

Summary of Industrial Catalytic Processes

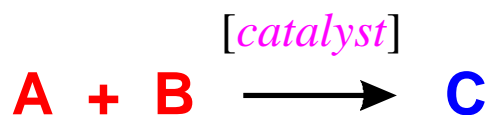
Process	Typical Catalysts
Petroleum Refining	
Cracking	Pt/Re on alumina, Zeolites
Reforming	Pt/Re/Ge/Sn on alumina (dehydrogenation)
Hydrocracking	alumina, zeolites, Pt
Alkylation	H ₂ SO ₄ , HF
Hydrodesulfurization	(Mo-Co) oxides, (Mo-Ni) oxides
Hydrodenitrogenation	(W-Ni) oxides
Chemical Manufacturing	
Natural Gas desulfurization	ZnO, Cu, Fe on activated C
Hydrogenations	Raney Ni, Raney Co, Pt, Rh
Ammonia synthesis	promoted Fe
Methanol synthesis	Cu-ZnO
Dehydrogenation	Butadiene: Fe ₂ O ₃ , Pt/Re on alumina styrene: Zn, Cr, Fe or Mn oxides
Oxidations	ethylene oxide: Ag nitric acid: Pt/Rh mesh/gauze sulfuric acid: V ₂ O ₅ maleic, phthalic anhydrides: V ₂ O ₅ formaldehyde: Ag or Cu; Mo, Fe, V oxides
Polymerizations	Ziegler-Natta polypropylene: Al alkyls + TiCl₃ Dow single site polypropylene: Ti metallocene Phillips -- Cr oxide on silica Polyethylene (low density): peroxides, peresters Polystyrene: benzoyl peroxide Urethanes: amines, organo-tin, phosphine oxides
Hydroformylation	Union Carbide/Hoechst/BASF: Rh/PPh₃ Exxon/BASF: HCo(CO)₄ Shell: HCo(CO)₄(PR₃) (R = bulky alkyl)

Catalytic Production of the Top **Organic** Industrial Chemicals

Ranking	Chemical	Production
#4	Ethylene 33 billion lbs	Steam Cracking of Hydrocarbons: larger hydrocarbon \longrightarrow smaller hydrocarbon + H ₂ $C_2H_6(g) \longrightarrow C_2H_4(g) + H_2(g)$ Catalyst: Zeolites, Pt/Re on Al₂O₃ support Conditions: 850°C, 20-50 atm
#10	Propylene 18 billion lbs	Steam Cracking of Hydrocarbons: $C_3H_8(g) \longrightarrow C_3H_6(g) + C_2H_4(g) + CH_4(g) + H_2(g)$ Catalyst: Zeolites, Pt/Re on Al₂O₃ support Conditions: 850°C, 20-50 atm
#12	Dichloroethane 15 billion lbs	<i>Direct Chlorination:</i> $C_2H_4(g) + Cl_2(g) \longrightarrow ClCH_2CH_2Cl(g)$ Catalyst: FeCl₃ or AlCl₃ <i>Oxychlorination:</i> $2C_2H_4(g) + 4HCl(g) + O_2 \longrightarrow 2ClCH_2CH_2Cl(g) + 2H_2O$ Catalyst: Cu salts on SiO₂ or Al₂O₃ supports
#16	Benzene 10 billion lbs	Hydrocarbon Reforming (dehydrogenation) $C_6H_{14}(g) \longrightarrow C_6H_{12}(g) + H_2(g)$ Endothermic! $C_6H_{12}(g) \longrightarrow C_6H_6(g) + 3H_2(g)$ Endothermic! toluene \longrightarrow benzene + methane Catalyst: Pt/Re/Ge/Sn on Al₂O₃ support
#17	Ethyl Benzene 9 billion lbs	$C_6H_6(g) + C_2H_4(g) \longrightarrow C_6H_5C_2H_5$ 1. Catalyst: Liquid phase system with AlCl₃ 2. Catalyst: Zeolite – Lewis Acid based gas phase process Classic Friedel-Crafts rxn.
#19	Vinyl Chloride 8 billion lbs	$ClCH_2CH_2Cl(g) \longrightarrow H_2C=CHCl(g) + HCl(g)$ This reaction is often coupled with the oxychlorination reaction to produce dichloroethane, this allows recycling of the HCl.
#20	Styrene 8 billion lbs	Dehydrogenation of ethyl benzene Catalyst: Fe oxides on Al₂O₃ support Conditions: 550-600°C
#21	Terephthalic Acid 8 billion lbs	<i>Amoco Process:</i> $p-CH_3-C_6H_4-CH_3 + 3O_2 \longrightarrow p-HOOC-C_6H_4-COOH + H_2O$ Catalyst: Co/Mn salts (with some heavy metal bromides) Conditions: liquid acetic acid solution, 200°C, 20 atm Ti or Hastelloy C lined reactor (very corrosive)

#22	Methanol	$\text{CO} + \text{H}_2 \longrightarrow \text{CH}_3\text{OH}$ <p>Catalyst: ZnO/Cu salt</p> <p>Conditions: > 100 atm, 200-300°C</p>
	7 billion lbs	
#24	Ethylene Oxide	$\text{C}_2\text{H}_4(\text{g}) + \frac{1}{2}\text{O}_2 \longrightarrow \text{ethylene oxide}$ <p>Catalyst: Ag</p> <p>Conditions: 300°C</p>
	6 billion lbs	
#26	Toluene	<p>Catalytic Reforming of methyl cyclohexane and derivatives</p> <p>Catalyst: Pt/Re on Al₂O₃ support</p> <p>Conditions: 500°C and 25 atm</p>
	6 billion lbs	
#27	Xylenes	<p>Catalytic Reforming of 1,4-dimethylcyclohexane</p> <p>Catalyst: Pt/Re on Al₂O₃ support</p> <p>Conditions: 500°C and 25 atm</p>
	5.5 billion lbs	
#28	Ethylene Glycol	$\text{ethylene oxide} + \text{H}_2\text{O} \longrightarrow \text{HOCH}_2\text{CH}_2\text{OH}$ <p>Catalyst: H₂SO₄ (0.5 - 1%), 50°-70°C</p> <p>Conditions: Thermal @ 195°C and 15 atm.</p>
	5 billion lbs	
#29	Butylaldehyde	<p><i>Hydroformylation -- Union Carbide/Celanese/BASF</i></p> $\text{propylene} + \text{H}_2 + \text{CO} \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ <p>Catalyst: <i>homogeneous Rh/PPh₃ catalyst</i></p> <p>Conditions: 100-125°C, 8-25 atm</p>
	5 billion lbs	
#31	Cummene	$\text{benzene} + \text{propene} \longrightarrow \text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2$ <p>1. Liquid phase catalysts: H₂SO₄, AlCl₃, HF</p> <p>2. Gas phase catalyst: H₃PO₄ on SiO₂</p> <p>Friedel Crafts reaction</p> <p>Conditions: 35-40°C, 7 bar (liquid); 200-300°C, 20-40 bar (gas)</p> <p>Cumene is mainly used to produce phenol and acetone.</p>
	3.7 billion lbs	
#32	Acetic Acid	$\text{CH}_3\text{OH} + \text{CO} \longrightarrow \text{CH}_3\text{COOH}$ <p>Catalyst: <i>homogeneous RhI₂(CO)₂⁻</i> <i>(Monsanto Acetic Acid process)</i></p> <p>Conditions: 150°C, 35 atm</p>
	3.5 billion lbs	

Homogeneous Catalysis



Remember that thermodynamics and equilibrium still rule!! A catalyst only speeds up the rate at which a chemical reaction reaches equilibrium. The actual equilibrium constant (thermodynamics) is NOT affected by the catalyst. Therefore, non-spontaneous reactions are usually NOT suitable for catalytic applications.

Advantages/Disadvantages of **Homogeneous** Catalysts Relative to **Heterogeneous** Catalysts

Good **homogeneous** catalysts are:

- good*
- generally far more selective for a single product
 - far more active
 - far more easily studied from chemical & mechanistic aspects
 - far more easily modified for optimizing selectivity
- bad*
- far more sensitive to permanent deactivation
 - far more difficult for achieving product/catalyst separations

Heterogeneous catalysts dominate chemical and petrochemical industry: ~ 95% of all chemical processes use **heterogeneous** catalysts.

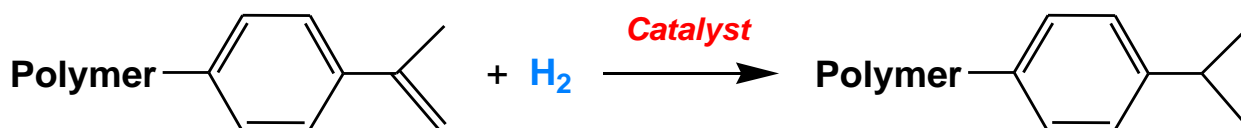
Homogeneous catalysts are used when *selectivity* is critical and product-catalyst *separation problems* can be solved.

Homogeneous or Heterogeneous?

Because many **homogeneous** catalysts decompose to form **heterogeneous** catalysts, and some **heterogeneous** catalysts can dissolve to form **homogeneous** catalysts, one should always be careful about making assumptions on what type of catalyst one is using in any new catalytic experiment. There are several general ways to test whether a catalyst is **homogeneous** or **heterogeneous**.

- 1) Exposure to elemental Hg will generally poison a **heterogeneous** catalyst
- 2) Exposure to polythiols will poison most **homogeneous** catalysts
- 3) Light scattering studies to identify the presence of colloids (**heterogeneous**)
- 4) Product selectivity studies

e.g., polymer bound alkenes:

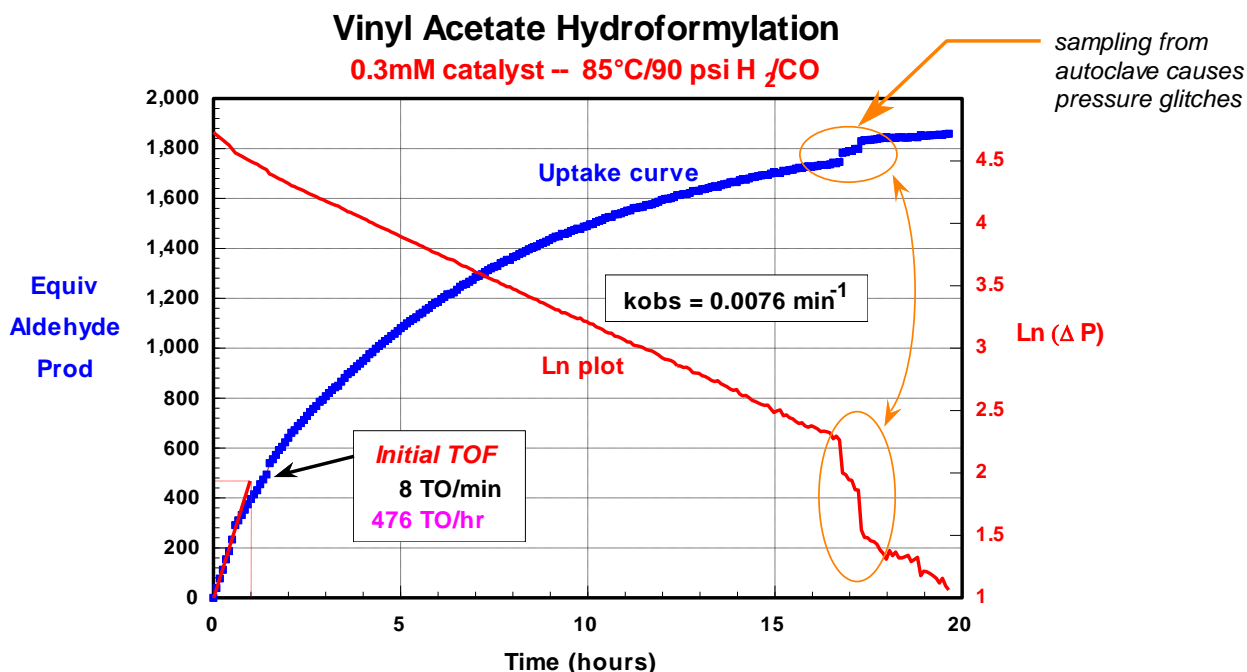


Catalyst	Homo/Hetero	% Yield
RhCl(PPh ₃) ₃	<i>homo</i>	100
Ni(OAc) ₂ + NaBH ₄	<i>hetero</i>	--
[Rh(nbd)(PR ₃) ₂] ⁺	<i>homo</i>	90
Pd/C	<i>hetero</i>	--
[Ir(cod){P(i-pr) ₃ }(py)] ⁺	<i>homo</i>	100

Some Catalysis Terminology

Turnover (TO) -- one loop through the catalyst cycle. Typically one equivalent of reactant is converted to one equivalent of product (per equivalent of catalyst).

Turnover Frequency (TOF) or Turnover Rate -- the number of passes through the catalytic cycle per unit time (typically sec, min or hrs). This number is usually determined by taking the # of moles of product produced, dividing that by the # of moles of catalyst used in the reaction, then dividing that by the time to produce the given amount of product. The units, therefore, are usually just $time^{-1}$. Note that the rate of a batch catalytic reaction is fastest at the very beginning of when the reactant concentration is the highest and generally slows down as the reaction proceeds -- stopping when all the reactant is used up. Note the graph below for the production of aldehyde product from the homogeneously catalyzed reaction of vinyl acetate, H_2 , and CO.



The TOF, therefore, will vary throughout the course of a batch reaction. The **Initial TOF** is defined as the initial part of a catalytic reaction where the rate is the fastest and essentially linear. A far better measure

of rate is the observed rate constant k_{obs} , which allows one to reproduce the entire product production curve given a set of reactant & catalyst concentrations. In the above graph, the reaction is pseudo-first order in excess reactant alkene (vinyl acetate concentration ~ 0.6 M, catalyst 0.3 mM) and k_{obs} is determined from a \ln plot of the change in H_2/CO pressure (reactant concentration) versus time for this rxn. When reporting k_{obs} chemists often normalize it to a certain catalyst concentration (1 mM, for example).

Turnover Number (TON) -- the absolute number of passes through the catalytic cycle before the catalyst becomes deactivated. Academic chemists sometimes report only the turnover number when the catalyst is very slow (they don't want to be embarrassed by reporting a very low TOF), or decomposes quite rapidly. Industrial chemists are interested in both TON and TOF. A large TON (e.g., $10^6 - 10^{10}$) indicates a stable, very long-lived catalyst. TON is defined as the amount of reactant (moles) divided by the amount of catalyst (moles) times the % yield of product. Authors often report mole % of catalyst used. This refers to the amount of catalyst relative to the amount of reactant present. 10 mole % = 10 TO, 1 mole % = 100 TON, 0.01% = 10,000 TON.

ee (enantioselectivity) – this defines the enantioselectivity of an asymmetric catalyst that produces more of one optically active enantiomer (*R* enantiomer, for example) than the other (*S* enantiomer).

ee is defined as:

$$ee = \frac{|R - S|}{R + S} \times 100\%$$

A catalyst that makes an equal amount of *R* and *S* enantiomers has 0% ee (a racemic mixture). 85% or higher is generally considered a good ee, although that depends on what the best known catalyst can do relative to that being reported.

Catalysis Data in Publications

There is a lot of mediocre/bad catalysis reported all the time in chemistry publications. One often has to dig into the data to figure this out. The things one wants to typically look for to tell whether there is “good” catalysis or not include:

- 1) # of turnovers performed – more is better
- 2) TOF (turnover frequency) – faster is better
- 3) Good selectivity for the product – this includes chemoselectivity, regioselectivity, and enantioselectivity (if applicable)
- 4) Reaction conditions – harsh? Mild? Unusual? Concentrations?

To figure out the number of turnovers you need to know the amount of substrate (reactant) and catalyst:

$$\text{Turnovers} = \frac{\# \text{ moles (equivalents) reactant (substrate)}}{\# \text{ moles (equivalents) catalyst}}$$

But authors often list these values in different ways and you may have to do some interpreting. The most common alternate way of representing the substrate:catalyst ratio is **mole %**. This is especially common for organic chemists doing Pd-catalyzed coupling reactions. 10 mole % catalyst means that there is 10% as much catalyst as substrate on a molar basis. This is equivalent to 10 turnovers.

10 mole % catalyst = 10 turnovers

5 mole % catalyst = 20 turnovers

1 mole % catalyst = 100 turnovers

0.1 mole % catalyst = 1000 turnovers

0.01 mole % catalyst = 10,000 turnovers

These represent the theoretical maximum # of turnovers. One also has to note the % yield or the % conversion of substrate into product to figure out the actual # of turnovers!!

Example: Consider the following catalytic data reported in a *J. Am. Chem. Soc.* communication (very prestigious) a number of years ago:

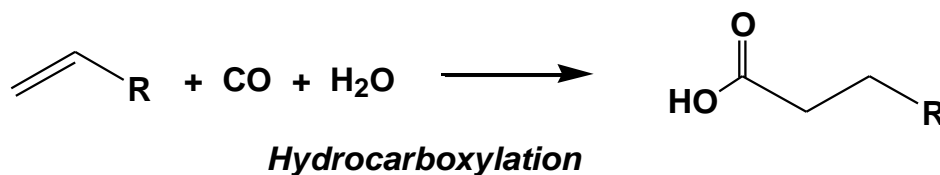


Table I. Hydrocarboxylation of *p*-Isobutylstyrene (**1**) and 2-Vinyl-6-methoxynaphthalene (**2**)

substrate	L*	1 (or 2)/ L*/PdCl ₂	product yield, ^a %	optical yield, ^b %
1	(<i>S</i>)-BNPPA	7.7/0.38/1.0	89	83 (<i>S</i>)
	(<i>S</i>)-BNPPA	7.7/0.77/1.0	80	55 (<i>S</i>)
	(<i>R</i>)-BNPPA	7.7/0.38/1.0	81	84 (<i>R</i>)
2	(<i>S</i>)-BNPPA	4.2/0.42/1.0	46	72 (<i>S</i>)
	(<i>S</i>)-BNPPA	10/0.5/1.0	71	85 (<i>S</i>)
	(<i>R</i>)-BNPPA	4.2/0.42/1.0	48	76 (<i>R</i>)
	(<i>R</i>)-BNPPA	7.7/0.38/1.0	64	91 (<i>R</i>)

^aYield of pure material. ^bDetermined by optical rotation measurements, relative to those for the pure enantiomers, reported in the literature^{9,10} and confirmed by independent measurements of authentic pure *S*-(+) enantiomers in the authors' laboratory.

Let's look at the last line of data from the table since that had the highest ee. The third column contains the important information about the ratio of reactant (often referred to as substrate), chiral chelating ligand L*, and PdCl₂.

The authors had 7.7 equivalents of reactant, 0.38 equivalents of chiral ligand, and 1 equivalent of Pd. This means that the maximum number of turnovers they could do is defined by the amount of reactant (moles or equivalents) divided by the amount of catalyst (moles or equivalents).

$$\text{max turnovers} = \frac{\text{equivalents reactant}}{\text{equivalents catalyst}} = \frac{7.7}{1.0} = 7.7$$

7.7 turnovers is small and not at all impressive. Hydrocarboxylation, however, is a difficult catalytic reaction and doing it asymmetrically is even more impressive.

Of course, 7.7 turnovers assumes 100% yield, which they did not get. The actual number of turnovers needs to be reduced by the % yield, which they report as 64%, so the actual number of turnovers is:

$$\text{actual turnovers} = 7.7 \times 0.64 = 4.9$$

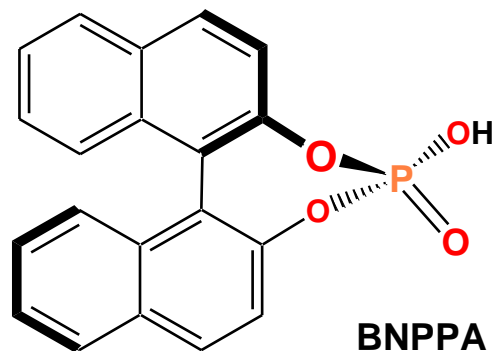
4.9 turnovers is barely catalytic. What about the TOF? Well you have to read a little footnote to find how long they ran the reaction to get their 64% yield: 18 hours at 1 atm of CO. The TOF is the number of turnovers divided by the time:

$$\text{TOF} = \frac{4.9 \text{ turnovers}}{18 \text{ hr}} = 0.27 \text{ hr}^{-1}$$

Well, 0.27 turnovers/hr is also barely catalytic. But that 91% ee is quite impressive isn't it. Or is it?

The authors only added 0.38 equivalents of chiral ligand to 1 eq of PdCl₂ to generate, at most, 0.38 equivalents of chiral catalyst (assuming one ligand per Pd). This is rather unusual, since one usually adds a little excess of chiral ligand to generate a chiral catalyst, even when dealing with a chelating ligand. There are examples where one can add less ligand than metal complex due to the fact that the metal-ligand catalyst generated is much more active than the starting metal complex itself. But one almost always adds enough ligand (or extra since the ligand can dissociate) to generate as much of the presumed catalytically active species as possible.

The ligand that the author is using is:



This is being used under rather acidic conditions (typically needed for Pd-catalyzed hydrocarboxylation) and under these conditions it is highly unlikely that it would be able to function as a ligand. Remember that the late transition metals don't particularly like oxygen donor ligands (weaker bonding).

This fact makes the high ee's rather suspect. And a number of research groups (Hoechst Celanese, Union Carbide, etc.) have found (although not published) that the actual ee for this "catalyst" is close to 0.

So it is often important to read the experimental conditions very carefully and with a critical eye.

Problem: Consider the following catalytic data reported in a recent publication. What information is missing?

Table 1 Biphasic hydrogenation reactions of arenes in the [bmim][BF₄] ionic liquid and water with [H₄Ru₄(η^6 -C₆H₆)₄][BF₄]₂ as the catalyst precursor

Substrate	Reaction system	Reaction conditions	Con- version (%)	Catalytic turnover ^a / mol mol ⁻¹ h ⁻¹
Benzene	Ionic liquid	60 atm H ₂ , 90 °C, 2.5 h	91	364
	Water	60 atm H ₂ , 90 °C, 2.5 h	88	352
Toluene	Ionic liquid	60 atm H ₂ , 90 °C, 3 h	72	240
	Water	60 atm H ₂ , 90 °C, 3 h	78	261
Cumene	Ionic liquid	60 atm H ₂ , 90 °C, 2.5 h	34	136
	Water	60 atm H ₂ , 90 °C, 2.5 h	31	124

^a Catalytic turnover is calculated on the assumption that the tetra-ruthenium catalyst does not break down into monoruthenium fragments which is entirely consistent with the data.

Notes and references

† The ionic liquid [bmim][BF₄] was prepared using the literature method.⁶ [H₄Ru₄(η -C₆H₆)][BF₄]₂ is very soluble and stable in this ionic liquid and is readily characterised in the ionic liquid using ¹H NMR spectroscopy which revealed a spectrum similar to that in conventional solvents.

Hydrogenations were carried using a Parr stainless steel autoclave (300 ml) fitted with either a glass or PTFE liner. The catalyst [H₄Ru₄(η^6 -C₆H₆)][BF₄]₂ was added together with the required amount of [bmim][BF₄] ionic liquid. The autoclave was then sealed and purged with hydrogen gas (99.9995% purity) and the appropriate reaction pressure was then set at room temperature. The autoclave was then sealed and heated to the required reaction temperature and stirred for the time period required. After reaction the contents were then separated into organic and ionic liquid phases and the products analysed by ¹H NMR spectroscopy and GC. The only products observed were the perhydrogenated cycloalkanes, there was no evidence for the formation of partially hydrogenated products or polymeric by-products.

Problem: Beller and coworkers have reported (*Angew. Chem.*, **2001**, *40*, 3408-3411) on hydroformylation catalysis using HRh(CO)(Naphos). The table of catalytic data from their paper is shown below. For experiment # 1, how many turnovers did the authors do? Clearly show how you calculate your number. Is there any important data missing from this table?

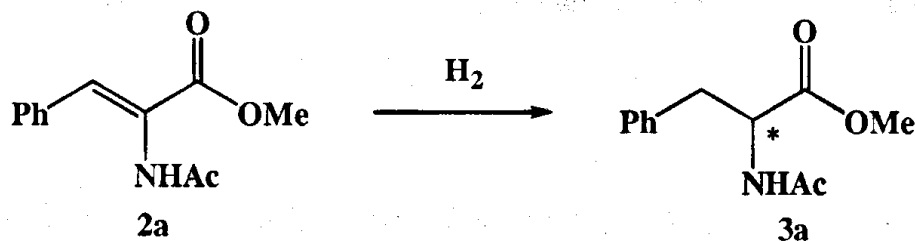
Table 1. Hydroformylation of 1- and 2-pentene with NAPHOS.^[a]

Entry	Olefin	<i>p</i> [bar]	<i>T</i> [°C]	Yield ^[b] [%]	<i>n:i</i>	TOF [h ⁻¹]
1	1-pentene	10	120	76	99:1	475
2	1-pentene	50	120	88	97:3	550
3	2-pentene	10	120	22	89:11	138
4	2-pentene	50	120	7	55:45	44

[a] Reaction conditions: olefin (70.0 mmol; 40 mL solution), [Rh(acac)-(CO)₂] (0.01 mol %; 20.7 ppm Rh), NAPHOS:Rh = 5:1, *t* = 16 h. [b] No significant amounts (> 1 %) of other products apart from isomerized olefin were detected.

Problem: What information is missing from the following Table of catalytic results (they defined the ligands used elsewhere in the paper). How many turnovers are they doing?

Table 1 Asymmetric hydrogenation of methyl α -acetamidocinnamate^a



Entry	Ligand	Solvent	Conv.	Ee [%]	t/2 [min]
1	1a	toluene	100	47 (R)	6
2	1b	toluene	100	46 (R)	4
3	1c	toluene	100	20 (R)	52
4	1d	toluene	100	90 (R)	50
5	1e	toluene	100	74 (R)	12
6	1f	toluene	100	82 (R)	36
7	1g	toluene	100	67 (R)	17

^a Conditions: 1 mmol substrate; 0.01 mmol [Rh(COD)₂]BF₄; cat.:ligand = 1:2; 15 ml solvent; 25°C