# Efficient homogeneous catalytic hydrogenation of $CO_2$ and hydrogencarbonate mediated by the *cis,mer*-[$IrH_2Cl$(*m*tppms-Na)$_3$] complex catalyst

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## Introduction

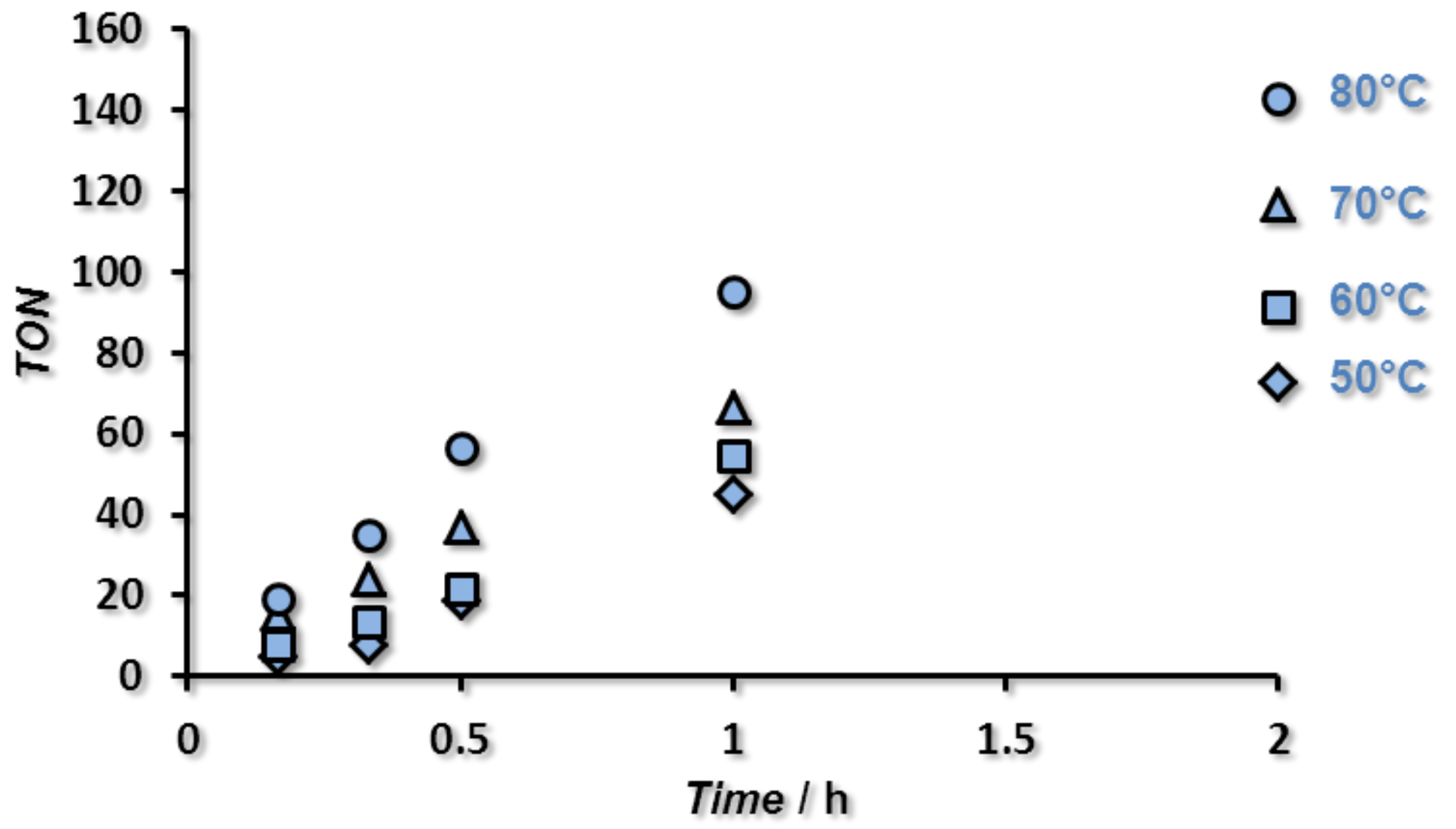
Whenever possible, we should prioritize the use of environmentally friendly ("green") technologies and energy sources, such as hydrogen, which is a promising alternative energy carrier. One of the key advantages of hydrogen is its high energy content – approximately 120 MJ/kg. Additionally, hydrogen combustion or its use in fuel cells does not emit carbon dioxide or other primary pollutants. However, due to its low density, the safe storage and transportation of hydrogen is a critical challenge. Currently, the most common method involves storing hydrogen in gas cylinders or tanks under high pressure – typically hundreds of bars. An alternative, potentially safer, long-term hydrogen storage solution is formic acid. Using a suitable catalyst, hydrogen can be stored as formic acid via the hydrogenation of $CO_2$, yielding a stable compound.

For this hydrogenation process, the water-soluble complex *cis,mer*-[$IrH_2Cl$(*m*tppms-Na)$_3$] has proven to be an effective catalyst. It is also active in the reverse reaction, enabling efficient hydrogen release.

## $CO_2$ and bicarbonate hydrogenation

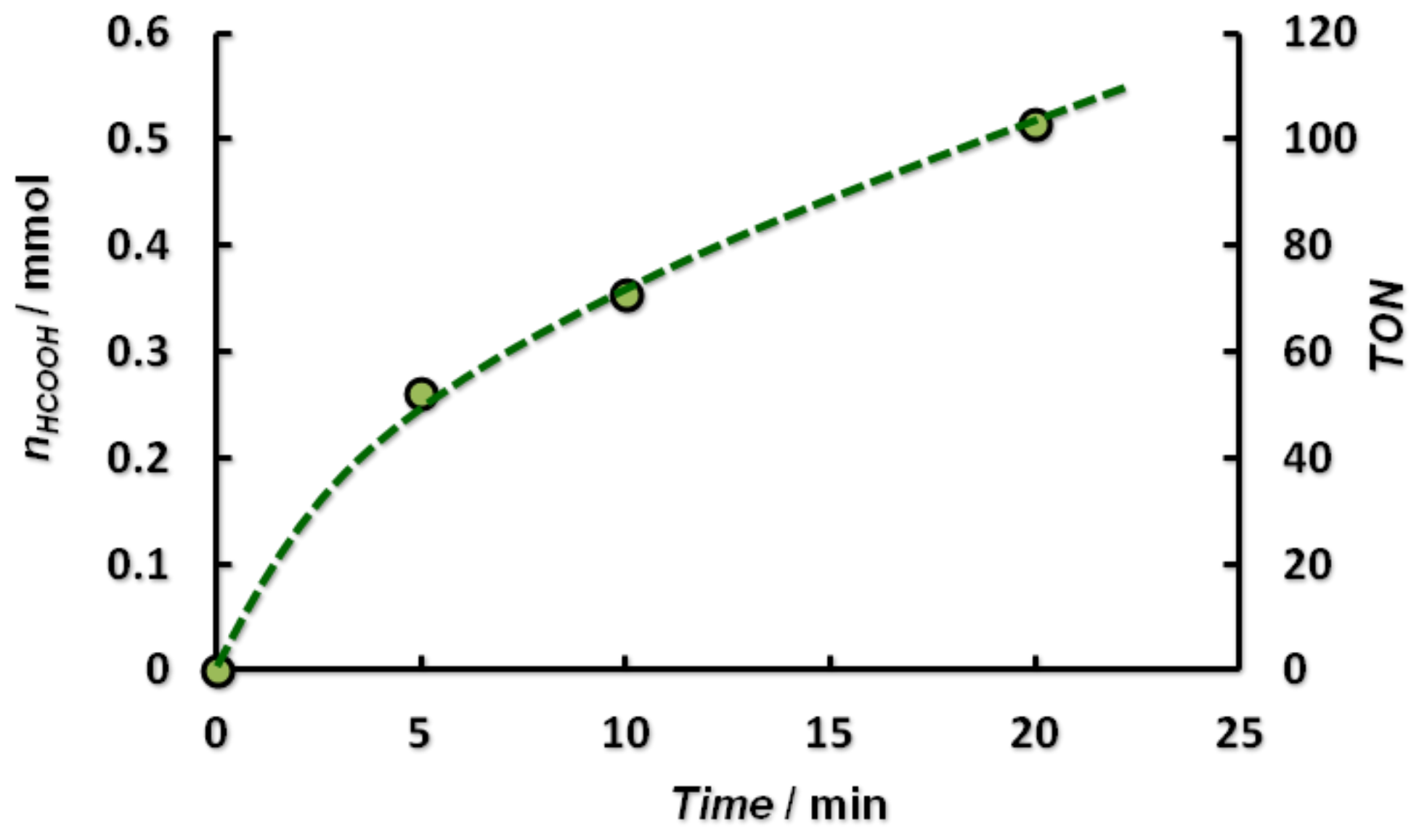
With the first reactions we performed, we proved that this Ir-complex is a promising catalyst, since we achieved turnover numbers
(TON = $n_{product}/n_{catalyst}$)
as high as 100 at only 10 bar of pressure.

$pH = 7.0$ $c_{Ir} = 0.5$ mmol/dm$^3$; $t = 1$ h
$p(CO_2) = 5$ bar; $p(H_2) = 5$ bar



Hydrogenation of $CO_2$ – up to 100 bar

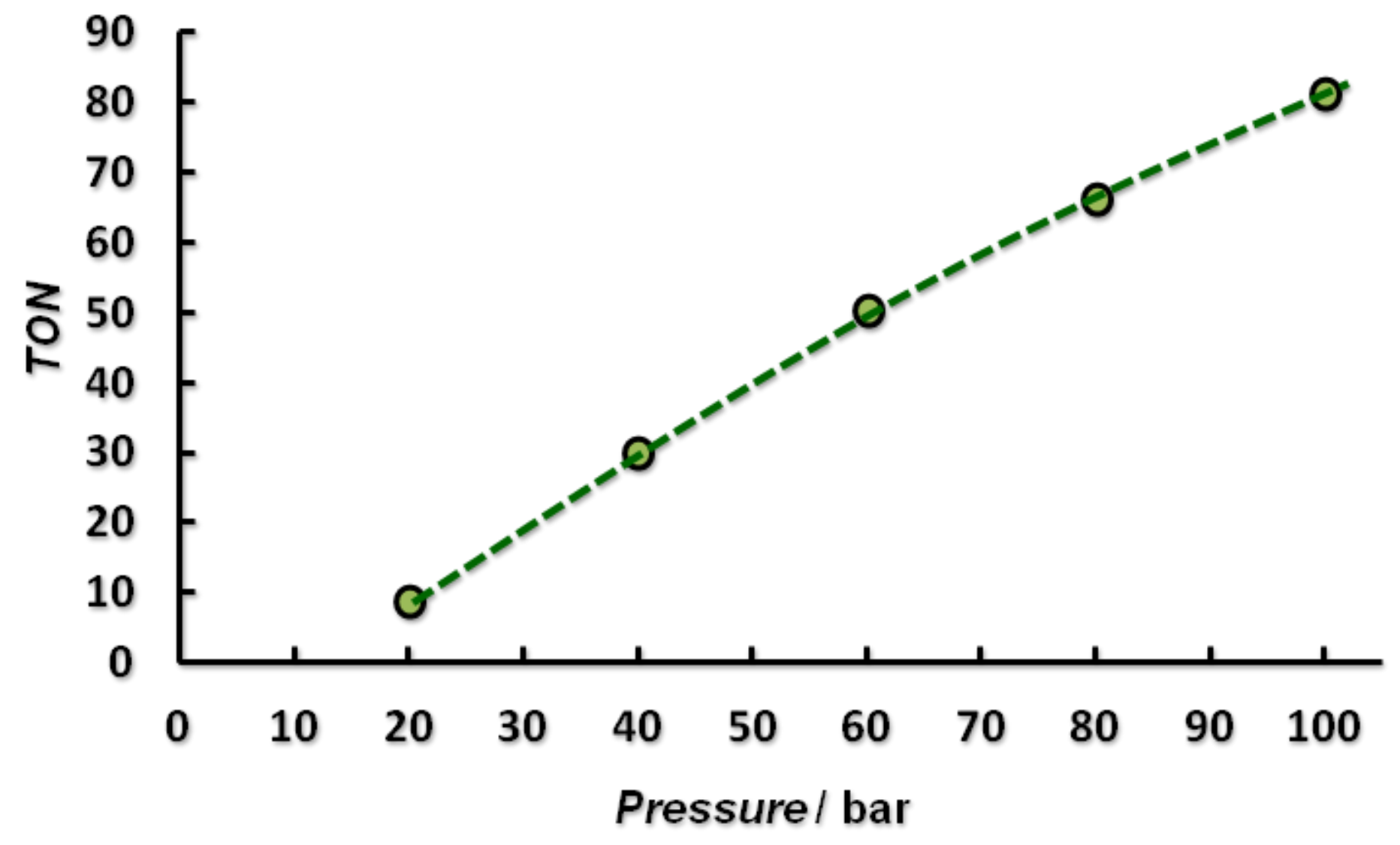
$c_{Ir} = 0.5$ mmol/dm$^3$; $p(H_2) = 50$ bar; $p(CO_2) = 50$ bar; $T = 85$°C; unbuffered solution ; $pH \sim 3\text{-}4$

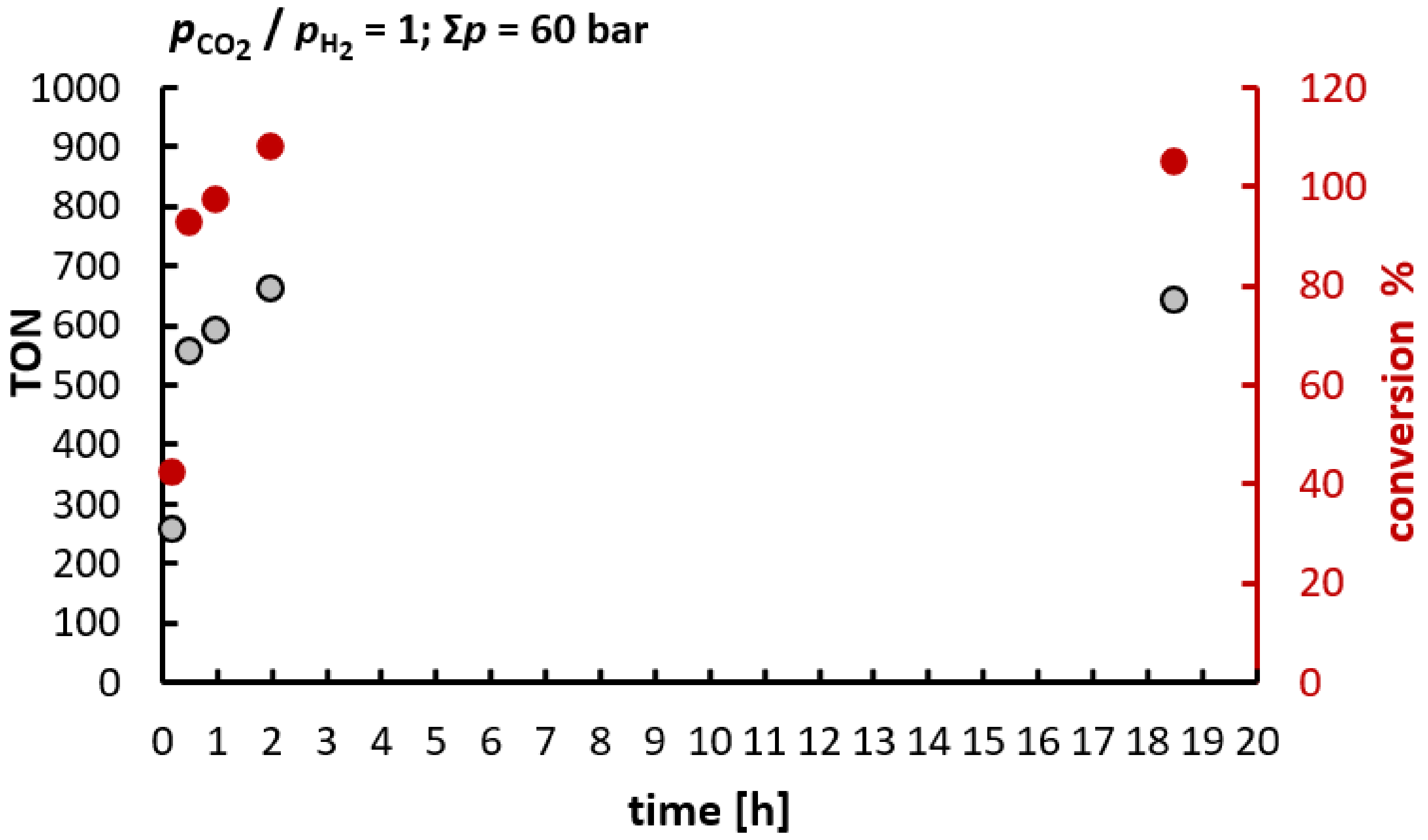


**$iTOF = 980$ h$^{-1}$**

The catalyst was also tested at a mild temperature, even at 40°C, we obtained a TON value higher than 80.

$c_{Ir} = 0.5$ mmol/dm$^3$;
$p(H_2) / p(CO_2) = 1$; $T = 40$°C; $t = 30$ min;
unbuffered solution; $pH \sim 3\text{-}4$



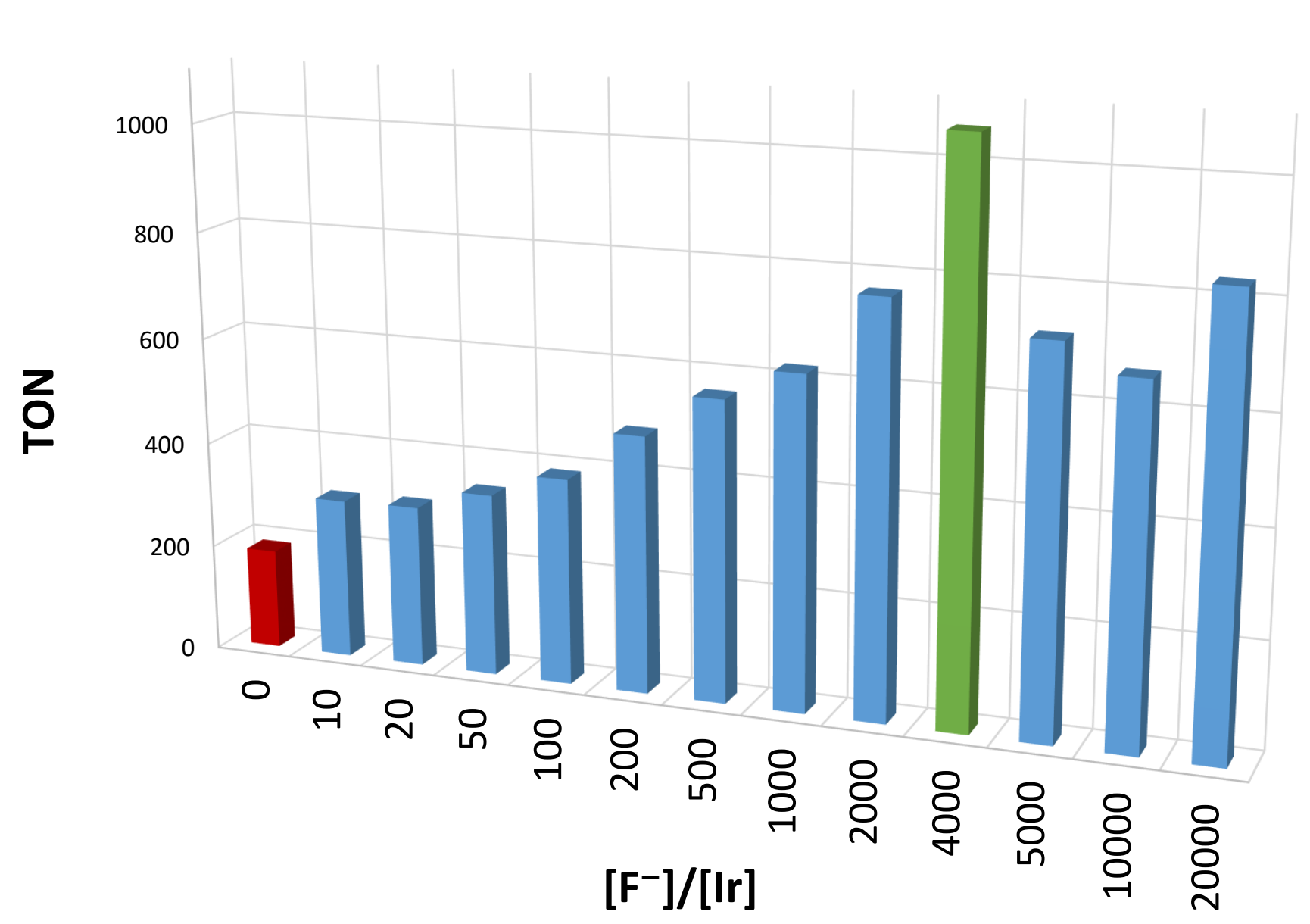


We performed hydrogenation reactions at different pressures, and at 100 bar ($CO_2/H_2$=1), we reached turnover numbers as high as 790 ($n_{Ir} = 10^{-5}$ mol; $n_{NaHCO_3} = 6\times10^{-3}$ mol; $V = 200{,}0$ mL; $T = 100$ °C; $t = 1$ h). In this case, we also added $NaHCO_3$, so the formed HCOOH did not decompose (the conversion is due to the bicarbonate, and it can exceed 100% because both $CO_2$ and bicarbonate are hydrogenated). Higher pressures correspond to higher TON values because of the greater number of moles of $H_2$ and $CO_2$.

## Effect of fluoride ions in $CO_2$ hydrogenation

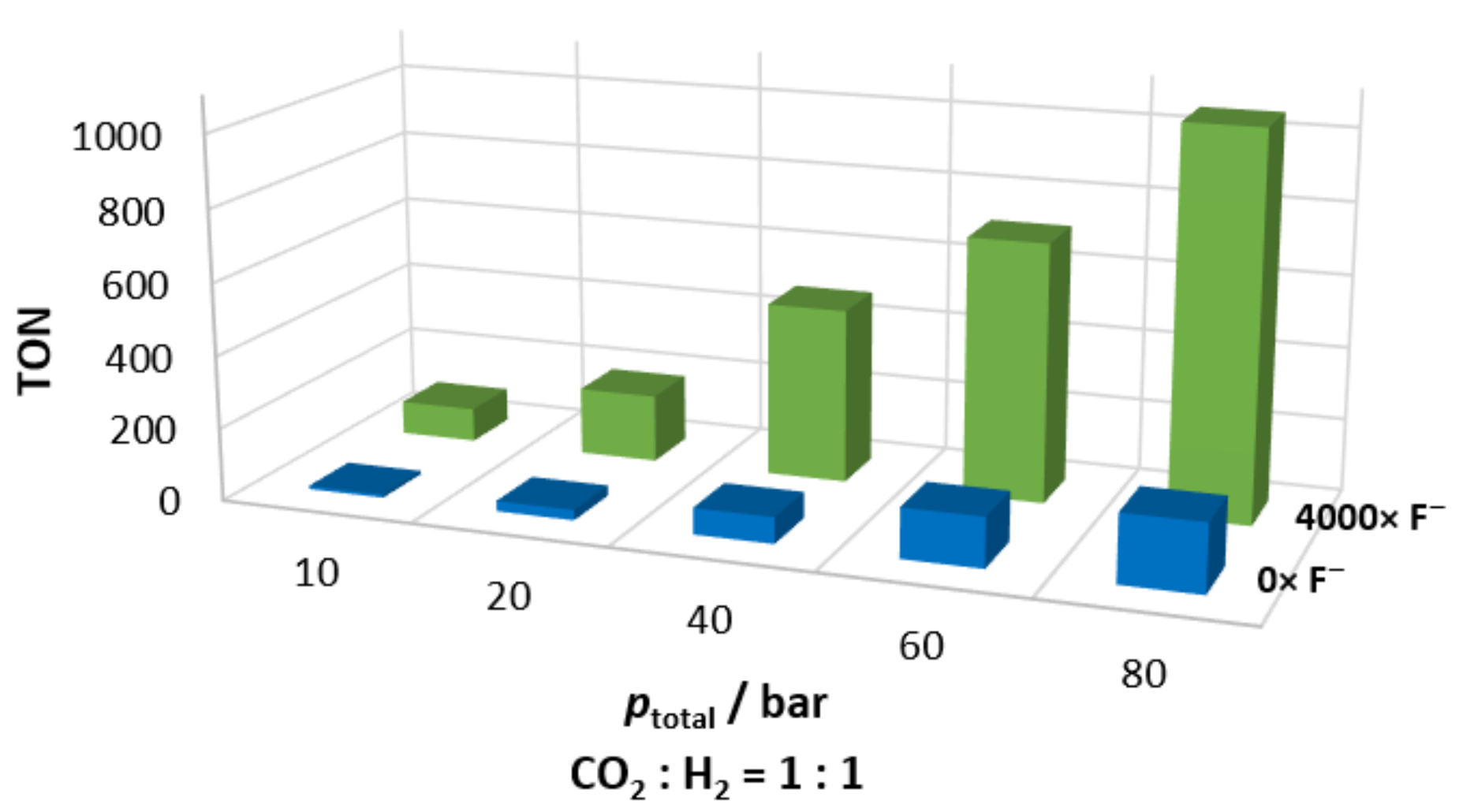
We performed carbon-dioxide hydrogenation ($n_{Ir} = 10^{-5}$ mol; $p(CO_2) = 40$ bar; $p(H_2) = 40$ bar $V = 200{,}0$ mL; $T = 80$°C; $t = 1$ h), at first without adding NaF to the reaction so that we could comprehend the results with the fluoride-ions' effect. Adding fluoride salt (amounts starting at 10× the moles of the Ir-catalyst) immediately increased the TON of the reaction. The more fluoride ions we added, the higher the turnover number we achieved, up to 4000× equivalent, where we obtained an outstanding result: TON = 1060. DFT calculations were performed to determine the effect that increases the reaction rate, and the result was that the effect of $F^-$ is not realized through the iridium complex, but instead, HF is formed. This hydrogen fluoride inhibits the proton transfer in the mechanism, thereby increasing the rate of hydrogen evolution.

Effects of $F^-$-ions in $CO_2$-hydrogenation



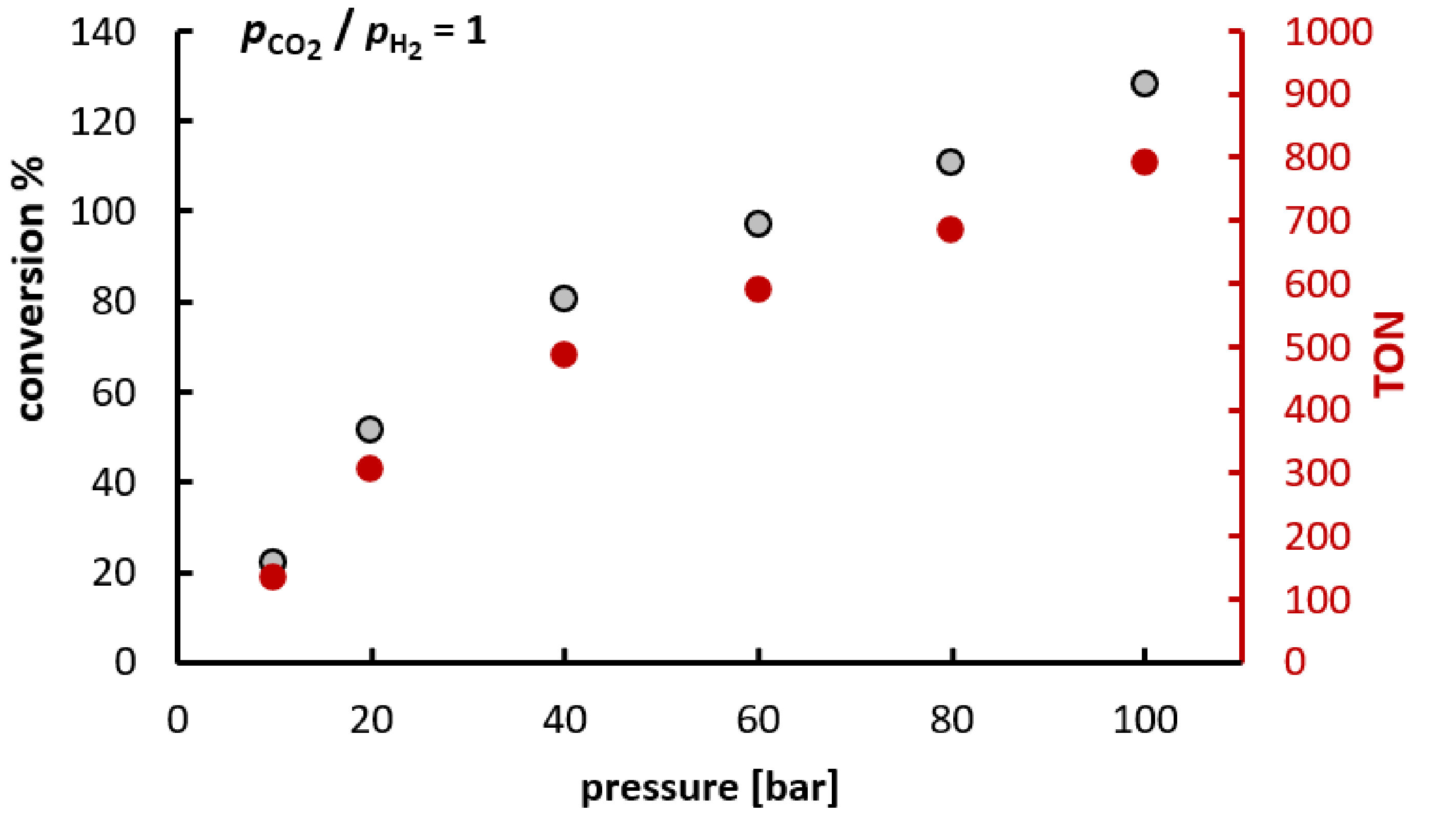
The effect of the $F^-$ was tested at different pressures, ranging from 10 to 80 bar. Reaction conditions were the following: $n_{Ir}=10^{-5}$ mol; $n_{F-} = 0{,}04$ mol; V=200,0 mL; T=80 °C; t= 1 h. As shown in the figure, higher total pressures led to higher TON in both cases. However, the reactions with added NaF show a huge difference compared to the basic reactions.

$p_{total}$ effect in $CO_2$-hydrogenation



We examined the amount of time needed to reach the reaction equilibrium and found that after two hours the reaction is complete. The conditions were the following:

$n_{Ir} = 10^{-5}$ mol; $n_{NaHCO_3} = 6\times10^{-3}$ mol; $p(CO_2) = 30$ bar; $p(H_2) = 30$ bar;
$V = 200{,}0$ mL; $T = 100$ °C.



## Conclusions

The *cis,mer*-[$IrH_2Cl$(*m*tppms-Na)$_3$] complex has a huge potential in homogeneous catalytic hydrogenation, as we look at the enormous TONs we achieved in our reactions. We can state that this complex is active even at mild reaction conditions, however the best results are earned on 100 °C. It is important to emphasize that this complex is water soluble, thus no organic solvents are needed for the hydrogenation reactions (green chemistry). The addition of fluoride-ions also has a great impact on the hydrogenation process and we are planning to perform experiments in the presence of $F^-$ with other catalysts too.

## References

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2. Czuna Alexandra: Halogenid ionok tanulmányozása a *cisz,mer*-[$IrH_2Cl$(*m*tppms)$_3$] komplex katalizált HCOOH-bontásban, 2021.

## Acknowledgement

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