switching from hydrogen-rich to carbon-rich mixtures. When maximum amplitude experiments were carried out in which the feed varied between pure carbon monoxide and pure hydrogen, performance was significantly better, but still failed to attain the levels possible with steady-state operation. Thus, in this paper, we examine periodic forcing with carbon dioxide.

EXPERIMENTAL

The question addressed in our experimental program was whether periodic pulsing of the reaction system with carbon dioxide could increase the production rate of methanol to a greater extent than maintaining a small bleed of the same gas into the system. Only exploratory experiments were carried out. These employed the stoichiometric hydrogen-carbon monoxide mixture for methanol synthesis of 2:1. In one of the source gases, carbon dioxide was added to a level of 2% by volume. The experiments were then carried out by periodically switching the feed from the source containing carbon dioxide to the source free of CO_2 . Referring to Figure 1, the variables explored were period and the length of exposure to the gas containing carbon dioxide, referred to earlier as the cycle split. All experiments were carried out at a pressure of 2.52 MPa and 250°C. The catalyst used was a commercial low temperature water gas shift catalyst with the following formulation: Cu/Zn/Al = 29/47/24. BET surface area of this catalyst was 80.0 m^2/g and its pore volume was measured as 0.470 mL/g. Thus, the mean pore diameter was 240 Å. Auger spectroscopy showed the presence of copper as Cu^+ on the surface. Transmission electron microscopy indicated the catalyst was a finely dispersed mixture of various phases.

Measurements were carried out using a Berty reactor. This reactor behaves as totally backmixed which simplifies experimentation, as well as interpretation of the results. It has the disadvantage, however, that the reactor contains a significant dead volume which limits the switching frequency in cyclic operation. If this frequency is too high, the well stirred dead volume smooths out the concentration pulse so that the catalyst phase sees no change in composition with time. The arrangement of the experimental equipment is shown schematically in Figure 2. Details of the experimental equipment are available elsewhere (Jain et al., 1983; Nappi et al., 1984). The only change made from the reactor described in these publication is that the interior has been electroplated with copper in an attempt to reduce the methanation activity.

Blank runs were performed to check methanation activity. It was found that a very small amount of methane was produced; however, it is not certain whether this methane was produced on the reactor walls or in the low temperature, catalytic oxygen scavenging unit located upstream from the reactor. Methane found in the blank runs, in any case, was well below the methane contained in the source cylinders feeding the reactor. Corrections were made for both methane sources.

Analyses were performed by gas chromatography using a 3-m Porapak Q column and a hot wire detector in series with a flame ionization detector.

It was found experimentally that a cyclic stationary state was achieved after about two cycles between the CO₂ containing and CO₂ free synthesis gas mixtures. In most cases the experiment was carried out over a time frame of many hours so that up to 20 complete cycles were run. Sampling was done intermittently, but sufficient measurements were made to characterize completely the time-varying methanol and methane yields.

EXPERIMENTAL RESULTS

Table 1 summarizes the experimental results for methanol production. Of the two variables that were explored in these measurements, the period was only examined at 12 and 30 minutes. Decreasing the period effected a small improvement. Reactor dead space and mixing rendered experiments much below 12 minutes unproductive. As the cycle split is decreased, however, the effect is the opposite, the rate of methanol production decreases. This is, of course, expected because it has been demonstrated that at low levels of carbon dioxide in the feed, methanol production becomes proportional to the concentration of this component. Thus, as the cycle split is decreased, the quantity of carbon

Table 1
Time-Average Rate of Methanol Production as a Function of
Period and Cycle-Split With CO₂ Dosing

τ (min)	Cycle Split	Quasi-Steady- State Rate (10 ⁻⁷ mol/g cat*s)	Transient Average Rate (10 ⁻⁷ mol/g cat*s)	*Normalized Rate
12	0.05	7.10	8.25	1.16
12	0.10	7.38	9.34	1.27
12	0.25	8.22	9.89	1.20
12	0.50	9.61	10.1	1.05
12	0.75	11.0	11.4	1.03
30	0.50	9.61	9.97	1.04

* The transient rate was normalized with respect to the quasi-steady-state rate.

dioxide the catalyst sees within a cycle falls. It is incorrect, therefore, to compare the measurements from the cyclic operation to the steady state measurements with CO₂ free synthesis gas. The proper comparison is with the steady state results at the same mean level of CO₂ used in a complete cycle in the

periodic forcing experiments. For example, if the cycle split were 0.5 and the two source gases contained 2% and 0% CO₂, the mean level would have been 1%. Unfortunately, a complete set of steady-state experiments at different CO₂ levels was not made. However, it is possible to estimate these steady state rates by assuming a linear relationship between the mole % CO₂ in the gas and the rate of methanol formation. If this is done, and the estimated steady state value is divided into the measurements shown in Table 1, the normalized rate is obtained. These are found in the last column of the table. Normalized results reflect the improvement in methanol yield over the comparable steady state through periodic forcing.

Adding 2% CO₂ by volume to the stoichiometric mixture increases the steady-state methanol formation from 6.8×10^{-7} to 12.4×10^{-7} mol/g cat*s. Evidentially, periodic forcing is capable of further increasing the methanol production rate by about 25%. Worth noting is that the measurement reported in this paper are of a screening nature and no attempt has been made to optimize the periodic dosing sequence.

Table 2 shows our methane production results. Introduction of a steady stream of CO₂ into the feed gas dramatically suppresses the steady-state rate of formation of methane in this reaction system from 3.4×10^{-8} to 5.4×10^{-9} g mol/g cat*s. Although the methane formation rate for this catalyst in the absence of carbon dioxide is only about 5% of the formation rate for methanol, the introduction of CO₂ suppresses this rate to just 0.4% of the methanol rate. Table 2 shows that cycle period has a much stronger effect on methane than on methanol production. Unlike methanol production however, periodic pulsing with CO₂ reduces methane formation substantially and shortening the pulse length exerts just a small effect on the rate of formation.

Table 2

Time-Average Rate of Methane Production as a Function of Period and Cycle-Split With CO₂ Dosing

τ (mins)	Cycle Split	Quasi-Steady-State Rate (10^{-9} mol/g cat*s)	Transient Average Rate (10^{-9} mol/g cat*s)	*Normalized Rate
12	0.05	32.6	3.10	0.095
12	0.10	31.2	3.42	0.11
12	0.25	26.9	3.39	0.13
12	0.50	19.7	2.98	0.15
12	0.75	12.6	5.83	0.46
30	0.50	19.7	5.87	0.30

* The transient rate was normalized with respect to the quasi-steady-state rate.

If the rate of formation of methane is proportional to the carbon dioxide concentration, the rate of formation at quasi-steady-state will be a close estimate of the steady state for CO₂ levels between 0 and 2 vol%. These values are appropriate for comparison with the time-average rates of methane formation under periodic pulsing. We have assumed appropriateness and the last

column in Table 2 compares the time-average cyclic rates with the assumed steady-state ones. These results indicate the large influence of dosing time on methane formation.

Periodic sampling through the gas chromatograph permits a reconstruction of the change of rate with time inside a dosing cycle. These reconstructions are shown in Figures 3 and 4 for two quite different cycling conditions: the first is for a short pulse of CO₂ containing feed while the second figure considered a relatively long pulse. Immediately upon introduction of the CO₂-containing gas, methane production falls to a level which cannot be detected with our analytical equipment. In Figure 4, when the CO₂-free gas stream is introduced, the methane concentration builds up to about one. The measurements have been normalized with exit concentration measured at steady state with the CO₂-containing gas. If a short CO₂ pulse is used, Figure 3 shows the normalized concentration rising to about 2.4. In both cases, these values are well below the steady state values expected for a CO₂-free synthesis.

In both figures, methanol production changes very little. Although it is shown in the figures, the CO₂ detected in the stream leaving the reactor changed very little within the dosing cycle.

DISCUSSION

The failure of the methanol production rate to follow the changes in the CO₂ content of the gas coupled with the dramatic 20 to 25% improvement in production rate with respect to steady state strongly suggests that the introduction of CO₂ causes a restructuring of the surface and/or reoxidation of the sites in the system. These sites, or surfaces, however, are not corrected immediately back to their starting condition when CO₂ is removed. Restructuring or reductions appears to be very slow. A long-term decay of the copper/zinc oxide catalyst activity in the absence of CO₂ in the feed gas is observed, of course, in steady state operation. If a massive reoxidation of copper in the catalyst were occurring on the introduction of CO₂, methanol production would have changed much more sharply than what can be seen in the data shown in Figures 3 or 4.

A sharp change in production rate does appear, however, for methane. It seems likely that the explanation for this is a wholesale destruction of the sites responsible for methane production by the introduction of CO₂. Evidentially, these sites must be quite different from those for methanol formation judging from the sharply different behaviour when CO₂ is either introduced or removed from the system. Substantial adsorption of CO₂ accounts for the lack of change in CO₂ levels in the exit stream. The presence of CO₂ when the feed is CO₂-free seems to result from methane formation. Methane formation is favoured thermodynamically at the operating conditions employed so that CO₂ suppression cannot occur through an equilibrium interaction because the reaction system operates so far away from equilibrium.

ACKNOWLEDGEMENTS

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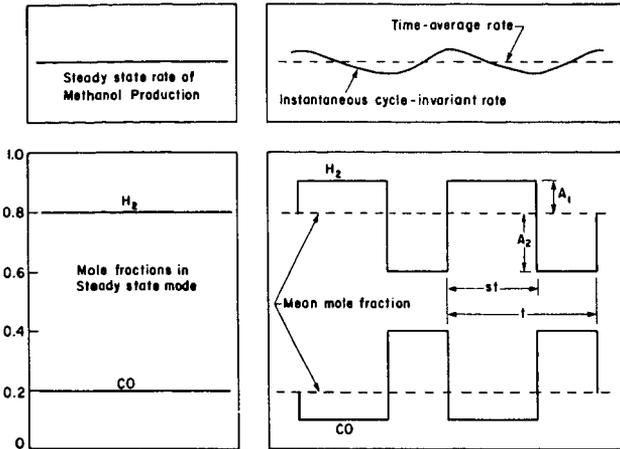


Figure 1 Schematic of the Periodic Operation of a Catalytic Reactor.

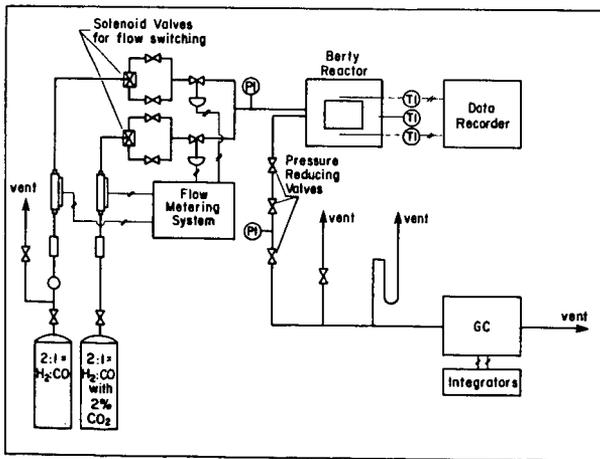


Figure 2 Schematic of the Experimental Apparatus (PI = pressure gauge, TI = thermocouple, GC = gas chromatograph)

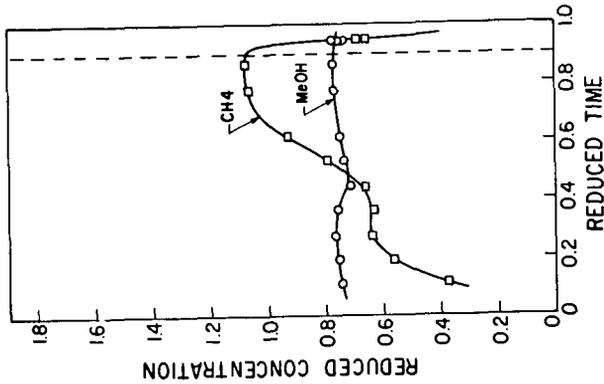


Figure 3 Time Variation of Product Concentrations Under Periodic Dosing with 2 vol. % CO₂ for $\tau=12$ Minutes, $*s=0.10$ (Concentrations Normalized With Steady State Product Concentration Using 2 vol.% CO₂ in Feed, 250°C 2.513 MPA).

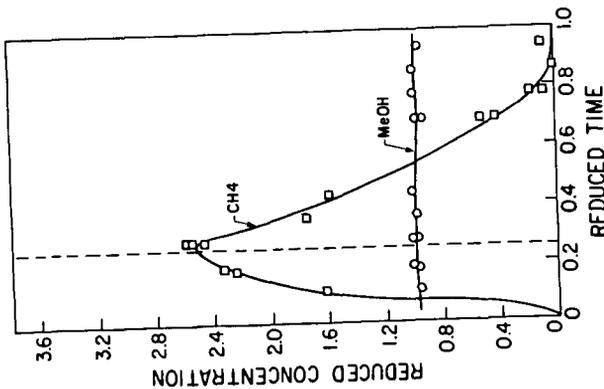


Figure 4 Time Variation of Product Concentrations Under Periodic Dosing with 2 vol. % CO₂ for $\tau=12$ Minutes, $*s=0.75$ (Concentrations Normalized With Steady State Product Concentration Using 2 vol.% CO₂ in Feed, 250°C 2.513 MPA).

$*s$, defined as the ratio of the CO₂-rich portion of the cycle to the cycle period.