

Screening of ortho-parahydrogen catalysts

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Abstract. The growing demand for liquefied hydrogen (LH₂) results in an increased need for ortho-parahydrogen catalysts. Currently, the LH₂ supply chain relies heavily on a single catalyst product: hydrous ferric oxide, commercially available as “Ionex-Type OP Catalyst” (Ionex) from Molecular Products. On the one hand, this reliance poses a supply vulnerability for liquefaction plants under construction. On the other hand, previous research indicates the potential for much more active catalysts based on other materials. This holds promise for optimizing liquefaction plants thermodynamically and substantially reducing the size of the ortho-para converters. To identify alternative catalyst options, a screening of several catalyst samples was conducted as part of the HyCat project. The samples were synthesized by specialized manufacturers and tested at 77.3 K and 2.5 bar(a) in the Ortho-Para Catalyst Test Facility at TU Dresden. This work presents the results of the screening, including some promising candidates suitable for further development and potential use in large-scale hydrogen liquefaction.

1. Introduction

Catalytic ortho-para conversion is essential during the hydrogen liquefaction process. In large-scale facilities, the conversion typically takes place in catalyst-filled channels of plate-fin heat exchangers (PFHXs) or in several reactor vessels located between heat exchanger stages. Maintaining the ortho-para ratio close to the equilibrium ratio is essential for the efficient removal of reaction heat. Beyond large-scale liquefaction, catalytic ortho-para conversion is also relevant in several other applications, such as in cryogenic neutron moderators [1][2], parahydrogen-induced polarization in NMR/MRI [3], shield cooling for liquid hydrogen (LH₂) storage tanks, and specific scientific applications like fluid property measurements of ortho- and parahydrogen.

The current standard catalyst is hydrous ferric oxide, which is in use since the 1950s and commercially available as “Ionex-type OP Catalyst” (short “Ionex”) from Molecular Products. However, hydrous ferric oxide has some drawbacks: its activity is only moderate, necessitating large catalyst volumes (particularly problematic in high-capacity liquefiers), and the material exhibits a strong decrease in catalytic activity at temperatures above 77 K, leading to less efficient conversion in higher-temperature sections of cryogenic heat exchangers, and rendering the material rather unsuited for normalization at room temperature. This behaviour was shown earlier [4][5] and confirmed in recent measurements performed at TU Dresden [6]. Normalizers using Ionex need to be extremely voluminous if a complete para-ortho conversion at room temperature is required, which is a considerable obstacle to certain lab applications.

Developing alternative catalysts is highly desirable to foster competition (improving price and supply security) and achieve higher volumetric activity in the full temperature range between



300 and 20 K — allowing for smaller, less expensive converters and associated cold boxes, potentially increasing overall efficiency during liquefaction, and enabling para-ortho converters at elevated temperatures ($> \sim 100$ K) and normalizers of acceptable size. Previous studies have demonstrated that catalysts exhibiting activities multiple times higher than that of hydrous ferric oxide are possible [7][8][9]. However, no such catalyst is available at present.

Within the HyCat project, a versatile and highly specialized experimental setup was established that allows testing ortho-para catalysts in a wide range of conversion conditions. Following the generation of new kinetic data for Ionex (currently being published), this work presents results from the systematic screening of several alternative catalyst materials performed under standardized conditions, aiming to identify promising new catalyst materials.

2. Experimental

2.1 The Ortho-Para Catalyst Test Facility

The experiments were conducted using the Ortho-Para Catalyst Test Facility (CTF) located at TU Dresden, which is designed for the comprehensive investigation of catalytic ortho-parahydrogen conversion. The system is described in detail in a previous publication [10]. A simplified process and instrumentation diagram is shown in Figure 1. The facility allows catalyst testing under a wide range of conditions relevant to hydrogen liquefaction and other applications, enabling the independent variation of temperature (18 – 200 K, and 300 K), pressure (2 – 80 bar(a)), flow rate (0.33 – 24.7 L/min at STP¹), and inlet parahydrogen percentage (25 – 99.99% p-H₂). However, for the sake of screening, typically only the “screening conditions” are employed (at TU Dresden defined as 77.3 K, 2.5 bar(a), 25% p-H₂ at inlet). These conditions were selected as they are readily reproducible on simpler LN₂-cooled setups, ensuring comparability with most other studies.

The CTF comprises four main subsystems: The **Catalyst Test Cryostat (CTC)** is a cryocooler-based cryostat housing an exchangeable Sample Reactor (SR) where the catalyst specimen is placed. Accurate temperature control is achieved using heaters. The gas entering the Sample Reactor is precooled to the conversion temperature using two heat exchangers.

The **Ortho-Para Precision Converter (OPPC)** [6][10] is a second cryostat, designed to produce hydrogen streams of accurately adjustable parahydrogen fractions by catalytic conversion in an oversized catalyst bed at controlled temperatures (15 – 200 K). If any other composition than normal hydrogen (n-H₂) is needed, it supplies the desired inlet composition to the CTC and provides nearly pure parahydrogen for calibration of the Ortho-Para Measurement System. For the screening purposes in this work, however, only n-H₂ is used and hence, the OPPC is inactive.

The **Ortho-Para Measurement System (OPM)** is used for highly accurate, real-time measurements of the parahydrogen fraction. Depending on its operating conditions, it can achieve a total measurement uncertainty better than $\pm 0.11\%$ p-H₂ (without correction of systematic errors) or $\pm 0.06\%$ p-H₂ (with correction of systematic errors, coverage factor $k = 2$) [6]. The parahydrogen fraction is determined based on the speed of sound, measured with a commercial

¹ STP: 1.0 bar(a) and 273.15 K in accordance with the current IUPAC definition

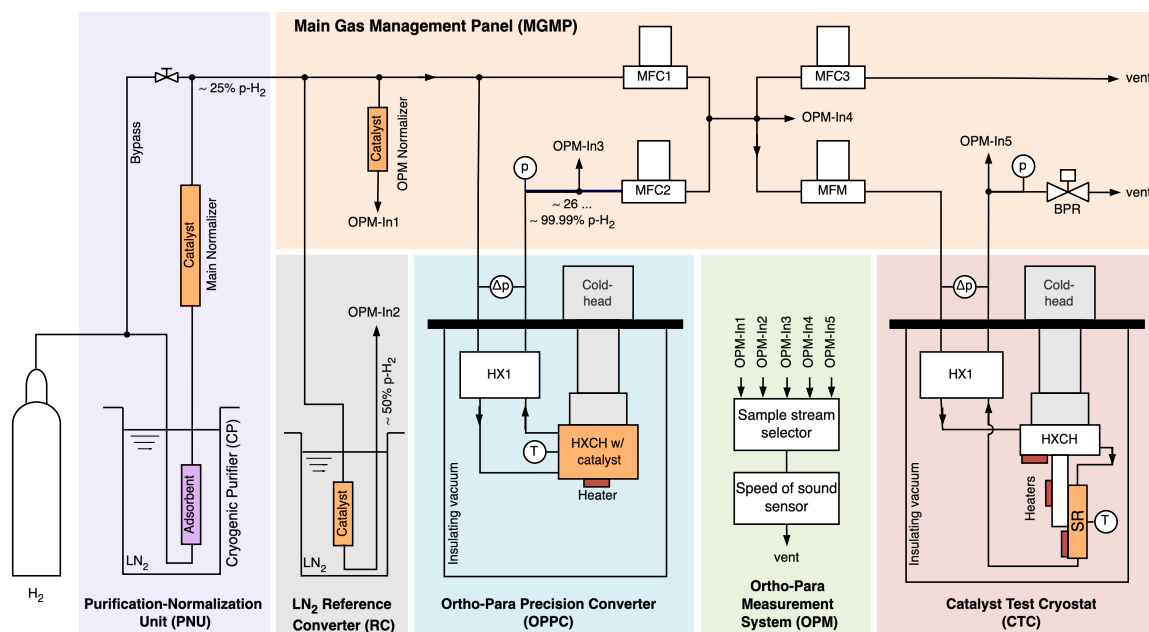


Figure 1. Simplified P&ID of the Ortho-Para Catalyst Test Facility. Abbreviations: **MFC** – Mass flow controller, **MFM** – Mass flow meter, **BPR** – Back-pressure regulator, **HX1** – Counter-flow heat exchanger, **HXCH** – Coldhead heat exchanger, **SR** – Sample reactor.

binary gas analyzer (Stanford Research Systems BGA 244). The system requires regular calibration using reference gases ($n\text{-H}_2$, $e\text{-H}_2$, 77.3 K, and optionally nearly pure $p\text{-H}_2$ from the OPPC).

The **Main Gas Management Panel (MGMP)** manages gas supply and routing, controls flow rates and the CTC pressure level and allows for the mixing of $n\text{-H}_2$ streams with streams of variable composition produced using the OPPC.

To prevent catalyst deactivation during extended measurement runs due to trace impurities in the feed gas (hydrogen 5.0), a cryogenic purifier (150 ml of zeolite adsorbent at 77 K) followed by a large normalizer (500 ml of Ionex) were installed upstream of the MGMP (**Purification-Normalization Unit**). This upgrade was added after the initial commissioning of the facility and is therefore not included in the previously published system description [10]. Both the purifier and the normalizer can be bypassed. The bypass capability is particularly relevant for conducting catalyst activation under realistic conditions, since activation with hydrogen of a purity grade better than 5.0 is unlikely most applications.

3. Results

The materials tested in this study and the corresponding results are summarized in Table 1. Figure 2 visualizes the obtained rate constants.

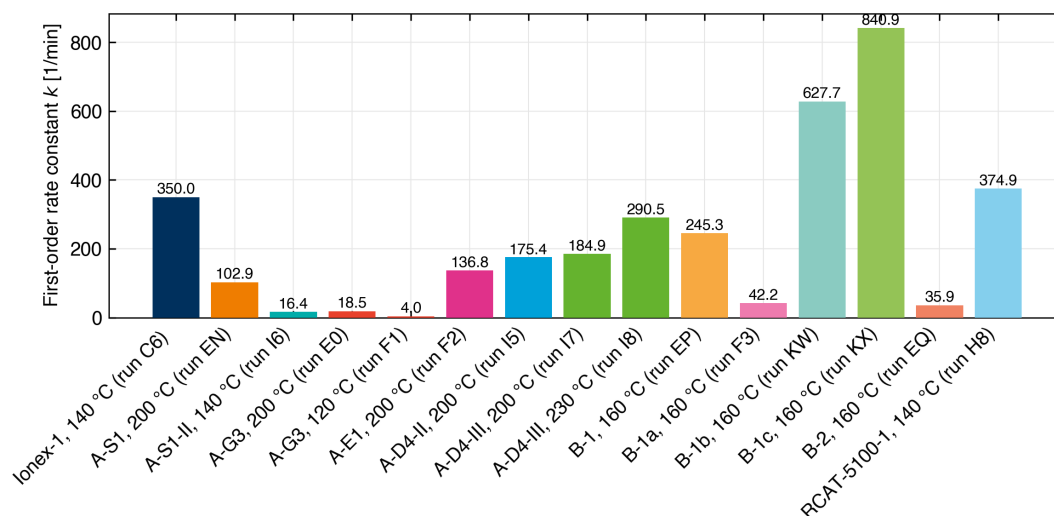


Figure 2. Overview of catalyst activities expressed in terms of the first-order rate constants.

For reference, two commercial catalysts are included: Ionex from Molecular Products and RCAT®-5100 from Ranido. The rest of the materials were specifically synthesized for this catalyst screening by specialized manufacturers; no pre-existing, off-the-shelf materials were utilized. Two groups of materials were investigated: Group A, comprising iron-based catalysts, and Group B, consisting of nickel-based catalysts. All newly developed materials have a macroscopic morphology comparable to the one of Ionex (which is characterized by irregularly shaped particles of sizes between 300 and 600 μm). Further material properties, such as specific surface area or pore size distributions, are not known as they were not shared by the manufacturers and not determined in-house.

The screening experiments were performed at 77.3 K and 2.5 bar(a), with (volumetric) space velocities at standard temperature and pressure ($SV_{\text{vol,STP}} = \dot{V}_{\text{STP}}/V_{\text{cat}}$) ranging from ~ 300 1/min to ~ 2900 1/min. All samples underwent in-situ activation under hydrogen for 16 h at 1.5 bar(a) and a low flow rate of approximately 0.1 $L_{\text{STP}}/\text{min}$. The activation temperature varied between samples and was set as indicated by the respective manufacturers.

Upon activation, several processes can occur in addition to the mere desorption of impurities from the active surface, such as alterations of the oxidative state of the active species. In the context of this study, it seems advantageous to perform the sample activation using hydrogen as it allows for the reduction of the samples (which can have a major effect on activity). Observations of color and color shifts are included in Table 1 as these serve as clear visual cues of changes in chemical composition, which can be linked to reduction processes. For example, a shift from brown to black in the iron-based samples indicates a (partial) transition from Fe_2O_3 to Fe_3O_4 .

For Ionex, an activation temperature of 140°C was chosen. In prior investigations (results to be published separately), this temperature was found to be optimal for the material and it is therefore the standard activation condition for kinetic measurements using Ionex at TU Dresden. For RCAT®-5100, the same temperature was selected for the sake of direct comparability with Ionex².

² For RCAT®-5100, the optimal activation temperature was found to be around 180°C, yielding an approximately 19% higher rate constant than the activation temperature of 140°C.

Table 1. Screening materials and results overview. Abbreviations: **HFO** – Hydrous ferric oxide, **SAPO** – Silicoaluminophosphate

Batch ID	Composition (initial) ^a	Run ID	ρ^b [g/ml]	T_{act} [°C]	Color / color shift upon activation	k [1/min]
Ionex-1	HFO	C6	1.26	140	Black-brown (no change)	350.0
A-S1	Fe ₂ O ₃ / SAPO (<10 wt% Fe)	EN	0.56	200	Slight shift from light brown to light grey	102.9
A-S1-II	Ferric oxide ^c / SAPO (<10 wt% Fe)	I6	0.60	140	Light gray (no change)	16.4
A-G3	Fe ₂ O ₃ / SiO ₂ (<10 wt% Fe)	E0	0.46	200	Shift from dark red-brown to black-brown	18.5
		F1	0.40	120	Dark red-brown (no change)	4.0
A-E1	Fe ₂ O ₃ / Al ₂ O ₃ (<10 wt% Fe)	F2	0.56	200	Marked shift from ocher-brown to black	136.8
A-D4-II	Ferric oxide ^c / BEA zeolite (<10 wt% Fe)	I5	0.49	200	Gray-black (no change)	175.4
A-D4-III	Fe ₂ O ₃ / BEA zeolite (<10 wt% Fe)	I7	0.54	200	Slight shift from ocher-brown to ocher-gray	184.9
		I8	0.55	230	Marked shift from ocher-brown to gray-black	290.5
B-1	Ni(OH) ₂ · nSiO ₂ (15 wt% Ni)	EP	0.31	160	Light green (no change)	245.3
B-1a	Ni(OH) ₂ (60 wt% Ni)	F3	1.13	160	Shift from green to green-black	42.2
B-1b	Ni(OH) ₂ · nSiO ₂ (31 wt% Ni)	KW	0.41	160	Slight shift from light green to light green-gray	627.7
B-1c	Ni(OH) ₂ · nSiO ₂ (35 wt% Ni)	KX	0.48	160	Slight shift from light green to light green-gray	840.9
B-2	Ni-MOF-74 / boehmite (1.8 wt% Ni)	EQ	0.69	160	Yellow-ocher (no change)	35.9
RCAT-5100-1	n/a	H8	0.92	140	n/a	374.9

^a Composition before activation. Notation follows conventions used in heterogeneous catalysis: “/” separates active species and support material, “·” indicates mixes phases.

^b Bulk density before activation.

^c Fe₃O₄ assumed to be dominant, however, an exact statement on oxidative state is not possible.

The sample activity is expressed quantitatively by means of the first-order rate constant k , calculated from the measurement data as follows:

$$k = \frac{(\ln|x_{p,eq} - x_{p,in}| - \ln|x_{p,eq} - x_{p,out}|)}{\tau} \quad (1)$$

where $x_{p,eq}$ is the equilibrium parahydrogen fraction at the conversion temperature, $x_{p,in}$ and $x_{p,out}$ are the parahydrogen fractions at the reactor inlet and outlet, respectively, and τ is the residence time. The latter is defined as $\tau = V_{cat}/\dot{V}$, where V_{cat} is the catalyst bulk volume and \dot{V} is the hydrogen flow rate at the conversion temperature and pressure. Therefore, k is a measure of the *volumetric* activity of the material. The rate constants shown in Table 1 were evaluated only at the highest space velocity SV_{STP} tested for each sample (typically between 2750 and 2900 1/min). This choice was made because the rate constant is typically not constant across the entire space velocity range. It is lower at low space velocities and asymptotically approaches a maximum value at higher space velocities. This behavior is not yet fully understood and could be linked to either mass transfer limitations or limited suitability of the first-order model.

The two commercial catalysts, Ionex (lot no. L03A-2314) and RCAT®-5100 (lot no. M230210K), show comparable activity under the chosen activation conditions, with RCAT®-5100 being approximately 7% more active. The catalysts from Group A (iron oxide on various support materials) generally exhibited lower activity than Ionex. The batches A-G3 and A-D4-III were tested at two different activation temperatures. In both cases, the higher activation temperature resulted in a higher activity and a more marked color shift. This strongly suggests that a reduction of Fe_2O_3 towards Fe_3O_4 is beneficial for ortho-para conversion.

As an activation at temperatures as high as 200°C is not feasible in most liquefaction facilities, the reduction step should ideally be incorporated into the synthesis process. Following this line of thought, some batches were pre-reduced by the manufacturer (before the in-situ activation). Those batches, assumed to contain mostly Fe_3O_4 a priori, were expected to perform better than their counterparts containing Fe_2O_3 (e.g., A-S1-II vs. A-S1 and A-D4-II vs. A-D4-III). This was, however, not the case. Possible explanations may be found in an insufficient purity of the forming gas used for reduction (which could lead to deactivation), over-reduction, or other deviations in the preparation procedure.

Sample A-D4-III, activated at 230°C, showed the highest activity in Group A, reaching an activity of roughly 83% of that of Ionex. This is noteworthy, considering its much lower iron content (assuming that Ionex can best be described as $FeO(OH)$ and therefore would have a gravimetric iron content of about 63%). The overall best performance was observed for batches B-1b and B-1c, with activities reaching 179% and 240% of that of Ionex, respectively. For batches B-1, B-1b and B-1c, consisting of mixed phases of $Ni(OH)_2$ and SiO_2 , the correlation between nickel content and activity is apparent. Batch B-1a, which in contrast is composed solely of $Ni(OH)_2$, shows much lower activity despite its higher nickel content.

The comparability of these results is limited, however. To obtain a truly fair comparison with respect to activation, all tests would have needed to be done with the same activation temperature. The fact that the activation temperatures were not consistent across all materials is owed to the manufacturers' different preferences. To obtain a fair comparison of the intrinsic *potential* of each material, complete activation studies (varying activation conditions) would be required for each individual batch. This was not feasible within the scope of the present study due to the enormous experimental effort associated with varying activation conditions.

While the Catalyst Test Facility is one of the most capable experimental facilities for testing ortho-para catalysts currently available, it is optimized for large measurement campaigns in a

wide range of conversion conditions with relatively few catalyst samples, not for screening large amounts of materials under identical screening conditions. To overcome this limitation and enable more comprehensive screenings in the future, a new catalyst screening device is planned as a drop-in module for the current Catalyst Test Cryostat. The device will enable testing several samples, each exposed to different activation temperatures, in one experimental run.

4. Conclusion

Developing highly active alternatives to Ionex is desirable for several reasons and would be beneficial for the scale-up of the liquid hydrogen supply chain. This study represents a first step in this direction, presenting initial screening results for new ortho-parahydrogen catalyst materials synthesized by specialized manufacturers. These materials were broadly categorized into iron-based (Group A) and nickel-based (Group B) systems. Furthermore, a new commercial ortho-para catalyst (RCAT®-5100 from Ranido) was added to the comparison. It showed a slightly higher activity than Ionex under identical activation conditions.

The screening identified several high-potential materials that serve as a strong basis for further development. Notably, nickel-based samples B-1b and B-1c demonstrated high performance, with activities reaching 179% and 240% of Ionex's under the tested conditions. The iron-based samples also showed promise; variation of the activation temperature indicated that reduction towards Fe_3O_4 is likely necessary for achieving high activity. Future catalyst design should aim to incorporate this reductive step in the synthesis process.

No premature conclusions on the ultimate suitability of the presented materials should be drawn based on this study, as small changes in preparation methods can significantly impact catalytic activity. More comprehensive screening will be required to fully assess and optimize the presented materials and future candidates, which will be facilitated by a more efficient screening apparatus that is currently being planned.

Acknowledgments

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