Iron-doped Pillared Laponites as Catalysts for the Selective Conversion of Syngas into Light Alkenes

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Stable, active and shape selective catalysts for the transformation of syngas into light hydrocarbons (C_2—C_3 alkenes) have been prepared by ion exchanging a laponite with mixed polyhydroxycations of Fe and Al; these results clearly show that mixed $AlFe_xO_y$ species are active and selective sites for syngas conversion.

While most of the early studies on alumina- and zirconia-pillared clays[1,2] were motivated by the possible use of these materials as catalysts in selective hydrocarbon conversion,[3] the more recent studies on the introduction of transition metal ions either into the Al- or Zr-pillars or on the clay surface[4—8] open a way to a variety of other reactions such as the conversion of synthesis gas.[4,7]

We report here results which demonstrate for the first time that Fe^{III} doped Al-PILC'S can act as selective catalysts in the conversion of syngas into light hydrocarbons even at high temperature (700 K). Pillaring was achieved by using mixed Fe^{III}–Al polyhydroxycations, prepared *in situ* within the clay suspension. This *in situ* method, not yet reported in the literature, was operated by adding dropwise and simultaneously 1 l of 0.12 M NaOH and 0.2 l of a 0.5 M ($AlCl_3$ + $FeCl_3$) aqueous solution to 0.5 l of a 2% (w/w) suspension of the clay in water, at 313 K. The total NaOH/metal chloride ratio was 1.2. The pH of the starting suspension is 9.9. The rate of addition was adjusted in order to complete the addition of the base and the metal ions at the same time, after about 1 h. The pH drops to 4.0 within the first 5 minutes and remains constant afterwards. After addition of the solution, the suspension was left to age for 48 h, without stirring at room temperature; the clear supernatant was then removed and the concentrated suspension was dialysed until no more chloride was detected. The dialysed suspension was aged for 7 days and freeze-dried. One sample was prepared without Al and without NaOH. The d_{001} spacings at room temperature were all in the range 1.8—1.84 nm and the N_2 (BET) surface areas were all around 400 m^2/g (±50). The amount of iron reduced by hydrogen at 773 K was below 0.8.

Table 1 shows the activity and the selectivity of one Al-pillared laponite (laponite is a synthetic hectorite), two Fe–Al pillared laponites and one Fe-pillared laponite. We observe that, with mixed pillared laponites, more than 70% of the carbon monoxide is converted into C_2—C_5 hydrocarbons (balance without CO_2) containing mainly ethene and propene. On the other hand we noticed that the Al-pillared laponite was quite inactive in syngas conversion and that a Fe-pillared laponite had a very low selectivity in light alkenes, the main products being methane and carbon dioxide.

Moreover the hydrocarbon distribution obtained with mixed pillared laponites does not follow Schulz–Flory law. An unusual and large selectivity for C_2—C_3 molecules is obvious from the results presented in Figure 1. This selectivity is comparable to the shape selectivity observed with zeolite-

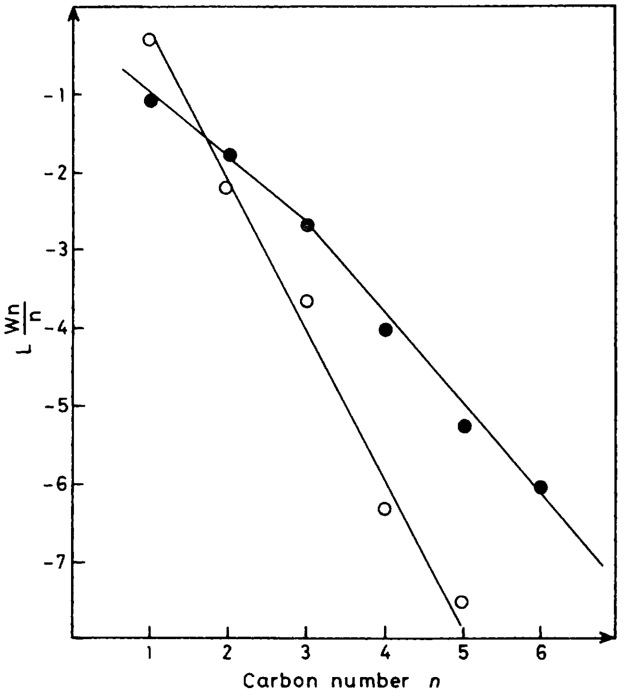

Figure 1. Hydrocarbon distribution from syngas conversion on Fe–Al and Fe-pillared laponites. (●) LAP 80/20 (○) LAP 0/100. Results from Table 1.

Table 1. Conversion of syngas in presence of Fe–Al containing pillared interlayered laponites. P = 1 atm, H_2/CO = 3, m/F = 0.66 g h l^{-1}. Before use, solids were reduced with hydrogen at 773 K for 10 h.

Al/Fe[a]	LAP 100/0	LAP 90/10	LAP 80/20	LAP 0/100
Iron content (%)	0	4.33	6.73	22.4
T_{reaction} (K)	650—750	696	685	693
Activity (×10^3)				
mol h^{-1} g^{-1} catal.	0	0.96	1.33	7.22
mol h^{-1} g^{-1} Fe	0	22.3	19.8	32.2
Selectivity (%)				
CO⟶Cn				
CH_4		30.5	27.7	45.5
C_2H_4		19.8	21.3	2.3
C_2H_6		6.4	6.5	12.9
C_3H_6		15.6	16.5	2.5
C_3H_8		ε^c	ε^c	3.0
C_4H_8		4.6	4.9	ε^c
C_4H_{10}		0	0	0.5
C_5		1.7	2.0	ε^c
C_6		1.1	1.2	0.4
C_7^{+b}		ε^c	ε^c	2.0
CO_2		20.4	20.0	31.0

[a] Atomic ratio. [b] Hydrocarbons containing 7 or more carbon atoms. [c] $\varepsilon \leqslant 0.1\%$

encapsulated metal clusters in the conversion of syngas or methanol into light olefins[9] or fuels.[10—12] However in the present case, in addition to their specific selectivity, these catalysts have fair stability which is not characteristic of zeolite catalysts.

In conclusion these results demonstrate that iron-aluminium oxide species are selective and active sites for syngas conversion into alkenes and that a shape selectivity leading specifically to light alkenes can be obtained when these species are intercalated in hectorite clays. Moreover these catalytic properties are obtained at high temperature (700—800 K) which is also a very important feature for the use of a catalyst in an exothermic reaction.

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