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Artículo Científico

Hydrocarbon synthesis using Iron and Ruthenium/SiO_2 with FISCHER-TROPSCH catalysis.

Y.J. Fonseca[1], B. Fontal[1], M. Reyes[1], T. Suárez[1], F. Bellandi[1], R. R. Contreras*[1], P. Cancines[1], A. Loaiza[2], M. Briceño[3].

(1) Laboratorio de Organometálicos, Facultad de Ciencias, Universidad de Los Andes (ULA), Mérida, Venezuela.
(2) Laboratorio de Cinética y Catálisis. Fac. Ciencias, ULA, Mérida.
(3) Laboratorio de Microscopía. Fac. Ciencias, ULA, Mérida.

(*) ricardo@ula.ve

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Resumen:

Se utilizaron los cúmulos $Fe_2(CO)_9$, $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ como precursores para soportar estos metales en sílice. Las sílices impregnadas se obtuvieron utilizando solventes orgánicos en atmósfera inerte y tanto los complejos absorbidos como los metales reducidos fueron caracterizados por medio de FTIR, SEM, EDX y HRTEM. Se observó una buena actividad catalítica en reacciones Fischer–Tropsch (FT); los productos, analizados por GC-MS, fueron principalmente alcanos, alquenos, y alcoholes medios y altos. El catalizador de rutenio presentó una alta selectividad hacia los alcoholes. El HRTEM mostró nanoparticulas de rutenio. **Palabras clave**: Fischer-Tropsch, gas de síntesis, catalizador, nanopartículas.

Abstract

$Fe_2(CO)_9$, $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ clusters were used as precursors for silica supported metals. The impregnated silica solids were obtained in organic solvents under inert atmosphere and the adsorbed complexes and reduced metals characterized by FT-IR, SEM EDX and HRTEM. The catalysts showed good Fischer–Tropsch (FT) activity; the main products were alkanes, alkenes and medium and higher alcohols as analyzed by GCMS. The Ru catalysts showed higher alcohols selectivity. HRTEM showed Ru nanoparticle size. **Keywords**: Fischer-Tropsch, syngas, catalyst, nanoparticles

Introduction

Transition metal carbonyl clusters on inorganic oxides supports have been used in catalytic synthesis with highly dispersed metal particles[1] to give industrial products with high activity, selectivity and stability[2]. Numerous heterogenization methods have been investigated for FT synthesis[3,4]. Traditional low dispersion FT catalysts produce gasoline and diesel[5]. New F-T catalysts with nanoparticles of different metals have been reported[6,7]. New demands for higher contents of oxygenated compounds on gasoline and diesel have favored catalysts with highly dispersed small size particles[8]. We report here the synthesis of a series of FT catalysts with nanoparticle size Fe and Ru metals with high hydrocarbons and oxygen compounds activity. All the solid supported catalysts reported were tried, but here only a representative sample is presented and compared.

Experimental

General Procedure: Metal complex solutions were handled under Ar using standard Schlenk techniques. THF was distilled from sodium/benzophenone under Ar before use. Ruthenium trichloride and iron pentacarbonyl (Aldrich) were used without further purification. Catalysts precursors $Ru_3(CO)_{12}$, $Fe_3(CO)_{12}$ and $Fe_2(CO)_9$ were obtained as described elsewhere[9,10,11]. Silica (Aerosil, large surface area, 200 m^2g^{-1}, Degussa) was vacuum dehydrated (423 K, 2 hr.) in a Schlenk tube, dry THF (50 mL) containing $Ru_3(CO)_{12}$, $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ in different proportions, to get the desired metal content, was then added and stirred for 24 hours at 348 K. The colored solutions get decolorized with time, as the metal complexes get adsorbed on the silica surface. The excess of THF was separated, the solids were washed several times with fresh THF and vacuum dried at room temperature. The supported catalyst precursors were characterized by IR (FTIR Perkin Elmer 1725 X in KBr pellets). The metals were reduced with H_2 gas (flow, 20

ml/min; 673 K, 2 hr). The amount of supported Ru and Fe was estimated by SEM with EDX analysis (Hitachi S-2500). This analysis was performed at 75 kV, with an emission of radiation-X angle of 35º during 100 sec. (See Table 1 for the EDX values).

Dispersion and particle size were determined by HRTEM analysis (Hitachi-600; working at 200 kV); the solid catalysts were ultrasonically dispersed in isopropyl alcohol, then one drop of this suspension was placed on a copper support with a graphite cover.

Catalytic Runs: In a typical experiment, freshly reduced catalyst solids (0,15 g) were rapidly introduced into a glass-lined stainless steel reactor (Parr, 75 ml), with mechanical stirring (1500 rpm); purged with a 1:1 syngas mixture and then charged at the required syngas pressure (200 Psi), and heated to 473 K and 24 hours. After the reaction, the reactor was cooled, the remaining gases were released (the gaseous F-T products are included in these remaining gaseous part) and liquid samples were extracted with dry ether and analyzed by GC–MS (Hewlett-Packard 5890 - MS 5988-A, HP–1 methyl silicone gum, 50m X 0.51mm column.).

Table 1. The different preparation variables for the catalysts.

Catalytic Precursor	**Pre-treatment SiO_2 (h)**	**Aged Time (h)**	**Supported-metal %** [a]	**Catalytic Precursor**	**Pre-treatment SiO_2 (h)**	**Aged Time (h)**	**Supported-metal %** [a]
$Fe_2(CO)_9$	Vacuum x 2h	48	2,10	$Ru_3(CO)_{12}$	▲ 150ºC 16h	24	1,70
$Fe_2(CO)_9$	Vacuum x 2h	48	2,42	$Ru_3(CO)_{12}$	▲ 150ºC 16h	48	1,50
$Fe_2(CO)_9$	Vacuum x 2h	72	5,31	$Ru_3(CO)_{12}$	▲ 150ºC 22h	48	7,30
$Fe_3(CO)_{12}$	Vacuum x 2h	24	4,00	$Ru_3(CO)_{12}$	▲ 150ºC 22h	48 reflux 60ºC	5,84
$Fe_3(CO)_{12}$	Vacuum x 2h	48	3,90	$Ru_3(CO)_{12}$	▲ 150ºC 22h	48 reflux 60ºC	6,00
$Fe_3(CO)_{12}$	▲ 150ºC 24h	24	5,00	$Ru_3(CO)_{12}$	▲ 150ºC 24h	72 reflux 60ºC	3,24
$Fe_3(CO)_{12}$	▲ 150ºC 24h	48	3,05	$Ru_3(CO)_{12}$	▲ 150ºC 24h	72 reflux 60ºC	9,00
$Fe_3(CO)_{12}$	▲ 150ºC 24h	48	8,50	Bimetallic Fe/Ru	▲ 150ºC 16h	72 reflux 60ºC	Fe: 6,30 Ru: 5,50
$Fe_3(CO)_{12}$	▲ 150ºC 24h	48	10,00	Bimetallic Fe/Ru	▲ 150ºC 16h	72 reflux 60ºC	Fe: 7,54 Ru: 5,47
$Ru_3(CO)_{12}$	Vacuum x 2h	24	2,50	Bimetallic Fe/Ru	▲ 150ºC 16h	24 reflux 60ºC	Fe: 3,33 Ru: 2,74
$Ru_3(CO)_{12}$	Vacuum x 2h	72	4,44	Bimetallic Fe/Ru	▲ 150ºC 20h	24 reflux 60ºC	Fe: 5,90 Ru: 6,70
$Ru_3(CO)_{12}$	▲ 150ºC 16h	24	0,65	Bimetallic Fe/Ru	▲ 150ºC 20h	24 reflux 60ºC	Fe: 9,00Ru: 10,00

[a] % Supported metal determined by EDX analysis ; the THF solutions used for impregnation contain different concentrations of the metallic precursors, to obtain the desired % metal content upon complete adsorption.

Results and Discussion

Catalyst Preparation. The different preparation variables for the catalysts are shown in Table 1. In all cases, the concentration of the THF solution of the metallic precursor was calculated to obtain the desired percentage of metal supported on the high surface area silica, assuming complete adsorption from solution. The optimum impregnation and % supported metal (EDX analysis) is obtained with longer silica dehydration times, longer contact times, accompanied by longer reflux times. In these cases, the % supported metal is near the expected value from complete deposition from the organic solvent solution.

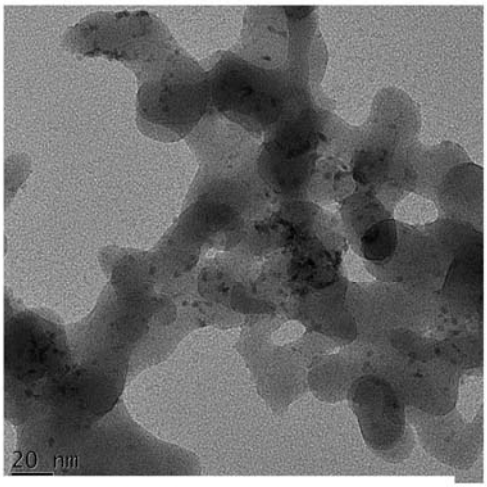


Figure 1. TEM photo of silica-supported Ru nanoparticles 6%

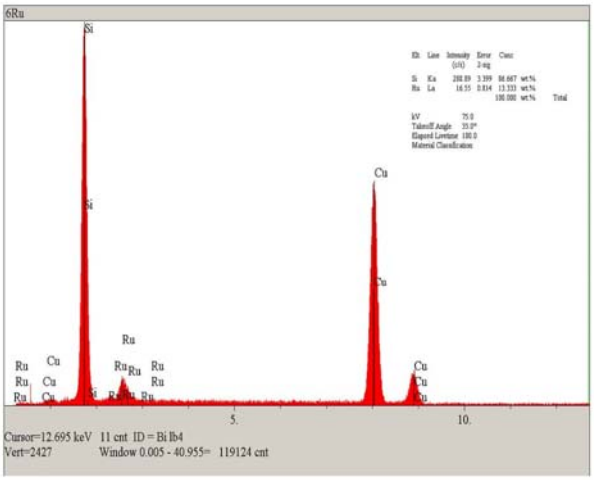


Figure 2. EDX spectrum for catalyst Ru/SiO_2 6%

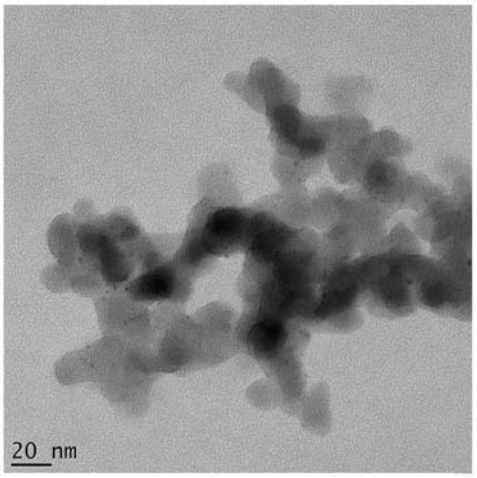


Figure 3. TEM photo of silica-supported 1,5 % Ru nanoparticle

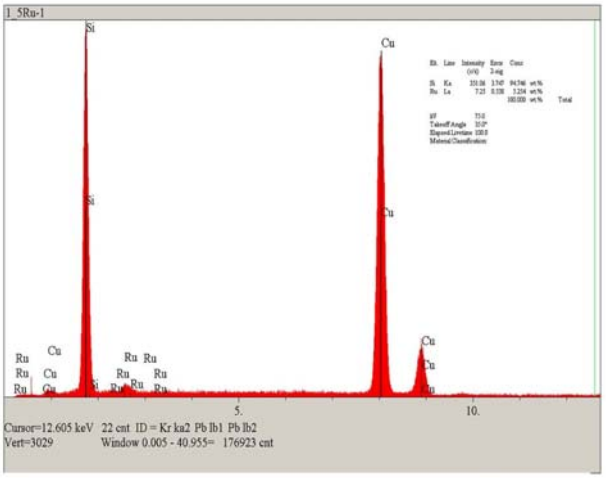


Figure 4. EDX spectrum catalyst $Ru/SiO_2$1,5%

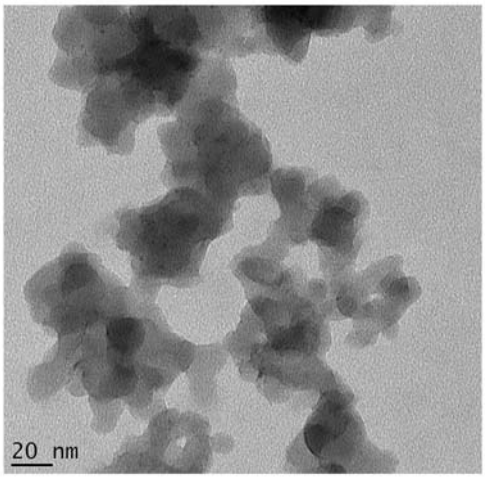


Figure 5. TEM photo of silica-supported Ru nanoparticle 1,5%

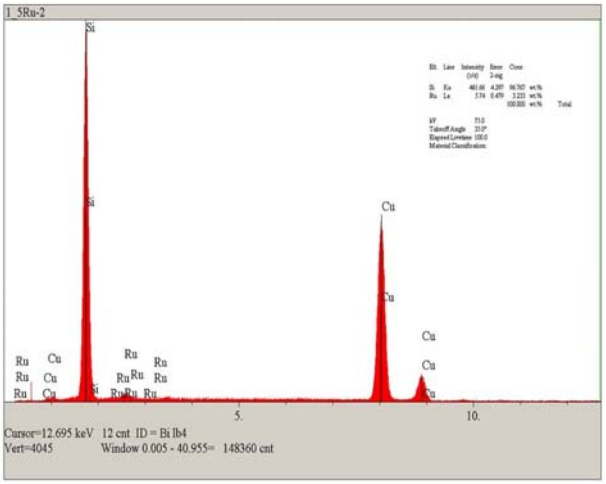


Figure 6. EDX spectrum catalyst Ru/SiO_2 1,5 %

*TEM, EDX Analysis***.** From the TEM analysis, it is possible to identify (Ru/SiO_2 6,0%) ruthenium particles with size between 4 to 8 nm, with morphology not well defined.(See Figure 1) The shape of these particles could be originated by smaller ruthenium particles agglomerations, with a size under the instrument detection limit. The metal content of these particles are corroborated with Ru peaks showed by EDX analysis coupled to the TEM instrument. The size distribution of the ruthenium particles in the Ru/SiO_2 1,5% catalyst, (as indicated in the photographs in Fig. 3 and 5) varied between 1 to 3 nm, showing a better dispersion and homogeneous distribution. Almost all the particles also present a smaller morphology and spherical shape. In the EDX analysis (Figures 4 and 6) it is possible to observe a constant metal concentration that reflects the uniformity in the size of the particles

FTIR Characterization. The IR spectra for supported $Ru_3(CO)_{12}$ catalytic precursor shows strong bands at 2060 and 1990 cm-1,assigned to terminals carbonyls; this positions are similar to those reported in the literature[11]. Infrared spectrum for supported $Fe_3(CO)_{12}$ catalytic precursor shows bands at 2050, 1858 y 1825 assigned to bridged and terminals carbonyls and are similar to those reported in the literature[10]. These bands disappear when the solids are oxidized and then reduced with H_2 to the metal particles.

Fischer-Tropsch Reactions. In Figures 7, 8 and 9 are shown typical chromatograms for the separation of the liquid reaction products for the Ru/SiO_2, 6%, Fe/SiO_2, 4% and $Fe/Ru/SiO_2$, 6,3% / 5,5% catalysts respectively, as representative systems. The reaction products as characterized by MS are indicated at the bottom of the Figures. These products were compared with the bibliographic data base from MS and their fragmentation patrons of the HP instrument. The low molecular weight gaseous products are diluted in the gaseous un-reacted syngas and could not be quantified. All the other catalysts systems reported in Table 1 were tried under similar F-T conditions and present results with similar products distribution.

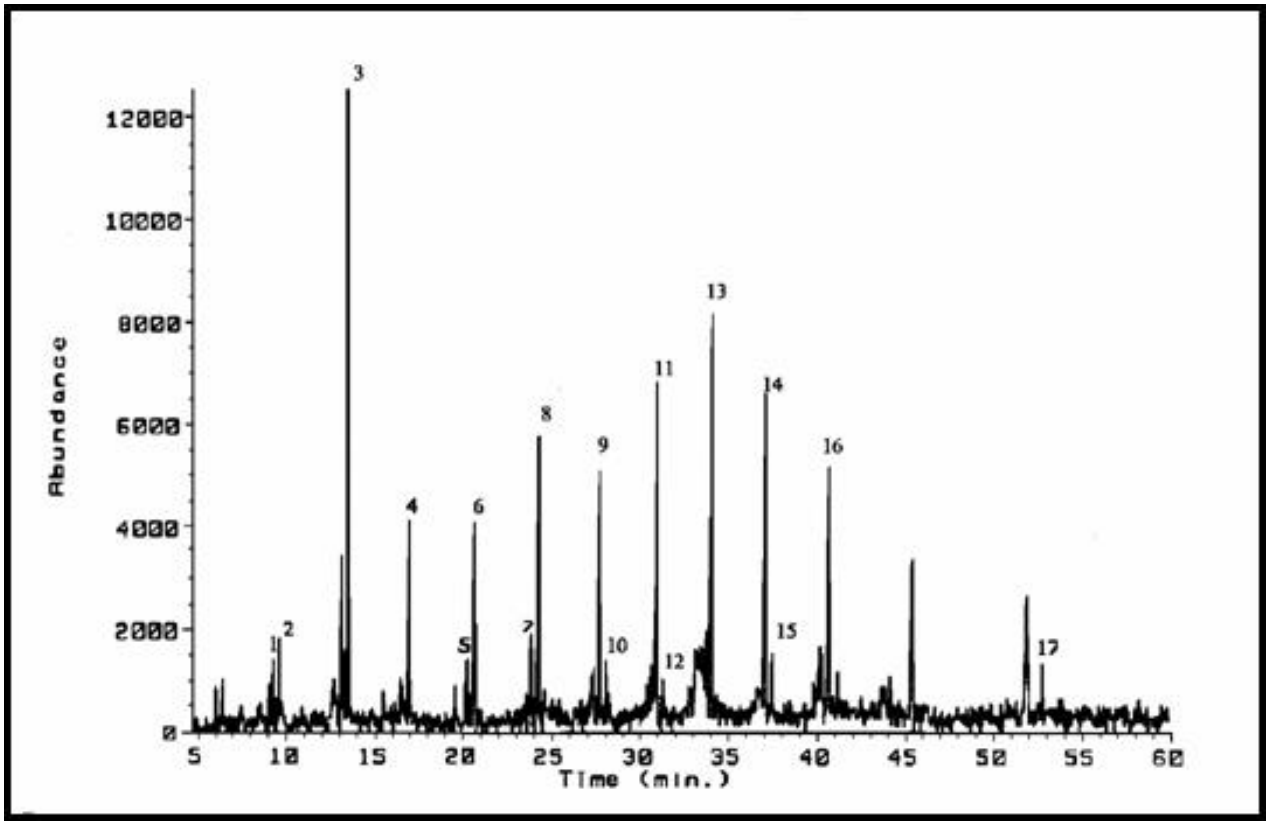


Fig. 7 Reaction Products Chromatogram (Ru/SiO_2, 6% catalyst). 1) 1-pentadecanol, 2) Decycloxietanol, 3) Octane, 4) Eicosane, 5) Pentadecanol (isomer), 6) Tetradecane, 7) 1-Heptadecanol, 8) Tetradecane (isomer), 9) Octane 2,4,6 – Trimetil, 10) Pentadecanol (isomer), 11) Hexadecane, 12) Heptadecanol (isomer), 13)Heptadecane, 14) Tetradecane (isomer), 15) Heptadecanol (isomer), 16) Octadecane, 17) Pentadecanol (isomer).

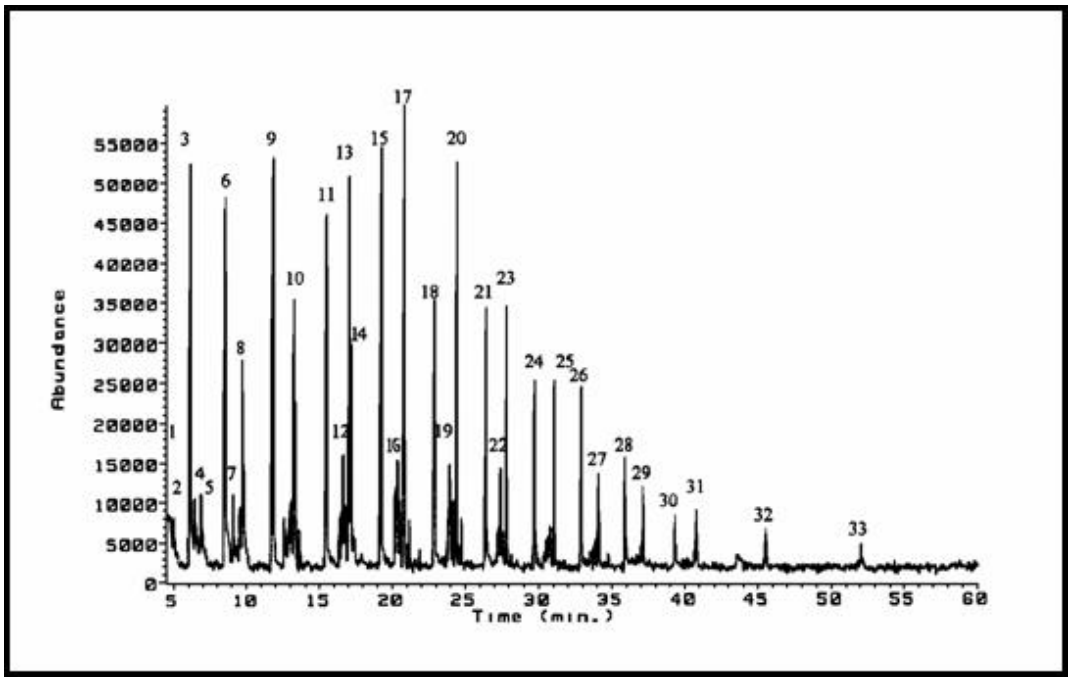


Fig. 8 Reaction Products Chromatogram (Fe/SiO_2, 4% catalyst). 1) Hexanal, 2) Heptane, 3) 1-Pentanol, 4) Decanal, 5) Heptane (isomer), 6) 1-Pentene-2-Metil, 7) Nonane, 8) 1-Heptanol, 9) Dodecane, 10) 1-Octanol, 11) 5-Undecene, 12) Decane 2,3,5-Trimetil, 13) 1-Heptadecanol, 14) 1-Nonanol, 15) 5-Dodecene, 16) Heptadecane, 17) 1-Decanol, 18) 4-Nonene, 19) Tridecane, 20) Ciclohexane 1,2,3 –Trimetil, 21) 1-Octadecanol, 22) Heptadecane (isomer), 23) 1-Dodecene, 24) Tetradecane, 25) 9-Octadecene, 26) Heptadecane(isomer) ,27) 1-Heptadecanol, 28) Heptadecane (isomer), 29) 1-Octadecanol, 30) Pentadecane, 31) Dodecane 1,1 Oxybis, 32) Ciclopentane 1-etil.

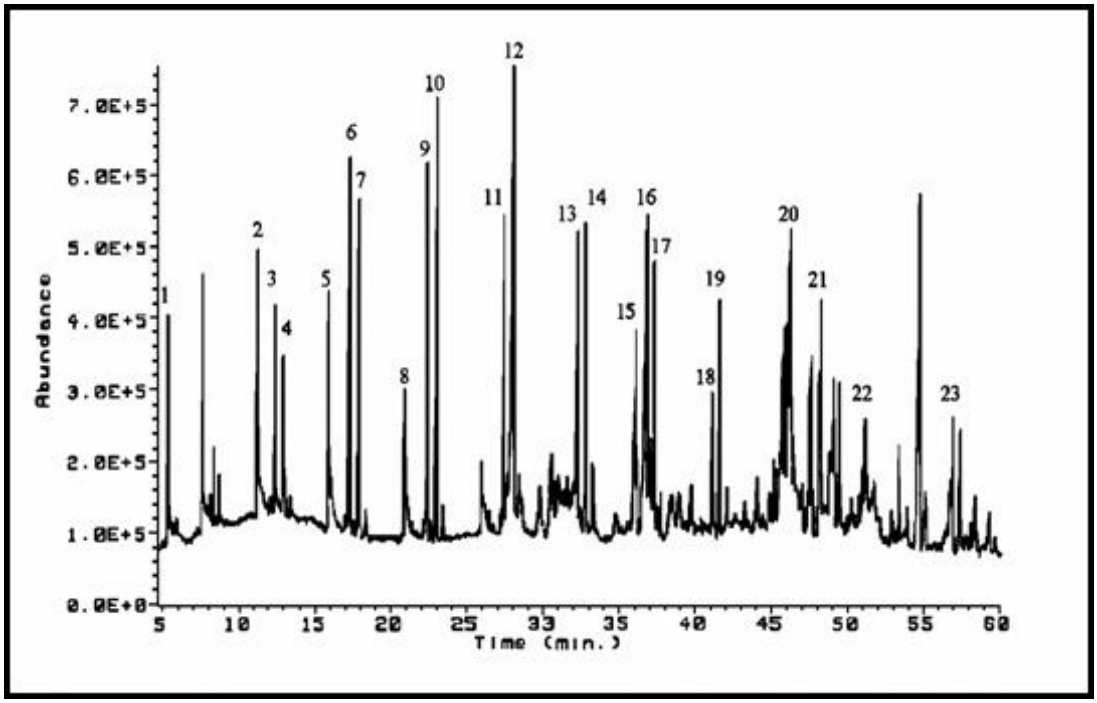
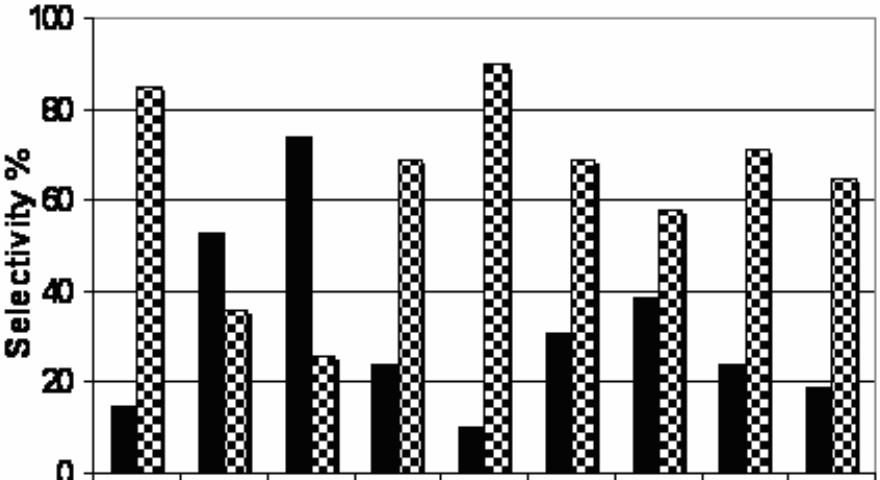


Fig. 9 Reaction Products Chromatogram ($Fe/Ru/SiO_2$, 6,3%/ 5,5% catalyst). (*) 1) 1-Butanol, 2) 1-Butanol-3-metil, 3) Ciclopentane, 4) Nonane, 5) 1-Heptanol, 6) 1-Octanol, 7) Tetradecane, 8) 1-Octanol, 9) Ciclooctane, 10) Undecane, 11) Ciclobutane 1-butil 2-etil, 12) Dodecane, 13) 5-Tetradecene, 14) Heptadecane, 15) Bencen propanoic acid, 16) Propanedioic acid, 17) Heptadecane (isomer), 18) Tetradecane(isomer), 19) Hexadecane, 20) Heptacosane, 21) Pentadecane, 22) Decane 6-etil, 2-metil, 23) Tridecane.



	Ru 0,7%	Ru 3,2%	Ru 6,0%	Ru 9,0%	Fe 2,1%	Fe 3,0%	Fe 4,0%	Fe 8,5%	Fe 6,3% Ru 5,5%
■ alcoh/Prod tot	15	53	74	24	10	31	39	24	19
▨ HdC/Prod tot	85	36	26	69	90	69	58	71	65

Fig. 10. Fischer-Tropsh reaction selectivity from supported ruthenium, iron and bimetallic Fe/Ru catalysts.

All the catalysts studied show a good Fischer-Tropsch activity under the reaction conditions tried. The three systems reported as typical (Figures 7, 8, 9) indicate a product distribution as expected for mainly linear alkanes and alkenes and little cyclical hydrocarbons and varying amounts of oxygenated products, mainly terminal alcohols. There product distribution and especially the presence of oxygenated compounds, varies with the type of metal used, and shows some dependence with the percent metal content of the catalyst. This is summarized on Figure 10, for a few of the systems tried; that presents the total % selectivity to hydrocarbons and oxygenated products as deduced from the MS-GC studies. For the Ru metal catalysts, the low metal content catalyst favors hydrocarbon products and there is a marked increase in oxygenated products as the supported Ru content increases reaching a maximum (75% oxygenated products) for the Ru/SiO_2 6% catalyst. A similar behavior is observed with the Fe catalysts, but the selectivity to oxygenated products is lower, reaching a maximum for oxygenated products with the Fe/SiO2 4% catalyst. The bimetallic catalyst reported (Fe 6,3%, Ru 5,5%) shows low oxygenated compound selectivity. Similar F-T behavior has been noted for Co and Co/Fe supported catalysts prepared by a similar method, using THF soluble Co and Fe carbonyl complexes and will be reported in a future publication.

Conclusions

Silica supported ruthenium, iron and Ru/Fe bimetallic catalysts were synthesized by the impregnation method using THF soluble metal carbonyl complexes; this method was very successful for obtaining nanoparticle metallic size. The use of high surface area silica, low metallic content, and long contact time, favors high metal dispersion and minimal metal conglomeration. This has been corroborated by TEM studies. The catalytic reactions show a high F-T activity for alkane, alkene and oxygenated compounds. Ru/SiO_2 catalysts show a higher selectivity for oxygenated products and show some dependence with the percentage of Ru metal content, while the Fe/SiO_2 and the $Fe/Ru/SiO_2$ catalyst show less selectivity for oxygenated compounds. The use of very reactive nanoparticle size dispersed metal catalysts shows a very promising type of catalyst for important industrial processes, such as the Fischer- Tropsch synthesis.

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