A Statistical Evaluation of Preparation Conditions on the Performance of Ce-Promoted Co-Mo Fischer-Tropsch Catalyst

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Abstract–This paper describes a statistical approach to the optimal selection of preparation conditions for a ceria-promoted Co-Mo catalyst used during CO hydrogenation. Eight catalyst samples based on a full factorial design were prepared via incipient wetness method. Evaluation was carried out in laboratory packed bed reactor using synthesis gas containing H_2:CO=2 at 280 °C and 110 kPa. BET was unaffected by pH although increased calcination temperature induced only a small drop in total surface area. More significantly, catalysts calcined at low temperature (350 °C) suffered a 3-fold loss in metal surface area when treated at high temperatures (550 °C) while an increase in pH improved the metal area value. pH values above the isoelectric point (IEP=5.65) and low calcination temperature favoured activity and alkene selectivity. High reduction temperature, however, appeared to enhance methane suppression. Additionally, 2-factor interactions were statistically more significant than 3-factor interactions at 95% confidence level. Optimisation of the polynomial models describing the response data was also consistent with qualitative inferences.

Key words: Fischer-Tropsch Synthesis, Statistical Evaluation, Co-Mo Catalyst, Optimal Catalyst Design

INTRODUCTION

The ultimate performance of a catalyst is determined by the interplay of several physical and chemical processes involved in its formulation. The preparation of a catalyst may be broadly classified into three stages: chemical synthesis, calcining and activation. One of the major drawbacks in catalyst design for tailored applications is the inability to systematically relate innate physicochemical properties and intrinsic performance (activity and selectivity) to original preparation conditions. This often makes it difficult to compare catalysts from different sources albeit with similar composition. This is especially true for the Fischer-Tropsch synthesis, FTS-(a class of CO hydrogenation reactions) catalysts where a multitude of preparation factors dictate catalyst behaviour [Bartholomew, 1991; Anderson, 1984]. The traditional technique of conducting experimental multivariable optimisation using the 'one-factor-at-a-time' approach is both labour-intensive and time-consuming for catalyst design. A statistical approach is very useful in the analysis of complex multivariate systems particularly when the independent variables may themselves produce interactions with significant effects on the chosen response variable. Two-level factorial designs have a practical appeal to multivariable systems since they can indicate major trends with promising directions with relatively fewer runs in the factor space [Box et al., 1978]. Additionally, effects of factor interactions may be uncovered if runs are replicated. Moreover, as an orthogonal main effect plan, data from factorial design runs may be conveniently represented by orthogonal polynomial models for descriptive and predictive purposes and, by inference, form the basis of an optimisation strategy within the factor space.

Transition metals supported on a variety of oxides such as silica, alumina, titania, zirconia and magnesia are commonly employed as Fischer-Tropsch catalysts. Although Fe, Co and Ru are generally favoured, Fe catalysts are easily oxidised under reaction conditions and require high operating pressure (>1 MPa). Co-based catalysts are, however, selective for gasoline-range hydrocarbons at low operating pressure (0.1-0.3 MPa) and thus, more attractive for laboratory studies. Under the same conditions, Ru offers mainly waxy products and is also significantly more expensive than cobalt. A substantial body of evidence suggests that bimetallic catalyst formulations have synergistic effects on both activity, olefin selectivity and product distribution in the FTS [Stoop and van der Wiele, 1986; Ishihara et al., 1991; Bessell, 1993; Cooper and Frost, 1990]. Whereas these previous investigations have employed bimetallics from traditional FT single metal catalysts, pairing with adjacent elements to the Group VIII members has unique advantages. Mo, for example, is a good desulphurisation catalyst and may therefore confer sulphur-resistant properties on the FT catalyst since commercial syngas contains copious amounts of sulphur. Interestingly, Mo carbide reportedly has FT activity [Park et al., 1991], and in a previous work, we observed the methane-suppression characteristics of a Mo-containing catalyst [Chen and Adesina, 1994]. Ceria in steam reforming catalysts offers anti-coking properties and its addition to the present catalytic system will minimise carbon deposition which is often responsible for on-line activity loss during FT synthesis over cobalt catalysts. As a result, in this study, silica-supported 4Ce : 6Co : 1Mo catalysts

Table 1. Summary of all results

Catalyst code	Preparation condn.			Activity $[\text{mol g}^{-1}\text{s}^{-1}\times10^8]$	EMR	MFOPR	TOPR	α	A_{BET} $[\text{m}^2\text{g}^{-1}$ of unreduced catalyst]	$A_{metal\ area}$ $[\text{m}^2\text{g}^{-1}]$
	pH	T_C [°C]	T_R [°C]							
C11	4.65	350	350	6.02	0.1261	1.7737	0.2311	0.4691	123.50	0.515
C12	4.65	350	350	5.95	0.1255	1.7910	0.2351	0.4313		
C13	4.65	350	350	5.82	0.1194	1.7101	0.2246	0.4343		
C21	4.65	550	350	1.41	0.1272	0.3808	0.1690	0.6273	117.47	0.1536
C22	4.65	550	350	1.52	0.1414	0.4520	0.1906	0.6162		
C31	6.65	350	350	5.96	0.1253	1.7971	0.2335	0.4373	124.24	0.6334
C32	6.65	350	350	6.01	0.1325	1.8249	0.2419	0.4373		
C41	6.65	550	350	3.71	0.1480	1.2346	0.2451	0.4843	117.89	(0.272)
C42	6.65	550	350	3.61	0.1543	1.2269	0.2495	0.4849		
C_{high_TR}	4.65	350	550	1.02	0.0993	0.2314	0.1350	0.7256	123.5	0.515
C51	4.65	350	450	4.23	0.1185	1.0244	0.1857	0.4387	123.5	0.515
C52	4.65	350	450	4.43	0.1130	1.0289	0.1844	0.4407		
C61	4.65	550	450	1.04	0.0986	0.2335	0.1346	0.7203	117.47	0.1536
C62	4.65	550	450	1.01	0.1052	0.2328	0.1382	0.7336		
C71	6.65	350	450	3.08	0.1317	0.8204	0.1968	0.4806	124.24	0.6334
C72	6.65	350	450	3.22	0.1355	0.8658	0.2060	0.4850		
C81	6.65	550	450	1.87	0.1299	0.5015	0.1759	0.5622	117.89	(0.272)
C82	6.65	550	450	1.85	0.1307	0.4984	0.1761	0.5639		

have been prepared via incipient wetness. The present composition was informed by previous experiments carried out in our laboratory. Among others, the most important and easily quantifiable preparation variables are pH, calcination temperature and the reduction temperature. The predominant surface charge on the catalyst support may be positive or negative depending on whether the pH of the solution is below or above the isoelectric point (IEP) of the support material. This affects the adsorptivity and dispersion of the impregnating species. Furthermore, thermal treatment (calcination and reduction) influences catalyst morphology, metal particle size and the impregnant profile within the porous support. Thus, reaction temperature is often used as the lower limit for calcination/reduction temperature. The role of all three factors has been discussed in detail [Adesina, 1996].

EXPERIMENTAL DETAILS

The experimental apparatus is a standard laboratory set-up consisting of a gas purification and delivery section, reaction unit and a product composition analysis station [Chen and Adesina, 1994]. All gases (H_2, CO, He and air) were research grade purity supplied by BOC Gases, Sydney. Even so, an oxy-trap and hydro-purge (Alltech, Sydney) were installed on the feed line (CO/H_2 mixture) to remove oxygen and moisture impurities. Catalyst samples were prepared via incipient wetness technique using quantitative mixtures of aqueous cobalt nitrate and ammonium molybdate in a beaker containing weighed amount of the silica support. Preliminary experiments gave the IEP of silica as 5.65, thus, two pH values, 1 unit above and below the IEP were used, i.e., 4.65 and 6.65. Control of pH was administered via addition of HNO_3 or NH_4OH to the slurry. Calcination temperatures of 350 °C and 550 °C were employed. FTS is rarely carried out

above 350 °C, while an upper level temperature of 550 °C was selected to avoid excessive loss in surface area due to collapse of silica pores at higher temperatures. Reduction was carried out at 350 °C and 450 °C. H_2 reduction at 550 °C gave poor activity as may be seen on Table 1. Consequently, eight catalyst samples were examined (2^3 factorial design). Low temperature N_2 adsorption and H_2 chemisorption (at 100 °C) were employed to determine the BET area and metal surface area, respectively. Catalyst evaluation was carried out by passing a feed containing H_2:CO ratio of 2 over 0.2 g of catalyst particles (d_p=180-250 µm) mixed with 1 g of inert quartz particles of similar size in the packed bed reactor at 280 °C. The reactor was a 9.525 mm OD copper tubing placed in a temperature-controlled tubular furnace. Space velocities in excess of 200 mlg^{-1}min^{-1} were used to avoid transport effects. Only C_1-C_5 hydrocarbons were monitored on the FID-GC due to the differential conversions (<0.5%) occasioned by these experimental conditions. Performance was assessed in terms of catalyst activity, chain growth probability, α, given by the Anderson-Schulz-Flory (ASF) model [Anderson, 1984] and alkene selectivity. The latter may be further decoupled as ethylene-to-methane ratio (EMR), total olefin-to-paraffin ratio (TOPR) and the methane-free olefin-to-paraffin ratio (MFOPR). Thus, there are five response variables. Replicated measurements allowed independent estimation of the error variance for the data.

RESULTS AND DISCUSSION

1. The Effect of Preparation Factors on Physical Attributes

Area measurements from both low temperature N_2 adsorption and H_2 chemisorption were used to assess the impact of preparation conditions on the catalyst structural properties. As may be seen from Table 1, the total area (A_{BET}) was practically

Table 2. Calculated effects and standard errors

Response (run average)±standard error					
Activity×10^8	EMR×10^2	MFOPR×10	TOPR×10^2	α×10^2	Effect type
3.42±0.011	12.73±0.065	9.75±0.035	19.89±0.085	52.6±0.125	average
0.48±0.022	1.73±0.13	2.42±0.069	3.33±0.17	−6.8±0.25	pH
−2.84±0.022	0.42±0.13	−7.6±0.069	−2.81±0.17	14.62±0.25	T_C
1.04±0.022	0.53±0.13	2.99±0.069	2.02±0.17	−8.24±0.25	pH*T_C
−1.67±0.022	−1.39±0.13	−6.49±0.069	−4.85±0.17	5.43±0.25	T_R
−0.65±0.022	0.58±0.13	−2.00±0.069	−0.54±0.17	0.77±0.25	pH*T_R
0.55±0.022	−1.27±0.13	1.92±0.069	−0.89±0.17	3.76±0.25	T_R
−0.029±0.022	−.0038±0.13	−0.74±0.069	−0.86±0.17	−2.11±0.25	pH*T_C*T_R

constant with pH. The average BET area for all samples was estimated as 121.08±3.24 m^2g^{-1} which is close to a value of 120 m^2g^{-1} for the pure silica support. It would therefore appear that changes in pH on either side of the IEP induced neither pore blockage nor creation of new smaller pores. Similarly, the biggest loss (ca. 5%) in BET area was seen only for a change in T_C from 350 to 550 °C. Multivariable linear regression of the data gave:

$$A_{BET}=123.50+2.025X_{pH}-29.02X_{T_c} \qquad (1)$$

where, the dimensionless variables for pH, X_{pH}, and calcination temperature, X_{T_c}, are defined

$$X_{pH}=\frac{pH-5.65}{pH}; \quad X_{T_c}=\frac{T_C-200}{T_C}; \quad X_{T_s}=\frac{T_R-200}{T_R} \qquad (2)$$

From this analysis, it seems unlikely that there will be significant morphological changes with variation in preparation conditions. Chen [1995] had come to similar conclusions using XRD and EDS-TEM data.

The metal surface area (A_{metal}) was, however, strongly influenced by both pH and T_C. Increase in pH improved the metal surface area by as much as 23% (between C1 and C3 specimens) suggesting that high pH favoured better metal dispersion probably due to facilitated transport of positively charged Co and Mo species into the pores in an alkaline environment. This is in agreement with the work of Huang et al. [1986] for Ni catalysts. Nevertheless, a 3-fold drop in A_{metal} was witnessed by simply changing T_C from a value of 350 to 550 °C. Eq. (3) describes the multidimensional linear model for the metal area data.

$$A_{metal}=1.33+0.324X_{pH}-1.739X_{T_c} \qquad (3)$$

Due to an unexpected equipment (Micromeritics ASAP 2000) break-down, the metal area values for C4 and C8 catalyst samples could not be experimentally obtained but were estimated to be 0.272 m^2g^{-1} by using Eq. (3). Eqs. (1) & (3) suggest that the improvement in both BET and metal surface area could be realized by calcining as close as possible to the base temperature of 200 °C (since X_{T_c} will be zero under this condition) and selecting pH higher than the IEP. These tentative inferences regarding the physical attributes are, however, constrained by other factors as will be discussed later.

2. Effect of Preparation Factors on Catalyst Performance

Yates' algorithm provides an efficient and rapid method for the analysis of effects from 2^k factorial design data. The computational procedure used here is well outlined in Box et al. [1978]. Table 2 presents the estimates of the various effects and the associated errors. Amongst the 40 effects shown, the 3-factor interaction effects for activity and EMR are smaller than the corresponding standard error. In all cases, however, 2-factor interactions are quite significant at 95% confidence level This suggests that the effect of the primary factors cannot be interpreted without considering the 2-factor interactions.

2-1. Effect of pH

The pH of the impregnating solution may affect the surface charge of the support and extent of metal dissolution [Huang et al., 1986]. As a result, catalyst activity is influenced since the amount of metal ions adsorbed or deposited controls metal dispersion. Huang and Schwarz [1987] have also observed that C_2 and C_3 selectivity increased at higher impregnating pH consistent with the view that basic support enhances alkene selectivity. It is apparent from Table 2 that increasing pH has a positive effect on all response variables save the chain growth probability, α. At pH values above the IEP, the support surface is predominantly negatively charged; thus, Co and Mo species in solution will experience easier mobility into the pore and hence, higher dispersion. Interestingly, the 2-factor interaction, pH*T_C, also has a positive sign suggesting that a concurrent increase in T_C is required to match an increase in pH in order to improve activity, MFOPR and TOPR. This may, however, be counter-productive for the main effect of T_C (negative sign implies a lowering of T_C is beneficial) on these variables as seen on Table 2. On the other hand, the negative sign for the pH*T_R interaction for any response variable indicates that a lowering of reduction temperature must accompany increase in pH or vice versa.

2-2. Effect of T_C

Calcination is generally carried out in oxidising atmospheres at moderate to high temperatures (300-600 °C) to decompose the metal precursor compounds. This step often has a marked effect on metal dispersion, metal reducibility and alloy formation or metal support interactions. Ishihara et al. [1991] have indicated that alkene selectivity was favoured on catalysts calcined at low temperatures (close to the reaction temperature). However, stability was compromised on these catalysts. On the other hand, high calcination temperature was accompanied by a substantial reduction in BET area, promoted methane formation and low chain growth probability. Interestingly, Rankin and Bartholomew

[1986] reported that mild calcination treatment at 100 °C dramatically influenced the activity and selectivity of Fe : K : SiO₂ catalysts resulting in a non-ASF product distribution. They found that higher calcination temperatures reduced the catalyst adsorption capacities for H_2 and CO and increased the binding energies for these gases. In the present investigation, activity, MFOPR and TOPR decreased with increased T_C in agreement with the studies of Ishihara et al. [1991]. This may be attributed to better dispersion caused by demetallisation at low T_C. Although the effects of T_C and T_R are both negatively signed, the interaction factor, T_R*T_C, has a positive effect for activity suggesting a mutual enhancement between these two factors.

2-3. Effect of T_R

The last step in catalyst preparation, the activation process (or metal oxide reduction) also affects catalyst performance. Reduction temperature determines the extent of oxide reduction, metal particle size and dispersion [Reuel and Bartholomew, 1983]. All response variables except α were favoured at low T_R. This observation may also be due to poor metal dispersion at higher reduction temperatures [Ishihara et al., 1991]. Metal atom agglomeration at high reduction temperatures will reduce the population of potential active sites and, hence, overall activity. Nevertheless, since large metal crystallites will provide adequate sites for growing carbon chain, it is not surprising that high T_R favoured α.

2-4. Model Building and Optimisation Strategy

Further to the qualitative insights provided by the statistical method, a polynomial of the type

$$Y_i = a_0 + a_1 X_{pH} + a_2 X_{T_c} + a_3 X_{T_R} + a_4 X_{pH} X_{T_c} + a_5 X_{pH} X_{T_R} + a_6 X_{T_c} X_{T_R} \qquad (4)$$

may be used to model the data.

Table 3 displays the coefficients of the model for various response variables. The leading coefficient, a_0, represents the response estimate for a catalyst synthesised at the base conditions of pH=5.65, $T_C=T_R=200$ °C. The sign of a_1-a_6 indicates the direction in which the associated factor must be changed (from the base case) to improve the response variable in question. Good agreement between this model and data is reflected by excellent correlation coefficients, R>0.95 in all cases. Moreover, since the model is unimodal, the values of the preparation factors 'best favoured' for a particular response may be obtained from multivariable optimisation of the model by solving the set of simul-

Table 3. Coefficients of orthogonal polynomial arising from statistical analysis of the catalyst design

Response coefficient	$Y_{activity}$	Y_{EMR}	Y_{MFOPR}	Y_{TOPR}	Y_α
a_0	28.035	−8.734	92.805	27.945	71.267
a_1	0.589	−15.040	7.131	−7.899	80.639
a_2	−33.176	49.963	−105.738	21.382	−76.700
a_3	−36.076	41.281	−131.496	−2.980	−107.715
a_4	27.294	13.993	78.740	53.270	−217.098
a_5	−28.069	25.052	−86.254	−23.058	33.187
a_6	41.404	−96.546	145.682	−67.459	284.617
Correlation coefficient, R	0.999	1	0.9956	0.9847	0.9882

Table 4. Values of "best" factor levels for the FT catalyst

Factor	Y_{act}	Y_{EMR}	Y_{MFOPR}	Y_{TOPR}	Y_α	Avg.
pH	5.38	3.67	4.84	3.81	4.93	4.53
T_C	550 (1226)	281	550 (1018)	227	331	387
T_R	550 (1210)	357	550 (1088)	188	237	376

taneous equations, $\partial Y_i/\partial X_j=0$ for all factors for each response variable, i. The outcome of this exercise provides the optimum preparation factor values as shown in Table 4. In practice, silica support suffers significant loss in total area at temperatures above 550 °C; thus numerical optimum T_C and T_R have been capped at this limit. The estimates in brackets are those for the unconstrained conditions. Since it is desirable to design a catalyst that will be most suitable for all five performance indices, an arithmetic average of optimum values has been proposed in the last column as the "best" for the catalyst. These mean values are in good agreement with the qualitative consensus earlier established in the literature. For example, Huang et al. [1986] observed an optimum pH range of 4-5 for the Ni/Al₂O₃ catalyst, while the wealth of information in Anderson [1984] recommends thermal treatment of 350-400 °C to facilitate metal precursor decomposition and metal reducibility for most FT catalysts. In particular, the availability of a mathematical model between preparation conditions and catalyst performance indices now makes it possible to further introduce catalyst synthesis conditions into standard kinetic rate expressions (such as Langmuir-Hinshelwood equations) which can then be directly used in overall reactor modeling and optimization following classical protocols.

CONCLUSIONS

This study has demonstrated that a statistical approach to catalyst design offers insights into the general trends of preparation factor effects. The role of factor-interactions can also be significant and may indeed modulate optimum factor levels in a multi-objective catalyst design exercise. For instance an optimum pH lower than the IEP is a reflection of the attenuating effects occasioned by the 2-factor interactions considered in the optimization strategy as distinct from inferences from single-objective considerations. Statistical design is also useful for procuring a reliable model that relates preparation factors to catalyst performance and ultimately for optimal catalyst synthesis. Moreover, this investigation opens the way, for the first time, for a distinct possibility of carrying out integrated optimization for catalyst design and reactor operation in terms of basic manipulated variables due to the availability of a quantitative relationship between preparation factors and reactor indices via standard kinetic models.

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