JOURNAL OF CATALYSIS 137, 127–138 (1992)

The Selective Synthesis of Acetonitrile from Carbon Monoxide, Hydrogen, and Ammonia over Mo/SiO_2

KYUNG N. KIM AND ALAN M. LANE[1]

Department of Chemical Engineering, The University of Alabama, Tuscaloosa, Alabama 35487

Received August 29, 1991; revised February 3, 1992

The selective synthesis of acetonitrile from $CO/H_2/NH_3$ over Mo/SiO_2 was investigated. The effects of temperature, space velocity, and reactant compositions on conversion and selectivity were explored with a two-level factorial designed experiment. High selectivities (37–96% excluding CO_2) were achieved at reasonably high conversions (29–64%). The product's carbon number distribution differed significantly from that obtained from a CO/H_2 feed under identical conditions. The results are explained in terms of three competing reactions: water–gas shift, Fischer–Tropsch synthesis, and nitrile synthesis. Other experiments are described that indicate a nitrile synthesis mechanism involving a C–N intermediate which further reacts with a carbon species to form the acetonitrile. A mechanistic hypothesis involving an isocyanide ligand is proposed.

INTRODUCTION

The production of hydrocarbons from synthesis gas characteristically results in a product with a broad molecular weight distribution much like a polymerization reaction. While this distribution may be acceptable in fuel production, it is not economical for specific chemical intermediates. This research focuses on the selective production of acetonitrile in a Fischer–Tropsch synthesis modified by the addition of ammonia.

Reactions of third molecules with synthesis gas sometimes are selective. For example, olefins can be hydroformulated with CO/H_2 to selectively yield alcohols of one-higher carbon number (*1*). This differs from the title reaction in that no CO–CO linkage occurs. Ammonia has also been added to synthesis gas over promoted chromite catalysts to form trimethylamine with 99% selectivity (*2*). However, there is no carbon–carbon bond formation so this would not be an example of enhanced Fischer–Tropsch synthesis (FTS) selectivity. The ammonia-modified synthesis reaction has also been carried out over Fe catalyst to yield an unselective range of products with a Schulz–Flory distribution (*3*). Examples of selective reactions with CO–CO linkage are rare.

Olive and Olive patented a process for Monsanto for preparing acetonitrile with high selectivity from $CO/H_2/NH_3$ (*4, 5*). It operated at 350–550°C, 1–10 atm, and 150–2000 hr^{-1} space velocity using reduced Fe and Mo catalysts. Only carbon dioxide, methane, and traces of propionitrile were coproducts. Auvil and Penquite (*6, 7*) improved this process by adding carbon dioxide to minimize the water–gas shift (WGS) reaction and increased the acetonitrile selectivity as high as 80%. They also found hydrogen cyanide, which simply may have been missed in the earlier patents. Henrici-Olive and Olive hypothesized that methylamine dissociates to the carbene or dehydrogenates to hydrogen cyanide (*8*). Finally, hydrogen cyanide inserts into the carbon–metal bond of the dissociation product.

Recently, Tatsumi *et al.* described acetonitrile formation over Mo catalysts at 250–450°C (*9*). Two additional significant products were hydrogen cyanide and, at low

---

[1] To whom all correspondence should be addressed.

0021-9517/92 $5.00

temperatures, methylamine. Experiments with various probe molecules added to the CO/H_2 feed led them to hypothesize that hydrogen cyanide is the principal intermediate which inserts into a surface carbene from normal carbon monoxide hydrogenation. The yield of acetonitrile attained a maximum at 450°C with a selectivity of 50% and conversion of 16%.

This report describes new information on the performance and mechanism of this reaction. The objective is to systematically explore the reaction parameters and gain mechanistic insight on how the unusually high selectivity is achieved. This is accomplished by conducting a two-level factorial designed experiment on the effects of temperature, space velocity, and reactant concentrations on the conversion and selectivity. The designed experiment is supplemented by three other experiments: examining the product distribution under ammonia-deficient conditions; examining the product distribution under hydrogen-deficient conditions; and examining the transient response to alternating feeds of ammonia and carbon monoxide. Finally, a new and more detailed mechanism involving an isocyanide intermediate is hypothesized and discussed in the context of the other competing reactions.

METHODS

The reaction was carried out in a 0.95-cm diameter 304 stainless steel tube used as an upflow reactor. It showed no activity in a blank run without catalyst. The use of 316 stainless steel produced small amounts of acetonitrile without using catalyst, probably because it contains 2% Mo. The effluent line was heat-traced to prevent formation of ammonium carbonate (from carbon dioxide and ammonia below 58°C) which plugs the lines.

The reactant gases were hydrogen (99.995%), carbon monoxide (99.3%), ammonia (99.99%) and inert helium (99.99%) used without purification. Feed rates were regulated by mass flow controllers. The reactor was heated using a fluidized sand bath with a furnace and temperature controller. The reaction temperature was measured with a thermocouple placed in the middle of the catalyst bed.

The Mo/SiO_2 catalyst was prepared by impregnating Degussa Aerosil-200 (BET surface area = 196 m^2/g) with a molybdic acid solution to incipient wetness. The paste was dried, crushed, and sieved to 28–35 mesh size. The catalyst was pretreated by oxidizing with flowing oxygen at 475°C for 5 hr and reducing with hydrogen at 500°C for 12 hr.

The reaction products were sampled with a 25-μl gas sampling valve connected to an HP 5890 gas chromatograph equipped with a TCD and FID. Helium was the carrier with a flow rate of 20 cc/min. A Haysepe C column (0.32 cm × 0.91 m) was used in series with a Porapak Q column (0.32 cm × 3.66 m). For GC/MS, a methylsilicon column (DB-1, 30 m, 0.25 μm film thickness) was used. Both hydrogen cyanide and ammonia produced some troublesome tailing, possibly due to adsorption on the walls of the gas sampling valve (*10*). Nevertheless, the results were reproducible.

The GC/MS was used to positively identify the acetonitrile product. An FID was used to verify the absence or presence of some expected products such as methylamine or hydrogen cyanide. The GC was run for an extended time with ramped temperature to verify that no higher molecular weight products were missed. Elemental balance calculations on both carbon and nitrogen gave recoveries of 95–97% and 96–98%, respectively.

RESULTS

Under most conditions the main products were acetonitrile and methane with coproducts carbon dioxide and water. Only small amounts of other hydrocarbons were found. These included ethane, ethylene, propane, propylene, butylene, and propionitrile. Methylamine was not detected and hydrogen cyanide was found only with low hydrogen

TABLE 1

Two-Level Factorial Designed Experiment

Reaction variables (design levels)					Products (nmol)			Calculations (mol%)		
T	SV	CO	H_2	NH_3	CO_2	CH_4	MeCN	X	$S1$	$S2$
−	−	+	+	−	122.6	22.0	22.7	61.5	23.1	61.4
−	−	−	+	+	60.9	10.4	14.4	63.9	28.2	69.9
−	−	+	−	+	104.8	1.6	21.1	46.5	28.4	96.3
−	−	−	−	−	57.8	2.4	13.2	54.1	30.4	91.6
−	+	+	+	−	72.2	10.1	15.1	36.1	26.2	70.3
−	+	−	+	+	33.3	4.9	7.9	33.8	29.2	76.2
−	+	+	−	+	70.8	1.7	10.2	29.1	21.9	92.1
−	+	−	−	−	41.4	3.0	10.8	41.4	32.8	87.8
+	−	+	+	−	90.3	24.6	14.6	46.4	19.7	50.3
+	−	−	+	+	40.9	11.5	9.3	44.7	26.1	61.2
+	−	+	−	+	83.8	5.3	18.5	39.5	29.3	87.3
+	−	−	−	−	40.7	16.9	5.3	43.3	15.4	37.3
+	+	+	+	−	73.4	16.4	14.5	38.1	23.9	60.1
+	+	−	+	+	33.5	9.3	7.2	36.2	24.8	59.1
+	+	+	−	+	76.2	3.8	16.1	35.1	28.7	89.4
+	+	−	−	−	34.7	9.7	7.3	37.4	24.5	58.4

Note. Design Level	−	+	
T (°C)	475	525	
SV (min^{-1})	4.7	9.4	
Conc. (cc/min)	3	6	(at SV = 4.7)
	6	12	(at SV = 9.4)

feed ratios. The conversion and product distribution reached approximate steady state after 1–2 hr and a slow deactivation was observed.

Designed Experiment

A two-level factorial designed experiment was performed to determine the effects of temperature, space velocity, and reactant concentrations on conversion and selectivity. The design is shown in Table 1 along with the results. The design and analysis of such experiments is discussed in many texts including a good introduction by Hendrix (*11*).

The parameter ranges were based on examples given in the Monsanto patents (*4–7*) and our own preliminary experiments. Temperature was tested at 475 and 525°C and space velocity at 4.7 and 9.4 min^{-1}. The concentrations were actually the flow rates which combine to give the desired space velocity. Helium made up the difference in the case of all three components having a low value. The catalyst was 1 g of 9% Mo/SiO_2.

The product gases are reported as the moles present in the 25-μl gas sampling valve. They were analyzed using a thermal conductivity detector. The sensitivity is not as high as with an FID, so compounds in small amounts such as propionitrile were difficult to detect. Also, the broad ammonia and water peaks covered up some small peaks such as propylene and butylene. Only carbon monoxide, carbon dioxide, ammonia, methane, ethane, ethylene, and acetonitrile were quantified. Table 1 only shows carbon dioxide, methane, and acetonitrile; all other products had much smaller concentrations.

The catalyst is prone to some deactivation and care was taken to assure that the activity was reasonably constant within the designed experiment. This was accomplished by allowing the catalyst to equilibrate for a few hours, minimizing the time between design levels, and checking activity at base line conditions ($CO:H_2:NH_3 = 6:6:6$). The low-temperature experiments were run first and fresh catalyst was activated for the second batch of experiments at the high temperature. The activity decreased less than 10% during each temperature series and was equivalent between them. To minimize the impact of the slight deactivation on the results, experiments were performed in random order within each temperature level.

The conversion and selectivity are also shown in Table 1. Conversion is defined here as the moles of carbon monoxide reacted divided by the moles of carbon monoxide fed. Selectivity is defined in two ways. *S*1 is the moles of acetonitrile produced (times two since there are two carbons per molecule) divided by the moles of all products including carbon dioxide. *S*2 excludes carbon dioxide and is much higher.

Reaction under Ammonia and Hydrogen-Deficient Conditions

The reaction was run with ammonia and hydrogen-deficient feeds with all other conditions remaining constant. Space velocity was kept constant by adding makeup helium. The specific reaction conditions were 475°C and 4.7 min^{-1} space velocity; 0.8 g of 10% Mo/SiO_2 catalyst was used. A flame ionization detector was used to obtain a sensitive measure of all the FTS and nitrile synthesis products.

Figure 1 shows the concentrations of the product gases for decreasing ammonia feed concentration. This was done to compare the modified FTS distribution with the conventional FTS distribution under identical conditions. The reaction products are the total amount of each carbon number species. For instance, C2 refers to ethylene and ethane. Although not shown, in the presence of hydrogen the alkane was the dominant product and without hydrogen, the alkene became dominant.

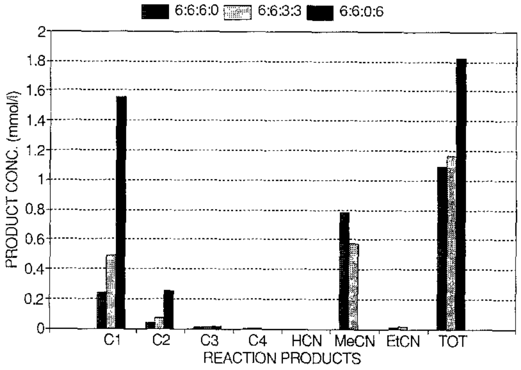


FIG. 1. Product distributions for various feed rates of $CO:H_2:NH_3$: He (cc/min) trending towards ammonia-deficient conditions.

Figure 2 shows the concentrations of the product gases for decreasing amounts of hydrogen. Removal of hydrogen was motivated by patent claims that acetonitrile could be produced even without hydrogen. The designed experiment also showed that hydrogen had a large effect on the selectivity (*S*2).

These tests were run over a period of 800 min and show some deactivation. The total activity as represented by carbon monoxide

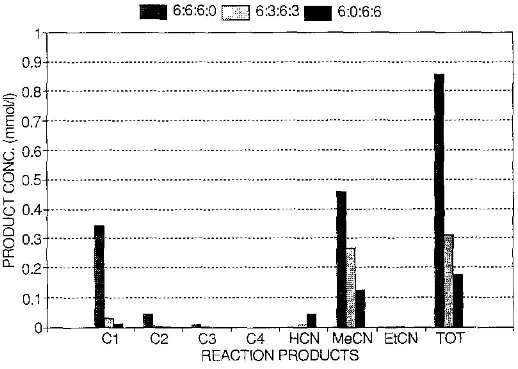


FIG. 2. Product distributions for various feed rates of $CO:H_2:NH_3$: He (cc/min) trending towards hydrogen-deficient conditions.

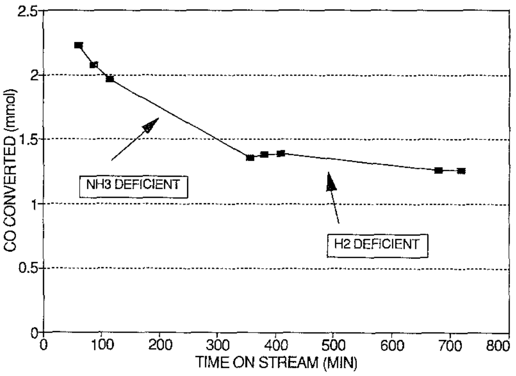


FIG. 3. Activity profile of the baseline conditions ($CO : H_2 : NH_3 : He = 6 : 6 : 6 : 0$ cc/min) before, during, and after the ammonia- and hydrogen-deficient reaction experiments.

conversion is shown in Fig. 3. This is only conversion to the FTS and nitrile synthesis products; the WGS reaction was not monitored. The data points refer to the base line condition ($CO : H_2 : NH_3 = 6 : 6 : 6$), which we returned to occasionally to compare activity. The periods in between refer to the experiments at ammonia- and hydrogen-deficient conditions. Since hydrogen and ammonia significantly affect activity, these data are not plotted. This curve indicates the type of deactivation profile encountered. The deactivation may be caused by a slow buildup of nitride.

Transient Response to Alternating Flows of Carbon Monoxide and Ammonia

The order in which the reactants combine is of interest. For instance, carbons could polymerize by a Fischer–Tropsch mechanism and then the ammonia could act as a chemical trap. Another possibility is that a carbon reacts with nitrogen to form an adsorbed intermediate which then reacts with another carbon species as suggested by Tatsumi *et al.* (*9*) and Henrici-Olive and Olive (*8*).

One test of this is to alternately feed carbon monoxide and ammonia to the reactor and see which step produces the acetonitrile. We could do this with a GC because the retention time for the acetonitrile was significantly longer than the other products.

One gram of 10% Mo/SiO_2 was pretreated by the normal procedure. Ammonia or carbon monoxide was fed for 30 min each with 1-min nitrogen flushes in between, as shown in Table 2. The second carbon monoxide addition produced large amounts of acetonitrile and this was consistent through further NH_3–CO cycles. Although we did not attempt to quantify the response, it appears that the carbon monoxide was titrating some species from the surface. The same type of response was observed if a combined CO/H_2 feed was used or if CO was fed first.

DISCUSSION

Designed Experiment

This experiment allows us to compare the average of eight experiments at each level for five variables while only conducting 16 experiments. The net effect of temperature on conversion, for example, is obtained by multiplying each measured conversion by a -1 or $+1$ (depending on the design level), summing the products, and dividing by the total number of experiments. Thus the average effect of increasing temperature from 475 to 525°C on conversion was -2.9% out of a total span of 35%. The effects of all variables on conversion and selectivity are shown in Table 3. The range of values is

TABLE 2

Acetonitrile Production from Alternating Feeds of CO and NH_3

Feed	Time (min)	MeCN (area × 10^{-3})
NH_3	30:00	N.D.
CO	30:00	Trace
NH_3	30:00	N.D.
CO	0:40	N.D.
	1:20	15.1
	2:00	7.2
	2:40	4.6
	3:20	3.0
	30:00	N.D.

Note. N.D. = not detected.

TABLE 3

The Effects of Changing Reaction Variables from Low to High Value

Reaction variables	CO_2	FT (nmol)	MeCN	*X*	*S*1 (mol%)	*S*2
T	-5.6	+2.5	-2.8	-2.9	-1.7	-8.9
SV	-10.4	-2.7	-3.7	-7.1	+0.7	+2.4
CO	+21.9	+1.8	+7.2	-1.4	-0.6	+4.1
H_2	+1.1	+5.1	+0.4	+2.1	-0.6	-8.2
NH_3	-1.8	-4.5	+0.1	-1.9	+1.3	+7.1
Range	89.3	27.1	34.8	34.8	17.4	58.9

given to help put the individual effects in perspective. Note that the individual effects are averages and the absolute values do not necessarily add up to the total range of values.

The most immediate observation from the designed experiment (Table 1) is that under these conditions significant conversions ranging from 29 to 64% were achieved. The selectivity to acetonitrile based on all products ranged from 15 to 33%. If carbon dioxide is not included, the selectivity to acetonitrile ranged from 37 to a very high 96%.

These results are in general agreement with other accounts of the high acetonitrile selectivity (*4–7*, *9*). One notable difference is the absence of hydrogen cyanide in our reaction products. The original two Monsanto patents (*4*, *5*) also reported no hydrogen cyanide, but mentioned material balance problems that could cut reported selectivities in half. The later two Monsanto patents (*6*, *7*) did report small amounts of hydrogen cyanide. The feed ratios in their examples that produced significant amounts of hydrogen cyanide were hydrogen-deficient ($CO:H_2:NH_3 = 1:0.5:2$) compared to our feeds. Indeed, when we ran with low hydrogen feeds we did produce hydrogen cyanide (Fig. 2). Tatsumi *et al.* (*9*) also produced hydrogen cyanide (and methylamine at low temperatures), but their highest temperature (450°C) was less than our lowest design temperature (475°C). Even as low as 400°C our preliminary experiments did not produce hydrogen cyanide. Since Tatsumi *et al.* (*9*) did not mention their feed composition, it is very difficult to speculate on the discrepancy.

Three general reactions occur and the results are best discussed in this context. First, Mo is a very good water–gas shift (WGS) catalyst and the reaction is probably near equilibrium (*12*). Second, the Fischer–Tropsch synthesis (FTS) continues even in the presence of ammonia. The third reaction is the synthesis of nitriles.

In addition to the conversion and selectivity, any measured quantity can be used as the response to the five design parameters. Table 3 shows the effects of the reaction parameters on the total moles (in the gas sampling valve) produced of carbon dioxide, FTS products (mostly methane), and acetonitrile which represent the products of the three reactions discussed above. The amounts are presented as the carbon monoxide required to create the product.

Effect of temperature. Increasing temperature has a positive effect on the FTS but decreases the WGS and the nitrile synthesis reactions. The reaction effects combine for a surprising decrease in conversion over the 50°C temperature span. The WGS (*12*) and nitrile (*4*, *5*) reactions have been shown to be near equilibrium and the equilibrium conversion decreases with temperature. This outweighs the increase in rate for the FTS. Also, the catalyst may deactivate faster during the high-temperature runs, although we did not measure significant loss of activity. At the very least, temperature has very little effect on total conversion.

Since increasing temperature decreases the equilibrium position of both the WGS and the nitrile synthesis reactions, the major contributor to lowering the selectivity is the increasing FTS compared to the decreasing nitrile synthesis.

Effect of space velocity. Of course, space velocity has a large negative impact on conversion. Interestingly, it has a small positive effect on the selectivities. Carbon dioxide production is negatively affected by space velocity. Perhaps at high space velocities the shift reaction is not quite at equilibrium and thus increases selectivity ($S1$). The reason for its effect on $S2$ is not apparent.

Effect of feed concentrations. High levels of carbon monoxide have a positive effect on the amount of all three products but decrease conversion. The FTS products are least affected by the carbon monoxide level because there is plenty already on the surface and it competes too strongly with hydrogen (*12*). It has a large impact on production of carbon dioxide and acetonitrile. Both cases could be explained by simple mass action since they are assumed to be near equilibrium. Carbon monoxide increases the WGS reaction more than the nitrile synthesis and so decreases $S1$. Since it has little effect on the FTS, $S2$ increases.

Hydrogen levels have almost no effect on either carbon dioxide or acetonitrile production. It does have a major positive effect on the FTS products since it is the limiting surface species.

Ammonia has almost no effect on the carbon dioxide production since it is not involved in the reaction. It has a strong negative effect on the FTS products. This is probably a competitive adsorption effect. Ammonia is known to suppress the FTS on iron catalysts; the molybdenum nitride is even more stable (*12*). Surprisingly, ammonia has very little effect (in the design range) on acetonitrile production.

Optimum conditions. The ideal conditions within this design space can be determined from the data. Presumably, optimum selectivity for acetonitrile at reasonable conversion is the desired goal. The temperature should be low to minimize the formation of FTS products. There is a trade-off between conversion and selectivity with space velocity but since the major effect is on conversion, a low space velocity (high conversion) is best. High carbon monoxide concentration will promote the nitrile synthesis (and WGS) more than the FTS. Low hydrogen concentration interferes with the FTS. High ammonia concentration also maximizes acetonitrile selectivity, not because it increases the nitrile synthesis rate but because it severely limits the FTS. Thus the best conditions are $T = 475°\text{C}$, $SV = 4.7\ \text{min}^{-1}$, and $\text{CO} : \text{H}_2 : \text{NH}_3 = 6:3:6$. This condition produced an impressive 96% acetonitrile selectivity ($S2$) with 47% conversion.

Ammonia-Deficient Reaction: Comparison to an FTS Distribution

The product composition for varying amounts of ammonia was shown in Fig. 1. The activity (total moles produced) increased significantly when ammonia was removed from the reactants. This was accompanied by an increase in FTS products and elimination of nitriles.

The Schulz–Flory product distribution is expected for polymerization reactions such as the FTS (*14*). The weight fraction, M_P, of each carbon number is related to the probability of chain growth by

$$\log(M_P/P) = \log(\ln^2 \alpha) + (\log \alpha)P, \quad (1)$$

where P is the number of carbons in a molecule and α is the probability of chain growth. Carbon dioxide is not considered in the distribution since it comes from an entirely different reaction (WGS) and can be minimized by addition of carbon dioxide to the reactant gas (*4*, *5*). Also, the acetonitrile will be counted in this exercise as a two-carbon compound as would ethane or ethylene.

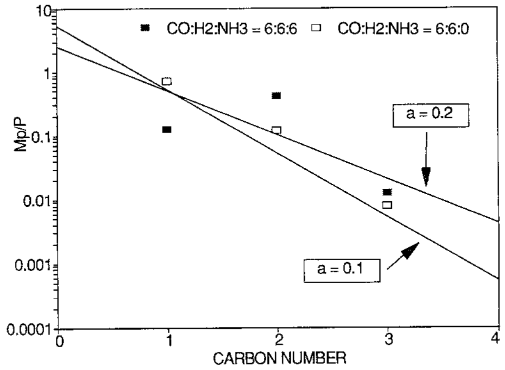


FIG. 4. Comparison of the Schulz–Flory distribution to the synthesis reaction with and without ammonia.

Two questions are (i) do the synthesis gas products under these reaction conditions follow the expected Schulz–Flory distribution and (ii) does addition of ammonia alter it?

Figure 4 presents the Schulz–Flory equation plotted for two values of α. The products from the $CO/H_2/He$ reaction fit the distributions well, demonstrating a probable polymerization-like mechanism. It is interesting that even the methane fits the curve; this is not always the case in FTS. However, the distribution for $CO/H_2/NH_3$ cannot fit the Schulz–Flory equation since it is far too selective for a two-carbon compound. Usually, if variations are seen, Cl is too high and C2 is too low, which is the opposite of that seen here.

Henrici-Olive and Olive (*15*) showed that amines formed from the ammonia-modified FTS over Fe catalysts followed a Schulz–Flory distribution. The ammonia was hypothesized to act as a chain-transfer agent, terminating growing hydrocarbon molecules. If the Mo-catalyzed reaction proceeded the same way, a Schulz–Flory distribution would also be expected. The dramatic difference between the product distribution found here compared to theoretical Schulz–Flory distributions or that found in the absence of ammonia is strong evidence that acetonitrile is produced by a mechanism quite different than the FTS and that ammonia is not a simple chain-transfer agent.

Hydrogen-Deficient Reaction

The reaction stoichiometry shows that reaction can be sustained even in the absence of hydrogen because of the WGS reaction:

$$\begin{array}{c} 2CO + 2H_2 + NH_3 \rightleftarrows CH_3CN + 2H_2O \\ \underline{2CO + 2H_2O \rightleftarrows 2CO_2 + 2H_2} \\ 4CO + NH_3 \rightleftarrows CH_3CN + 2CO_2 \end{array}.$$

Figure 2 shows that to be true, but hydrogen cyanide was also produced. It requires fewer hydrogens and in fact has a net hydrogen production via the WGS reaction:

$$\begin{array}{c} CO + NH_3 \rightleftarrows HCN + H_2O \\ \underline{CO + H_2O \rightleftarrows CO_2 + H_2} \\ 2CO + NH_3 \rightleftarrows HCN + H_2 + CO_2 \end{array}.$$

Removing hydrogen from the reactant mixture greatly reduced the activity. At half the baseline hydrogen concentration, the FTS products were virtually eliminated. The acetonitrile production was also decreased but much less than the FTS. The selectivity, $S2$, was much higher in this case. Complete removal of hydrogen produced significant quantities of hydrogen cyanide and further reduced the activity.

Transient Response to Alternating Feeds of Carbon Monoxide and Ammonia

The acetonitrile production can be observed with this experiment but other products cannot be measured. It would be interesting in future work to measure other products by directly feeding a portion of the reactor effluent to a mass spectrometer. The acetonitrile production on the second carbon monoxide addition indicates that carbon monoxide is the last species added to the acetonitrile intermediate. Further discussion of this experiment will be reserved until after the mechanism is discussed.

Mechanistic Implications

The FTS reaction has been studied for many years without a clearcut consensus of the mechanism, so one could not expect an

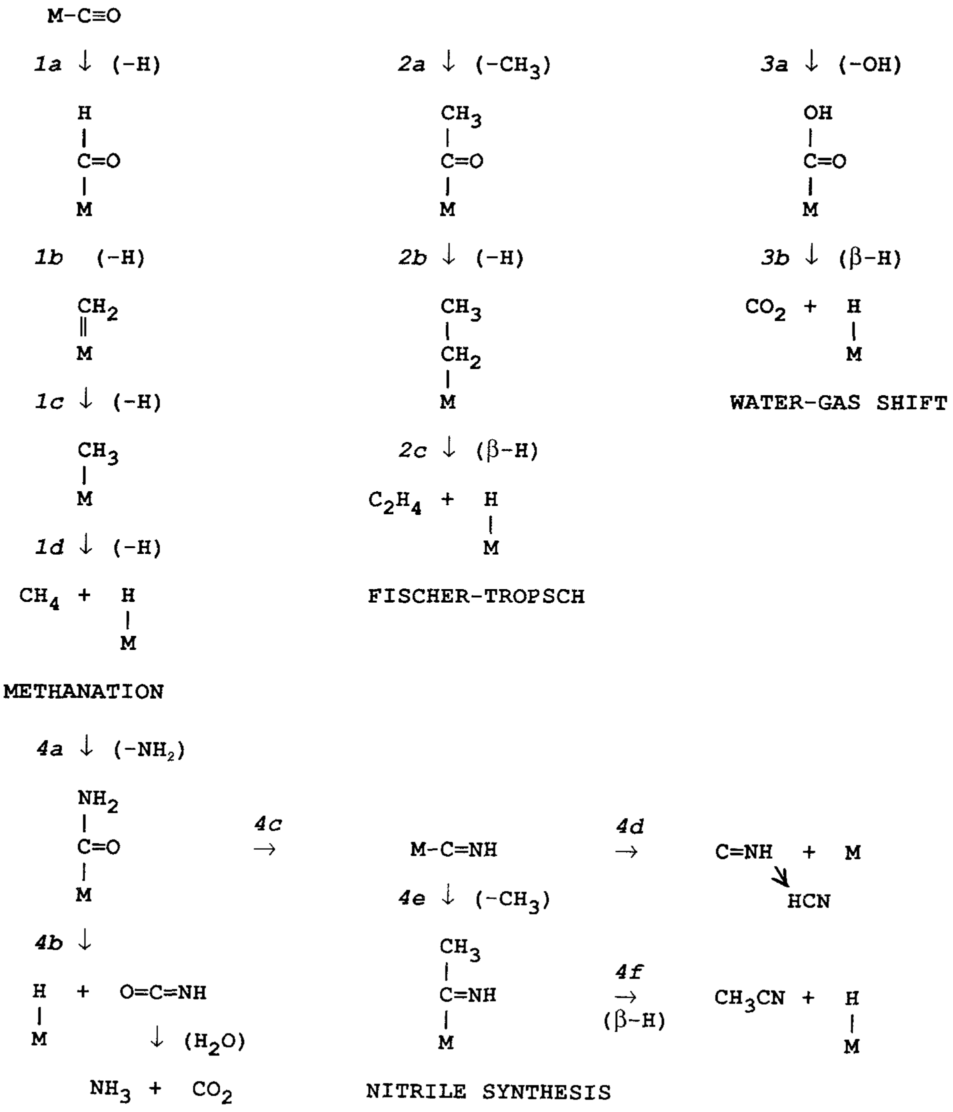


FIG. 5. Proposed mechanism for the modified Fischer–Tropsch reaction.

unambiguous mechanism from these modest experiments. However, the evidence is sufficient to corroborate and expand upon the mechanisms postulated by both Henrici-Olive and Olive (*8*) and Tatsumi *et al.* (*9*). They invoked the formation of a hydrogen cyanide intermediate that inserts into a metal carbene; in other words, a C–N–C reaction sequence. We have gathered sufficient evidence to elaborate further on the surface chemistry.

Our proposed mechanism is shown in Fig. 5. We have generally invoked the carbon monoxide insertion mechanism (scheme IVC in Anderson (*12*)). This scheme supposes that the important carbon monoxide dissociation step for the synthesis reactions occurs after activation by insertion into a σ-bonded molecule, even though Mo strongly dissociates carbon monoxide compared to other FTS metals. Insertion converts the linear, π-acceptor carbon monoxide ligand into a non-linear, σ-bonded ligand. The separate paths show the competing reactions: methanation [1]/FTS [2]; WGS [3]; and nitrile synthesis [4]. Note that they all begin by the insertion of carbon monoxide into a σ-bonded ligand. The symbols such as $-CH_3$ refer to reaction with an adsorbed ligand (on the same or nearby MO atom) and β-H means β-hydrogen elimination.

Path 1 shows the methanation reaction starting with the activation of carbon monoxide by insertion into a metal hydride bond (step 1a). The hydrogen atom can come from dissociation of molecular hydrogen, ammonia, or water. The enol can now dissociate and add hydrogen to form a CH_x ligand (steps 1b and 1c). Henrici-Olive and Olive (*16*) proposed that the enol hydrogenates to the alcohol, which then dehydrates. Another possibility is that carbon monoxide dissociates directly and then hydrogenates (carbide mechanism). All these mechanisms result in a CH_x surface species. The carbene ligand could participate as an active FTS intermediate (it can insert into σ bonds as does carbon monoxide). The methyl ligand can participate in the insertion reaction with carbon monoxide to form higher hydrocarbons, or simply hydrogenate to form methane (step 1d).

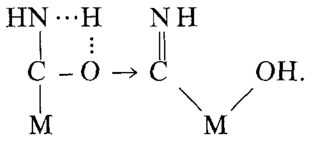
Path 2 shows the FTS with carbon monoxide insertion into an alkyl ligand (step 2a). The oxygen dissociates and the carbon hydrogenates to an ethyl ligand (step 2b). The ethyl group in this case either leaves as ethylene by β-H elimination (step 2c) or undergoes further carbon monoxide insertions to form higher hydrocarbons. The presence of alkanes in FTS products is usually attributed to hydrogenation of the primary alkene product in a secondary reaction.

The WGS reaction is shown in Path 3. A hydroxyl ligand is present either from partial hydrogenation of the oxygen from carbon monoxide dissociation or by dissociation of water. It then participates in a carbon monoxide insertion reaction (step 3a). The hydrogen leaves by β-H elimination (yielding a resonance-stabilized anion) producing carbon dioxide (step 3b). This is a very fast reaction and is usually assumed to be equilibrium limited (*12*, *13*).

The novel part of this scheme is the nitrile synthesis. The chemistry is hypothesized here in some detail and discussed in context with the other reactions. This is important since several analogies will be invoked. The first step is carbon monoxide insertion into the dissociated ammonia (step 4a). This is very similar to the first step of the WGS reaction and should be a very facile reaction. This reaction (and the WGS) could also occur by direct attack from the gas phase.

The molecule could leave after β-H elimination (just like CO_2 in the WGS reaction) as an amidic acid (4b) except that we do not have any evidence for the existence of this molecule in the product. If formed, it probably is destroyed by reaction with water to form ammonia and carbon dioxide. This would then be essentially an ammonia-assisted WGS reaction.

Alternatively, the oxygen could dissociate from the molecule to form either a cyanide or isocyanide ligand (step 4c). We discount the formation of an amine since these are not seen in our reaction products. The isocyanide ligand is proposed here first because it is a π-acceptor ligand like carbon monoxide and can participate in insertion reactions (*17*). This reaction could proceed through an intermediate such as:



Formation of hydrogen cyanide occurs by simple desorption (step 4d) similar to the reversible adsorption of carbon monoxide and followed by rearrangement. Alternatively, it can insert into an alkyl bond of which methyl groups are most predominant (step 4e). Now a hydrogen is available for β-H elimination and the product leaves and undergoes a rearrangement to acetonitrile.

This rearrangement would be difficult but could be assisted by the metal surface. It could also lose hydrogen by β-elimination from the nitrogen which would yield acetonitrile directly as shown in step 4f. Propionitrile is produced by insertion of the isocyanide ligand into an ethyl ligand.

An alternative to step 4c is to form a cyanide ligand. This could reductively eliminate by hydrogenation to hydrogen cyanide similar to the formation of methane. Alternatively, it could insert (perhaps by recoordinating through its π bonds) into a methyl ligand. This step would be accompanied by simultaneous desorption since the carbon is already saturated. We are not aware, however, of any evidence for this type of insertion reaction in the literature. Also, the requirement of hydrogen for desorption of hydrogen cyanide seems to conflict with the fact that small amounts of hydrogen prevent formation of hydrogen cyanide.

Step 4e in our mechanism seems to require the unlikely formation of two activated intermediates (isocyanide and methyl ligands) on the same or adjacent Mo atoms. Henrici-Olive and Olive (*14*) invoked related arguments that carbon monoxide or hydrogen are used in each step of the carbon monoxide insertion as evidence for that mechanism. This may not be a problem for the following reasons. We hypothesize that large amounts of isocyanide species (or cyanide) are present because of the ease of forming its precursor by analogy with the WGS reaction. Also, since gas phase and adsorbed carbon monoxide are easily exchanged, the isocyanide ligand might by analogy be easily displaced by incoming carbon monoxide and thus be relatively mobile. In the presence of significant hydrogen, no hydrogen cyanide is produced, so it appears that the isocyanide insertion into the methyl ligand is quite fast. However, in the absence of hydrogen, methyl groups are rarer and some isocyanide apparently leaves the catalyst as hydrogen cyanide after rearrangement.

Other mechanisms are plausible also. Schemes based on the carbide mechanism can be hypothesized. However, insertion of a carbene into an ammonia ligand would yield a saturated amine on the surface. Formation of acetonitrile would then require substantial dehydrogenation.

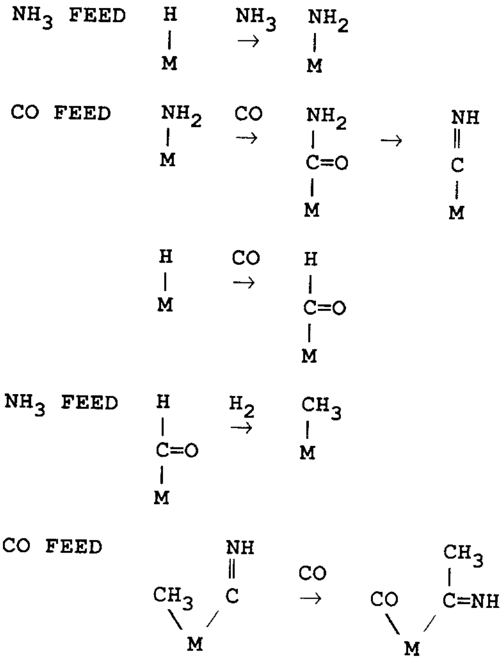


FIG. 6. Proposed mechanism for the transient response experiment.

The transient experiment can now be explained in greater detail and the hypothesized mechanism is shown in Fig. 6. After pretreatment, the molybdenum surface is covered with hydrogen atoms. The first pulse of ammonia lays down NH_x ligands. On the next pulse, carbon monoxide readily adsorbs on the surface and reacts with the ammonia ligands. Not enough hydrogen is present to completely dissociate and hydrogenate the adsorbed carbon monoxide. The next ammonia pulse acts mainly to add hydrogens to form the methyl ligands. Presumably, this ammonia pulse could be replaced with hydrogen for similar results. The two proposed precursors for acetonitrile are now present but gas-phase carbon monoxide is necessary to force the insertion reaction by displacement. This happens with the second carbon monoxide pulse which does not actually incorporate into the acetonitrile. This hypothesis could be tested with labeled carbon monoxide in the second pulse.

Several significant questions remain. What similarities are there between the water–gas shift reaction and the initial reaction between ammonia and carbon monoxide? Is the active intermediate actually an isocyanide, cyanide, or something else? Why does just a small amount of hydrogen suppress the formation of hydrogen cyanide? These questions are being addressed in our current research.

CONCLUSIONS

The designed experiments showed that selectivity for acetonitrile as high as 96% (excluding carbon dioxide from the water–gas shift reaction) at 47% conversion could be achieved. The selectivity for acetonitrile is optimized primarily by minimizing the competing Fischer–Tropsch synthesis reaction. These conditions include low temperature, low space velocity, high carbon monoxide concentration, low hydrogen concentration, and high ammonia concentration. These results strictly apply only to the range of parameters studied in the designed experiment.

The chemistry of this process is a combination of the water–gas shift reaction, the Fischer–Tropsch synthesis, and a nitrile synthesis. The nitrile synthesis seems to occur by the initial formation of a CN intermediate which then inserts into a CH_x species. The proposed mechanism involves an isocyanide ligand which undergoes an insertion reaction into an alkyl ligand.

ACKNOWLEDGMENTS

This research was supported in part by a grant from the Research Grants Committee of The University of Alabama. Professor Curt Conner is thanked for initially bringing this reaction to our attention.

REFERENCES

1. Falbe, J., "Carbon Monoxide in Organic Synthesis." Springer-Verlag, Berfico, 1970.
2. Nozaki, K., and Cerrito, E., U. S. Patent 3,410,904 (1968) to Shell.
3. Kliger, G. A., Glebov, L. S. Popova, T. P., Marchvskaya, E. V., Beryezkin, V. G., and Loktev, S. M., *J. Catal.* **111,** 418 (1988).
4. Olive, G., and Olive, S. U.S. Patent 4,179,462 (1979) to Monsanto.
5. Olive, G., and Olive, S., British Patent 1,496,649 (1976) to Monsanto.
6. Auvil, S. R., and Penquite, C. R., U.S. Patent 4,272,451 (1981) to Monsanto.
7. Auvil, S. R., and Penquite, C. R., U.S. Patent 4,272,452 (1981) to Monsanto.
8. Henrici-Olive, G., and Olive, S., *Angew. Chem. Int. Ed. Engl.* **17,** 862 (1978).
9. Tatsumi, T., Kunitomi, S., Yoshiwara, J., Muramatsu, M., and Tominaga, H., *Chem. Lett.* **3,** 223 (1989).
10. Zhang, Q. W., Hathcock, L., and Bertsch, W., *J. High Resolut. Chromatogr.* **13,** 683 (1990).
11. Hendrix, C. D., *Chemtech* **9,** 167 (1979).
12. Anderson, R. B., "The Fischer-Tropsch Synthesis." Academic Press, Orlando, FL, 1984.
13. Murchison, C. B., *in* "Proceedings, 4th Internation Conference on Uses Chm. Molybendenum, 1982."
14. Olive, S., and Henrici-Olive, G., "Catalyzed Hydrogenation of Carbon Monoxide." Springer-Verlag, Berlin, 1984.
15. Henrici-Olive, G., and Olive, S., *J. Mol. Catal.* **4,** 379 (1978).
16. Henrici-Olive G., and Olive, S., *Angew. Chem. Int. Ed. Engl.* **15,** 136 (1976).
17. Cotton, F. A., and Wilkinson, G., "Advanced Inorganic Chemistry." Interscience, New York, 1981.