Selective synthesis of α-olefins on Fe–Zn Fischer–Tropsch catalysts

Stuart L. Soled^a, Enrique Iglesia^b, Sal Miseo^a, Bruce A. DeRites^a and Rocco A. Fiato^c

 ^a Exxon Research and Engineering Company, Rt. 22 East, Annandale, New Jersey 08801, USA
^b Department of Chemical Engineering, University of California, Berkeley, CA 94720, USA
^c Exxon Research and Engineering Company, PO Box 101, Florham Park, New Jersey 07932, USA

Fe/Zn oxides promoted with K and Cu selectively produce α -olefins at typical Fischer– Tropsch synthesis conditions (2/1 H₂/CO, 1 MPa, and 270°C). The simultaneous presence of K and Cu introduces a synergistic activity enhancement while maintaining the high olefin selectivity obtained by alkali promotion. Structural and morphological differences in Fe–Zn oxides prepared from ammonium glycolate complexes or precipitated from nitrate solutions have only a small influence on catalytic properties. Catalyst behavior is strongly influenced by synergistic promoter effects (Cu, K) and by the controlled in situ conversion of iron oxide precursors to carbides.

Keywords: Fischer-Tropsch; a-olefins; iron-zinc oxides

1. Introduction

Synthesis gas conversion to linear α -olefins in the C₇-C₁₄ molecular weight range produces high value plasticizer and detergent intermediates. Several recent reviews have addressed the conversion of synthesis gas to light (C₂-C₄) olefins [1,2]. Our studies address the synthesis of larger olefins, predominantly in the C₅-C₁₅ range.

Recent studies show that primary α -olefin products of the Fischer-Tropsch (FT) synthesis on Fe undergo secondary reactions [3]. As CO dissociates, surface carbidic species form CH₂ monomers, which add to growing chains described approximately by Flory polymerization kinetics [4]. Chains can terminate either by β -hydrogen abstraction to form α -olefins or by H-addition to form paraffins [5]. Olefins undergo secondary isomerization, hydrogenation, or chain initiation to produce internal or branched olefins, paraffins, or larger hydrocarbons, respectively. In this work, we try to maximize α -olefin selectivity during FT synthesis by controlling these secondary reactions.

Several groups have studied FT synthesis in backmixed slurry reactors because these reactors are well-suited for exothermic reactions and require low capital and operating costs [6]. In a well-mixed slurry reactor, the feed gas composition equals that of the exit gas, so the entire catalyst is exposed to a gas stream at the same redox potential. With concurrent water-gas shift, the effective H_2/CO ratio in a backmixed system increases dramatically as conversion increases. Obtaining high olefin selectivities at conditions that favor secondary hydrogenation reactions presents a significant challenge. The CO₂ formed during water-gas shift reactions also limits carbon utilization efficiency, so reducing shift activity during Fecatalyzed FT synthesis also presents an important challenge.

Here, we compare Fe–Zn catalysts formed from oxide precursors with different structure, surface area, particle size, and morphology. We have prepared spinel (Fe₃O₄-related) precursors by decomposing ammonium glycolate complexes and corundum (Fe₂O₃-related) precursors by precipitating aqueous nitrate solutions with base and have compared the performance of the resulting catalysts in slurry and fixed-bed reactors. Our previous studies have shown the importance of forming and maintaining an iron carbide phase free of polymeric carbon in order to maximize olefin selectivity [7]. The current catalysts, designed on these prior criteria, produce α -olefins in the C₅–C₁₅ range with high selectivity (~ 70%). We have used zinc oxide as a structural promoter rather than manganese oxide because zinc will maintain its divalent state during controlled pH precipitation, thereby facilitating the formation of ternary oxide phases, whereas manganese easily oxidizes and phase segregates.

2. Experimental

2.1. CATALYST PREPARATION

All catalysts were prepared as oxides, promoted with Cu and K, and then activated in situ using synthesis gas at reaction conditions. Iron oxide/zinc oxide catalyst precursors were prepared using three procedures: (i) decomposition of mixed-metal ammonium glycolate complexes, (ii) increasing pH precipitation (final pH \approx 9.5) of aqueous iron/zinc nitrate solutions using ammonium hydroxide, and (iii) constant pH (pH = 7) precipitation of aqueous iron/zinc nitrate solutions with ammonium carbonate. Catalyst precursors with iron to zinc atomic ratios from 3/1 to 19/1 were prepared. The K, Cu promoter levels were chosen as atomic (Fe + Zn)/Cu: 100/1 and (Fe + Zn)/K: 100/2 from extensive tests previously carried out on related Fe–Mn catalysts [8,9].

For the ammonium glycolate synthesis method (i), we adopted a procedure first described by Courty and Delmon [10]. Fe and Zn nitrates (Baker, Reagent Grade) were dissolved in deionized water. To an aqueous solution containing glycolic acid (molar ratio: glycolic acid/(Fe + Zn) = 4/1), a sufficient quantity of NH₄OH

was added to raise the pH to 6.5, and this solution was added to the Fe/Zn nitrate solution. As this combined solution dried, a foam-like X-ray amorphous solid formed. After calcination at 350°C for 1 h, the X-ray spectrum showed a single phase spinel structure, isostructural with Fe₃O₄, but with a slightly smaller lattice constant. This oxide was promoted by adding 2 at% K (using a K_2CO_3 solution) and/or 1 at% Cu (using a Cu(NO₃)₂·3H₂O solution), and then dried at 120°C.

In the increasing pH precipitation technique (ii), Fe and Zn nitrates were dissolved in water and the two solutions were mixed and then heated to 80°C. A sufficient quantity of NH₄OH (\sim 14 M) was added until the solution pH reached 9. The resulting precipitate was filtered, washed with several liters of water (25°C), dried at 100°C overnight, and calcined at 350°C for 1 h. X-ray diffraction showed primarily a corundum phase isomorphous with Fe₂O₃. Promoters were added as described above for the glycolate-derived sample.

In the constant pH precipitation technique (iii), Fe and Zn nitrate solutions (1 M) were mixed together to obtain a given atomic Fe/Zn ratio. A 1 M solution of ammonium carbonate was prepared separately. The mixed nitrate solution was added at approximately 15 cm³/min flow into a large flask held at 80°C, while its contents were continuously recirculated through a centrifugal pump to achieve thorough mixing. The ammonium carbonate solution was fed separately and its flow was controlled to maintain the slurry pH at 7. Within 1–2 min of initiating the process, the pH equilibrated at 7.0 (±0.1), where it remained throughout the preparation (~ 1 h). The resulting precipitate was washed with water, dried at 110°C overnight, and calcined at 350°C for 1 h. X-ray diffraction revealed a corundum phase. This material was promoted with 2% K, 1% Cu as described for the other samples.

2.2. CATALYST CHARACTERIZATION

Powder X-ray spectra were collected using a wide angle X-ray diffractometer and Cu K α radiation. Surface areas were measured by a multipoint N₂ BET measurement on an Omnisorb model 360. SEM micrographs were taken on a Jeol 35C scanning electron microscope operating at 15 kV electron energy. Iron-57 Mössbauer spectra were collected in transmission mode (at Mössbauer Spectroscopy Consultants) and fitted to a Lorentzian profile on samples.

Catalytic tests were performed in both stirred and fixed-bed reactors. The stirred reactor consisted of a 300 cm³ Parr autoclave mixed by an impeller at 600 rpm without gas recirculation. The slurry liquid initially consisted of distilled $385^{\circ}C^{+}$ FT synthesis products. The reactor was loaded with 90 g of this liquid and 0.75– 2.5 g of catalyst and then heated in 2/1 H₂/CO to 260°C at about 120°C/h. In fixed-bed runs, 1 g (0.9 cm³) of catalyst was charged into a tubular reactor (20 inch length and 0.5 inch diameter). The catalyst was mixed with quartz chips (150– 220 µm, HNO₃-washed, rinsed, and calcined at 600°C) such that the total volume of catalyst charge (catalyst + diluent) was 18 cm³ with a catalyst to diluent volume ratio of 0.1/1. A 12-point thermocouple monitored the axial temperature gradient. In all runs, the catalysts were pretreated in a $2:1 \text{ H}_2/\text{CO}$ feed during a 3-5 h ramp to reach reaction temperature.

Synthesis gas was purified using activated charcoal (Matheson-454) and 13X zeolite (Matheson-451) canisters. Pre-mixed cylinders of 2.04 $(\pm 0.05)/1$ ratio H_2/CO containing 7% nitrogen as an internal standard (Air Products, 99.9+%) were used. Gas feed rates were controlled by Brooks mass flow controllers.

The products were partially condensed in a vessel kept at 125°C, and the remaining products were analyzed on-line by an HP 5880 gas chromatograph, CO, CO₂, N₂, and $C_1 - C_4$ hydrocarbons were separated by Porapak R (Supelco) columns and detected by thermal conductivity or flame ionization detectors. A second FID connected to a capillary column (HP-Crosslinked Methyl Silicone Gum) was used to detect C_{1} - C_{13} hydrocarbons, as well as alcohols and aldehydes. C_{16+} samples were removed from the condenser vessel. These products were analyzed up to C_{50} using a capillary column and a FID detector. For the fixed bed runs, we combined the online C_{13-} analysis with an off-line analysis of the C_{16+} collected fraction and interpolated points in between. For the stirred reactor runs, we only used the on-line C_{13-} analysis to avoid any interference from the higher boiling slurry solvent. Selectivities were calculated from these data and are reported as the percentage of reacted CO that appears as a given product, i.e. on a total C basis. We used a N_2 internal standard in order to ensure accurate material balances. The runs were carried out for several days and products were collected and analyzed after reaching steady-state liquid compositions (24-36 h).

The effects of particle size, synthesis gas and CO_2 pressures were examined in the fixed-bed reactor. Separate particle fractions with average diameters of 0.10, 0.26 and 1.5 mm were obtained from promoted powders by crushing and sieving large pelletized particles. For the CO_2 addition experiments, a carbon dioxideargon mixture (90/10) was added to the synthesis gas (H₂/CO/N₂) to set the CO_2/CO ratios at 0.2 and 0.4.

3. Results and discussion

3.1. PREPARATION AND CHARACTERIZATION OF CATALYST

Our previous studies showed that selectivity to α -olefins is high when Fe catalysts contain (1) carbided surfaces, (2) low amounts of polymeric carbon, (3) high surface area stabilized by a non-reducible metal oxide as a structural promoter and (4) alkali *and* copper promoters. In our samples, the zinc oxide component acts as a structural promoter by inhibiting sintering of iron carbide. Alkali reduces the extent of secondary hydrogenation and acid-catalyzed reactions, while copper lowers the temperature required to convert the oxide to carbide [7–9]. Potassium may also increase the surface coverage of CO during FT synthesis and thus increase olefin selectivity and product molecular weight. The conversion of the oxide precursor to iron carbide is required for high olefin selectivity [7]. We attempted to facilitate the reduction by preparing small particles of the ternary iron oxide precursors. We used a technique involving the formation of fine particle mixed metal oxides from ammonium glycolate complexes [10]. When drying a solution of the component nitrates, glycolic acid and ammonium hydroxide, a low density amorphous solid forms; on calcination it converts to an oxide isomorphous with Fe_3O_4 (i.e. with a spinel structure). Snel has recently reported the synthesis of Fe-base catalysts using citrate complexes related to our glycolate precursors [11].

The oxides derived from the glycolate precursors form small particles. Figs. 1a and 1b show representative scanning electron micrographs, revealing the spongelike appearance of the glycolate-prepared oxides, where the void areas apparently result from expulsion of gases during calcination. This appearance differs from that of the precipitated oxide particles (fig. 1c), which appear larger and more densely packed. The glycolate derived oxides had higher surface areas (53–76 m²/g) than the precipitated catalysts (21–26 m²/g). The scanning electron micrographs indicate smaller particles are formed from ammonium glycolate precursors. The oxides convert to carbide on exposure to H₂/CO at reaction conditions. Although the smaller particles of the glycolate-derived oxide may reduce at slightly lower



Fig. 1. Scanning electron micrographs of Fe–Zn oxides. (a) and (b): Fe_{2.8}Zn_{0.2}O₄ prepared from an ammonium glycolate precursor, and (c) constant pH precipitated Fe/Zn (19/1) oxide.



Fig. 1. (Continued.)

temperature, the results below suggest that once converted to carbides, the different oxide precursors contain a similar number and type of active sites.

Catalytic tests were used to determine the effect of changing chemical and promoter composition. Three catalysts of differing iron zinc ratio (19/1, 5/1 and 3/1) were prepared from ammonium glycolate precursors, promoted with 2 at% K and 1 at% Cu, and tested in a 300 cm³ stirred autoclave. The catalysts were run for 40–100 h and showed constant activity and selectivity after an initial 2–4 h activation period during which the active carbide forms. The experimental conditions and results are shown in table 1. Catalysts with the higher Fe/Zn ratios (5/1, 19/1) show both high activity and α -olefin selectivity, while the lower Fe/Zn ratio catalyst (3/1) was less active. Ternary iron oxide phases containing more difficult to reduce transition metal elements reduce and carbide at higher temperatures than pure iron oxides. The results in table 1 suggest that samples with higher Fe content reduce and carbide readily at 270°C, and form active and selective olefin synthesis catalysts.

We also examined the role of Cu and K promoters in achieving high olefin selectivity and high activity. Table 2 shows the effect of the individual K and Cu promoters, as well as their combined effect for a 19/1 Fe/Zn oxide catalyst prepared by precipitation with NH₄OH. Table 2 shows that simultaneous promotion of Fe–Zn with K and Cu leads to high activity and high olefin selectivity. The catalyst promoted with just K showed similar olefin selectivity as the doubly promoted catalyst, but much lower activity. This synergistic effect has been previously observed with Fe–Mn and Fe–Co catalysts [8,12].

	Fe _{2.8} Zn _{0.2} O ₄	$Fe_{2.5}Zn_{0.5}O_4$	Fe _{2.25} Zn _{0.75} O ₄
Fe/Zn ratio	19	5	3
g-at%K	2	2	2
g-at%Cu	I	1	1
catalyst weight (g)	2	2	2
temperature (°C)	270	270	270
pressure (kPa)	500	500	500
H_2/CO ratio	2	2	2
H_2/CO flow (cm ³ /min)	180	180	180
CO conv. (%)	80	84	32
carbon selectivity (%)			
CH4 (total C basis)	1.7	1.7	2.3
CO ₂	40	38	40
olefins in $C_2 - C_4$ (%)	93	92	85
C ₁₀ composition			
α-olefin (%)	63	61	n.l.o. ª
<i>n</i> -paraffin (%)	14	15	n.l.o.
other components (%)	23	24	n.l.o.

Table 1 Determination of optimum Fe/Zn ratio

^a n.l.o.: no liquid obtained.

Promoters	None	К	Cu	K and Cu
g-at%K	0	2	0	2
g-at%Cu	0	0	1	1
catalyst weight (g)	2	2	2	2
temperature (°C)	270	270	270	270
pressure (kPa)	500	500	500	500
H_2/CO ratio	2	2	2	2
H_2/CO flow (cm ³ /min)	180	180	180	180
CO conv. (%)	41	33	34	73
carbon selectivity (%)				
CH4 (total C basis)	13.7	2.0	10.1	1.9
CO ₂	37.9	34	52	40
C ₄ olefin/paraffin ratio	0.11	8.0	0.44	7.9

Table 2 Contrast of singly and doubly promoted Fe/Zn(19/1) catalysts

The presence of dual promoters exerts the strongest influence on catalytic performance, with physical morphology and particle size differences playing a secondary role in determining the number of available surface sites in the active forms of the working carbide catalysts. For similar Fe/Zn ratio and Cu, K promoter level as seen in table 3, the glycolate and controlled pH catalysts are more active than the ascending pH precipitated catalyst.

At 1 MPa and 270°C, we observe a range of productivities with different preparations ranging from 2.7 to 4.5 ℓ of CO converted per gram of catalyst per hour, about an order of magnitude higher than with a fused promoted iron (ammonia synthesis) catalyst run under comparable conditions [13].

3.2. FIXED-BED AND STIRRED REACTORS

Previous studies have shown that reaction environment (e.g., extent of backmixing) influences catalyst structure, concentration of carbide and oxide phases, and

	Ammonium glycolate precursor	NH₄OH precipitated	Controlled pH precipitation
catalyst weight (g)	2	2	2.5
temperature (°C)	270	270	270
pressure (kPa)	500	500	500
H_2/CO ratio	2	2	2
H_2/CO flow (cm ³ /min)	180	180	400
CO conv. (%)	80	73	54
C selectivity (%)			
CH4 (total C basis)	1.7	1.9	2.4
CO ₂	40	41	40
C ₄ olefin/paraffin ratio	7.9	7.2	6.5

K, Cu-promoted Fe/Zn (19/1) oxides prepared with different precursors

Table 3

FT synthesis selectivity [6]. In fig. 2, we compare the doubly-promoted precipitated Fe-Zn catalyst in stirred and fixed-bed reactors. In both reactors, the catalysts were activated at 500 kPa in 2/1 H₂/CO and then the pressure was increased to 1 MPa. The average particle size of the fixed bed catalyst was 100 um. Similar synthesis rates and selectivities were observed with a step change occurring as the operating pressure was raised from 0.5 to 1.0 MPa. No appreciable deactivation occurred in the stirred autoclave during 150 h runs, whereas in the fixed-bed reactor. the catalyst deactivated slowly (69 to 62% conversion in 150 h). Fig. 3 shows that the methane selectivity remains similar in stirred and fixed-bed reactors in runs exceeding 300 h. Methane is slightly higher in the fixed-bed than in the stirred reactor as expected from the larger average catalyst particle size, which introduces transport restrictions and higher intraparticle effective H_2/CO ratios near active sites [14]. In both units, CO₂ selectivities lie between 42 and 49%, near the thermodynamic equilibrium of the water-gas shift at reaction conditions (see table 7). Thus. we conclude that in the absence of significant transport limitations, synthesis rates and selectivities in these plug-flow and backmixed reactors are similar.

3.3. EFFECT OF REACTION CONDITIONS ON RATE AND SELECTIVITY

Higher temperatures lead to faster CO hydrogenation rates and higher α -olefin selectivity, but also increase deactivation rates and decreases product molecular weight. As conversion increases, in both the stirred tank and fixed-bed reactors, C₄ and C₉ α -olefin/*n*-paraffin ratios and CH₄ selectivity increase. This CH₄ selectivity trend parallels that of supported cobalt catalysts, but the increase in olefin content with conversion is opposite to the behavior of supported cobalt. This difference in behavior between Co and Fe during FT synthesis may result from the



Fig. 2. CO conversion for precipitated Fe-Zn/2K, 1Cu in stirred autoclave and fixed-bed at 15000 v/v/h, 270°C, 2/1 H₂/CO.



Fig. 3. CH₄ selectivity for precipitated Fe–Zn/2K, 1Cu in stirred autoclave and fixed-bed at 15000 v/v/h, 270°C, 2/1 H₂/CO.

simultaneous shift reaction that occurs during Fe-catalyzed synthesis. This increases the effective H_2/CO ratio with increasing conversion and therefore increases methane selectivity. The increasing α -olefin/*n*-paraffin ratio observed with increasing conversion suggests that at higher conversions and especially in backmixed reactors, secondary olefin hydrogenation reactions are inhibited by the water produced during FT synthesis and their contributions diminish even as the H_2/CO ratio increases [15].

Table 4 summarizes the selectivity parameters for the stirred reactor at 500, 1000 and 2000 kPa. Increasing pressure increases synthesis rates, but decreases average molecular weight and olefin content in products. We find that increasing H_2/CO gas ratios between 0.5 and 2.0 increases synthesis rate, lowers the olefin content slightly, and decreases the deactivation rate. For H_2/CO ratios less than one, deactivation becomes significant, as coke deposition rates apparently increase. In addition to *n*-paraffins and α -olefins, small amounts of alcohols and aldehydes (~ 7-10%), internal olefins (~ 5%), and minor amounts of other oxygenates (acids, ketones) and methyl-branched olefins are formed.

	500 kPa	1 MPa	2 MPa
CH ₄ (CO ₂ -free) (%)	4.5-5.5	5.2-6.6	6.1-6.9
CO ₂ (%)	45	44	43
α-olefin/n-paraffin			
C ₄	5.3	4.5	3.0
C ₉	4.6	3.5	2.4
C ₁₃	3.8	2.6	1.9

Stirred reactor selectivities with Fe-Zn/2K, 1Cu, at 270°C, 2/1 H₂/CO, at conversion above 60%

Table 4

	500 kPa	1 MPa	
$\overline{CH_4(CO_2-free)}$	4.7	5.9	
CO ₂	43	42	
α-olefin/n-paraffin			
C ₄	4.2	2.8	
C9	3.6	3.0	
C ₁₂	3.1	2.1	

Table 5 Selectivities in fixed-bed reactor for Fe–Zn/2K, 1Cu, 0.15–0.43 mm particles, 270°C, 2/1 H_2/CO , 15000 v/v/h

Selectivities obtained during the fixed-bed runs at 500 kPa and 1 MPa are listed in table 5. The results are similar to those reported for the same catalyst in a stirred reactor.

3.4. PARTICLE SIZE EFFECTS IN FIXED-BED REACTOR RUNS

We observed modest changes in selectivities with changes in particle size (table 6). For the largest particles, the iron-time yield (moles CO converted/g-at Fe h) drops markedly, while CH₄ increases and olefin/paraffin ratio decreases gradually with increasing particle size. This behavior arises from intraparticle transport restrictions of the CO reactant. These CO transport restrictions increase H_2/CO ratios near active sites and decrease both FT synthesis rates and chain growth probability.

3.5. MOLECULAR WEIGHT DISTRIBUTION

The reported molecular weight distributions for iron catalysts in small laboratory reactors is controversial, with some workers fitting the distributions with two or three values of α [15]. Recently, Iglesia et al. reported a detailed molecular weight distribution analysis for FT synthesis products formed on cobalt, ruthenium and iron catalysts [13,16]. They quantitatively account for the curvature by

Particle size effects for $Fe-Zn/2K$, ICu in fixed-bed, at $2/0^{\circ}C$, 24–60 h on stream					
Pressure (psig)	ParticleFe time yield (molessize (mm)CO conv./g-at Fe h)		%CH ₄ C ₄ 0 (CO ₂ -free)		
75	1.5	1.3	5.8	3.20	
75	0.26	5.4	5.3	3.93	
75	0.10	5.2	4.7	4.22	
150	0.10	6.8	5.5	n/a	
150	0.26	6.7	5.8	n/a	

Table 6 Particle size effects for Fe-Zn/2K, 1Cu in fixed-bed, at 270°C, 24-60 h on stream

assuming an increasing probability for olefin readsorption and chain initiation as the larger olefins face more severe transport restrictions as they are removed from catalyst pores. Our Fe–Zn catalysts show similar curvature in the Flory plot (fig. 4).

3.6. CO₂ COFEED EXPERIMENTS

The effectiveness of the proposed α -olefin synthesis scheme is limited by the loss of carbon to CO₂ as well as by the formation of products outside the desirable size range. During FT synthesis, about 50% of the CO is converted to CO₂ in secondary water-gas shift reactions that are near equilibrium during CO hydrogenation. By including CO₂ with the H₂/CO reactants to shift the equilibrium, the reaction can be run with lower or even zero net CO₂ production. Table 7 illustrates this effect where two ratios of CO₂ were cofed with CO and the resulting product stream contained decreasing amounts of CO₂. Calculations indicate that at the conditions of this experiment, we would require a CO₂/CO ratio of 16/1 to avoid any CO₂ formation in the water-gas shift reaction.

3.7. MÖSSBAUER SPECTROSCOPY

Mössbauer spectra were collected on samples embedded in slurry wax following runs in the stirred tank or fixed bed at 270°C, 1 MPa, and 2/1 H₂/CO. The data were fitted to Lorentzian profiles, for mixtures of chi and epsilon prime carbides and magnetite. For the stirred tank run, a nearly equal mixture of ε' and χ' carbide was present with a small amount of magnetite (~ 10%). For the fixed-bed run, a sample taken from near the top of the bed contained almost pure ε' carbide.



Fig. 4. Flory plot for precipitated Fe–Zn/2K, 1Cu in fixed bed at 15000 v/v/h, 270°C, 2/1 H₂/CO, 1 MPa.

CO ₂ /CO feed ratio	Space velocity (v/v/h)	CO conversion	Experimental net CO ₂ selectivity (%)	Predicted net CO ₂ selectivity (%)
0	9200	56	42.7	48.6
0.2	9200	59	37.2	46.3
0.4	9700	55	35.3	43.0
16.6	_	56	-	0

Table 7 CO₂ effects on water-gas shift selectivity for Fe/Zn/2K, 1Cu, 0.1 mm particles, 1 MPa, 270°C

4. Conclusions

Fe/Zn oxide precursors promoted with K and Cu produce active and selective olefin synthesis catalysts. Oxides prepared from glycolate precursors or controlled pH precipitation were slightly more active than those prepared by ascending pH. The catalysts behave similarly in stirred and fixed-bed reactors as long as small particles (<0.1 mm) are used in both reactor systems. At 1 MPa, 270°C and 2/1 H₂/CO maximum productivities of about 5 ℓ CO converted per gram of catalyst per hour were obtained. C₅-C₁₅ olefin yields were approximately 25% of the hydrocarbon fraction.

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