Hydrogenation of Citral Over Carbon Supported Iridium Catalysts

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Abstract Hydrogenation of citral (3,7-dimethyl-2,6-octadienal) was carried out in a batch reactor at atmospheric hydrogen pressure and 70 °C over Sibunit (mesoporous carbon) supported iridium catalysts with different metal loadings. The major products were isopropyl ethers of geraniol and nerol (2-propanol was used as solvent), but also geraniol, nerol, citronellal di-isopropyl acetal and citronellal were formed. The metal particle size was determined by CO-chemisorption and varied from 2 to 6 nm. The turnover frequency for hydrogenation reactions increased with the metal particle size.

Keywords Catalysis · Hydrogenation · Citral · Iridium

1 Introduction

Hydrogenation of α,β -unsaturated aldehydes is an important reaction, which has recently been reviewed [1–3]. Citral (3,7-dimethyl-2,6-octadienal) belongs to this class of compounds and is also valuable in industrial processes for the synthesis of fragrances, flavours and pharmaceuticals. Hydrogenation of citral gives valuable products, including

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citronellal, geraniol, nerol, and citronellol. Hydrogenation of citral has been studied using Ru [4-9], Pt [7, 10-15], Pd [7, 16, 17], Rh [6, 7, 11], Au [18], Ni [6, 7, 19, 20], Ir [7, 21–23], Co [7], Os [7], Ag [24] and bimetallic [12, 21, 25– 29] catalysts. Citral contains three double bonds of which two are conjugated (C=O and C=C) and the third is isolated. Hydrogenation of the C=C bond is thermodynamically more favourable than the C=O bond making the selective hydrogenation of the C=O bond challenging and a topic of continuous research. Selective hydrogenation of the C=O bond can be achieved using homogeneous catalysts but heterogeneous catalysts are more environmentally friendly and easier to separate and re-use than their homogeneous counterparts [1]. Different factors influence chemoselectivities in selective hydrogenations, such as the metal type, metal particle size and morphology, the use of second metal, electronic and steric influence of the support, metal-support interactions with partially reducible supports, steric effects of the substituents at the conjugated double bond, reaction conditions, and use of additives or promoters (Lewis acids or bases) [24].

In this work, iridium catalysts supported by Sibunit were used in the hydrogenation of citral in a batch reactor under atmospheric hydrogen pressure. Sibunit is a class of porous carbon–carbon composite materials combining advantages of graphite (chemical stability and electric conductivity) and active carbons (high specific surface area and adsorption capacity) [30, 31]. Sibunit is produced in the form of powders with particle sizes of 5–200 μ m, spherical granules of 0.2–4 mm diameter, extrudes in the shape of cylinders, tubes, trefoils, and quatrefoils, and blocks of honeycomb structure. The aim was to hydrogenate citral selectively to either citronellal or geraniol and nerol. Savchenko et al. [23] reported 100 % yield of geraniol using catalysts supported on activated carbon with iridium

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content of 4.7 and 4.9 wt% and boron content of 0.08 and 0.1 wt% (no reaction conditions were given). Singh and Vannice [7] used Ir/SiO₂ and obtained 52 % selectivity to citronellal, but no geraniol and nerol at 27 °C, atmospheric hydrogen pressure and hexane as a solvent. Reves et al. [21] used TiO₂ and SiO₂ supported monometallic and bimetallic iridium catalysts reduced at low (200 °C) and high temperatures (500 °C) at 67 °C, 4.1 bar hydrogen pressure with ethanol as a solvent. It was observed that the selectivity to nerol and geraniol varied with the catalyst reduction temperature. The selectivity to geraniol was 100 % at 37 % conversion for Ir-Ge/TiO₂ reduced at high temperature and the selectivity to nerol was 100 % at 3 % conversion for Ir/TiO₂ reduced at low temperature. The selectivity to citronellal was zero for most of the catalysts and at highest 12 % at 14 % conversion (Ir-Ge/TiO₂ reduced at low temperature).

2 Experimental

2.1 Catalyst Synthesis

Mesoporous graphite-like carbon material of the Sibunit family was used as a support material to prepare the iridium catalysts. The preparation procedures and properties of Sibunit carbons are described elsewhere [30]. Textural characteristics of the mesoporous graphite-like carbon material Sibunit (fr. 40–100 µm, $S_{\text{BET}} = 350 \text{ m}^2/\text{g}$, total pore volume 0.6 cm³/g, mean pore diameter 7 nm) were obtained from the data on nitrogen adsorption measured at 77 K with an automatic volumetric device ASAP 2400 (Micrometritics).

Prior to use, the support was washed to remove any impurities, first by boiling Sibunit with distilled water to remove suspended coal dust, then washing with HCl (2 M) under reflux for 4 h, and finally washed with distilled water and dried at 120 °C. The iridium catalysts used in the experiments were prepared using solutions of reagent grade IrCl₄·*n*H₂O in HCl (0.5 M) (Ir content 52.9 %, JSC "The Gulidov Krasnovarsk non-ferrous metals plant") by two different procedures: incipient wetness impregnation (IWI) and deposition-precipitation (DP). Iridium catalysts (Ir/C-1, Ir/C-3) were prepared by DP using the following procedure. To prepare Ir/C-1 catalyst sample the carbon support was dispersed in water. An appropriate amount of an aqueous solution of H2IrCl6 was added dropwise under moderate stirring, followed by addition of Na₂CO₃ (1 M) aqueous solution, reduction by NaBH₄, separation by filtration, washing with water until the pH of the rinsing waters reached a value of 6, and finally dried overnight at 120 °C. The procedure of Ir/C-3 sample preparation was similar to Ir/C-1 except that catalyst sample after mixing with the aqueous solution of Na_2CO_3 was washed, dried overnight at 120 °C and reduced by hydrogen at temperature ramp 2 °C/min up to 350 °C.

Iridium catalyst (Ir/C-2) was prepared by incipient wetness impregnation where the precursor solution was poured down onto the support by drops in a single step using the appropriate concentration to obtain required metal content. The sample was kept sealed at room temperature overnight, then dried and reduced by hydrogen similarly to Ir/C-3 sample.

2.2 Catalyst Characterization

To determine the metal particle size and dispersion, samples were analysed by CO pulse chemisorption (Autochem 2910, Micromeritics) where 0.1-0.3 g of the sample was placed into a quartz sample tube containing silica wool. The tube was inserted to the system and the sample was treated in a stream of helium (AGA) gas at 50 °C for 30 min. After that, the sample was reduced at 400 °C for 1 h in hydrogen (AGA) using helium as a carrier gas, after which it was flushed with helium (still at 400 °C) for 1 h, cooled to room temperature, placed on water bath, and subsequently the CO pulses were introduced (10 % CO in helium, helium as a carrier gas) until adsorption was complete. The dispersion was calculated from the amount of CO consumed, assuming the CO:Ir stoichiometry to be unity [32].

Quantitative analysis of iridium concentration was performed using wavelength dispersive X-ray fluorescence (WDXRF) spectrometry with pressed powder pellet method. Test samples (0.1 g) were diluted with cellulose (0.9 g). Resulting samples were ground in a ball mill for 30 min and pelletized in 20 mm diameter die using handpress. Calibration samples with iridium content from 0.5 to 3 % were prepared utilizing the same technique by mixing an appropriate amount of cellulose with iridium containing substance with known iridium content. The intensities of iridium La1 lines in samples were measured on an ARL Advant'X spectrometer equipped with a rhodium anode X-ray tube. Excitation conditions were as follows: tube voltage of 50 kV; current of 40 mA; collimator with a divergence of 0.25°; LiF200 crystal was used as a monochromator; scintillation counter was used as a detector; counting time was 12 s.

The SEM analysis was performed with a LEO Gemini 1530 with a Thermo Scientific UltraDry Silicon Drift Detector (SDD), equipped with SE (secondary electron), BSE backscattered electron) detectors, as well as an In-Lens detector.

X-ray photoelectron spectra (XPS) were recorded using SPECS spectrometer with PHOIBOS-150 hemispherical energy analyzer and MgK α X-ray irradiation (h ν = 1253.6 eV,

100 W). Binding energy scale was preliminarily calibrated by the position of the peaks of Au4f_{7/2} (84.00 eV) and Cu2p_{3/2} (932.67 eV) core levels. For spectra recording the samples were supported to the conductive copper scotch tape. The binding energy of peaks was corrected to take into account the sample charging by referencing to the C1s (284.5 eV) (internal standard). The ratio of surface atomic concentrations of the elements was calculated from the integral intensities of photoelectron peaks corrected by corresponding atomic sensitivity factors (ASF) [33]. In addition to the survey photoelectron spectra, more narrow spectral regions C1s, Ir4f, Cl2p, and O1s have been recorded. For the survey spectra the pass energy of the analyzer was 50 eV, while for the narrow spectral regions the pass energy was 20 eV.

2.3 Experimental Procedure

The experiments were performed in a stainless steel shaking reactor with a shaking frequency of 4 double movements per second. Citral and 2-propanol were from Sigma-Aldrich (>99.8 %) and hydrogen from AGA (99.999 %). The reactant concentration was 0.02 M and the amount of catalyst in the experiments was 0.2 g (<40 μ m). The iridium catalysts were reduced ex-situ at 400 °C (heating rate 5 °C/min) for 1 h in hydrogen flow. The catalyst was pre-treated additionally in situ at 70 °C in 70 ml solvent for 45 min in hydrogen flow. The experiments were conducted at 70 °C under atmospheric hydrogen pressure. The reactant in 30 ml solvent was injected to a bubbling unit and hydrogen was bubbled through for 5 min. The reactant solution was led to the reactor, the reaction time was set to zero and the reaction was started.

Samples were taken at different time intervals and analyzed by a gas chromatograph (GC). The samples were prepared for GC using 0.5 ml of the sample taken from the reactor and to this 0.5 ml of internal standard, consisting of 0.02 M cyclohexanone in cyclohexane, was added. An aliquot of 1 μ l of the sample was injected with an autosampler to the GC. The injector temperature was 220 °C and the split ratio 50:1. A Supelco B-Dex-225 column was used and the helium gas flow rate was 0.9 ml/min and the temperature program 78 °C for 85 min, 1 °C/min to 90 °C and 10 °C/min to 165 °C for 10 min. The flame ionization detector (FID) was kept at 300 °C. The products were identified by GC–MS.

3 Results and Discussion

3.1 Catalyst Characterization

The Ir contents of Ir/C-1, Ir/C-2, Ir/C-3 catalysts were measured using X-ray fluorescence (XRF) technique. The

results are presented in Table 1. Ir/C-1 had 0.55 wt% iridium (will be denoted as 0.55 wt% Ir/Sibunit hereon), Ir/C-2 had 2.97 wt% iridium (denoted 3 wt% Ir/Sibunit), and Ir/C-3 had 0.99 wt% (denoted 1 wt% Ir/Sibunit).

The catalysts were characterized by CO chemisorptions and SEM-EDX. The results from CO chemisorptions are presented in Table 2. For the Sibunit supported catalysts the metal dispersion varied from 18 % for 1 wt% Ir/Sibunit to 37 and 53 % for 0.55 and 3 wt% Ir/Sibunit, respectively. Figure 1 shows the results from SEM, confirming that the catalyst particles are spherical. EDX showed that no other metals than iridium were present.

The XP spectra of 3 wt% Ir/Sibunit are shown in Fig. 2. They were recorded after (1) the catalyst reduction has been performed at 300 °C, (2) heating at 500 °C in vacuum for 1 h, (3) heating at 500 °C in O₂ for 1 h. One should note that the intensities of Ir4f were normalized to the intensity of C1s level of Sibunit support. The value of binding energy of Ir4f level in the sample treated with H₂ is 61.5 eV, while heating of the sample in vacuum shifts this line to 61.2 eV, which is typical for Ir^0 in the bulk (BE = 60.9 eV) [34]. One the contrary sample heating in O₂ shifts the peak to higher values of BE (62.0 eV) characteristic for Ir in the oxide. It can be concluded therefore that in the initial 3 % Ir/Sibunit highly dispersed species have been formed with Ir in the metallic state. Heating of the sample in vacuum results in sintering which is evidenced by a decrease of Ir/C ratio (Table 3) and a subsequent shift of Ir 4f level towards value characteristic for bulk metal.

The Ir 4f spectra for 0.55 wt% Ir/Sibunit, 1 wt% Ir/Sibunit, and 3 wt% Ir/Sibunit are displayed in Fig. 3. Two of these catalysts, namely 0.55 wt% Ir/Sibunit and 3 wt% Ir/Sibunit contain predominately Ir(0) with a small amount of Ir(III). Contrary to it 1 wt% Ir/Sibunit contains mainly Ir(III) with minor quantities of Ir(0), indicating that during

Table 1 Ir content in catalysts samples determined by XFA

Sample	Ir content (%)
Ir/C-1	0.55
Ir/C-2	2.97
Ir/C-3	0.99

 Table 2
 Catalyst characterization data

Catalyst	Ir dispersion (%)	Ir particle size (nm)		
0.55 wt% Ir/Sibunit (Ir/C-1)	37	3		
1 wt% Ir/Sibunit (Ir/C-3)	18	6		
3 wt% Ir/Sibunit (Ir/C-2)	53	2		



Fig. 1 Scanning electron micrograms of 3 wt% Ir/Sibunit ×25,000



Fig. 2 Ir4f core-level photoelectron spectra of the 3 wt% Ir/Sibunit catalyst

the preparation procedure treatment with hydrogen was not sufficient, thus it was completed with ex-situ pre-reduction prior to experiments at 400 °C. Moreover, analysis of the samples for chlorine showed that 1 wt% Ir/Sibunit had much more chlorine than the two other, which is in agreement with the presence of Ir(III) in 1 wt% Ir/Sibunit.

Table 3 XPS binding energies

and Ir/C ratios

The intensities of Ir4f line in 0.55 and 3 wt% Ir/Sibunit catalysts are concomitant indicating similar content of Ir species in the same electronic state [Ir (0) and Ir(III)]. As expected, significant differences in the Ir/C atomic concentration ratios were detected for 0.55 and 3 wt% Ir/ Sibunit contrary to 1 wt% Ir/Sibunit (Table 3). In the 1 wt% catalyst, Ir/C ratio on the surface is lower than that in the bulk as compared with 0.55 wt% catalyst suggesting a lower dispersion of the Ir particles in agreement with CO chemisorption results. At higher Ir loading (3 wt% prepared by impregnation) this Ir/C ratio remains almost the same as for Ir 0.55 wt% indicating approximately the same Ir dispersion as well as predominate core-shell distribution of Ir in 0.55 wt% Ir/Sibunit with lower bulk Ir concentration. It is worth to note that the surface Ir/C ratio is independent on the preparation method.

3.2 Hydrogenation of Citral

The reaction scheme for the hydrogenation of citral is shown in Fig. 4. The starting material consists of *E*-citral (geranial) and *Z*-citral (neral) with about 50 % of each (the ratio changed slightly during the reaction). When the C=O bond is hydrogenated the reaction products are geraniol and nerol. When the conjugated C=C bond is hydrogenated, the reaction product is citronellal. Citronellol is formed when the double bond in geraniol and nerol or when the C=O bond in citronellal is hydrogenated. Citronellol can be further hydrogenated to 3,7-dimethyloctanol, but this did not take place in our case. Side reactions such as etherification of geraniol and nerol as well as acetalization of citronellal also took place. Moreover, decarbonylation and cyclization can occur, but we did not notice these.

The conversion profiles as a function of time for different Sibunit catalysts are given in Fig. 5. The conversion was 31 % in 4 h for 0.55 wt% Ir/Sibunit, 58 % for 1 wt% Ir/Sibunit and 99 % for 3 wt% Ir/Sibunit. The selectivity to citronellal (CAL) as a function of conversion is shown in Fig. 6. The selectivity is highest in the beginning, but decreases with conversion for 3 and 1 wt% Ir/Sibunit, but is relatively constant around 12 % for 0.55 wt% Ir/Sibunit.

Semula	1-46	C1a	L./C	
Sample	If41 _{7/2}	CIS	II/C	
0.55 wt% Ir/Sibunit (Ir/C-1)	61.6	284.5	0.0026	
1 wt% Ir/Sibunit (Ir/C-3)	62.6	284.5	0.0013	
3 wt% Ir/Sibunit (Ir/C-2)	61.5	284.5	0.0027	
3 wt% Ir/Sibunit, vacuum, $T = 500$ °C	61.2	284.5	0.0021	
3 wt% Ir/Sibunit, oxygen, $T = 500$ °C	62.0	284.5	0.0027	



Fig. 3 Ir4f core-level photoelectron spectra of the Ir/Sibunit catalysts

The highest selectivity was 18 % for 1 wt% Ir/Sibunit at around 20 % conversion.

The selectivity to geraniol (G) and nerol (N) as a function of conversion is shown in Figs. 7 and 8, respectively. As can be seen, the selectivity was lower for 1 wt% Ir/Sibunit with 6 nm metal particles compared to the other catalysts (with 2 and 3 nm). This suggests that the selectivity to geraniol and nerol is depending on the metal particle size. Galvagno et al. [5] found no influence of particle size on the selectivity to geraniol and nerol when Ru/C catalyst was used, which is different from the current data for iridium. The selectivity to geraniol increased with conversion for 0.55 wt% Ir/Sibunit from around 11 to 15 %. For 1 wt% Ir/ Sibunit the selectivity to geraniol was around 6 % and for



Fig. 5 Hydrogenation of citral, conversion versus time, *filled diamond* 3 wt% Ir/Sibunit (2 nm), *filled square* 1 wt% Ir/Sibunit (6 nm), and *filled triangle* 0.55 wt% Ir/Sibunit (3 nm)

3 wt% Ir/Sibunit the selectivity decreased with conversion from around 14 % to ca. 11 %. The selectivity to nerol was mostly 4 % for 0.55 wt% Ir/Sibunit, and for 3 wt% Ir/Sibunit the selectivity was constant ca. 4 % decreasing slightly after 80 % conversion. The selectivity to nerol for 1 wt% Ir/ Sibunit was constant (ca. 2 %).

The selectivity to isopropyl ethers of nerol (NE) and geraniol (GE) (identified by GC–MS that gave a molecular weight of M_w 196 and the isopropyl mass fragment M/e^+ 59) is presented in Figs. 9 and 10, respectively. It can be noticed, that the selectivities were close to each other in the case of 0.55 and 1 wt% Ir/Sibunit, but much higher for 3 wt% Ir/Sibunit. The explanation could be that 3 wt% has much more metal and this could have an influence on the selectivity. Etherification is mostly done using acidic catalysts without metal [35, 36]. However, previously etherification was observed on carbon nanofiber supported palladium





Fig. 6 Selectivity to citronellal as a function of conversion, *filled diamond* 3 wt% Ir/Sibunit (2 nm), *filled square* 1 wt% Ir/Sibunit (6 nm), and *filled triangle* 0.55 wt% Ir/Sibunit (3 nm)



Fig. 7 Selectivity to geraniol as a function of conversion, *filled diamond* 3 wt% Ir/Sibunit (2 nm), *filled square* 1 wt% Ir/Sibunit (6 nm), and *filled triangle* 0.55 wt% Ir/Sibunit (3 nm)



Fig. 8 Selectivity to nerol as a function of conversion, *filled diamond* 3 wt% Ir/Sibunit (2 nm), *filled square* 1 wt% Ir/Sibunit (6 nm), and *filled triangle* 0.55 wt% Ir/Sibunit (3 nm)

catalysts where the main reaction was hydrogenolysis [37]. In [37] more ether was formed with less acidic catalyst (the selectivity to hydrogenolysis product was lower for less acidic catalyst). We excluded the acidity function since the pH of the materials were the same, 7.1, when dispersed in water, which suggests that the materials were not acidic after



Fig. 9 Selectivity to nerol isopropylether as a function of conversion, *filled diamond* 3 wt% Ir/Sibunit (2 nm), *filled square* 1 wt% Ir/Sibunit (6 nm), and *filled triangle* 0.55 wt% Ir/Sibunit (3 nm)



Fig. 10 Selectivity to geraniol isopropylether as a function of conversion, *filled diamond* 3 wt% Ir/Sibunit (2 nm), *filled square* 1 wt% Ir/Sibunit (6 nm), and *filled triangle* 0.55 wt% Ir/Sibunit (3 nm)



Fig. 11 Selectivity to citronellal di-isopropylacetal as a function of conversion, *filled diamond* 3 wt% Ir/Sibunit (2 nm), *filled square* 1 wt% Ir/Sibunit (6 nm), and *filled triangle* 0.55 wt% Ir/Sibunit (3 nm)

reduction at 400 °C. The selectivity to nerol isopropyl ether was around 7 % for 0.55 wt% Ir/Sibunit, from 8 % in the beginning at lower conversion to 12 % at higher conversions for 1 wt% Ir/Sibunit and decreasing from 23 % at lower



Fig. 12 Turnover frequency of hydrogenation reaction (excluding acetalization and etherification) at 30 min as a function of Ir particle size

conversion to 19 % at higher conversion for 3 wt% Ir/Sibunit. The selectivity to geraniol isopropyl ether was around 17 % for 0.55 wt% Ir/Sibunit, from 17 % up to 28 % for 1 wt% Ir/Sibunit. For 3 wt% Ir/Sibunit initial selectivity to this compound was 48 % at lower conversion and decreased to 43 % at higher conversion. 3 wt% Ir/Sibunit also behaved differently from the other catalysts regarding formation of citronellal di-isopropyl acetal (CALacetal, Fig. 11), displaying lower selectivity. The selectivity varied from 24 % at lower conversion to 32 % at higher conversion for 0.55 wt% Ir/Sibunit and around 33 % for 1 wt% Ir/Sibunit. 3 wt% Ir/Sibunit exhibited just 4 % selectivity towards citronellal acetals in the beginning and 14 % in the end of the experiment. Note that acetalization is an acid catalyzed homogeneous reaction [6] that does not require metal. However, the materials were not acidic since the pH of the catalyst slurries were as high as 7.1.

The metal particle size had an influence on turnover frequency, as seen from Fig. 12 where the turnover frequency (TOF) of hydrogenation reactions (excluding acetals and ethers) is plotted as a function of metal particle size, showing TOF increase as the metal particle size increased. Reyes and Rojas [15] used Pt and Pt–Fe/SiO₂ catalysts and investigated the influence of metal particle size in the range of 1.6 to 3.8 nm. The metal particle size did not affect the TOF in their case.

An overview of TOF for hydrogenation reactions and selectivity to different products at 30 % conversion is given in Table 4. The selectivity to nerol and geraniol ethers was high, as high as 72 % in the case of 3 wt% Ir/ Sibunit. Since the amount of ether is so high, that would explain why the selectivity to geraniol and nerol was moderate as they reacted further to form ethers. However, the lumped selectivity to geraniol, nerol and their ethers was 90 % for 3 wt% Ir/Sibunit, 38 % for 1 wt% Ir/Sibunit and 45 % for 0.55 wt% Ir/Sibunit. It seems that the amount of surface metal affects the C=O group hydrogenation; the more surface metal is available the more of the C=O bond is hydrogenated (the dispersion for 1 wt%) Ir/Sibunit is low compared to 0.55 wt% Ir/Sibunit thus that the amount of surface metal is actually higher for 0.55 wt%). Moreover, several unknown products, which were not isopulegol, menthol, citronellol or 3,7-dimethvloctanol, were formed when 0.55 and 1 wt% Ir/Sibunit were used.

4 Conclusions

The hydrogenation of citral was carried out in a batch reactor over Sibunit (mesoporous carbon) supported catalysts with 0.55, 1 and 3 wt% iridium. Isopropyl ethers of geraniol and nerol (2-propanol was used as a solvent), geraniol, nerol, citronellal di-isopropyl acetal and citronellal were obtained as products. The iridium particle size was determined by CO-chemisorption and varied from 2 to 6 nm. The turnover frequency for hydrogenation reactions increased when the metal particle size increased. The formation of geraniol and nerol was lower for 1 wt% Ir/Sibunit, which had larger metal particles, higher chlorine content and different oxidation state than the other two catalysts. The etherification was the highest for the catalyst with the highest metal loading (3 wt%), while the least amount of acetals was formed with the same catalyst. The results cannot be attributed to acidity function, since the pH of the catalyst slurries was 7.1, which means that the catalyst was not acidic.

Table 4 Hydrogenation of citral using carbon supported catalysts

Catalyst	TOF $(h^{-1})^a$	Sel CAL (%) ^b	Sel G $(\%)^{b}$	Sel N (%) ^b	Sel GE + NE $(\%)^{b}$	Sel CALacetal (%) ^b	Sel unknown (%) ^b
0.55 wt% Ir/Sibunit	117.0	11	15	5	25	31	13
1 wt% Ir/Sibunit	174.8	10	5	1	32	33	19
3 wt% Ir/Sibunit	37.0	6	14	4	72	4	0

^a Moles hydrogenated (excluding acetalization and etherification) in 30 min per mole of surface metal

^b Selectivity at 30 % conversion

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