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Fischer–Tropsch synthesis on ruthenium supported ETS-10 titanium silicate catalysts ☆

R. Carli [1], C.L. Bianchi and V. Ragaini

Department of Physical Chemistry and Electrochemistry, University of Milan,
Via Golgi 19, 20133 Milan, Italy

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Titanium silicate ETS-10 was found to be a suitable metal catalyst support, having high surface area, high ion exchange capacity and no acidic functions. In this work, ETS-10 was used as a support in preparing ruthenium supported catalyst for Fischer–Tropsch synthesis. Ru/M-ETS-10 catalytic systems (M standing for Na or K) showed some important characteristics, as good metal dispersion and shape selectivity. Moreover, no side reactions due to acidic functions were evidenced; indeed readsorption of olefins on active metal centers was found to control the activity of the catalysts.

Keywords: Fischer–Tropsch synthesis; titanium silicate molecular sieves; ruthenium supported catalysts; olefins readsorption

1. Introduction

CO hydrogenation on classical Fischer–Tropsch (FT) catalysts leads to the formation of a wide distribution of products, according to the Anderson–Schulz–Flory (ASF) chain-growth probability. Attempts to control the product selectivity have been made, involving molecular sieves as catalyst support for metals which are known to be active catalysts in FT synthesis (ref. [1] and references therein). Geometric or diffusional constraints on the product molecules coupled with strong acidic functions greatly influenced the normal chain-growth process in FT synthesis.

In many studies, a large variety of molecular sieves have been used, such as zeolites of FAU, MFI, MOR, LTL and ERI structure types in their acidic or alkaline forms. There have been a significant number of recent promising developments in FT catalyst technology based on zeolites, leading to a new class of zeolite-based multifunctional metal catalysts. In this work we propose to use a titanium-

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[1] To whom correspondence should be addressed.

containing molecular sieve as metal catalysts support, in order to combine the shape selectivity with the electronic properties of a well-known FT-catalyst support, such as TiO_2.

Molecular sieves, containing titanium in framework position, have been synthesized with MFI [2,3] and MEL [4,5] structure types. These titanium silicalites, TS(1) and TS(2), show interesting catalytic activities in oxidation reactions probably due to titanium centers in tetrahedral coordination [6,7]. It is important to note that these materials have no ion exchange sites, because framework titanium (tetrahedral coordination) is present as Ti^{4+}. Consistently with these characteristics, no relevant results have been obtained with ruthenium supported TS(1) catalyst used in FT synthesis [8].

In order to enable a suitable interaction between support and Ru centers in the final catalyst, a new class of titanium-containing molecular sieves composed of tetrahedral and octahedral oxide polyhedra have been used as catalyst supports. Titanium silicates such as ETS-4 and ETS-10, recently synthesized by Engelhard's researchers, have all the properties of classical molecular sieves with small (ETS-4) or large (ETS-10) pore channel systems [9,10]. ETS-10 shows high ion exchange capacity, high BET surface area ($\sim$ 300 m^2/g) and no acidic functions [10]. The structure of ETS-10 has been recently solved by Anderson et al. [11]. They pointed out that the pore system of ETS-10 contains 12-membered rings (0.76 × 0.49 nm) and displays a considerable degree of disorder. These important characteristics make ETS-10 molecular sieve a suitable catalyst support.

2. Experimental

2.1. CATALYST PREPARATION

Na-Y zeolite (LYZ-42, Si/Al = 1.5, from UOP) and ETS-10 titanium silicate (potassium form, Si/Ti = 5.0, from Engelhard) were used as catalyst supports. A particular sodium form of ETS-10 was prepared by multiple ion exchange with NH_4Cl solution (1.0 M, 20 $ml/g_{ETS} \equiv 5 \times 4$ meq/g_{ETS}) and subsequently with NaCl solution (1.0 M, 20 $ml/g_{ETS} \equiv 5 \times 4$ meq/g_{ETS}). The supports were calcined at 773 K for 4 h.

Catalyst samples were prepared by slurry impregnation of the calcined support with a solution of $Ru(AcAc)_3$ in ethanol (both from Fluka). The support is stirred into the precursor solution at 313 K for 12 h, then the excess ethanol is evaporated under vacuum. The recovered powders were reduced in flowing H_2 at 623 K for 4 h. The final content of ruthenium for all the samples was 1 wt%.

All the samples were characterized by means of ESCA measurements (MProbe, Surface Science Instruments) and ICP-AES analyses.

Metal dispersions (D_m) were measured by single-introduction–back-sorption coupled methods on the basis of irreversibly adsorbed hydrogen, as described elsewhere [12,13]. Data on metal dispersion of catalyst samples, named Ru/NaY, Ru/Na-ETS-10 and Ru/K-ETS-10, are summarized in table 1. By means of ESCA measurements it was possible to determine the complete reduction of ruthenium after in situ treatment in flowing hydrogen (5 ℓ/h) at 623 K for 4 h.

2.2. CATALYTIC REACTION TESTS

Reaction tests were performed in a bench scale reactor especially designed for FT synthesis of hydrocarbons (C_n: $n < 15$). The apparatus, sketched in fig. 1, was composed of the following parts: (A) gas supply unit equipped with mass flow controllers (Matheson, P601EA); (B) copper coated stainless steel reactor heated by a furnace (Brignole, AU8.5ML) equipped with an electronic heating controller (Ascon, XS); (C) on-line connected gas chromatograph (HP-5890) equipped with an automatic sampling valve (VALCO Inst., VICI A60HT). For further details see ref. [13].

In a standard run, 1 g of fresh catalyst, packed into the reactor body, was activated in flowing H_2 (12 ℓ/h) at 623 K, 800 kPa, for 12 h. The FT reactions were carried out with a mixture of CO and H_2 (High Purity Gas, SIAD) which were purified in a molecular sieve trap. The H_2/CO ratio of the inlet mixture was 2. The catalyst samples were studied at 500–573 K, 500 kPa, and space velocity, GHSV, of 2160 V/V · h (space velocity, GHSV, is defined as the gas hourly reactant flow at STP per total bed volume).

The reaction products, passing through the outlet line kept at 573 K by a thermostatic switch, were directly injected into the gas chromatograph by means of the automatic sampling valve. The products, separated using a capillary column (Wide-Bore Poraplot, Chrompack, 0.53 mm × 25 m), were analyzed with a TCD. The column was initially at 258 K and heated to 453 K at a rate of 10 K/min, followed by heating and holding at 513 K to separate higher hydrocarbons.

3. Results and discussion

Activities, selectivities and turnover frequency, TOF, for all catalyst samples are summarized in table 2. TOFs were calculated using estimated site concentra-

Table 1
Catalyst metal dispersions (D_m) estimated on the basis of irreversibly adsorbed hydrogen as described in refs. [12,13]

Sample	Ru[a] (wt%)	D_m
Ru/NaY	1.0	53.1
Ru/Na-ETS-10	1.0	57.0
Ru/K-ETS-10	1.0	57.5

[a] From ICP-AES analysis.

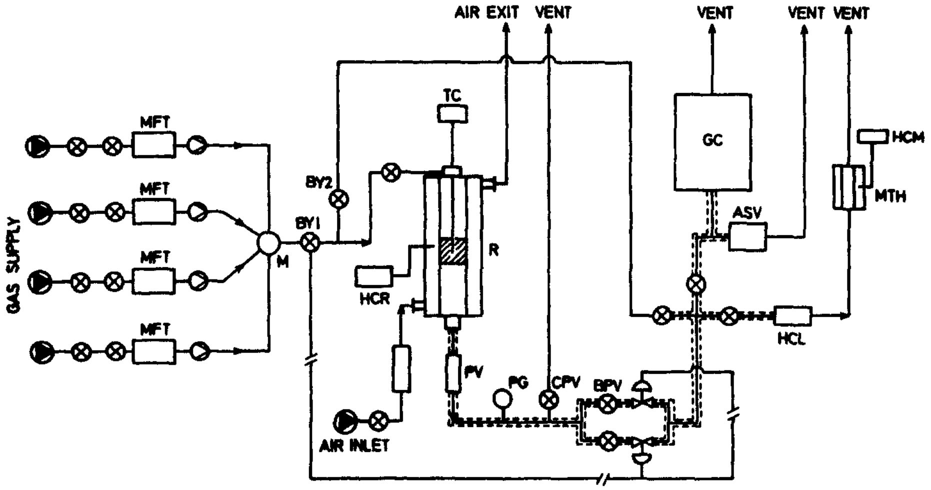

Fig. 1. Apparatus for reaction tests. MFT: mass flow transducer; M: mixer; BY1, BY2: bypass; R: reactor body; HCR, HCM, HCL: heat controllers (reactor, methanizer, exit line); TC: thermocouple; PV: poppet valve; PG: pressure gauge; CPV: cracking pressure valve; BPV: back pressure valves; ASV: automatic sampling valve; GC: gas chromatograph; MTH: methanizer. See also text.

tions provided by hydrogen chemisorption measurements. In order to understand these experimental results on the basis of support nature, some observations have to be noticed.

It is important to stress that for all samples the production of hydrocarbons is limited to the C_7 fraction, present in only a few percent, as a result of reaction parameters and a significant "cage effect". Thus, ETS-10 titanium silicate actually acts as a molecular sieve showing shape selectivity as high as for Na-Y zeolite. Product distribution curves as a function of carbon number for all samples at 548 K are reported in fig. 2. TOF values of catalyst samples evidence no effects of support acidity on catalytic activity, considering a strong decrease in support acidity from Ru/NaY to Ru/M-ETS-10 samples (M standing for Na or K); as men-

Table 2
Activities and selectivities of catalyst samples

Sample	Temp. (K)	CO conv.[a] (%)	CH_4	CO_2	C_{2+}[b]	$C_{3=}/C_3$	TOF[c] ($s^{-1} \times 10^2$)
Ru/NaY	548	7.3	72.6	3.2	24.1	0.5	1.24
Ru/Na-ETS-10	508	2.9	42.3	11.4	46.3	2.0	0.46
	548	8.0	53.7	7.0	39.3	1.1	1.27
Ru/K-ETS-10	508	3.4	33.5	36.0	30.5	3.7	0.53
	548	8.5	43.4	33.5	23.1	3.3	1.33

[a] Reaction parameters: GHSV = 2160 V/V · h; $H_2/CO = 2$; 1 g of fresh catalyst.
[b] C_{2+} stands for hydrocarbons C_2–C_7.
[c] TOF estimated on D_m values. See table 1.

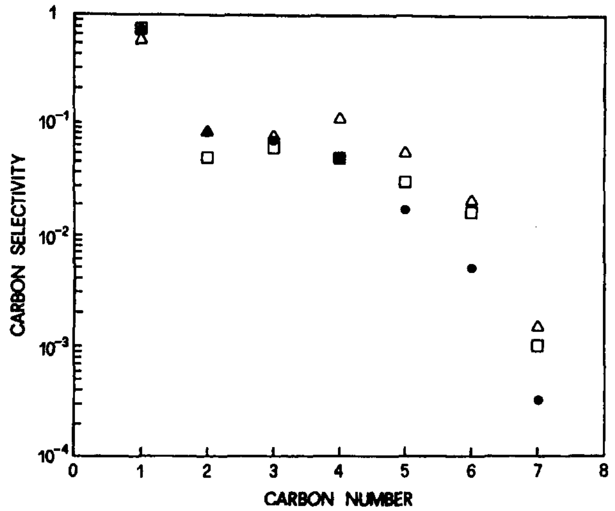

Fig. 2. Carbon number distribution of catalyst samples ($T = 548$ K, GHSV = 2160 V/V · h, $H_2/CO = 2$, 1 g of fresh catalyst).

tioned above ETS-10 materials show no acidic functions [10]. This result is very consistent with data published by Oukaci et al. [15]. On the other hand, the selectivities of the catalysts appear to be strongly affected by the nature of the support. Indeed, experimental selectivities of Ru/Y and Ru/M-ETS-10 catalyst samples seem to be due to some chemical and structural factors: (i) support acidity; (ii) electronic interactions of ruthenium centers with supports and/or alkaline metals (Na^+, K^+); (iii) variations in pore channel structure [15–17].

Ru/NaY and Ru/M-ETS-10 show similar CO conversions at 548 K but significantly different selectivities. In fact, while the selectivity to CH_4 decreases, the selectivity to olefins, as depicted from $C_{3=}/C_{3-}$ values, increases from Ru/NaY to Ru/Na-ETS-10 samples. This trend of CH_4 and olefins selectivities is in complete agreement with the differences in support acidity.

The activity of catalyst samples toward C_1 ($CH_4 + CO_2$) and C_{2+} (C_2–C_7 hydrocarbons) products is a very interesting result. High production of C_{2+} hydrocarbons correlated with low selectivity to C_1 in Ru/Na-ETS-10 catalyst marks this sample from Ru/NaY and Ru/K-ETS-10. Moreover, comparing Ru/NaY and Ru/K-ETS-10 samples in terms of C_1 and C_{2+} selectivities, it becomes evident that they show similar behavior: the only significant difference appears in CH_4–CO_2 and olefins production data.

Actually, differences between Ru/NaY and Ru/M-ETS-10 can still arise from acidic nature of the supports but this is not the case when comparing activities of Ru/Na-ETS-10 and Ru/K-ETS-10 samples.

It is possible to explain the above experimental evidence taking into account that readsorption of olefins seems to be a fundamental step in FT synthesis of hydrocarbons, as recently shown by Iglesia et al. (ref. [18] and references therein).

Slow removal of olefins from catalyst pores by diffusive processes increases the extent of readsorption leading to: (i) improvement of the effectiveness of the chain-growth process; (ii) increase of secondary product formation (isomers, internal olefins, etc. . . .).

It is worth noting that for molecular sieve structures exchange of sodium ions for larger potassium ions produces a change in the void volume of the pores. Thus it seems reasonable that, during catalyst preparation and/or activation, ruthenium diffuses inside the M-ETS-10 supports to a depth which depends on the ionic radius of M-cation. XPS measurements on Ru and Ti signal area ratio, $R = \mathrm{Ru}(3\mathrm{d}_{5/2})/\mathrm{Ti}(2\mathrm{p}_{3/2})$ showed that R values for Ru/Na-ETS-10 and Ru/K-ETS-10 were respectively $R_{\mathrm{Na}} = 0.1$ and $R_{\mathrm{K}} = 0.3$, suggesting that ruthenium was closer to the outer surface of particles in Ru/K-ETS-10 than in the Ru/Na-ETS-10 sample (R values as from ICP-AES analysis were for both samples 0.05). Therefore, readsorption of olefins was a much more favorable process in Ru/Na-ETS-10 than in Ru/K-ETS-10 catalyst and, as mentioned above, the selectivity to secondary products was enhanced in Ru/Na-ETS-10 catalyst.

In order to further validate this explanation, some catalytic tests were performed analyzing the reaction products by means of a GC-MSD (HP-5890 equipped with mass selective detector HP-5971A, capillary column HP1). The average values of normal hydrocarbons, n-C, and isomers, i-C (estimated for C_4 and C_5) showed that production of isomers is higher in Ru/Na-ETS-10 than in the Ru/K-ETS-10 sample ($[n\text{-C}/i\text{-C}]_{\mathrm{Na}} \approx 1$; ($[n\text{-C}/i\text{-C}]_{\mathrm{K}} \approx 5$), confirming that the formation of secondary products such as isomers, increases in the Ru/Na-ETS-10 sample.

Thus, it may be concluded that, when a possible effect of support acidity functions on FT synthesis can be completely ruled out (Ru/M-ETS-10), catalysts activity and selectivity depend on the effectiveness of the olefin readsorption process as described by Iglesia et al. [18]. By contrast, if support acidity is not negligible (Ru/NaY) the catalysts behave as described by Oukaci et al. [15]: acidic functions conceal the expected reaction path allowing relevant side processes (cracking, oligomerization, . . .), although a direct interaction with active metal centers cannot be excluded.

4. Conclusions

Experimental results presented in this work show that ETS-10 titanium silicate is a very interesting catalyst support. In particular ETS-10 shows high ion exchange capacity but no acidic functions.

ETS-10 used as support in Fischer–Tropsch ruthenium supported catalyst showed the following characteristics: (1) good metal dispersion; (2) "cage effect" on selectivity; (3) no side reactions due to acidic functions. Comparison made between catalysts prepared with NaY zeolite and ETS-10 showed that, when a possible effect of support acidic functions on Fischer–Tropsch synthesis can be completely ruled out, readsorption of olefins on active metal centers controls the activity and the selectivity of the catalysts.

Further work is needed in order to fully exploit the peculiar properties of ETS-10 titanium silicate.

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