



Study of syngas conversion to light olefins by statistical models



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HIGHLIGHTS

- Application of the response surface models in CO hydrogenation to light olefins has been studied.
- Catalyst was a Fe–Co–Mn prepared with precipitation method.
- A quadratic polynomial for CO hydrogenation and alkene yields was successfully fitted to the experimental data.
- The RSM simulated data were also employed to kinetic study of CO hydrogenation.
- A rate equation based on direct reaction of hydrogen from gas phase with molecularly adsorbed CO were proposed.

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ABSTRACT

This paper presents the application of the statistical models in CO hydrogenation to light olefins studies. The effect of support content as a structural variable of a precipitated Fe–Co–Mn catalyst in conjunction with two reactor variables, temperature and total pressure was investigated via an Orthogonal Second-order Design. A quadratic polynomial was successfully fitted to the experimental data and the significance of regression coefficients was statistically investigated by *t*-student test. The results were also compared with simulated artificial neural network results that was constructed and trained based on data collected according to the experimental designs. The response surface model (RSM) simulated data were also employed to kinetic study of CO hydrogenation under condition of support 20%, temperature 340–380 °C, pressure 3–7 bar and a rate equation based on direct reaction of hydrogen from gas phase with molecularly adsorbed CO were proposed. The estimated activation energy under above conditions was 40 kJ/mol.

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1. Introduction

Light olefins are commercially desired products of CO hydrogenation over transition metals. The role of catalyst is very critical and its performance is determined by several important and complex aspects such as preparation method (chemical synthesis, calcining and activation steps), metal, support and promoter type/amount which beside the reaction variables (temperature, pressure, feed ratio and space velocity) determine the final activity and selectivity to the light olefins [1,2]. As mentioned by Mirzaei et al. [2], with a multitude of factors, there is a need for a statistically designed program for CO hydrogenation catalyst development both from the standpoint of runs minimization and information maximization and also the future CO hydrogenation catalyst design will benefit immensely from the application of

statistical tools in the formulation of a well-understood and predictive catalytic system.

Among the different statistical tools, the response surface methodology is a famous procedure in scientific studies. This methodology is a collection of statistical techniques for designing of experiments, building the models, evaluating the effects of factors and searching for the optimum conditions. The classical experiment designs of the methodology are Central Composite Design (CCD) and Box Behnken design. Although statistical methodologies and RSM have been used extensively in various scientific fields as well as catalysis science [3–5], a few study for CO hydrogenation are based on statistical methodologies [6,7] and no study has been conducted based on response surface methodology.

The purpose of RSM is establishing the systematic modeling, demonstrating and optimizing the behaviors via regression/statistical/graphical tools which lead to more efficient understanding of the complicated processes. There are several studies that employed all aspects of response surface methodology. Elavarasan et al. [4]

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Nomenclature

%CO	CO conversion (%)	X_i^*	uncoded value of the <i>i</i> th independent variable at the center point
K	equilibrium constant of elementary reactions	ΔX_i	step change value
k	rate constant	Y	predicted response
m_{cat}	catalyst mass (g)	F_{CO}	molar stream of CO (mol/s)
P	total pressure in the reactor (bar)	<i>Abbreviation</i>	
P_{CO}	CO pressure (bar)	ANN	artificial neural network
P_{H_2}	hydrogen pressure (bar)	ANOVA	analysis of variance
$-r_{CO}$	rate of CO appearance (mol/g s)	LHHW	Langmuire Hinshelwood Hougan Watson
R^2	correlation coefficient	MARI	most abundant reactive intermediate
R_{adj}^2	adjusted correlation coefficient	RSM	response surface methodology
T	value of student's <i>t</i> -test:		
V	volume flow rates (ml/min)		
x_i	coded value of the <i>i</i> th independent variable		
X_i	uncoded value of the <i>i</i> th independent variable		

employed Box-Behnken design to study the combined effect of temperature, time, reactant ratio and amount of ionic liquid catalyst on phenol conversion and selective yield of *p*-cresol in batch alkylation process. Malleswara optimized the amount of V_2O_5 and MoO_3 in a heterogeneous catalysis of ODH reaction (oxidative dehydrogenation) by RSM [5].

The effects of structural variables such as type of the catalyst, promoters and supports, preparation method as well as operating conditions on conversion of syngas, and product contents on monometallic catalysts have been addressed in numerous publications mainly without statistical approaches [1,2]. While the major disadvantage of traditional one-variable-at-a-time techniques are that they do not include interaction effects among the variables, RSM demonstrates complete effects of the parameters on the process with minimum number of experiments. Bimetallic catalysts such as Fe–Co Fe–Mn and Co–Mn are also important commercially in conversion of syngas gas to desired products and have also been investigated in several literatures [2,8,9] without statistical approaches. Ishihara et al. have also investigated Fe–Co, Co–Ni and Ni–Fe over various supports and found that Fe–Co catalysts were the best light olefin products. The employments of ternary Fe–Co–Mn catalysts which are prepared by different techniques and different supports have also been conducted in our laboratory. It was observed that co-precipitation method and MgO as support give very good selectivity to light olefins.

In this study, we have presented the application of the response surface methodology in modeling of CO conversion and light olefin yields on Fe–Co–Mn/MgO supported catalysts. A simple kinetic study was also conducted with the aide of RSM simulation data.

2. Experimental

The effect of support content and reactor condition on CO conversion and yield of light olefins has been studied. The active metals were a ternary mixture of Fe–Co–Mn which is prepared with precipitation method. A Box Behnken design has been employed for simultaneous study of structural factor (support content) and operating factors (reactor temperature and pressure). The levels of the factors were as follows:

– MgO (%): 5–25, Pressure (bar): 1–7, Temperature (°C): 280–380

The support of this catalytic system was MgO. The choice of support for CO hydrogenation catalyst is dictated by several considerations including basicity, electronic modification, dispersion and metal-support interactions. Four popular supports, SiO_2 , TiO_2 , Al_2O_3 and MgO were employed in primary studies to check the activity

and selectivity to light olefins and it was observed that MgO gives satisfied results, so it was chosen in the present study [10].

In the co-precipitation method, aqueous solutions of cobalt nitrate, iron nitrate and magnesium nitrate with similar molar ratios were pre-mixed and the resulting solution heated to 70 °C in a round-bottomed flask fitted with a condenser. Aqueous Na_2CO_3 was added to the mixed nitrate solution with stirring while the temperature was maintained at 70 °C until optimized pH was achieved. It is important to that the optimized PH value has been determined according to the analytical calculations, the optimized PH value of co-precipitation was 9.7. The resulting precipitate was left in this medium for 2 h. The aged suspension was after that filtered, washed several times with warm distilled water until no further Na^+ was observed in the washings tested by flame atomic absorption.

The precipitate was then dried in the oven (120 °C, 16 h) to give a material denoted as the catalyst precursor, which was subsequently calcined in static air in the furnace (600 °C, 6 h) to give the final catalyst. For preparation of the supported catalysts, the different amount (5, 15 and 25 wt.%) of MgO support has been added separately to the mixed solution of iron and cobalt and magnesium nitrates.

The CO hydrogenation reaction was conducted in a 1 cm diameter tubular fixed bed micro-reactor with a composite catalyst of 1 g. The catalyst was diluted with quartz wool for heat dissipation during CO hydrogenation process. The reaction tube was placed in a furnace equipped with temperature controller (JUMO IMAGO 500 Co.). Prior to the reaction, the catalysis was activated in situ using H_2 (30 ml/min) and N_2 (30 ml/min) gas mixture at 400 °C for 2 h. After reduction, purified H_2 , CO and N_2 gas were fed into the reactor. The flow rates of H_2 , CO and N_2 were controlled by three mass flow controllers (BROOKS 5850E). It was possible to divert the feed mixture entering or the products leaving the reactor to the GC for analysis. The feed and product gases were analyzed for CO and C hydrocarbons by an on-line GC model UNICAM Pro GC + (THERMO ONIX Co.).

The GC has three channels; Hydrocarbon channel equipped with a capillary column type *CSAlumina* (length 30 m, diameter 0.53 mm), hydrogen channel consists of two packed column, *Haysep Q*, 60–80 mesh (length 1.5 m, diameter 0.125 in) and *MolSieve 5A* (length 2 m, diameter 0.125) and Permanent gases channel equipped with two columns, *Haysep QS*, 60–80 mesh (length 3 m, diameter 0.125) and *MolSieve 5A* (length 2 m, diameter 0.125). The hydrogen and permanent channels are related to a TCD and hydrocarbon channel are contacted to an FID. The volume flow rate of H_2 , CO, N_2 and ratio of H_2/CO was kept constant (30 ml/min, 15 ml/min, 30 ml/min and 2, respectively) in all experiments.

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