

Improved direct production of 2,3-dimethylbutenes and 3,3-dimethylbutene from 2-methylpropene on tungsten hydride based catalysts

*Anthony Garron, François Stoffelbach, Nicolas Merle, Kai C. Szeto, Sébastien Norsic, Jean Thivolle-Cazat, Jean-Marie Basset and Mostafa Taoufik**

Supporting Information

- *General procedures*

All experiments were carried out by using standard Schlenk and glove-box techniques. Solvents were purified and dried according to standard procedures. Isobutene was deoxygenated before use by passing it through freshly regenerated R-315 catalysts (BASF). $\text{Al}_2\text{O}_3\text{-(500)}$ was prepared with Alumina from Degussa (specific area of $100 \text{ m}^2 \text{ g}^{-1}$), which was partly dehydroxylated at $500 \text{ }^\circ\text{C}$ under high vacuum (10^{-5} Torr) for 15 h. Gas-phase analyses were performed on a Hewlett-Packard 5890 series II gas chromatograph equipped with a flame ionization detector and an $\text{Al}_2\text{O}_3/\text{KCl}$ on fused silica column (50 m X 0.32 mm). Elemental analyses were performed at the CNRS Central Analysis Department of Solaize (metal analysis) or in the LSEO (Dijon, for C, H analysis). IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer by using a DRIFT cell equipped with CaF_2 windows. The samples were prepared under Ar within a glove-box. Typically, 64 scans were accumulated for each spectrum (resolution 4 cm^{-1}). Catalyst evaluation: the solid catalyst was charged using a glove box, into a stainless steel $\frac{1}{2}$ ' cylinder reactor which can be isolated from atmosphere. After connection to the gas lines and purge of tubes, a flow of isobutene controlled by a Brooks® mass flow-meter was sent onto the catalyst bed which was heated at $150 \text{ }^\circ\text{C}$. Hydrocarbon products and hydrogen were analyzed on line by GC (HP 8890 chromatograph fitted with an $\text{Al}_2\text{O}_3/\text{KCl}$ $50\text{m} \times 0.32\text{mm}$ capillary column, FID detector for hydrocarbons and a 3Å molecular sieve column, TCD detector for hydrogen).

- Conversion of Isobutene on W-H/Al₂O₃-(500)

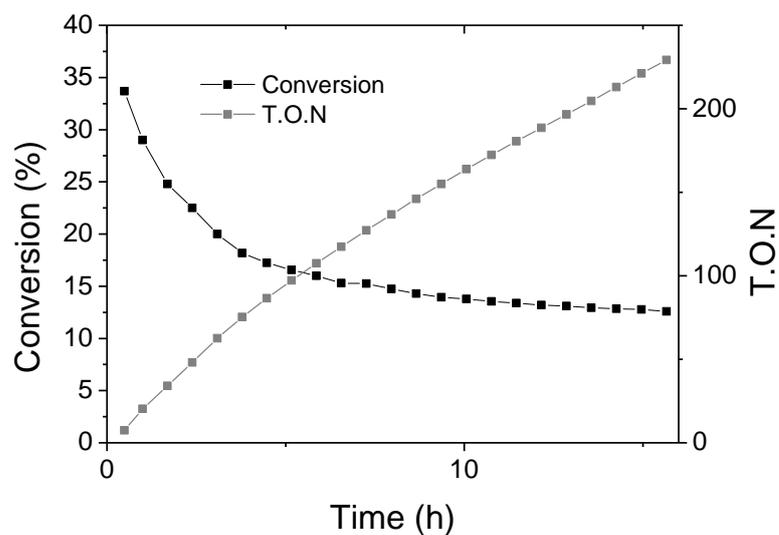


Figure S1: Conversion of isobutene catalysed by W-H/ Al₂O₃-(500) (3.86 wt% W): (a) conversion of isobutene (■) and T.O.N (■).

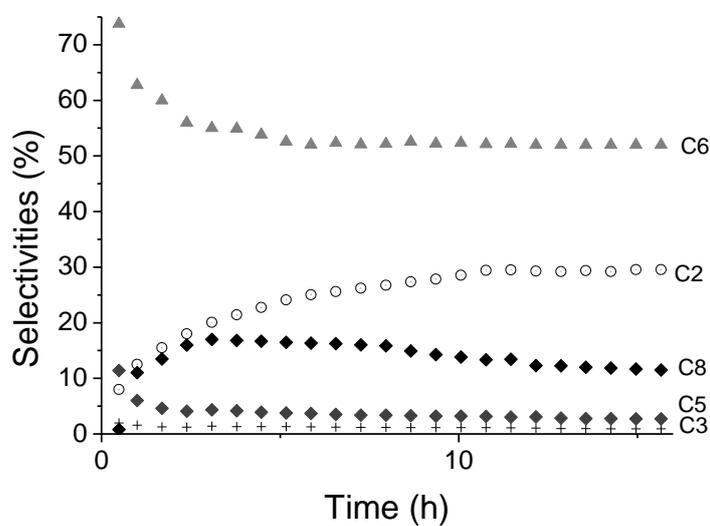


Figure S2: Selectivities: (▲) branched hexenes; (◆) DIB; (○) ethylene; (◆) 3-methylbut-1-ene; (+) propylene.

- Dimerisation of isobutene on γ -Alumina

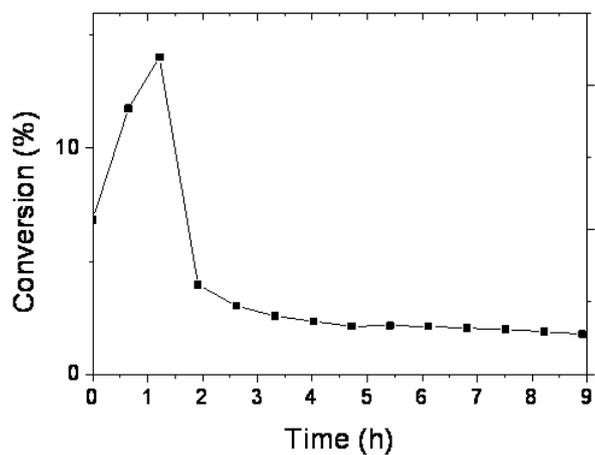
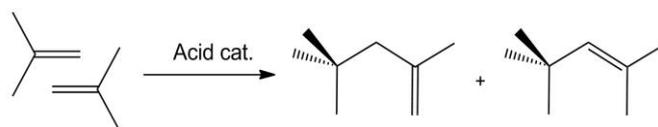


Figure S3: Conversion of isobutene on γ -Al₂O₃-(500).

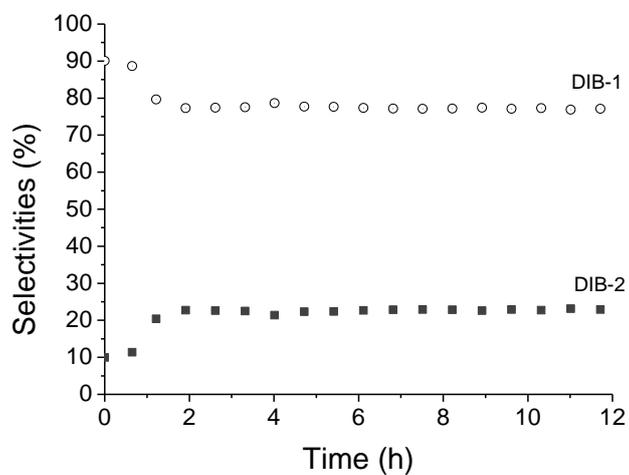


Figure S4: Selectivities in products during the conversion of isobutene on γ -Al₂O₃-(500).

- Cross metathesis reaction between DIB and ethylene.

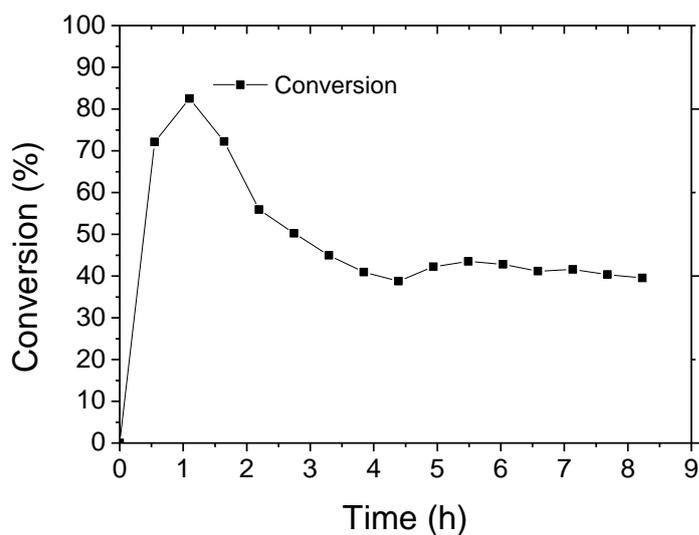
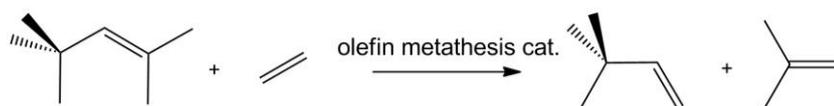


Figure S5: Conversion of DIB catalysed by W-H/ Al_2O_3 - (500) (3.86 wt% W).

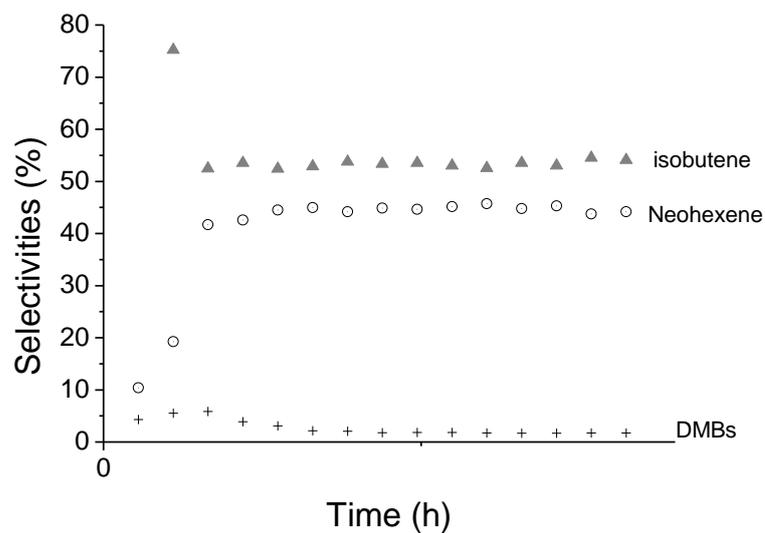


Figure S6: Selectivities: (○) neohexene; (+) DMBs; (▲) isobutene.

-Isomerisation reaction of 2,3-dimethylbutene-2



Equation S1. isomerisation of 2,3-dimethylbutene-2

Preparation and characterization of *W-H/Ni*_{1%}-*Al*₂*O*₃₋₍₅₀₀₎

According to the procedure patented in [1], γ -alumina from Degussa with a specific area of $100 \text{ m}^2 \cdot \text{g}^{-1}$ has been impregnated with an aqueous solution of nickel sulphate hexahydrate ($\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$) at 25°C under air for 1 hour in order to fix 1wt% Ni on the alumina on the final catalyst. The solution was evaporated under vacuum in a rotovapor system before drying overnight at 110°C . Finally the powder was calcined at 500°C under synthetic air flow (N_2/O_2) for 12 h before reduction of nickel at 390°C under pure hydrogen for 20 h. After evacuation of the powder in high vacuum at 500°C for 2h, the $\text{Ni}_{1\%}\text{-Al}_2\text{O}_{3-(500)}$ support was obtained. Then a mixture of $[\text{W}(\equiv\text{C}^t\text{Bu})(\text{CH}_2^t\text{Bu})_3]$ (115 mg, 0.246 mmol) and $\text{Ni}_{1\%}\text{-Al}_2\text{O}_{3-(500)}$ (0.8 g) in pentane (10 mL) was stirred at 65°C for 4 h. After filtration, the solid was washed three times with pentane and all volatile compounds were condensed into another reactor (volume known > 6 L) in order to quantify neopentane evolved during the impregnation. The resulting yellow-brown solid was dried under vacuum (10^{-5} Torr) Then the solid previously obtained was heated at 150°C in the presence of a large excess of anhydrous H_2 (550 Torr). After 15 h, the gaseous products were quantified by GC. Elemental analysis: 2.2 wt% W, 1 wt% Ni

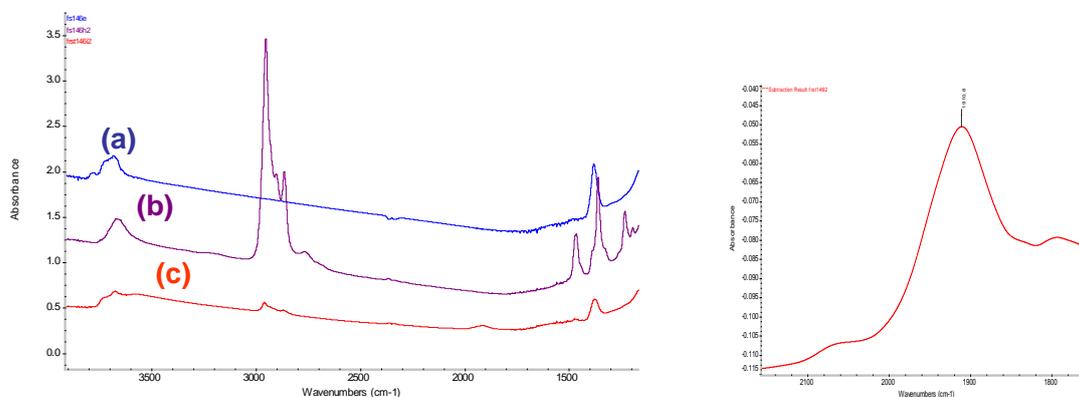


Figure S7: IR Spectra of a) $\text{Ni}_{1\%}\text{-Al}_2\text{O}_{3-(500)}$ b) $[\text{W}(\equiv\text{C}^t\text{Bu})(\text{CH}_2^t\text{Bu})_2]/\text{Ni}_{1\%}\text{-Al}_2\text{O}_{3-(500)}$ and c) $\text{W-H}/\text{Ni}_{1\%}\text{-Al}_2\text{O}_{3-(500)}$.