

Estimation Of Surface Site Density On Iron Fischer-Tropsch Catalysts By Means Of A Test Reaction

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Introduction

Surface titration methods such as selective chemisorption have great utility in any catalyst development program. Nevertheless, they are difficult to apply to iron Fischer-Tropsch (FT) catalysts for several reasons. First, an FT catalyst, although often initially reduced in hydrogen, is rapidly transformed during reaction to a combination of bulk iron carbide phases and magnetite [1,2]. The relationship of the bulk structure of the fully activated iron FT catalyst to the original catalyst bulk structure is difficult to establish, and the relationship between the characterized surface of the reduced catalyst and the uncharacterized state of the activated catalyst is therefore even less certain [3]. When the catalyst is generated by exposure of an oxide sample to syngas or CO with no preliminary H₂ reduction, there may even be no initially reduced, characterized sample with which to compare [4]. Second, no clear consensus exists for appropriate techniques for titrating a clean iron surface. Researchers have suggested each of the following provides a useful estimate of Fe⁰ surface sites: irreversible CO adsorption at 195 K [5, 6], total H₂ uptake at 473 K [7], H₂ desorption following cooling in H₂ flow to either 298 K [8] or 195 K [9], N₂ uptake at 573 K [7] or N₂ temperature-programmed desorption [10].

Measurement of the reaction rate of a structure-insensitive test reaction such as ethylene hydrogenation on a working FT catalyst offers an alternative method for estimating site density, one that characterizes the activated catalyst rather than a reduced precursor. Because the turnover frequency for these reactions is nearly independent of preparation method [11], measurement of the rate of the test reaction is similar to titrating site density. Reported here are the results of FT synthesis rate measurements made in a pressurized fixed bed reactor followed immediately by ethylene hydrogenation measurements. The freshly reduced catalyst precursors were also characterized by traditional titration techniques of H₂ temperature-programmed desorption and static CO chemisorption, and by N₂ BET surface area and x-ray diffraction. These measurements were conducted on a representative set of promoted iron FT catalysts prepared by precipitation, impregnation, and fusion.

Experimental

Two catalysts of promoted iron on alumina were prepared by impregnation of iron, copper, and potassium nitrates onto alumina (Catapal B, Vista Chemical). Elemental analyses of the dried, calcined precursors by means of atomic absorption gave compositions of 10.3 wt.% Fe, 0.5% Cu, 0.9% K, 29.6% Al (laboratory code FH1-137, designated here "Low K FeCu/Al₂O₃") and 11.1 wt.% Fe, 0.5% Cu, 4.5% K, 29.9% Al (laboratory code ED1-24, designated "High K FeCu/Al₂O₃"). The fused iron catalyst (C-73, Girdler) contained 68 wt.% Fe, 1.3% Al, 0.7% Ca, 0.2% Si, and 0.6% K. The precipitated iron catalyst ("Ruhrchemie", Hoescht Celanese) contained 45.76% Fe, 2.46% Cu, 2.18% K, 5.85% Si. Each catalyst sample was crushed into a powder clearing either 140 mesh for reaction experiments or 80 mesh for other experiments before use. These oxide precursors were pretreated by reduction in flowing H₂ at 723 K for 16 h, except for the Ruhrchemie catalyst, which was treated at 523 K or 723 K (the latter designated "High-T reduction").

Fixed bed FT synthesis experiments were conducted at 523 K and 1.30 MPa with 1:1 H₂:CO feed in a 0.305 cm ID brass reactor. Total flow rates of the gas was 100 cm³ min⁻¹ and 0.05-0.5 g of catalyst was used. All FT rates are reported after at least 24 h of H₂:CO exposure. Ethylene hydrogenation was conducted at 413-473 K and 0.10-1.30 MPa following FT synthesis with a 12.5:12.5:75 feed of H₂:C₂H₄:He. All ethylene hydrogenation rates are reported

after 2 h of $\text{H}_2:\text{C}_2\text{H}_4:\text{He}$ exposure. Each gas supplied to the reactor was obtained from a cylinder, purified, and metered through a Tylan mass flow controller. Gas-phase reactants and products were analyzed with a Hewlett-Packard 5890 gas chromatograph. A Chrompack PLOT column and flame ionization detector measured hydrocarbons while a Porapak R column and thermal conductivity detector (TCD) measured other gases. The H_2 temperature-programmed desorption experiments were performed on a reduced catalyst precursor in quartz U-tube in an Altamira AMI-1 apparatus. Each experiment was done with the method suggested by Jones and Bartholomew [9] unless otherwise noted. This method involved cooling the reduced catalyst from 723 K in flowing H_2 to dry ice temperature (195 K), flushing the system of excess H_2 , then measuring the H_2 desorbed in Ar flow as the sample temperature was increased to 723 K. In many cases, the TCD in the HP 5890 GC was used for improved sensitivity.

The CO chemisorption measurements and N_2 physisorption measurements were made in a Coulter 100CX adsorption apparatus. The CO chemisorption isotherms on reduced catalyst precursors were obtained following evacuation for 1.0 h at 673 K except where noted. The amount of chemisorbed CO was defined as the difference between total adsorption and reversible adsorption isotherms at 200 Torr [12] measured at 195 K [5,6]. Reduced samples were passivated in slow flow of 5% $\text{N}_2\text{O}/\text{He}$ before measurement of N_2 physisorption isotherm at 77 K. The total surface areas were calculated from application of the BET equation to physisorption isotherms. X-ray diffraction (XRD) measurements on reduced catalyst precursor samples were performed in a Rigaku diffractometer. Line broadening estimates were determined by applying the Scherrer equation analysis contained in the JADE software used for analyzing XRD data.

Results and Discussion

Table 1 presents characterization results for reduced catalyst precursors. Figure 1 presents a representative H_2 TPD scan. The total surface areas and the XRD line-broadening determination of Fe^0 crystal size show reasonable agreement. Less consistency is apparent in the results of H_2 TPD and of static CO adsorption measurements.

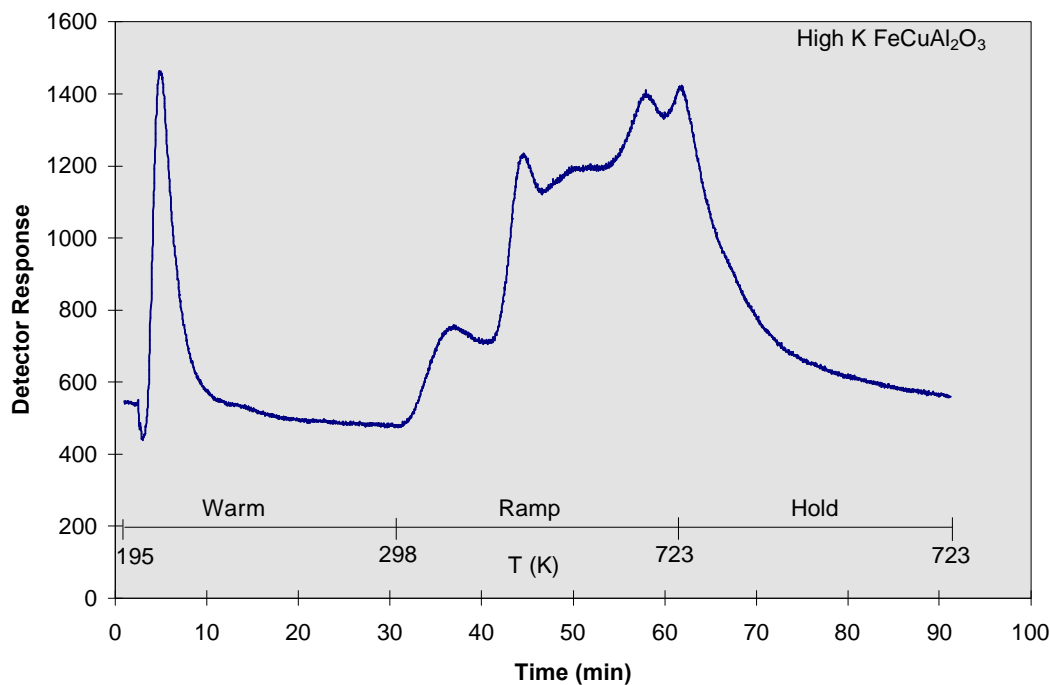


Figure 1. H_2 temperature-programmed desorption of reduced High K FeCu/Al₂O₃

Table 2 also displays H₂ and CO adsorption results for unsupported catalysts as a fraction of N₂ BET monolayer. Of the two techniques, the H₂ measurement appears to be the more consistent estimate of total Fe⁰ surface area. The Ruhrchemie sample and the High K FeCu/Al₂O₃ sample each showed relatively low CO uptake compared to the XRD, BET, and H₂ TPD results. The Fe surface of the Ruhrchemie sample may not be completely reduced by the 523 K pretreatment in H₂, while the high K loadings in High K FeCu/Al₂O₃ may selectively block CO adsorption. Table 2 also supports work elsewhere that H₂ TPD beginning at sub-ambient conditions yields higher estimates of H₂ surface coverage for Fe [13].

Table 1. Characterization of Reduced Catalyst Precursors

Sample	H ₂ ($\mu\text{mol g}^{-1}$)	CO ($\mu\text{mol g}^{-1}$)	Estimate: Relative Fe ⁰ geometric area ¹	Total surface area ($\text{m}^2 \text{g}^{-1}$)	d (nm)		
					H ₂	CO	XRD
Ruhrchemie	---	19.6 ²	4.20	115	---	---	10.9
Ruhrchemie (High-T reduction)	56.9	---	1.46	55.2	105	---	31.2
C-73	78.8	46.9	2.84	14.6	88.9	149.4	22.7
Low K FeCu/Al ₂ O ₃	58.1	34.5	0.75	123	18.3	30.8	13.8
High K FeCu/Al ₂ O ₃	80.0	8.8	0.77	71.6	14.3	130	14.5
Al ₂ O ₃ precursor	1.0	---	---	191	---	---	---

1. (Wt.% Fe in catalyst sample) / d, where d is taken from XRD line-broadening measurements

2. Evacuation for 2.0 h at 523 K before measurement

Table 2. Characterization of Unsupported Catalysts

Sample	X-ray diffraction		H ₂ TPD ¹ ($\mu\text{mol g}^{-1}$)	CO chemisorption ($\mu\text{mol g}^{-1}$)	Total surface area ($\text{m}^2 \text{g}^{-1}$)	Ratio to N ₂ BET monolayer	
	d (nm)	(Wt% Fe) / d				H ₂ ¹	CO
Ruhrchemie	10.9	4.20	---	19.6	115	---	0.017
Ruhrchemie (High-T reduction)	31.2	1.46	56.9 (46.2)	---	55.2	0.10 (0.082)	---
C-73	22.7	2.84	78.8 (50.8)	46.9	14.6	0.53 (0.34)	0.31

1. Numbers in parentheses are values for TPD commencing at room T rather than 195 K

The yields of FT synthesis and subsequent ethylene hydrogenation on these catalysts are shown in Table 3 and Figure 2. Conversions were kept low in all cases, so the yields reported should approach actual rate measurements. With one exception, FT synthesis rates correlate with rates of ethylene hydrogenation. The order-of-magnitude spread in rates for FT synthesis was matched by an almost three orders-of-magnitude range observed for ethylene hydrogenation. The rate of ethylene hydrogenation on one of two alumina-supported catalysts, the Low K FeCu/Al₂O₃, was higher than would be expected from the correlation curve due to additional ethylene

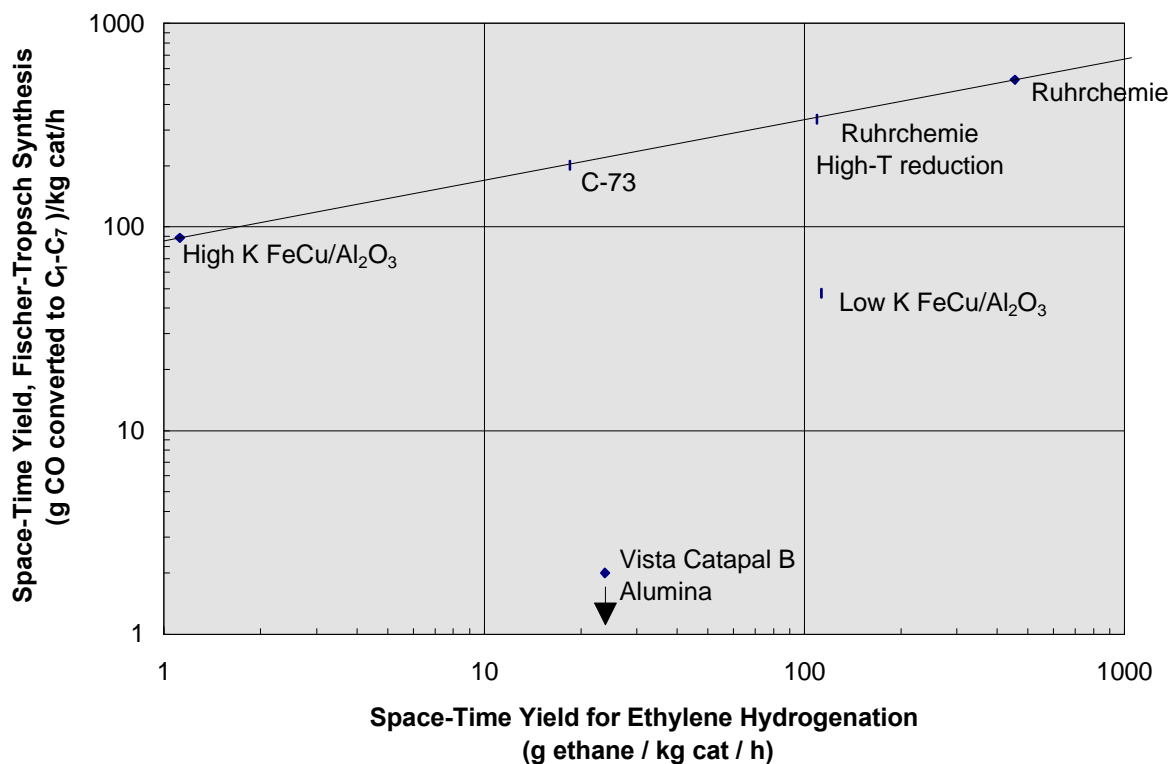


Figure 2. Yields for FT synthesis and subsequent ethylene hydrogenation. FT synthesis at 523 K and 1.30 MPa. Ethylene hydrogenation at 0.1 MPa and 413 K measured after 2 h of reaction.

hydrogenation on the alumina support. Alumina has activity at these conditions [14] as seen by the rate measured on the unimpregnated alumina precursor following hydrogen reduction. The fact that the rate is higher on Low K FeCu/Al₂O₃ than on the alumina suggests that the Fe and Cu additives promote ethylene hydrogenation on alumina, possibly through a spillover effect [15]. The fit with the correlation observed for High K FeCu/Al₂O₃ suggests that sites on the alumina responsible for ethylene hydrogenation are thoroughly blocked by the ten-fold higher K level on this catalyst. The lower total surface area of this sample is also consistent with this explanation.

Ethylene hydrogenation experiments on the initially reduced samples have begun recently. Figure 3 shows the ethylene hydrogenation yield on one catalyst as a function of time. Both the higher reaction yield and the deactivation trend in Figure 3 are typical of reported results for the reaction on iron and other catalysts [16, 17]. The kinetics of ethylene hydrogenation on metals mirrors that seen for the hydrogenation of CO during FT synthesis. Ethylene preferentially adsorbs over hydrogen on clean iron surfaces, which produces a surface that fills

with adsorbed carbonaceous species, leading to deactivation. The reported rate dependence on ethylene is roughly zero or even negative order, while the dependence on H₂ approaches first-order behavior, consistent with this picture that hydrogen uptake to a surface full of adsorbed C₂ species is rate-determining. The lower rates at higher temperatures observed for ethylene hydrogenation on iron FT catalysts suggest that much of the surface of an iron FT catalyst is unavailable for ethylene uptake when the gas composition is switched from H₂-CO to H₂-C₂H₄. This supports results of transient ¹²CO-¹³CO isotopic switching experiments on FT catalysts, which show that actively growing species leading to FT products occupy 10% or less of the total metallic surface area [18, 19].

Table 3. Yields for FT Synthesis and Subsequent Ethylene Hydrogenation.

Sample	FT Synthesis		Ethylene Hydrogenation	
	(g CO converted to C ₁ -C ₇) (kg cat) ⁻¹ h ⁻¹	% CO conversion	(g ethane) (kg cat) ⁻¹ h ⁻¹	% ethylene conversion
Ruhrchemie	529	0.759	454	2.605
Ruhrchemie High-T reduction (723 K)	339	0.453	109	0.584
C-73	201	0.536	18.5	0.197
Low K FeCu/Al ₂ O ₃	47.3	0.062	113	0.591
High K FeCu/Al ₂ O ₃	88.6	0.568	1.1	0.029
Vista Catapal B Alumina precursor	negligible	----	23.9	4.84

Summary

A linear correlation was found between the yields for FT synthesis and for ethylene hydrogenation on the activated FT catalysts. Initial FT synthesis activity and selectivity were reestablished following ethylene hydrogenation, suggesting that ethylene hydrogenation does not irreversibly alter the surface structure of the catalyst. Separate studies of ethylene hydrogenation on freshly reduced Fe catalysts were recently begun in order to better calibrate the correlation found between rates of FT synthesis and ethylene hydrogenation.

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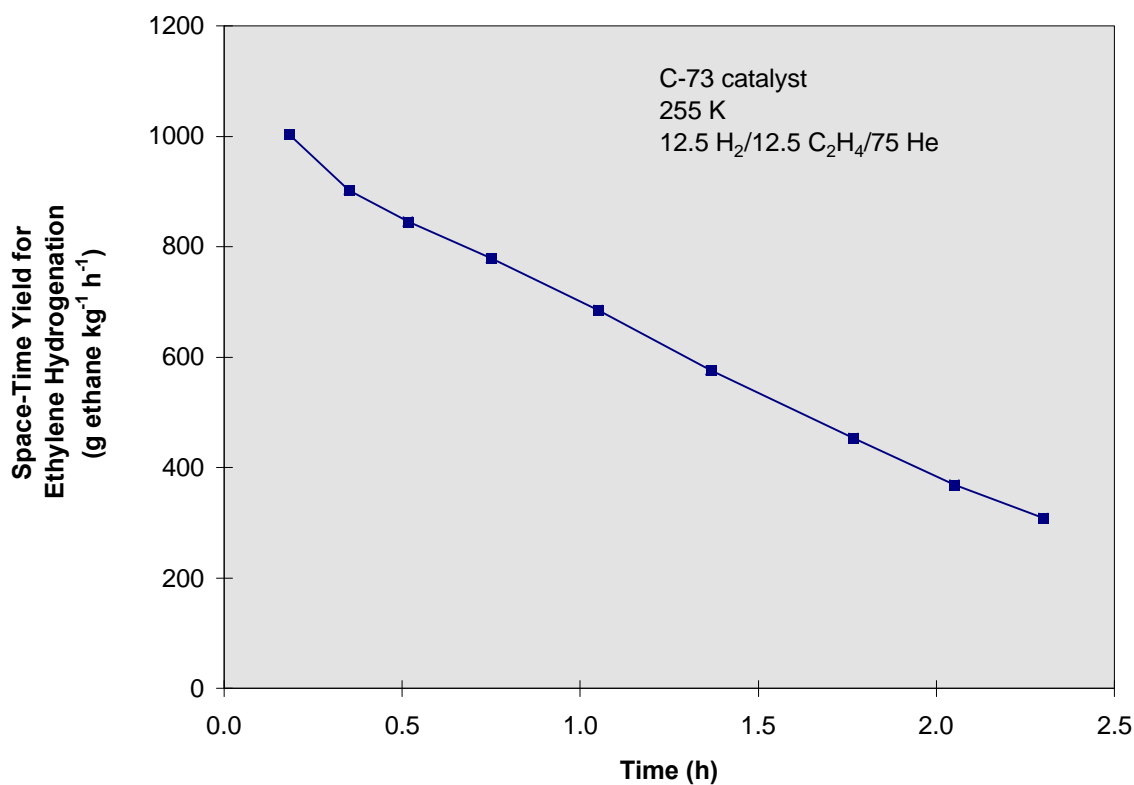


Figure 3. Ethylene hydrogenation on initially reduced iron