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To be cited as: *ChemCatChem* 10.1002/cctc.201901981

Link to VoR: http://dx.doi.org/10.1002/cctc.201901981

A Journal of ChemPubSoc Europe

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Selective hydrogenation of xylose to xylitol over Co/SiO$_2$ catalysts

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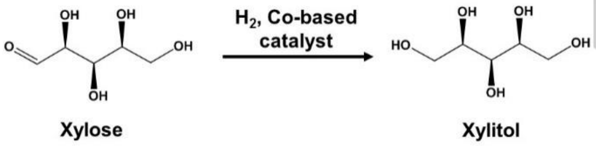
Dedication ((optional))

Abstract: Xylose can be selectively converted to xylitol in water, with an optimized yield of 98%, in the presence of a simple silica supported monometallic cobalt - Co/SiO$_2$ - catalyst. This catalyst displays initial outstanding catalytic properties in a proper solvent, the best results being obtained in pure water. Recyclability studies show a moderate deactivation of the catalyst, while selectivity to xylitol remains almost unchanged after 4 cycles, confirming that this catalyst formulation is very promising for the xylitol production process.

Xylose is a product issued from the hydrolysis of beechwood hemicelluloses. Different routes exist for the valorisation of xylose, amongst the selective hydrogenation to xylitol (scheme 1). Xylitol is an extensively used molecule in food, cosmetics, and pharmaceutical industry [1-4]. Xylitol has then been identified as one of the top-twelve value added chemicals that can be obtained from biomass [5]. As an example, xylitol is a valuable water soluble sweetener due to its atypical properties amongst, a higher sweetness strength and a lower energy capacity, as compared with sucrose. Nowadays, xylitol is widely incorporated in quotidian consumed products (chewing gums, chocolates, toothpastes, *etc.*) [6]. With an estimated market of 340 M$, xylitol is becoming the most popular "natural" sweetener [7]. Industrial production of xylitol by selective catalytic hydrogenation appears then as an economically viable approach.



Scheme 1. Hydrogenation of xylose to xylitol.

Xylitol can be produced by catalytic hydrogenation in the presence of RANEY® nickel. Reaction is performed in liquid phase, under high hydrogen pressure and temperature in batch-type reactors [8]. Selectivity above 90%, at a high conversion degree can be obtained at 80-130°C under 40-70 bar of H$_2$ (5 wt.% catalyst of the xylose mass, solution 40-60 wt.% of xylose in water) in the presence of RANEY® nickel. Despite the high selectivity and activity reached using this catalyst, with economic advantages related to the use of noble metal - free catalysts for the reaction, the intrinsic properties of the nickel, amongst toxicity and limited stability, [8-9] motivate the research of efficient catalyst substitutes. Food applications indeed implies the absence of any trace of nickel in the final product, nickel being recognized as a carcinogen compound. Most of recent studies were devoted to the study of supported noble metals, such as Ru, Rh and Pd, in monometallic or bimetallic catalytic systems, with the possible adding of dopants as Sn [8-15] Ru appeared as the most efficient. Hernandez-Mejia *et al*. [16] reported that xylose can be selectively converted to xylitol in the presence of rutile phase TiO$_2$ supported Ru (1 wt.%), despite the low surface area displayed by the rutile support. Authors then reported xylose yields higher than 90%, for a reaction performed in water at <140°C under 20 bar of H$_2$ and at a catalyst to xylose ratio (wt./wt.) of 1. Compared with rutile, the better dispersion of Ru over anatase does not allow to reach comparable activity nor selectivity to xylitol. As recently reviewed by Delgado Arcano et al., nickel and ruthenium catalysts then remains the most widely studied materials for the xylose to xylitol reaction, while titania is the most suitable support [15]. Replacement of noble metals in catalytic formulations is however preferable due to limited resources, fluctuating costs, and consumption by high - technology markets. Alternative catalysts, based on earth abundant transition metals such as cobalt, and in a lower extent copper, displaying lower toxicity than nickel demonstrated satisfying activity and stability in water under neutral to basic conditions for some hydrogenation reactions [17]. Thus, for some hydrogenation of biomass derived molecules, cobalt formulations are considered as very promising. Metallic cobalt indeed presents interesting activity for the hydrogenation of C=O bonds, as already observed for the selective conversion of cinnamaldehyde to cinnamyl alcohol [18-20], furfural to furfuryl alcohol [17,21], HMF hydroconversion [17,22] *etc.*

With this study, we demonstrated that, using a non-noble metal catalyst based on cobalt supported on a commercially Aerosil® 380 silica, high yields to xylitol can be obtained when reaction conditions are optimized. Furthermore, the catalyst can be reused at least three time before notable deactivation.

Silica supported cobalt oxide is prepared by Incipient Wetness Impregnation (IWI), starting from a hydrated cobalt nitrate precursor, a classical and industrialized approach. The oxide precursor, Co$_3$O$_4$/SiO$_2$, is obtained by calcination of the solid at 500°C under air. Formation of Co$_3$O$_4$ is confirmed by XRD (Figure 1(a)), with the presence of broad and poorly intense reflections corresponding to the expected crystalline phase (ICDD file n°42-

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1467). Considering the width of the reflections, the crystal domain size of the cobalt phase is relatively low (<10 nm). These results indicate that the impregnation used for the catalyst preparation is efficient to afford a high dispersion of the cobalt oxide phase.

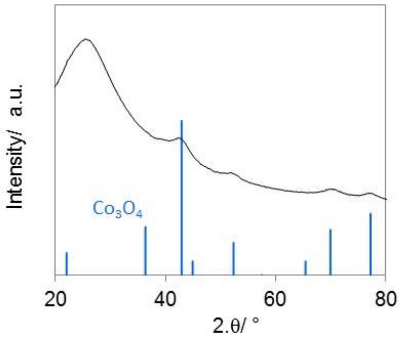

Figure 1. XRD analysis of Co/SiO_2 catalyst before (vertical bars, reference ICDD 42-1467).

In view of the catalyst application, the catalyst is first reduced under H_2 flow at 500°C for 10h. Main characteristics of the reduced catalyst (Co/SiO_2) are presented in Table 1. The solid retains satisfying textural properties, mainly large surface area and large pore diameter, compatible for liquid - phase catalytic reactions. In addition, the limited variation of the textural properties indicates adequate stability of the support (Table 1).

Table 1. Main characteristics of the Co_2O_3/SiO_2 and reduced Co/SiO_2 materials.

	Co_3O_4/SiO_2	Co/SiO_2
XRD phase	Poorly crystallized Co_3O_4	n.d.[a]
$D_{part.}$/[b] nm	n. d.[a]	Aggregates 10 to >100 nm Crystals <20 nm
S_{BET}/[c] $m^2.g^{-1}$	185	169
V_p/[c] $cm^3.g^{-1}$	0.71	0.63
D_p/[c] nm	15.0	14.7

[a] n.d.: not determined; [b] mean particle size obtained by TEM image observation; [c] surface area (S_{BET}), pore volume (V_p) and pore diameter (D_p) issued from N_2 physisorption at 77K.

Particle sizes and localization throughout the support porosity are not homogeneous (Figure 2). On large scale analysis, the aggregates of cobalt NPs are observed throughout the surface of the silica grains. The visible aggregates are of 20-100 nm in size. Focusing on the aggregates allowed to observe elementary particles of different sizes varying from 25 nm to less than 3 nm.

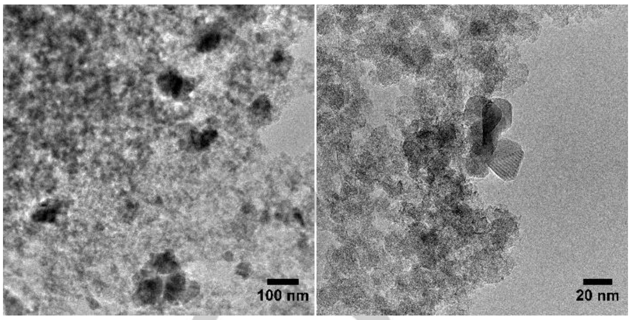

Figure 2. TEM images recorded for reduced Co/SiO_2 catalyst.

Activity of Co/SiO_2 is initially evaluated for the hydrogenation of 5 wt.% of xylose in 10 mL of water, with 5 wt.% of catalyst (toward xylose content). Reaction is performed at 150°C, under 5.0 MPa of hydrogen (Table 2, Entry 5). Figure 3 shows the evolution of the xylose conversion and the xylitol yield with reaction time. After only 30 min of reaction, the xylose conversion reaches 82%, with a xylitol yield of 77%. Xylose conversion and xylitol yield are observed to increase, to reach both 100% after 4 h of reaction. This noble metal - free catalyst, simply prepared by IWI over a commercial support is outstandingly active and selective for the hydrogenation of xylose to xylitol. However, when reaction time reaches 6 h, the xylitol yield starts to slightly decrease to 92%. Blank reaction performed under the same conditions, but without catalyst, led to a xylose conversion of 17% with no xylose being obtained (Table 2, Entry 1). This clearly shows that the selective conversion of xylose to xylitol is attributed to the presence of the cobalt-based catalyst.

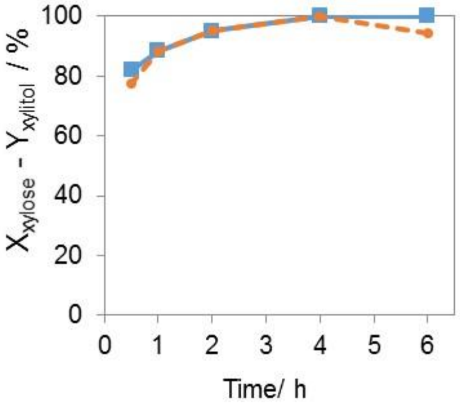

Figure 3. Hydrogenation of xylose to xylitol in the presence of Co/SiO_2 catalyst (full line: xylose conversion; dotted line: xylitol yield).

A comparison between the performances of Co/SiO_2 and a reference 1 (wt.%) Pd/C commercial hydrogenation catalyst (Table 2, Entry 2) demonstrated the high activity displayed by the Co/SiO_2 formulation, besides an exceptional chemoselectivity for the C=O bond hydrogenation. Under the exactly similar reaction conditions, the maximum xylitol yield obtained with 1%Pd/C, 58%,

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is achieved after 6 h of reaction (with a conversion of xylose limited at 81%). In addition, by-products form during reaction in the presence of Pd/C catalyst: tetrahydrofurfuryl alcohol (THFFA) and degradation products. The presence of tetrahydrofurfuryl alcohol was confirmed by mass spectrometry (signal at m/z = 102, with a fragment at m/z = 70 associated to $C_4H_7O_1^+$). Formation of THFFA is issued from the dehydration/hydrogenation of xylitol, occurring with the formation of 1,4-anhydroxylitol as intermediate.

Entry	Xylose content (wt%)	T (°C)	P(H_2) (MPa)	Conv. (%)	Xylitol Yield (%)
1 (No catalyst)	5	150	5	17	0
2 (1%Pd/C)	5	140	5	81	58
3	5	150	4.0	92	83
4			3.0	91	82
5		150	1.0	77	22
6	5	150	5.0	100	98
7		140		100	90
8		140[a]		98	90
9		130		82	78
10		100		69	65
11		100[b]		84	81
12	10	140	5.0	90	78
13	20	140	5.0	71	35
Ru/TiO_2[16]	1	120	2.0	100	98
Ru/C[14]	5	100-110	4.0-6.0	99.7	98.1
Raney Ni[23]	40-60	130	7	~92.5	~81
Raney Ni[24]	20	120	5.5	96.6	93.7
Ru/NiO-TiO_2[4]	20	120	5.5	99.9	99.7

[a] reaction time of 2h, [b] reaction time of 6h.

This is obviously not the case with the Co/SiO_2 catalyst. Activity, selectivity, and the absence of detectable by-products, clearly demonstrate the potential of the Co-based catalyst for the selective conversion of xylose to xylitol, when supported over silica. Comparison with available literature (Table 2) shows that the performances reported herein are directly comparable with the best ones available in the literature, over Ru- or Ni-based catalysts. The properties of Co/SiO_2 catalyst is further investigated under different experimental conditions (reaction temperature, pressure of hydrogen, solvent, xylose loading) in order to establish the suitable conditions for the hydrogenation of xylose to xylitol (Table 2, Entries 3-13).

The effect of the hydrogen pressure on activity and selectivity is first presented in Table 1 (Entries 3-6). An increase in hydrogen pressure from 1.0 MPa to 5.0 MPa leads to an increase in xylose conversion from 77% to 100%, while xylitol yield is observed to increase from 22% to 98%. These results demonstrate the necessity to apply a minimal pressure of 5.0 MPa to produce xylitol selectively. At lower H_2 pressure, the colour of the reaction media becomes dark. Such behaviour is indicative of the formation of decomposition products from xylose. The formation of such products originates from the limited H_2 solubility in water, resulting in reaction under hydrogen sub-stoichiometry to hydrogenate xylose to xylitol and making parallel reactions predominant (in our case, xylose decomposition reaction) [9, 24].

Impact of the solvent nature is also evaluated (Table 3). The reaction is carried out at 140°C, under 5.0 MPa of H_2 for 4 h. γ-valerolactone (GVL), ethanol, and water-ethanol mixture are studied. In GVL, a conversion close to 100% is obtained (Entry 2). The selectivity to xylitol remains however limited at 21% probably due to side reactions. In ethanol (Entry 3), a high conversion is obtained (> 95%), but selectivity is largely below the selectivity obtained in water. Again, the lower solubility of H_2 in ethanol than in water can be the reason of the selectivity decrease, with the formation of xylose decomposition products. In a water/ethanol mixture (Entry 4), the selectivity to xylitol remains comparable with than in water (Entry 1), but conversion is lower. Results presented in Table 3 then indicate that the best solvent for the xylose to xylitol selective conversion is water.

Table 3. Effect the solvent nature on the catalytic performances of Co/SiO_2 for the hydrogenation of xylose. Conditions: 140°C, 5 MPa H_2, 0.5 g of xylose, 10 mL of solvent, 5 wt.% of catalyst, 4 h of reaction.

Entry	Solvent	Conv. ‘%)	Xylitol selectivity (%)
1	water	100	90
2	GVL	97	21
3	ethanol	96	69
4	water/ethanol (1/1)	87	86

The effect of the reaction temperature on the Co/SiO_2 activity, in water as solvent, is reported in Table 2 (Entries 6, 7, 9, 10). The increase of the reaction temperature, from 100°C (Entry 10) to 150°C (Entry 6) allows to gradually increase the xylose conversion from 84% to 100% (at fixed reaction time of 4 h). Xylitol yields are observed to follow conversion evolution, with values increasing from 81% (100°C) to 98% (150°C). For all the studied temperatures, xylitol selectivity is above 90% (Table 2). Hence, reaction temperature only controls the hydrogenation reaction rate, with a very limited effect on the selectivity to xylitol. This is confirmed with the reaction performed at 100°C for different reaction times. When reaction time is prolonged to 6 h (Table 2, Entry 11), a xylose conversion of 84% and a xylose yield

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of 81% are obtained (xylitol selectivity of 96.5%). After 4 h of reaction under the exactly similar conditions (Table 2, Entry 10), selectivity to xylitol of 94.5% is obtained. These two values are directly comparable. A similar trend is observed at higher temperature (140°C), applying shorted reaction time (Table 2, Entries 6 (2 h) and 5 (4 h)): selectivity slightly varies, from 92% (2 h) to 90% (4 h).

The effect of the xylose content, from 5 wt.% to 20 wt.%, is finally reported at iso-catalyst loading (5 wt.% of catalyst, with respect to the xylose loading) (Table 2, Entries 7, 12,13). When the xylose loading increases from 5 wt.% to 20 wt.%, the conversion is observed to decrease from 100% to 71%, respectively. In parallel to the conversion decrease, a significant decrease in xylitol yield is observed from 90% (5 wt.% of xylose) to 35 % (20 wt.% of xylose). Selectivity then decreases up to ~50% at high xylose loading. These evolutions of conversion and selectivity are observed despite the maintaining, for the reaction, of the same xylose to catalyst loading ratio. This indicates that the selective conversion of xylose into xylitol is highly sensitive to the reactive concentration in water. At high-xylose loadings (10 and 20 wt.%), decline in the selectivity to xylitol can be explained by the formation of polymerisation and degradation products, as reported in the literature [25].

Due to the high yields to xylitol reported under selected reaction conditions (Table 2), recycling of Co/SiO_2 catalyst is further investigated. Successive reactions are performed during 2 h at 140 °C under 5.0 MPa of hydrogen and in 10 mL of water. Catalyst is recovered by filtration, without any intermediate treatment, and reused directly for a next run in the same experimental conditions. Evolution of xylose conversion and xylitol selectivity with reaction cycle is plotted in Figure 4. The catalyst can perform 2 successive reaction cycles without significant loss in xylose conversion and xylitol selectivity. The slight decrease observed can be related to the slight catalyst lost occurring during recovery process (< 5%).

For the third cycle, conversion is observed to decrease down to 83% (compared to 97% during the second cycle), while selectivity to xylitol decreases down to 84% (compared to 89% during the second cycle). For the fourth cycle, the conversion again decreases, up to 58%, even if selectivity to xylitol remains above 80%. During the third and fourth cycles, the measured decreases in conversion cannot be related only to the lost in catalyst weight occurring during the recovery process. Cobalt leaching in water (18 ppm) can be at the origin of the deactivation. To prove that cationic cobalt, in solution, is not active for the xylose conversion, the reaction is repeated a second time for 1 h. Thereafter, the catalyst is removed from the solution, and the reaction is prolonged for 1 h. After 1 h, and after catalyst removal followed by reaction for 1 h more, comparable xylose conversions (88±2%) and xylitol selectivities (95±2%) are measured. If the reaction is performed up to 3h after the catalyst removing, similar conversion is observed (90±2%) whereas the xylitol selectivity decreased from 95 to 70% due to side reactions as reported in the literature [16, 26]. These results confirms that the cationic cobalt species in solution are not active for the hydrogenation of xylose to xylitol.

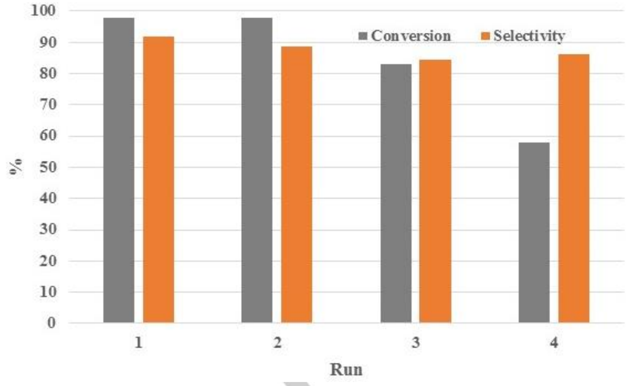

Figure 4. Evolution of the xylose conversion and xylitol selectivity with reaction cycle number. Reaction conditions: 140°C, 5.0 MPa of hydrogen, 2 h of reaction, 5 wt.% of xylose, 10 mL of water, 5 wt.% of catalyst with respect to xylose mass.

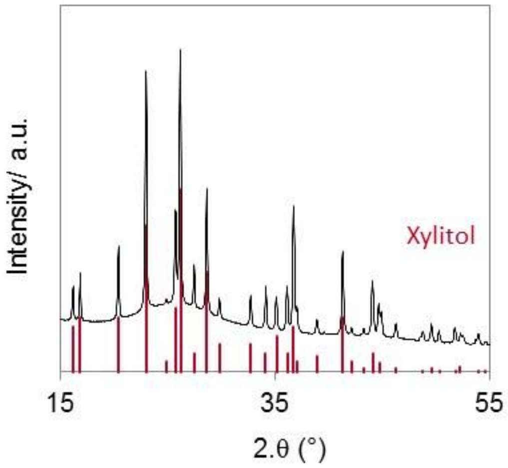

Figure 5. XRD analysis of Co/SiO_2 catalyst after 4 cycles of reaction.

XRD analysis is also performed on recovered catalyst (cycle 4), washed with water, ethanol and dried under vacuum (Figure 5). Pattern obtained for the used catalyst allows the detection of crystalline xylitol because an amount of xylitol can remain absorbed on the catalyst surface.

In line with XRD, thermal analysis under air (Figure 6) of the spent material shows that carbon species are indeed adsorbed on the catalyst, and they are oxidized at around 275°C. The active surface being covered by xylitol can be another reason of the activity loss during the third and fourth cycle. Then, intermediate reactivation treatment, including intermediate calcination (for organic decomposition) and reduction (reactivation), could be a viable strategy to recover initial activity.

Herein we report that a simple cobalt - based catalyst can be active and selective in the hydrogenation of xylose to xylitol, with a conversion of 100% and a yield to xylitol of 98 %, under optimized conditions. The nature of the solvent plays a key role in this reaction, the use of water being preferred to organic solvent like γ-valerolactone or ethanol. As concerning the reaction parameters, it was shown that H_2 pressure has a significant impact on the reaction rate and selectivity to xylitol, the best results being obtained for pressures up to 5 MPa. On the contrary, the main effect of the reaction temperature is on the reaction rate, which increases with temperature, while the catalyst remains selective to xylitol over the 100-150°C range. Finally, our study shows that a moderate catalyst deactivation occurs during the two first cycles of reaction, whereas further cycles induce a conversion decrease (58%) but the selectivity to xylitol remains at a high level (86%).

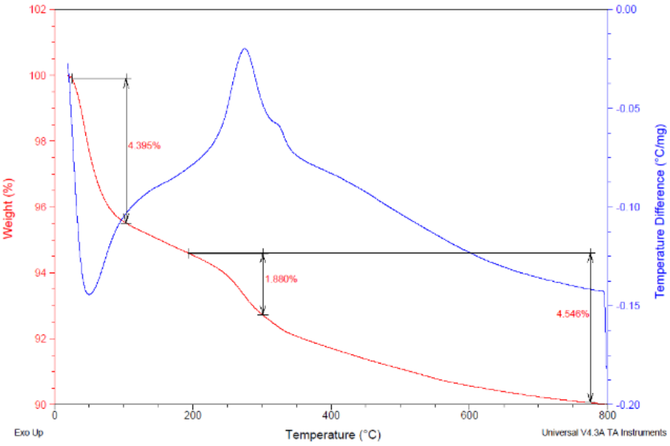

Figure 6. Thermal analysis of Co/SiO$_2$ catalyst after reaction.

Experimental Section

Catalyst preparation: The Co$_3$O$_4$/SiO$_2$ material, with a metal loading of 10 wt.% is prepared using incipient wetness impregnation method. To this end, 0.9975 g of Co(NO$_3$)$_2$ • 6H$_2$O is dissolved in 1,8 mL of water. Solution is added dropwise to 1.8 g of aerosil silica (380). Mixing is carried out until the formation of a homogeneous paste. After 2 h of ageing, the powder is dried in an over at 120 °C for 14 h. The dry solid is calcined at 500 °C for 6 h (heating rate of 1.5 °C.min^{-1}) to obtain the Co$_4$O$_4$/SiO$_2$ sample. Co$_2$O$_3$/SiO$_2$ is reduced under hydrogen flow (3L.h^{-1}) at 500 °C for 10 h (heating rate of 10 °C.min^{-1}).

Catalyst characterization: Co/SiO$_2$ catalyst was characterized by ICP-OES, XRD analysis, N$_2$-physisorption, Transmission Electronic Microscopy, Thermal analysis. ICP analysis is performed on a Perkin Elmer Optima 2000 DV instrument. Prior to analysis, samples are dissolved in HF-HCl solution and heated under micro-wave for digestion. N$_2$-physisorption experiments were obtained on an Autosorb 1-MP instrument, at 77K. Prior to the experiments, samples are heat treated under vacuum at 350 °C for 3 h. Surface area is determined on the linear zone of the Brunauer-Emmett-Teller (BET) plot. Pore size is determined on the desorption branch, applying the Barrett-Joyner-Halenda (BJH) algorithm. Finally, pore volume is determined on the adsorption branch of the isotherm at P/P$_0$=0.98. TEM experiments are performed on a JEOL 2100 UHR instrument operated at 200 kV, equipped with a LaB$_6$ source and a Gatan ultra scan camera. Thermal analysis were performed under 100 mL.min^{-1} of air (heating ramp of 10°C.min^{-1}).

General procedure for the hydrogenation of xylose: in a typical experiment, 0.5 g of xylose is added to 10 mL of water. 0,025 g of activated catalyst is added in a batch reactor of 75 mL total volume. The reactor is closed and pressurised under hydrogen. Then, the temperature is increased up to the desired reaction temperature, *i.e.* 100 °C to 140 °C. At the desired reaction time, the reactor is cooled down to room temperature, and liquid phase is analysed.

Analytical methods: yields in xylitol and conversion of xylose are determined by external calibration at 25°C, using HPLC equipped with a pump system (LC-20AD), an autosampler SIL-10A and a controller CBM 20A. Products of reaction are separated on a Varian 100-5 amino S 250 x 4.6 mm (NH$_2$) column, using a water/acetonitrile (2/8 vol.) as eluent, at a flow rate of 0.8 mL.min^{-1}. Quantification is performed using a refractive index detector (Waters 2410).

Acknowledgements

The authors would like to thank the Poitou-Charentes region for the funding of the PhD grant of Maïté Audemar. ANR agency for the funding of FurCab Project ANR-15-CE07-0016. Région Nouvelle Aquitaine for the funding of this project through the FR CNRS INCREASE 3707, the chaire TECHNOGREEN and FEDER, the University of Poitiers and the CNRS for their financial support. Chevreul Institute (FR 2638), Ministère de l'Enseignement Supérieur et de la Recherche and Région Hauts-de-France are also acknowledged for supporting this work.

Keywords: xylose • hydrogenation • catalysis • xylitol • cobalt

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10.1002/cctc.201901981

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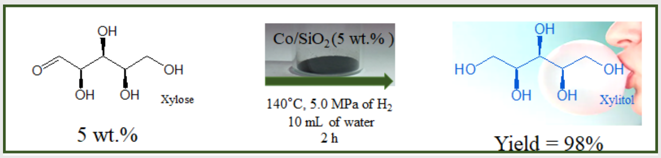

M. Audemar, W. Ramdani, T. Junhui, A. Raluca Ifrim, A. Ungureanu, F.Jérôme, S. Royer and Karine de Oliveira Vigier**

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Selective hydrogenation of xylose to xylitol over Co/SiO$_2$ catalysts

Xylitol, an interesting molecule in food, cosmetics, and pharmaceutical industry was selectively (98%) synthesized in the presence of a simple silica supported monometallic cobalt - Co/SiO$_2$ – catalyst in water from the hydrogenation of xylose. This catalyst shows interesting catalytic properties. The recyclability was investigated and moderate deactivation of the catalyst was observed and the selectivity to xylitol remains almost unchanged after 4 cycles.