

HYDROCONVERSION OF CARBON MONOXIDE IN ZEOLITIC MEDIA - A GENUINE FISCHER-TROPSCH REACTION ?

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ABSTRACT

The hydroconversion of Carbon monoxide over multicomponent zeolitic catalysts was reviewed. The Fischer-Tropsch (F.-T.) synthesis, as generally accepted was considered with reference to its obvious limitations : low overall conversion rate, broad product spectrum, and comparatively high methane yields. The design of active catalysts that circumvent the Schulz-Flory (S.-F.) distribution was the aim of most of the litterature disclosed initially. Later composite catalysts were designed to achieve depressed methane yields and narrower distributions : the quest for such catalysts was schematically analyzed : the first association of zeolites to metals known to be active in F.-T. synthesis was aimed at imposing cage and/or size effects so as to by-pass the S.-F. distribution. This idea slowly shifted to the use of intrinsically more selective catalysts for hydroconversion of CO stabilized in the zeolite cavities. These improved the selectivity but did not achieve the long sought higher rates. Composite catalysts including either an F.-T. conventional catalyst or a methanol synthesis catalyst and a shape selective zeolite were the most recent approaches directed at increasing yields and improving selectivities. However questions as to the operating pathways and the unexpected selectivity changes are still pending.

INTRODUCTION

The last decade has witnessed feverish efforts in the search of energy sources alternative to periodically dried up and yet ever lasting oil. Among the possible candidates renewable energy sources enjoyed an immense but fugacious popularity as cheap oil prices reassured the consumer for a new "period". By contrast coal still retains the attention of the professionals. The secret of this new infatuation for coal, in spite of all the heavy toll which traced the coal mining history up to very recently, may lie in the existing coal and coal-derived syn gas conversion

technology. Also the availability of coal in various parts of the world ensured an attractive reliable supply.

Syn gas conversion is a well known process to methanol and glycol, while Fischer-Tropsch synthesis to produce fuels, though not so popular as it used to be before the oil era regained some luster in recent years. Yet the F.-T. plants remained shut down. Only, in South Africa, probably on political grounds Sasol plants are operating. In order to gain Industrial significance, this process must meet the following conditions : the conversion rate, presently the lowest of all syn gas conversion processes, must be significantly enhanced ; the prevailing broad product distribution must be circumvented and the methane yield must be drastically cut down. Table 1 compares the production rates for methanol synthesis from various technologies and that of the Sasol plants as extract parts of the world ensured an attractive reliable supply.

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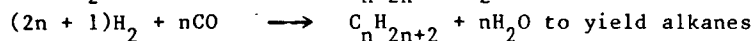
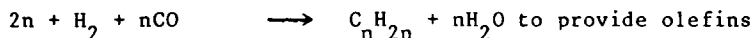
Table 1

Comparative rates for Methanol and F.-T. synthesis

Catalyst	temperature centigrades	pressure atmos.	space velocity h^{-1}	yield Kg/Kg/h	source [1,2]
CuO : ZnO : Al ₂ O ₃					
64 : 32 : 4	250	50	10 000	0.3	academic
"	300	50	10 000	0.9	"
CuO : ZnO : Cr ₂ O ₃					Power gas corporation
11 : 70 : 19	270	145	10 000	1.95	
31 : 38 : 5	230	50	10 000	0.755	BAST
33 : 31 : 36	250	150	10 000	1.1	academic
	300	150	10 000	2.2	"
Fe			2 000-3 000	0.01	Sasol

THE FISCHER TROPSCH SYNTHESIS PRINCIPLES AND LIMITATIONS

The syn-gas conversion occurs formally according to the simplified independent or sequential reactions :



The thermodynamic data [3,4] point to the following predictions :

- the equilibrium conversion will increase with increasing pressure and decrease temperature
- paraffins will be selectively produced in the operating temperature range (150-450°C)
- methane will be the dominant product which is a serious drawback.

But the most obvious limitation of the Fischer-Tropsch synthesis is its product distribution entirely dependent on its reaction mechanism :

Indeed there is a general agreement to ascribe the formation of hydrocarbons in syn-gas conversion to a polymerisation process involving a simple monomeric species. This monomeric species containing one carbon atom adds to the growing chain on the catalyst following the well established polymerisation kinetics with initiation, propagation and termination steps. Such a kinetic has been formulated mathematically [5] as follows

$$W_n = n \alpha^{n-1} (1 - \alpha)^2$$

W_n indicates the product weight fraction of carbon number n

α indicates the chain growth probability and is constant

α could be determined experimentally from the plot of $\log W_n/n$ against n .

Thus the distribution of the Fischer-Tropsch products appears to be predetermined by the chain growth mechanism. This type of product distribution is known as the "Schulz-Flory" distribution. Of course α varies with the nature of the catalyst and other experimental parameters. Nonetheless except where $\alpha = 0$ that is the methanation case, a whole product spectrum must be obtained with the relative concentrations strictly obeying the mathematical equation derived for polymerization schemes.

This is indeed a serious limitation which hinders the use of F.-T. synthesis to the production of a narrow range of chemicals. Though, possibly, parallel and sequential reactions may alter significantly this imposed distribution.

The second limitation is the very low activity of the Fischer-Tropsch catalysts compared to methanation and methanol synthesis catalysts (see table 1).

As to the major limitation i.e. broad spectrum of products, the literature data show that :

- a) Higher overall selectivities to lighter hydrocarbons may be reached by increasing either the H_2/CO ratio or the reaction temperature or by decreasing the residence time.

- b) As apparently olefins and/or alcohols are the primary products, these are favoured by low conversions achieved by high space velocities and/or low H_2/CO ratios. The selectivity towards these products will obviously depend on the hydrogenation ability of the catalyst. It would seem reasonable that alcohols should be favoured by high total pressures.
- c) Higher temperatures would favour olefins with respect to overall hydrocarbon production as increasing temperatures shift the hydrogenation dehydrogenation equilibrium towards olefins.

VIOLATION OF THE S.-F. DISTRIBUTION

Even though modest inflexions of the product selectivities may be achieved as mentioned above or by resorting to the variation in the reactor engineering, these selectivity changes are still achieved within the Schulz-Flory Distribution.

Ways to circumvent the CO hydrogenation were therefore sought in the catalyst design.

As zeolites always appeared as wonder catalysts, it was thought that these solids should be up to the expectation of the many scientists who engaged in the search for means to violate the S.-F. Distribution in order to render to the F.-T. synthesis some of its luster [6-9]. Indeed many reports on the violation of the S.-F. Distribution were issued following the use of zeolitic catalysts.

While this should appear as reasonable goal, a number of reports should be considered with caution.

In effect the following artifacts may well account for four apparently interesting non S.-F. Distributions :

In some cases, for obvious experimental constraints, usually fully mentioned by the authors, only a narrow fraction of products could be analyzed or collected, thus missing a representative picture of the actual distribution.

Analysis of the whole product spectrum may be hindered by a number of reasons from which we single out the following :

fractionation problems and incorrect sampling

condensation of long chain products on the catalyst surface or inside the pores.

preferential adsorption of some products.

Most of these problems may be overcome by running the F.-T. experiment over a long enough period, thus achieving high yields which minimizes the inherent errors to sampling, fractionation and product retention on/in the catalyst.

Alternatively a careful and accurate material balance would save erroneous and misleading conclusions.

Irrespective of the conclusions following a careful scrutiny of the available data reporting non Schulz-Flory distributions, several means were employed to circumvent the production of the entire spectrum of hydrocarbons.

The ideas behind the means were inspired by the belief that

- (i) metal support interaction may drastically influence both the activity and the selectivity of the supported metal. In particular the acid-base properties of the support were thought to be the most influential parameters that determine the modifications of the catalytic properties of the metal [10]
- (ii) the metal particle size is likely to influence the hydrogenation and hydrogenolysis activity of the metal [11] and possibly have sensitive effects on catalytic steps, such as carbene insertion into M-C bonds etc..., which govern the F.-T. synthesis mechanism.
- (iii) the chain growth mechanism may be strongly restricted by steric hindrance which may yield a stereoselective distribution appearing as a sharp cut off at a definite carbon number [12]. This latter way of thinking inevitably brought zeolites into play. The disclosure by Mobil of methanol conversion to hydrocarbons over various shape selective zeolites increased the attractive character of these solids as selective supports or components in F.-T. and F.-T. related synthesis.
- (iv) zeolites were well established as acid catalysts which perform cracking and isomerization of hydrocarbons. Therefore hopes were running high to modify the S.-F. distribution in a subsequent conversion step of the hydrocarbons produced on the F.-T. component.

In order to examine the accomplishments achieved by Zeolite "F.-T." synthesis as to the activity and the product distribution we shall consider separately the following topics which originate from the ideas outlined above as practiced by various groups.

Schematically these ideas inspired the emergence of :

- 1) bifunctional catalysts associating a metal, known to be F.-T. active, with zeolites
- 2) bifunctional catalysts associating an active component in hydroconversion of CO (usually a carbonyl complex) with various cage-type zeolites.
- 3) composite catalysts associating an active F.-T. catalyst with zeolites, which is the procedure used to up-grade F.-T. products.
- 4) composite catalysts associating an active CO hydrogenating catalyst (usually a methanol synthesis catalyst) with shape selective zeolites.

Roughly three approaches, which sometimes merge, dominated the disclosed data.

- (i) upgrading F.-T. products by addition of an acidic component possibly with shape selective properties.

(ii) diverting the CO hydrogenation from the F.-T. mechanism to produce oxygenated species, subsequently converted to hydrocarbons on acid catalys exhibiting (or not) shape selective properties.

While the first approach does not aim in principle at increasing the rate of reaction, the latter is also directed towards improving the yield as well as escaping the Schulz-Flory distribution.

However one more limitation which cannot be lifted upon choosing the first approach consists in unacceptably high methane yields. This feature, combined with low hydrocarbon production rates, and a broad product spectrum, contributed strongly to weight down the F.-T. process.

Therefore it would seem useful to examine the parameters which influence methane formation in order to depress methanation rates whenever possible.

METHANATION

Part of the dilemma in attempts to increase F.-T. synthesis rates is that it is necessary to increase the hydrogenation abilities of the catalyst which almost inevitably results in increased methanation rates as hydrogenolysis activity is also simultaneously increased. Thus both CO hydrogenation intermediates and hydrocarbon products all tend to be ultimately converted to methane the stable end product.

A well documented investigation by Lunsford and coworkers [13] has elegantly delineated the parameters which play a prominent role in methanation. Recent studies disclosed at this very meeting appear to be in agreement with Lunsford et al. and extend the investigation to the $H_2 + CO_2$ mixture [14].

Rabo and coworkers [15] have shown that supported metallic palladium produced essentially methanol from syn gas under specified pressure and temperature conditions. This result was ascribed to the unique property of palladium to adsorb CO associatively so as preventing methane formation, as this proceeds via dissociation of CO and subsequent hydrogenation of the resulting carbon. Lunsford and Coll. extended this pioneer work to palladium supported on a number of carriers including zeolites [13].

Large size palladium particles supported on HY and NaY zeolites were compared to similar size particles deposited on neutral silica and acidic silica.

Pd/HY appeared to be the most active methanation catalyst irrespective of particle size, while only silica-supported palladium exhibited a significant activity in methanol production. Under the same temperature and pressure condition Moreover methane production was shown to proceed by an independent route with respect to methanol formation and could not be due to sequential hydrogenation of methanol. Yet methane did not appear to be formed via CO dissociation. The weakl

adsorbed CO would appear to be the precursor to methanol, while strongly adsorbed CO would favour methanation. Changes in the CO adsorption strength were noticed upon varying the Palladium particle size. Larger particles favoured methanol formation.

The acidity effect seems, on the contrary, to enhance methanation rates (table 2). This was ascribed to an additional and simultaneous interaction of the Oxygen-End of the CO molecule with Brönsted acids, thus considerably affecting the CO bond strength enabling the C-O cleavage in subsequent steps to methanation. In a way, acid sites would provide "oxophile" for CO activation.

Table 2

rates of CH₄ and MeOH production on Pd supported over various acidic and neutral carriers in mmole per metal site per second T = 553 K ± 5 H₂/CO = 2.8 - 2.4
P = 1,51 MPa SV = 1200 ± 200 h⁻¹

Catalyst	support properties	rate CH ₄	rate CH ₃ OH
PdNaY	medium acidity	12 ± 4	-
PdHY	strong acidity	40 ± 3	1
PdSiO ₂ (01)	acid	2 ± 1	
PdSiO ₂ (57)	neutral	0.65	18
PdCab-O-Sil	fairly acid	1.2	4 ± 1

A recent report [16] on methanation supported Lunsford et al. [13] conclusions on the absence of any significant charge transfer between the support and the metal. It was suggested in addition that polarization of the chemisorbed CO followed by hydride transfer may enhance the rate of methanation as observed on acid supports. While it is clearly conceivable that hydride transfer may be favoured in this way, there is no obvious reason that this should be at the exclusive benefit of methanation. As no influence of the acidity was observed on methanol production rate this hypothesis could not be reconciled with experimental data. One would rather favour the acid-assisted CO dissociation mechanism in order to account for methanation rate enhancement.

Qualitative acidity effects were also investigated. It was reported that the effect varies in the following order HY > HZSM-5 > NaZSM-5 >> NaY > SiO₂ [16]. However too many influential parameters may have varied simultaneously to infer reliable conclusions. It is almost certain that the palladium particle size, the location of palladium particles and the vicinity of the metallic sites with the acid site may vary substantially from sample to sample.

However there should be no doubt that Brönsted acidity plays a major role in enhancing the methanation rate. Therefore acidic supports for Fischer-Tropsch catalysts should be prohibited on these grounds.

F.-T. Active metals supported on Zeolites. Such catalysts associating mainly ruthenium and iron with cage type zeolites were dealt with in many early investigations [6, 11, 17-19].

Jacobs and coworkers [11, 17] reported that a sharp cut off in chain growth occurred around C_9-C_{10} when ruthenium particles were supported on zeolites. Similarly Ballivet et al. [18] showed that iron-Y zeolites and $Fe_3(CO)_{12}$ -derived Iron Y zeolites produced C_1-C_{10} hydrocarbons for the latter and C_1-C_{12} hydrocarbons for the former. In both cases the probability in chain growth appeared not to be constant over the entire C_1-C_{12} range. A sharp decrease was observed past the C_9 hydrocarbons. This sharp decrease was attributed to a cage effect, as the $Fe_3(CO)_{12}$ -derived iron particles were thought to be located in the Y zeolite supercages.

However as the zeolite cages may have as a primary effect to stabilize metal particles that fit in these cages, it may well be that the interpretation must be considered in terms of particle size effects, regardless of the reason and the means used to develop such particles. Jacobs [6] reported such a drastic effect of the particle size over the hydrocarbon distribution obtained in the case of ruthenium supported on Y zeolites. For example particles sizes of 1.5, 2.5 and 4.0 nm limited the chain length of F.-T. products at 10, 5 and 1 carbon numbers respectively. Thus it would appear sensible to ascribe the observed distribution to particle size effects since the carrier did not change. Additionally, similar size ruthenium particles deposited on silica also produced similar effects which confirms that the F.-T. distribution is sensitive to the structure of the active component on which the actual chain growth does take place rather than to the porous structure of the matrix, except through secondary effects on the metal particle.

A curious distribution was recently reported where C_1-C_5 hydrocarbons were almost entirely absent from the products using a rod shaped ruthenium oxide supported on Y zeolites and subsequently reduced. However the actual operating catalyst has not been examined [20]. If confirmed this would be the most interesting structure sensitive example in F.-T. synthesis. This structure sensitivity would imply that only ensembles with as an optimum number of individual metal sites are able to initiate and/or effect the chain growth. It is again interesting to point out that larger particles produced essentially methane while smaller particles produced longer chains. This was further illustrated by investigating the activity and the product distribution exhibited by bimetallic catalyst. For example ruthenium associated with the F.-T. inactive copper in Y zeolite showed an overall decreased activity and additionally a comparatively lower methane yield [6].

A variant of the zeolite effect in F.-T. synthesis was exemplified by the addition (mechanical mixing) of HY zeolite to iron and/or ruthenium zeolite [18]. Under such circumstances a narrower range of product distribution was obtained, which was interpreted as the result of cracking of the longer chains. Also iso-products were produced in high yield probably via cracking and isomerization.

Active CO hydroconversion complexes entrapped in zeolites. It appeared that the methane rate depression obtained upon designing small metal particles or alloying F.-T. active elements by an inactive element was unfortunately accompanied by a depressed overall rate. Therefore another method was sought. Transition metal polynuclear carbonyls either adsorbed into- or synthesized within the zeolite were used. This was inspired by the fact that smaller ensembles may presumably totally inhibit methane formation, while preserving selective CO hydrogenation to higher hydrocarbons via non dissociated CO.

In fact, peculiar distributions were observed by combination of various size-cage zeolites and metals known to form stable polynuclear carbonyls. For example Gates and Coworkers [21] obtained a very narrow distribution in CO hydroconversion over CoII A zeolite subsequently reduced by metallic Cadmium. The narrow (almost C₃ hydrocarbons exclusively) distribution was ascribed to the formation of tiny metal particles in A zeolites as a first step followed by a slow conversion to Cobalt Carbonyl(s), as evident from the significant induction period preceding evolution of products. These results prompted further studies [22, 23]. An interesting feature in [22] is the high selectivity to olefins exhibited by Silicalite and concomitant methane rate depression. Silicalite has little (if any) acid sites which is not only in line with methane suppression (see methanation section), but also with the stability of zerovalent carbonyls, as these are readily oxidized by protons).

These features observed in [21, 22] result from :

- a low dissociation capacity of CO thus depressing methane yields.
- a low CH₂ or CO inserting activity into M-C bonds, which accounts for limited chain growth.
- a low hydrogenation activity as emphasized by the high olefin-to-paraffin ratio.

Diluted metal particles (alloys), as well as small metal particles are well known to possess poor CO dissociation as well as poor hydrogenation activity. Similar properties are also exhibited by metal carbonyl clusters. Such clusters are known to activate molecular hydrogen to form hydrides. Although CO or CH₂ insertion into M-H bond, which constitute the propagation steps in F.-T. synthesis [24] has not been reported for soluble polynuclear carbonyl clusters under normal temperature and pressure conditions, it is not excluded that this might occur under more severe

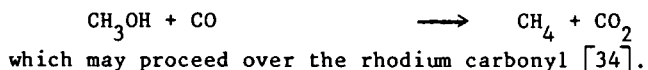
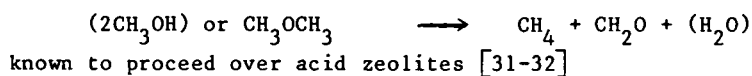
conditions. Metal formyls have been reported in solution, some of which result from the migratory insertion of CO into a Metal-hydride bond [25-28] in hydrido carbonyl complexes including Ta, Th and more interestingly Rhodium as the central atom. Such a rearrangement would be the initial step to subsequent hydrogenation of undissociated CO to form formaldehyde (either as such or dissociatively coordinated) and ultimately to yield methanol. Alternatively hydrocarbonylation of formaldehyde might lead to higher alcohols and olefins.

Drastic product distribution differences appeared upon reacting syn gas mixture over 20 Å zeolite entrapped rhodium particles and over well characterized $\text{Rh}_6(\text{CO})_{16}$ synthesized within Y zeolite cavities. The former catalyst produced essentially methane whereas the latter produced about 60 % methanol + ethanol + $\text{C}_2\text{-C}_5$ olefins and paraffins and only ~ 40 % methane. The overall conversion rate was by two orders of magnitude lower than the rate observed for the 20 Å metal particles.

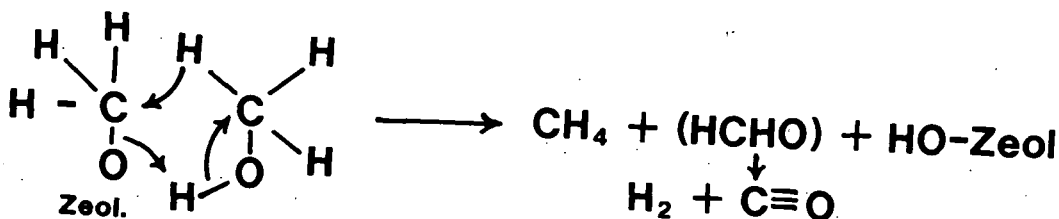
By contrast, 10 Å zeolite-entrapped Rhodium particles exhibited an intermediate behaviour : the initial predominant methane production declined with time on stream, while methanol, and $\text{C}_2\text{-C}_5$ hydrocarbon yield increased [29].

Inspection of the catalyst as it reached a steady state activity and selectivity, comparable to those recorded for $\text{Rh}_6(\text{CO})_{16}\text{-Y}$ catalyst, revealed that the metal particles were indeed converted to the hexarhodium-hexadecacarbonyl cluster [29, 30].

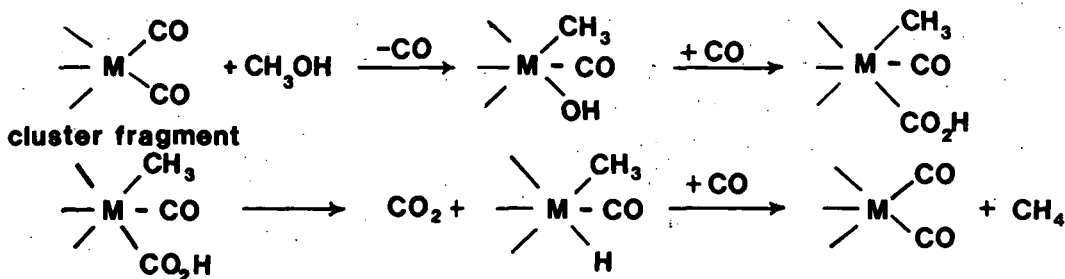
The depressed methane yield as metal particles were progressively converted into $\text{Rh}_6(\text{CO})_{16}$, together with the overall CO conversion decline, are indicative of a poor CO dissociation and CO hydrogenation activity of the polynuclear carbonyl. We even feel that methane produced in this case probably originates from a side reaction derived from methanol conversion



Recent results by Kubelkova and coworkers showed that methanol decomposed at low partial pressure on various zeolites to CH_4 and CH_2O , although it was not suggested that these two compounds were produced via the same pathway [31]. However earlier studies in our laboratory showed a clear correlation between methane and formaldehyde yields when methanol was reacted with a variety of cation exchanged Y zeolites [32]. Recently Chang proposed a concerted mechanism for CH_4 and $[\text{CH}_2\text{O}]$ formation upon reaction of methanol over adsorbed methoxide species [33].



Decomposition of Methanol to produce CO_2 and Methane was shown to occur on Methanol Carbonylation Catalyst via the following mechanism derived by Forster [34].



This approach of occluding well defined carbonyls within zeolites either by direct synthesis or via reduction of the active component using a procedure that prevents formation of protons and subsequent conversion to carbonyls by the H_2/CO mixture proved to be efficient in decreasing the methane yield and increasing the olefins and also to circumvent the S.-F. Distribution since the actual reaction pathway deviates substantially from the F.-T. mechanism [24]. Unfortunately as to the crucial activity problem the answer is not satisfactory as conversion of syn gas over such catalysts is even slower than that observed for conventional F.-T. catalysts already estimated to be rather poor contact masses.

COMPOSITE CATALYSTS

Composites associating a conventional F.-T. catalyst with a zeolitic component

In order to improve the selectivity of conventional F.-T. catalyst whatever its poor activity this approach favoured the adjunction of a zeolitic component meant both to upgrade the F.-T. products and hopefully to prolong the catalyst life time. This idea was first put into practice by Ceaser et al. [35] and by Chang et al. [36]. The results were beyond the initial hope as can be seen from table (3) which shows that a significant improvement is obtained not only considering the product distribution but also in view of the methane yield regression and the enhancement of the conversion rate which practically doubled while little activity improvement was expected.

Table 3

Comparison of the activity and Product distribution of plain F.-T. catalyst and composites F.-T. component + Zeolite component.

Catalyst	T K	P MPa	G HSV h ⁻¹	Conversion H ₂ +CO %	C ₁ %	Oxygenates	C ₅ ⁺	Ar/C ₅ ⁺
ZrO ₂	700	9.13	720	7.5	24.8	34.5	24.0	53.1
ZrO ₂ + ZSM-5	700	9.13	720	13.8	1.6	0	84.8	99.8

This improvement obtained upon mechanically mixing an F.-T. active component with a pentasil type zeolite should be connected to a rapid migration of mobil intermediates from the F.-T. component to be converted on the zeolite surface.

It is obvious, should this be the case, that profound alterations of the product distribution are to be expected following this diversion of the reaction intermediate from an F.-T. pathway to an acid type zeolite catalyzed process. The extent of such alterations is perfectly illustrated in table 3 and by results reported by Ceasar et al. [35], concerning the liquid fraction using a fused Iron-Zeolite composite. An increased stability against waxing was also observed due to cracking of long chain hydrocarbons. It was also shown that an optimum composition, far in favour of the zeolite, was necessary in order to avoid clogging.

The diversion from simple F.-T. mechanism, which is thought to be at the origin of increased life time, was related to the fate of terminal olefins. In a plain F.-T. process these were likely to reenter the propagation cycle and lead to long chains. If mobile enough, in a composite catalyst, they should be isomerized to internal olefins which cannot participate in the propagation step any more. Indeed, a much higher proportion of internal olefins was achieved in composite catalysts with reference to the simple F.-T. component.

These findings would suggest that higher benefits would be expected if the intimacy of the two components were improved, so as to enhance the migration of F.-T. intermediates to the zeolite surface, thus achieving simultaneously higher rates and narrower distributions.

Also, it was apparent that the best synergetic effect should be achieved when the "F.-T." intermediate is most likely to be rapidly converted by the zeolite component. As it is well known that zeolites, particularly those of the pentasil family, are tremendously active in methanol conversion, it was only logical that the next move was to associate a methanol component with a zeolite component.

Composite associating a methanol synthesis catalyst with a zeolitic component

Such catalysts are expected to benefit from the excellent activity of the methanol synthesis component since methanol conversion would not be the limiting step. However no matter how flexible a dual component catalyst might be, its limitations are inherent to its very nature of compromise type catalyst.

Nevertheless the expected benefits from such an association are the following :

- (i) as already mentioned a higher overall conversion rate, which would significantly improve the usual F.-T. rates to a level that would compare more favourably with rates encountered in methanol synthesis.
- (ii) a significant decrease in the total pressure. Indeed the usual pressures, employed in methanol synthesis in order to achieve acceptable rates at the most favourable thermodynamic conditions for methanol formation, may be cut down : conversion of the generated methanol would likely result in a significant equilibrium displacement making it possible to achieve reasonable conversion rates at significantly lower pressures.
- (iii) narrower product distribution, which should be the end products of methanol conversion under the operating conditions exclusively.

In fact, as already underlined, difficulties may be experienced in setting (adjusting) the optimum conditions to operate both components of the composite simultaneously. In particular the usual temperature range for zeolites to show optimum activity is significantly higher than the optimum range for methanol component.

On the other hand, zeolites used to exhibit an appreciable flexibility in directing the reaction towards the production of olefins or aromatics upon adjusting the experimental conditions (temperature and space velocities) and, to a lesser degree, the acidity of the alumino silicate. In the composite catalyst, however, both the activity and the selectivity pattern of the zeolite may be significantly affected by the presence of the other component and by the ambient $H_2 + CO$ atmosphere.

The activity of the dual component catalysts

Several components have been selected independently. The usual procedure was to achieve a fine mechanical mixing of a methanol catalyst : Pd/SiO₂ [37], Pd/MgO [38], Pd doped ZnO-Cr₂O₃, Cu-Pd/ZnO-Cr₂O₃ [39], CuO-ZnO/Al₂O₃ [37], CuO ZnO [40] and ZnO-Cr₂O₃ [39] with a zeolite component usually H type zeolites namely HY ; Hordenites either as prepared or modified, erionite, silicalite and HZSM-5 with various Si/Al ratios, with and without shape selective properties.

In all cases the activity of the composite catalyst was at least an order of magnitude higher than that of the methanol component under the same experimental conditions. This synergetic effect seems to depend on the nature of both components. Although this effect is interpreted in terms of equilibrium displacement by continuous consumption of the methanol produced, little is understood as to the origin of the variation of the extent of this synergetic effect.

Perhaps preparation methods and conditions which would offer the best intimate contact between the two phases, and thus enhance the methanol conversion rate, are not perfectly reproducible. It is not unreasonable, on the other hand, to assume that an intimate enough mixture would enable mobile enough intermediate species, in methanol synthesis, to migrate on the acidic surface of zeolite, to be directly converted into final products, thus bypassing the methanol step and therefore escaping the thermodynamic limitations. This hypothesis seems to be in accordance with the observation that both Pd/SiO₂ and CuO-ZnO/Al₂O₃ associated with the same zeolite did not achieve the same conversion, although their independent methanol synthesis rates were comparable under similar experimental conditions [37].

Pd/SiO₂ appeared to achieve a modest synergetic effect under identical conditions [37, 38]. This was ascribed to poisoning of palladium by aromatics [37]. In addition, although, no data is available as to the characterization of the catalysts, it should not be surprising that palladium particles exceed 50 Å in size and would, therefore, provide for a poor interface between the two components. One might expect that migration, over to the zeolite surface, may, permanently and dramatically, alter the final hydrocarbon distribution toward higher methane yields (see methanation section). Such ageing of palladium-zeolite composites has already been observed [37].

The likelihood of interception of methanol synthesis intermediate(s) which would account for synergetic effects seems to be supported by the steady increase of the yield of hydrocarbons with increasing reaction temperature on the composite catalyst, whereas methanol synthesis rates over the individual "methanol component" passed through a maximum as the reaction temperature increased and then declined drastically.

Also the observation that catalyst composition barely affects the conversion rate is yet another argument in favour of "interface sensitive" reaction than simple trivial multi-step reaction, one would expect that an optimum composition should exist whereby the rate of methanol synthesis on the methanol component should equal the rate of the subsequent conversion on the zeolite. In fact in academic systems the conversion rates achieved were slightly less than those of methanol synthesis though they were obtained under temperature and pressure conditions far away from the optimum thermodynamic conditions for methanol production. As the zeolite component is by far more effective than the other component one would at least

expect that, within a certain composition range, the overall conversion rate should increase linearly with the "methanol component" content in the composite. In fact this was not observed, which suggests that the intermediate migration onto the zeolite is likely to be realistic.

As expected, the nature of the zeolite appeared to be of importance. Silica-rich zeolites exhibited the highest rates, although faujasite type zeolites also exhibited synergetic effects.

By contrast product distributions were drastically dependent upon the nature of the zeolite. Little attention was devoted to the possible mutual influence on the catalyst stability. As already mentioned, the total pressure increase enhanced the yield while increased CO/H₂ ratios slightly depressed the overall production but had marked effects on the composite selectivity.

Selectivity : parameters and trends

Many parameters should affect the selectivity namely the total pressure, the temperature and the feed composition. On the other hand, the nature of the catalyst components and the principal characteristic of each of them : the hydrogenation ability of the MeOH synthesis component, its sensitivity to CO, its dispersion the acidity of the zeolitic component its Si/Al ratio and porous structure should dramatically influence the product distribution.

Too few studies were directed to pinpoint the influence exerted by each of these parameters independently. Rather, studies were directed towards obtaining a hydrocarbon distribution range or simply a desired product. Thus these parameters were optimized to achieve either a narrow spectrum of aromatics [36] or C₂-C₃ paraffin [41] or olefins [38]. However a more detailed study was disclosed by Tominaga and coworkers [37] which investigated the independent influence of a number of these parameters.

The prominent feature of selectivity trends is the total suppression of oxygenates as compared to all F.-T. and MeOH synthesis experiments. This is no surprise since the zeolitic component is usually chosen on the basis of its ability to convert alcohols and analogues at a very high rate.

The other important feature is the methane yield. The composite catalyst was designed to achieve a number of promises among which : increased activity with respect to classical F.-T. synthesis and a depressed methane yield.

The methane production appeared to depend on two main parameters : the temperature and the nature of the MeOH synthesis component and possibly a third parameter under particular circumstances.

The methane production is drastically enhanced by temperature increase this enhancement is well beyond the expected selectivity loss of the methanol synthesis. It probably stems from the subsequent conversion of hydrocarbons produced on the metal (oxide) component which hydrogenating abilities are increased by a temperature increase, as CO poisoning of those properties is partially removed.

The methane production enhancement is even more pronounced when the methanol synthesis component is metallic (usually palladium). It is even more so if one assumes that a temperature increase would result (i) in possible sintering of the metal to produce larger particles which exhibited high hydrogenation and hydrogenolysis activity. (ii) in possible migration from the initial MeOH synthesis carrier to the zeolite carrier which is more acidic and would therefore favour direct conversion of syn gas to methane (see methanation section).

An additional parameter which might influence the methane yield is the nature of the zeolite : while efficient methanol conversion catalyst of the pentasil family produce little methane, medium and large pore catalysts : faujasite, unmodified mordenites produced significant amounts of methane [33] following the reaction



Thus minimizing the methane yield requires low temperatures, oxide type methanol synthesis and pentasil type zeolites or modified mordenites.

The second feature, with few exceptions, is the increase of the paraffin/olefin ratio as compared to the direct methanol conversion on zeolite catalysts. This phenomenon is even more pronounced when the MeOH component is palladium. This is not surprising as the other component of the composite system has enhanced hydrogenating abilities with respect to the pure zeolite component. The possible way to preserving the higher olefin to paraffin ratio observed with straight forward methanol conversion should be sought through an increase of the CO partial pressure to inhibit subsequent hydrogenation of olefins. This however may result in a lowered overall activity.

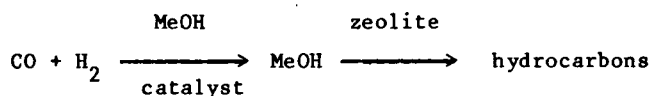
The next possible way which has been successfully investigated is the composition shift to a lower proportion of the MeOH synthesis component especially when it is palladium. In that case, it was observed not only that C₁ to C₃ yield in paraffins decreased but also that selectivity towards aromatics increased which is in line with decreasing hydrogenating and hydrogenolysis activity.

The last feature, we select, is the problem of aromatics production and distribution within the aromatic range. Clearly mordenites and pentasil type zeolites produce significantly more aromatics than any F.-T. catalyst, while composite catalyst including Y type faujasite produce almost exclusively aliphatics. This last observation is in line with previous reports concerning the simple

methanol conversion. This itself is a serious proof that the actual mechanism proceeds via methanol or a particular intermediate to methanol then subsequent conversion of the latter or of both.

Aromatic yield would depend on the possibility for olefins to oligomerize, which implies that the "methanol component" must not have a high hydrogenation activity or that the chances for olefins, when formed, to adsorb on the metallic or oxide component should be lowered. The yield in aromatics would become even lower when metallic components are present instead of oxide components.

The aromatic distribution however has been the subject of more concern and it even seemed to shed some doubt on whether syn gas conversion proceeded actually according the two step mechanism



The prominent feature of this distribution is a higher methylation of the aromatic ring, an important shift of aromatic hydrocarbons from the usual C₇, C₈, C₉ with a peak for xylenes to maximum C₁₀-C₁₁ production among aromatics on pentasil type composite catalysts and a maximum for aromatic distribution at C₁₁-C₁₂ expanding up to C₁₃ on mordenite composite catalysts.

Little has been proposed to account for this commonly recognized effect. Yet it has been observed that increasing CO partial pressure resulted in higher proportion of C₈-C₉ aromatics in the case of the palladium component. This suggests that the palladium component may well be active in the alkylation process (it may also disproportionate substituted aromatics, formed on/in the zeolite, the dealkylated molecules may be subsequently realkylated (by the zeolite) thus progressively shifting the aromatic distribution towards higher carbon numbers.

The alternative is that due to the fact the "methanol component" may only be vicinal to zeolite crystallites the methanol produced in a too low concentration (compared to a methanol feed) could well be converted significantly preferentially at the external surface thus undermining the shape selective property of the zeolite.

PROSPECTS

Too few investigations appeared to be directed at assessing the effect of the preparation method of the composite catalyst. One should think, however, that achieving a more intimate vicinity between centers effecting methanol synthesis or generating intermediate species to methanol and the zeolitic acid sites, would permit a better equilibrium displacement and/or more efficient intermediate interception, to form hydrocarbons, thus greatly improving the overall syn gas conversion rate.

However, in the case of methanol metallic component i.e. Pd the obvious pitfall would be the migration of the metallic component from its appropriate support to the acid zeolite support, which would switch the selectivity towards methane.

As to the selectivity of this process it would be desirable to depress tetra and penta methyl benzene yield. This could, for instance, be achieved by neutralization of the zeolitic external surface or by minimizing this surface using larger zeolite crystals.

In all, this procedure of circumventing the S.-F. Distribution would appear as the most promising especially that an important flexibility in the choice of the composite components is left at the will of the experimentalist.

As to the overall activity, this procedure also seems to yield the highest rates, as these approach the lower methanol production rates with the advantage over F.-T.-derived procedures of providing directly usable fuels.

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