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Effects of Calcination on the CO Hydrogenation Activity/Selectivity Properties of Potassium-Promoted Iron/Silica

INTRODUCTION

Much of the previous research in Fischer–Tropsch (FT) synthesis (*1–5*) has been directed toward development of catalysts having higher selectivities to premium hydrocarbon products such as light olefins or gasoline. Nevertheless, the product distribution of conventional, non-shape-selective FT catalysts is governed by Anderson–Schulz–Flory (ASF) polymerization kinetics (*6–8*) which place severe restrictions on the maximum yield of any given product or product range, e.g., a maximum of 47 wt%. C_5–C_{11} gasoline range hydrocarbons. Attempts to circumvent the limitations of ASF kinetics through incorporation of catalyst additives, strong metal–support interactions, and supported metal clusters have generally met with little success, although these catalyst modifications can be used to tailor catalyst selectivities for branched paraffins, olefins, and alcohols within the constraints of the ASF model.

It was reported in a very early work (*1*) and confirmed in more recent work (*9–16*) that alkali additives, typically in the form of potassium salts, improve the selectivity of iron catalysts for olefins and higher molecular weight hydrocarbons (*1*). Dry *et al.* (*9–16*) concluded that observed promoter effects, i.e., increases in chain propagation probability, and CO_2 production rate are explained by the surface basicity and electron donor character of the added alkali. However, there are still many aspects of potassium promotion that are poorly understood, for example, why potassium increases activity and liquid yields under certain reaction conditions while decreasing activity and increasing gas yields under another set of conditions (*16*). Recent studies (*17–19*) show that pretreatment and support can significantly influence the activity and selectivity properties of these catalysts.

This study was undertaken to determine the effects of potassium level and calcination pretreatment on the activity and selectivity properties of potassium-promoted Fe/SiO_2. The results reveal that a mild calcination treatment can dramatically influence the activity/selectivity behavior of $Fe/K/SiO_2$ catalysts, and they provide evidence of an alternative synthesis route in CO hydrogenation on these catalysts.

EXPERIMENTAL

A 15 wt% Fe/SiO_2 and a series of 15% Fe/SiO_2 catalysts containing 0.2, 1.0, and 3.0 wt% potassium were prepared by impregnation as described previously (*20*). Samples of each catalyst were then dried in air at 373 or calcined at 473 K for 2 h and reduced at 723 K for 36 h in flowing hydrogen that had been carefully purified (*20*). The physical and chemical properties of these catalysts were determined from H_2, CO, and CO_2 adsorption measurements, X-ray diffraction, temperature-programmed desorption, and Mössbauer spectroscopy in a companion study (*20*). Activity/selectivity tests were performed in a single-pass, differential, fixed-bed microreactor system at 1 atm total pressure, a H_2/CO feed ratio of 2, and temperatures of 473–523 K. Conversions were limited to 10% or less to ensure measurements of surface reaction rates in the absence of mass and heat transfer dis-

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TABLE 1

Effects of K-Level and Calcination Temperature on the CO Hydrogenation Activity of Fe/K/SiO_2 (H_2/CO = 2, 1 atm, 523 K)

Catalyst	Calcination (K)	% CO conv.	Reaction rate		N_{CO}[a] × 10^3 (s^{-1})	Activation energy[b] (kJ/mol)
			(nmol/g cat. s)	(μmol/g Fe s)		
15% Fe/SiO_2	373	3.9	380	2.5	3.2	93
15% Fe/SiO_2	473	5.0	180	1.2	1.6	110
15% Fe/0.2% K/SiO_2	473	1.6	29	0.19	0.27	104
15% Fe/1.0% K/SiO_2	473	0.83	7.0	0.047	0.12	72
15% Fe/3% K/SiO_2	473	0.39	3.0	0.020	0.063	32
15% Fe/3% K/SiO_2	373	8.6	370	2.4	5.9	124

[a] CO turnover frequency—molecules CO reacted per H adsorption site per second.

[b] Activation energy for CO conversion determined from CO turnover frequencies in the temperature range 473–523 K.

guises (*21*). Products were separated and analyzed using a Hewlett–Packard gas chromatograph (Model 5830A) equipped with a 30-m methyl silicone-coated capillary column and flame ionization detector. Fixed gases were separated and analyzed using a 1/8-in. × 10-ft. packed column of Chromosorb 102 and a thermal conductivity detector. The capillary column and ionization detector were calibrated for over 120 hydrocarbons and oxygenates ranging in carbon number from 1 to 25. Feed flow rates were monitored to ±0.1% using mass flow controllers (Brooks Instruments). Mass balances over the reactor closed within 1–2%.

RESULTS

Effects of potassium level and of calcination on specific activity in the form of CO turnover frequency (number of CO molecules converted per catalytic site per second) and on activation energy for CO hydrogenation are illustrated by the data in Table 1. For catalysts calcined at 473 K, the specific activity and activation energy decrease with increasing potassium content. For example, the specific activity of the catalyst containing 3% potassium is a factor of 25 lower than that of the catalyst containing no potassium; its activation energy of 32 kJ/mol is a factor of 3 lower. The specific activities of catalysts dried at 373 K are higher than for catalysts calcined at 473 K. Indeed, the activity of 15% Fe/SiO_2 calcined at 373 K is factor of 2 higher. Comparing the data for the catalysts containing 3% K it is evident that calcination at 473 K results in a factor of 100 decrease in specific activity and a factor of 4 decrease in the activation energy!

The specific activities and activation energies of the unpromoted and potassium-promoted Fe/SiO_2 catalysts dried at 373 K are in good agreement (i.e., within a factor of 2) with those reported earlier for Fe/SiO_2 and Fe/K/SiO_2 catalysts tested under similar conditions (*22–24*). The specific activity of a well-dispersed 5% Fe/7% K/SiO_2 prepared from iron carbonyl decomposition on silica (*24*) was reported to be about factor of 10 lower than the more conventional catalysts precalcined at 373–398 K. The activation energy for this catalyst of 7.5 kJ/mol was also dramatically lower than for the conventional catalysts. Thus the heavily promoted Fe/SiO_2 prepared from the carbonyl (*24*) behaves similarly to the 15% Fe/3% K/SiO_2 catalyst from this study precalcined at 473 K.

The effects of potassium level and calcination temperature on the product selectiv-

TABLE 2

Effects of Potassium Level and Calcination Temperature on Selectivity of K-Promoted Fe/SiO_2 Catalysts (H_2/CO = 2, 1 atm)

Catalyst	Temperature (K)		CO_2 select.[b]	Hydrocarbon selectivity[a] (wt%)				Olefin[c] / Paraffin	H_2/CO usage[d]
	Calcination	Reactor		C_1	C_2–C_4	C_{5+}	C_{OH}		
15% Fe/SiO_2[e]	373	498	47.0	30.2	50.9	5.7	13.2	0.33	—
15% Fe/SiO_2	473	473	5.8	26.5	46.0	23.1	4.4	1.1	2.1
		498	7.4	26.6	46.3	22.2	4.8	1.2	2.1
		523	13.9	25.0	48.5	23.0	3.5	1.2	1.9
15% Fe/0.2% K/SiO_2	473	473	30.4	19.0	81.0	0	0	8.2	1.25
		498	48.3	15.3	61.7	22.8	0.2	1.2	0.68
		523	44.1	11.1	45.1	42.9	3.5	0.77	
15% Fe/1% K/SiO_2	473	473	25.6	18.5	81.6	0	0	321	1.4
		498	34.9	20.7	75.0	4.3	0	11	1.09
		523	44.6	19.0	53.8	27.2	0.1	2.9	0.80
15% Fe/3% K/SiO_2	473	473	2.4	20.8	79.2	0	0	>400	2.15
		498	4.2	21.1	78.9	0	0	>400	2.1
		523	28.0	22.2	74.9	3.0	0	9.8	1.4
15% Fe/3% K/SiO_2	373	473	14.4	15.2	32.1	50.6	2.1	1.5	1.8
		498	17.7	15.9	33.6	49.4	1.0	2.0	1.7
		523	28.9	16.9	36.4	44.0	2.7	2.2	1.3

[a] Weight percentage hydrocarbon groups in the hydrocarbon product.

[b] Mole percentage of converted CO appearing as CO_2.

[c] C_2–C_4 fraction.

[d] Moles of H_2 used per mole of CO converted.

[e] Data obtained earlier using a 12-m glass capillary column.

ity are illustrated by the weight percentage carbon selectivity data in Table 2. The effect on the unpromoted Fe/SiO_2 catalysts of calcination is to increase the overall selectivity to hydrocarbons, while decreasing selectivity for CO_2; at the same time the selectivity to C_{5+} is increased and the olefin/paraffin ratio is increased from 0.3 to 2.1. In the case of the promoted catalysts containing 3% K, the calcination causes a significant shift from a broad distribution of C_1–C_{10} hydrocarbons to mainly C_2 and C_3 olefins; methane make is increased slightly. Indeed there is a progressive trend of decreasing C_{5+} hydrocarbon fraction and increasing C_2–C_4 olefin fraction with increasing potassium content.

The hydrocarbon product distributions for 15% Fe/SiO_2 (calcined at 473 K) and 15% Fe/3% K/SiO_2 (dried at 373 K) are typical of iron FT catalyst (see Figs. 1 and 2), i.e., involve products ranging from C_1–C_{10} hydrocarbons. Moreover, a plot of ln[mole fraction] versus carbon number is linear for both catalysts. However, the product distribution for 15% Fe/3% K/SiO_2 calcined at 473 K consists of only methane, ethylene, and propylene (see Fig. 3). In this case the plot of ln[M_n] versus carbon number is clearly not linear.

The hydrocarbon product distribution for unpromoted Fe/SiO_2 from this study is in very good agreement with the data reported by Amelse *et al.* (*23*); the olefin/paraffin ratio from this study is somewhat lower. The data for potassium-promoted catalysts are in fair agreement; however, the differences are probably explained by differences in potassium level and in analysis, since Amelse *et al.* (*23*) did not analyze for C_{6+} hydrocarbons and would have therefore reported artificially large C_1 and C_2–C_4 selectivities.

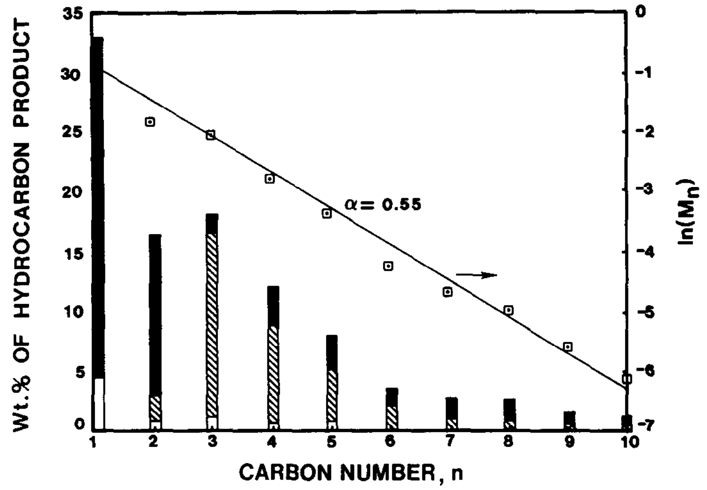

FIG. 1. Hydrocarbon product distribution and Schulz–Flory plot. 15% Fe/SiO$_2$ (calcined 473 K); 498 K, H$_2$/CO = 2, 1 atm. (■) Paraffins, (▨) olefins, (☐) alcohols.

The heavily potassium-promoted Fe/SiO$_2$ studied by McVicker and Vannice (*24*) behaved similarly to the 15% Fe/3% K/SiO$_2$ catalyst (calcined at 473 K) from this study in that it produced mainly methane, C$_2$–C$_3$ olefins, and no C$_{5+}$ products.

DISCUSSION

The results of this study indicate that potassium promotion may lead to either an increase or decrease in specific activity of Fe/silica, depending on the catalysts pretreatment. An increase in specific activity is observed if the catalyst is dried at 373 K prior to reduction, while drying and calcining at 473 K leads to a very significant decline in specific activity. It should be emphasized that because the specific activities reported in this study are based on the hydrogen adsorption capacities of the fresh catalysts, the observed decline in activity due to 473 K calcination is not a result of

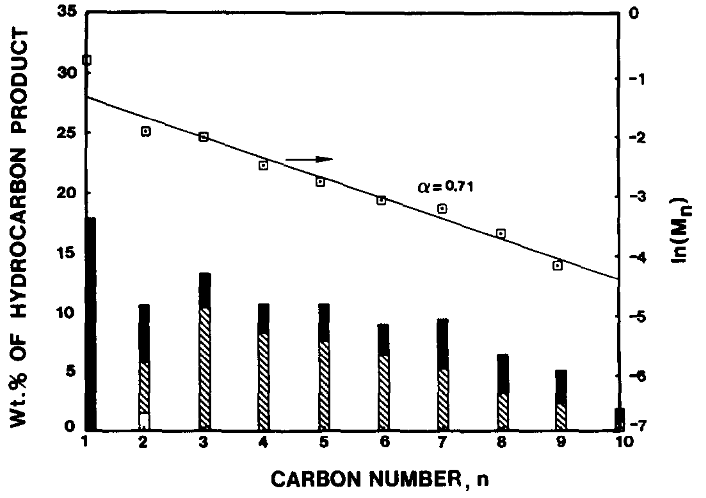

FIG. 2. Hydrocarbon product distribution and Schulz–Flory plot. 15% Fe/3% K/SiO$_2$ (calcined 373 K); 498 K, H$_2$/CO = 2, 1 atm. Symbols same as in Fig. 1.

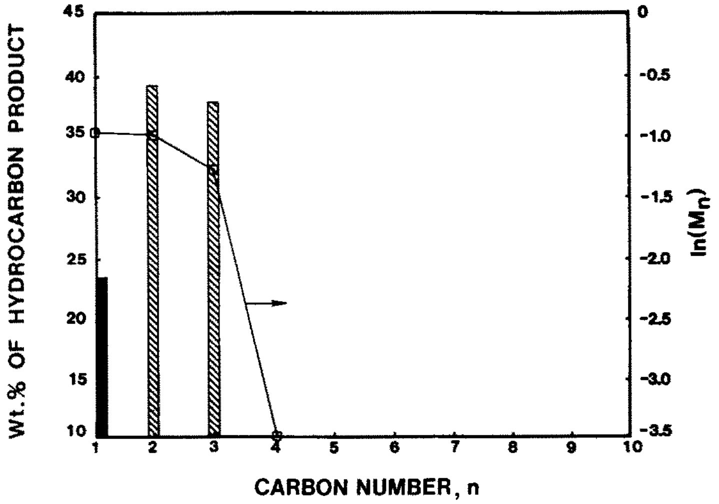

FIG. 3. Hydrocarbon product distribution and Schulz–Flory plot. 15% Fe/3% K/SiO_2 (calcined 473 K); 498 K, $H_2/CO = 2$, 1 atm. (■) Paraffins, ▨ olefins.

simple blocking of adsorption sites by surface contaminants. It should be further emphasized the results are *not* due to K-induced changes in iron crystallite size since in this group of catalysts it was the same within a factor of 2.

The 473 K precalcination of Fe/K/SiO_2 causes in addition to the decline in specific activity a dramatic decrease in the activation energy and a remarkable selectivity shift to a non-Anderson–Schulz–Flory distribution of methane and light olefins. These radical changes in activation energy and selectivity suggest that *a unique hydrocarbon synthesis mechanism is operative on the calcined catalysts*—one clearly different than conventional Fischer–Tropsch synthesis.

What changes in the operating catalyst might be responsible for this change in mechanism? The results of our companion investigation of the same catalysts (*20*) indicate that the 473 K calcination treatment leads to lower hydrogen and CO adsorption capacities, dramatic increases in the binding energy of hydrogen and the activation energy of hydrogen adsorption, a lower extent of reduction to iron metal, but no significant change in CO_2 adsorption capacity. These results are consistent with the formation of potassium or iron silicates during the calcination treatment which dramatically affect the kinetics of hydrogen chemisorption (*20*). Indeed, these results (*20*) indicate that hydrogen adsorption suffers severe kinetic limitations under reaction conditions typical of synthesis (180–300°C); these kinetic limitations could very possibly result in a deficiency of hydrogen atoms available for reaction on the surface. If so, this condition would explain both the observed lower specific activity for CO hydrogenation and significantly higher selectivity for olefins. Since CO hydrogenation on iron is typically first order in hydrogen (*25*) any decrease in the surface concentration of hydrogen atoms would significantly lower the reaction rate. The deficiency of surface hydrogen would also lower the rate of olefin hydrogenation. The deviation from Anderson–Schulz–Flory selectivities might be due to preferential termination of the adsorbed alkyl radical hydride via β-hydride elimination to the olefin.

While the above-discussed, calcination-induced changes in the intrinsic properties of Fe/K/silica can account for the observed behavior, there are at least two other explanations for the observed results. Dwyer (*26*) recently reported that potassium promotion of unsupported iron causes an order of magnitude loss in CO conversion activity and an increase in selectivity for high molecular hydrocarbons, while inducing the growth of a 2-nm-thick hydrocarbonaceous layer on the catalyst surface, which is not present on the unpromoted catalyst. Since Dwyer did not determine adsorption site densities for his catalysts, he was not able to report the effects of potassium on specific activity; nevertheless, his observed changes in selectivity were consistent with those observed in this study for the catalysts predried at 373 K (uncalcined). Thus, the changes in selectivity for the uncalcined Fe/K/silica catalysts might be explained, at least in part, by the presence of a condensed hydrocarbon layer on the iron surface. The unusual selectivity behavior of the 473 K-calcined catalyst might be similarly explained by changes in the thickness and composition of a hydrocarbonaceous layer on the iron surface.

Finally, a third alternative is that the presence at the surface of potassium oxide or hydroxide (*26, 27*) in the catalysts dried at 373 K and of potassium or iron silicates in the catalysts precalcined at 473 K affects the rate and extent of carbiding of iron near the surface. Indeed, the decreasing extent of reduction to iron metal with increasing potassium content and with calcination suggests that the extent of carbiding may be inhibited. Moreover, Schulz (*28*) has reported that oxides in "iron-matrix" catalysts have a high selectivity for olefins because the oxides suppress secondary hydrogenation and isomerization. Clearly additional investigations would be desirable to distinguish among these alternative explanations.

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