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Ranking of heterogeneous catalysts metals by their greenness

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ABSTRACT

Catalysis is very important process in industry and laboratory practice, especially from the point of green chemistry principles. However, eco-friendly character of heterogeneous catalysts, containing transition metal components has not been evaluated, yet. Therefore, we perform a comprehensive assessment of 18 heterogeneous metal catalysts (Pd, Pt, V, Co, Ni, Mo, Ru, Mn, Au, Cu, Cd, Zr, Fe, Rh, Ir, Sn, Zn, Ag) using multicriteria decision analysis approach. The ranking of alternatives according to relevant criteria like toxicity of pure metals and metal salts towards fish and *Daphnia magna*, algae/plants, metal toxicity towards rats via ingestion, carcinogenicity, the endangerment degree of metals, boiling point and energy for atom detachment, estimated as metal-metal bond strength in diatomic transition metal units, classification of elemental impurities according to International Conference on Harmonization (ICH)and their degree of importance is presented. Life cycle assessment (LCA) related parameters of metals have been also included. The assessment showed ruthenium, iron and molybdenum as the most favourable alternatives, in contrary to nickel, cobalt and rhodium. Results of environmental evaluation strictly depend on chosen scenario of assessment, in terms of toxicity, endangered elements or LCA. Sensitivity analyses towards variations in input data and applied weights, prove that results are reliable. Multicriteria decision analysis can be successfully applied in metal catalysts evaluation for particular case studies of different reactions.

Keywords: greenness assessment; green chemistry; heterogeneous catalysts; MCDA; sustainability assessment

Introduction

The concept of Green Chemistry was formulated in the 1990s. It may be defined as the "design of chemical products and processes to reduce or eliminate the use and generation of hazardous substances" [1, 2]. In other words, the aim of Green Chemistry is careful planning of chemical synthesis and molecular design to reduce some adverse consequences. The clue for chemists to achieve these goals could be 12 principles of green chemistry stated by Anastas and Warner [3]. Special attention should be paid to catalysis, a process by which a reaction rate is enhanced by a small amount of the catalyst, and it is usually not consumed or produced in the process, oppositely to surface or stoichiometric reactions [4, 5]. Principle no. 9 of the twelve principles concerns catalysis, indicating that catalysts (ideally as selective as possible) should be used instead of stoichiometric reagents. Furthermore, due to Anastas et al. [6], catalysis itself can be considered as primary tool for achieving all of the 12 principles of green chemistry. Analogously, some other concepts have been formulated with similar meaning, for instance by US Environmental Protection Agency (EPA), where the main areas for green chemistry have been narrowed down to the use of alternative synthetic pathways (natural processes such as photochemistry and biomimetic synthesis or alternative, harmless and renewable feedstocks as biomass), alternative reaction conditions or increased selectivity as well as reduced wastes and emissions (solvents with reduced impact on human health and the environment), design of eco-compatible chemicals (less toxic or more safe than traditional alternatives). These basics of green chemistry have been discussed and compared with objectives of industrial catalysis by Centi and Perathoner [7], taking into account examples of the old and new chemical routes.

According to many of researches, catalysis can significantly reduce the use and generation of hazardous substances. Notwithstanding, it may be problematic in case of complex ligands as well as while the use of catalysts in the presence of stoichiometric amounts or significant molar excesses of strong acids, bases, and other reagents. Therefore, an appropriate choice of the catalyst is very important and prospective. However, the selection between available options is not obvious and straightforward. Heterogeneous catalysts are generally characterized by simple separation, recovery and may be easily applied in case of continuous reactor operations. Nevertheless, they can be applied in form of different species: as metals, metal oxides, metal complexes catalysts, supported on different materials or not, in a form of nanoparticles, etc.

Considering for instance solvents, there are variety of greenness assessment systems based on Environment, Health and Safety (EHS) approach [8] or solvent selection guides developed by pharmaceutical sector [9, 10]. In the former case, the evaluation involves criteria such as release potential, fire/explosion and reaction/decomposition (as safety hazards), acute toxicity, irritation and chronic toxicity (as health hazards), persistency, air hazard and water hazard (as environmental hazards). As a result of the assessment, EHS indicator score is given for all solvents by summarizing points within these three fields of evaluation. Finally, by the application of solvent selection guides, every solvent is marked with color, by analogy to traffic lights, depending on its properties and recommendations for use or avoiding it.

Quite different approaches for solvents [11] and ionic liquids [12] have been proposed, both of them are based on MCDA (Multicriteria Decision Analysis) methodology application, where many criteria of assessment may be simultaneously included. Additionally, the possibility of assessing an appropriate weights to criteria, which reflect parameters importance, makes it more specific, flexible and comprehensive.

Some systems for solvents assessment are not specific for particular reaction or process. They are used in more universal manner (regardless of the type of synthesis reaction, extraction process, scale of process, etc.). It is in contrary to catalysts, where the label of being a green alternative is described in the context of the catalysis as a whole process. Accordingly, many publications may be found, in which the authors describe the green nature of the catalysis reactions. It was extensively summarized in supported materials in the **Table S1** (Based on an extensive conducted search particularly targeted library databases: ACS, Elsevier, Google Springer, Scopus, RSC, Web of Science – till first 100 hits, when available by the keywords “Green catalysis” or “green catalyst” with name of the element).Surprisingly, manganese is the only metal mentioned as a green catalyst (as a material).

Nevertheless, the estimation of greenness character of catalysts as a materials has not been done yet. In this work, 18different mostly transition metals, as a components of heterogeneous metal catalysts (Pd, Pt, V, Co, Ni, Mo, Ru, Mn, Au, Cu, Cd, Zr, Fe, Rh, Ir, Sn, Zn, Ag) have been evaluated using TOPSIS (The Technique for Order of Preference by Similarity to Ideal Solution) as MCDA algorithm. To our best knowledge, it is the first study that concerns wide variety of criteria and allows to rank heterogeneous catalysts from the most to the less recommended in respect to their environmental benigness. Results of such a study would be useful at the first stage of catalyst selection. They are not reaction or process-specific, as they do not include metrics suitable for reaction efficiency assessment. The criteria are selected in such a way that they cover spectrum of utilization processes and potential releases pathways to the environment. This approach gives a possibility to apply different weights if certain metal emission processes are more likely to occur, i.e. boiling points in case of high temperature processes or toxicity towards aquatic organisms in case of high probability of releases to water streams The results from this study, to some extent, would be helpful in synthesis and application of coordination polymers like metal-organic frameworks. In the metal-organic frameworks one and the same framework type may be obtained with different metal ions and for some specific applications one may choose the appropriate metal.

Materials

Data collection

The dataset concerns different heterogeneous catalysts, however only that ones used as a pure metals are included. This is because metalloid, metal oxides, metal nanoparticles are not characterized in an appropriate manner to be included in this assessment. Selected parameters for evaluation concern pure metals and their salts, therein: chlorides, bromides, fluorides, nitrates and sulfates. The majority of input data for analysis is taken from scientific papers. Some information are also provided by the Material Safety Data Sheets (MSDS) from *Sigma Aldrich* and *Merck* companies. Additionally, due to lack of information, properties such as boiling point of metal salts, toxicity of metal and its salts towards fish and *Daphnia magna* as well as toxicity of metals salts towards rats via ingestion are completed by information from other MSDS companies *(*Acros Organics, *Analytical Sensors & Instruments Ltd., Apollo Scientific, ATI, Avantor Performance Materials Poland, Carl Roth, Central Drug House (P) Ltd, ChemSrc,* Clearsynth, *Faggi Enrico Spa, Fluorochem Ltd., GFS Chemical Inc., Guide Chem, Multivalent Ltd, Nile Chemicals, Santa Cruz Biotechnology Inc., SrcChem, TCI Chemicals,* Thermo Fisher Scientific, *Wieland Edelmetalle GmbH).*Moreover, data about endangered elements according to ACS Green Chemistry Institute [13] as well as classification for residual metals in drug substances according to ICH (International Conference on Harmonization) [14] are also included. Moreover, life cycle data for the metals based on 5 characterization parameters is also added [15].TOPSIS analysis requires numerical values as input. Therefore, some collected information have been transformed, as described in details below. The numerical values for all criteria are summarized in the end of this subsection, **Table 1**.

Hazard statements

The hazard statements are taken from MSDS. Due to their descriptive character, they are transferred to numerical values according to the point system presented in **Table S2**. If the hazard is more serious, then the score is higher. Additionally, if hazard statements are in combination (two or more hazard statements summed up) their respective points are also summed up, such an approach has been used in assessment of derivatization agents greenness [16].

Precautionary statements

The precautionary statements are obtained from MSDS and transformed into points with the same procedure as in case of hazard statements. The results are summarized in **Table S3**. In case where, hazard statements are in combination (two or more hazard statements summed up) their respective points are also summed up.

Toxicity towards fish

The data on toxicity of metal and metal salts towards fish is taken from variety of MSDS and from some literature sources: [17, 18, 19, 20, 21, 22, 23, 24, 25,26]. Due to unavailability of data, the fish spices are different, however always the most unbeneficial solution is chosen as a first choice. Most often the data are related to fish species as: Feathed minnow (*Pimphale spromelas*), Carp (*Cyprinus carpio*), Rainbow trout (*Oncorhynchus mykiss*), Zebra fish (*Danio rerio)*. While defining the value of LC50 [mg/L], time of exposition is 96 h. Unfortunately, in case of Pd as a $PdCl_2$ and Mn as a $MnCl_2$, this time is shorter – 48 h (due to the lack of datapoints). Moreover, for Rh, Ru and Ir salts, there is no information about their toxicity. Therefore, we fulfill these gaps with the data concerning toxicity of different elements (Co) or their salts ($FeCl_3 \cdot 6H_2O$, $CoCl_2$), respectively. This transformation is done due to fact that element within the same group of periodic table, is characterized by similar properties to the given metal.

Toxicity towards Daphnia magna

The toxicity of metal and metal salts towards *Daphnia magna* is found in and articles: [20, 23, 27, 28, 29, 30]. As toxicity endpoints could be determined for different times, we decided to take the values for 48 h test, wherever possible. In case the endpoint for 48 h measurement was not available we took the values for 24 h test as in case of Pd as a $PdCl_2$. Of course, that values are chosen, which are characterizes by the most unwanted ranges. Unfortunately, for V and Mo salts, there are no information about toxicity. Therefore, we fulfill these gaps with the data concerning toxicity different element by different compounds of the elements Nb (as a $NbCl_5$) and Cr (as a $CrCl_3 \cdot 6H_2O$), respectively.

Toxicity towards rats via ingestion

Toxicity of metal catalysts salts towards rats via ingestion are taken from MSDS and literature sources: [31, 32, 33, 34]. Similarly as previously, LD50 values for salts are chosen to being the most unfavorable.

Boiling point

Values for metal salts boiling point are provided by MSDS and scientific papers: [35, 36, 37, 38, 39]. Regardless of the salt anion, least-beneficial values are always chosen – the lowest temperature that represents the possibility to be released from the metallic system.

Endangered Elements

Endangered Elements are critical elements i.a. rare earth elements, precious metals, and also some others that are essential to life, like phosphorus. This information is important from the point of sustainable development due to supply risks, extraction management, use, reuse and element dispersion. The Periodic Table of Endangered Elements conducted by the Chemical Innovation Knowledge Transfer Network and summarized by the ACS Green Chemistry Institute presents supply restrictions in the coming years [13]. These elements are distinguished by means of colors: grey for not endangered elements, yellow for elements with limited availability (future risk to supply), orange for elements with rising threat from increased use and finally red for elements characterized by serious threat in the next 100 years. Guided by the principle, the lower the better, for each group of elements appropriate points values are assessed: 0, 1, 2 and 3, respectively. This approach may put more attention for searching some alternatives, more efficient uses, recycling and recovery, that lower the risk and move industry towards sustainable supply chains.

Carcinogenicity according to IARC

According to IARC (International Agency for Research on Cancer) evaluation the carcinogenicity of chemical reagents to humans may be based on system of categories. This classification include several groups: Group 1 - Carcinogenic to humans, Group 2A - Probably carcinogenic to humans, Group 2B - Possibly carcinogenic to humans, Group 3 - Not classifiable as to its carcinogenicity to humans, Group 4 - Probably not carcinogenic to humans [40]. For metal catalyst points value are assessed: Group 1 – 2, Group 2A and Group 2B – 1, if no component of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC – then 0.

Energy for atom detachment, estimated as bond strength in diatomic metal compounds $M2 \rightarrow 2xM$

The data on energy for atom detachment is taken from the literature [41].In case of several values found, the least-beneficial one are always chosen – the lowest energy. This criterion reflects the possibility of releasing the metal atom from catalyst structure.

Toxicity towards algae/plants

Toxicity of metal/metal ions towards algae/plants are taken from scientific papers [42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53]. The toxicity endpoints as EC50 are determined for 72h, if not available, instead 96h are applied. In case of Ru and Ir, due to lack of data, different elements are applied, Co and Fe, respectively. This transformation is done with an assumption that element within the same group of periodic table, is characterized by similar properties to the given metal. This criterion is taken to consider toxicity towards organisms being low in trophic chain.

Classification for residual metals in drug substances (ICH guideline)

Alternative parameters to toxicity towards rats, that will properly describe human toxicity of metals is the permitted daily exposure (PDE) proposed by ICH (International Conference on Harmonization) in case of definition the residual metals in drug substances. Accordingly, metals are evaluated for their potential risk to human health and placed into classes as follows: Class 1 - Metals of significant safety concern, Class 2 - Metals with low safety concern, Class 3 - Metals with minimal safety concern, and Other element – that have not been established due to their low inherent toxicity and/or differences in regional regulations [14]. For metal catalyst points value are assessed: Class 1 – 3, Class 2 – 2, , Class 3 – 1, if metal is classified to Other, then – 0. Unfortunately, this risk evaluation involves only 24 metals, excluding Zr. Therefore we assume its low toxicity and assign to Class 3. The ICH guideline considers only those metals that are actually used for synthesis of drug substances and excipients as metal catalysts or reagents. The objective of this classification is to recommend, for the safety of the patient, maximum acceptable metal residues arising from the use of metals as catalysts or reagents in the synthesis of medicines (due to no therapeutic benefit from residual metals).

LCA for metals

LCA is a tool that allows to calculate and evaluate environmentally relevant inputs and outputs, as well as the potential environmental impacts of the life cycle of a product, material or service [54]. These potential environmental impact of product or process is related to chemical and biological reactions in air, water and soil and normalized to reference unit, using different factors. Environmental burdens are examined on the basis of some characterization factors that are estimated by metal life cycle stage, including mining, purification and refining. According to work provided by Nuss and Eckelman [15], the characterization factors of LCA as Global warming potential (GWP), Cumulative energy demand (CED), Terrestrial acidification, Freshwater eutrophication and Human toxicity (cancer and non-cancer) are applied. Due to the steadily increasing demand for metals, the their environmental burdens are likely to become more visible in the future. Therefore this criterion is important in case of finding sustainable metals for many processes.

Table 1. Summarized numerical data set for metal heterogeneous catalysts with assessed criteria` weights applied in ranking

Data for pure metals											**LCI/A for pure metals**					**Energy**	**Data for metal salts**		
Metal	**CAS no.**	**H – statements**	**P – statements**	**Endangered Elements**	**B.P. [°C]**	**Carc. IARC**	**ICH Class for metal residues**	**LC50 fish [mg/L] - 96 h**	**EC50 *Daphnia magna* [mg/L] - 48 h**	**EC50 algae/plant [mg/L] – 72/96h**	**GWP [kg CO2-eq/kg]**	**CED [MJ-eq/kg]**	**Terrestial Acidification [kgSO2-eq/kg]**	**Freshwater eutrophication[kg P-eq/kg]**	**Human toxicity [CTUh/kg]**	**Energy for atom detachment [eV]**	**LC50 fish [mg/L] - 96 h**	**EC50 *Daphnia magna* [mg/L] - 48 h**	**LD50 rats via ingestion [mg/kg]**
Pd	7440-05-03	12	23	1	100	0	2	0.2926	0.013	0.0065	3880	72700	1700	10	0.018	1.42	≤ 1*	0.2495*	200
Pt	7440-06-04	10	41	2	69.1	0	2	> 100	0.11	15	12500	243000	2200	51	0.092	3.19	2.5	0.082	980
V	7440-62-2	10	15	1	48.3	0	2	11.5	1.2	2.23	33.1	516	0.14	4.3E-07	4.4E-09	2.81	4.8	0.14**	160
Co	7440-48-4	13	73	1	> 74	10	2	1.406	0.71	0.59	8.3	128	0.089	0.004	3.8E-06	1.32	0.33	0.72	80
Ni	7440-02-0	24	23	1	103	10	2	1.3	0.65	0.002	6.5	111	1.5	0.014	0.000023	2.13	1.28	0.13	105
Mo	7439-98-7	17	48	1	25	0	3	800	1500	3.71	5.7	117	0.16	0.54	0.0009	4.54	> 1000	> 8.019**	200
Ru	7440-18-8	13	30	2	200	0	2	3810.81	12.3	2.75**	2110	41100	300	9.1	0.016	2.01	20.26**	53	> 579.6
Mn	7439-96-5	11	37	1	80	0	0	> 3.6	> 9.3	0.0364	1	23.7	0.0094	0.00067	3.3E-07	0.64	> 1000*	4.7	86
Au	7440-57-5	9	35	1	127	0	2	> 200	0.029	0.014	12500	208000	120	230	0.39	2.36	10.7	0.6	> 464
Cu	7440-50-8	13	13	1	83	0	1	0.0056	0.013	0.00011	2.8	53.7	0.39	0.13	0.00027	2.09	> 0.013	0.0094	> 140
Cd	7440-43-9	59	53	1	100	20	1	> 0.0004	0.0098	0.0004	3	53	0.022	0.0027	0.000014	0.08	> 0.0023	> 0.0093	88
Zr	7440-67-7	11	63	1	331	0	1	> 20.0	2.9	2,6	1.1	19.9	0.0058	0.00059	3.4E-07	3.11	51	2.9	98
Fe	7439-89-6	13	68	0	280	0	0	1.46	2.3	2.75	1.5	23.1	0.0052	0.00073	4.1E-07	1.23	4	7.6	319
Rh	7440-16-6	8	18	2	800	0	2	1.406**	0.29	5.23	35100	683000	5200	150	0.27	2.46	72	0.29	753
Ir	7439-88-5	8	44	2	687	0	2	1.406**	3	0.59**	8860	169000	3100	51	0.05	3.76	0.33**	3	1560
Sn	7440-31-5	7	20	1	114	0	1	>0.035	6.2	0.21	17.1	321	0.43	0.012	8.1E-06	1.94	480	6.2	700

Zn	7440-66-6	13	18	3	625	0	0	0.55	0.041	0.0009	3.1	52.9	0.039	0.0051	0.000059	0.23	0.1	0.47	350
Ag	7440-22-4	13	13	3	440	0	2	0.016	0.00091	0.16	196	3280	8.5	3.6	0.0069	1.69	0.0012	0.00091	1173
“Toxicity” scenario weights		0.01	0.01	0.05	0.01	0.03	0.1	0.12	0.1	0.1	0.02	0.02	0.02	0.02	0.02	0.03	0.12	0.1	0.12
“Endangered elements” scenario weights		0.01	0.01	0.4	0.01	0.05	0.03	0.08	0.05	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.02	0.08	0.05
“LCI/A” scenario weights		0.01	0.01	0.05	0.01	0.02	0.05	0.06	0.05	0.05	0.11	0.11	0.11	0.11	0.11	0.02	0.03	0.04	0.05

*Values for metal/metal salts with different time of exposition

**Values for metal/metal salts being a different compound - similar to the given one (within each group of periodic table)

*** Predicted values

Methods

TOPSIS algorithm

After preparing the dataset of heterogeneous catalysts and transformation them into numerical values, analysis using MCDA technique is performed.For this case study, the TOPSIS methodology (The Technique for Order of Preference by Similarity to Ideal Solution) developed by Hwang and Yoon [55], is selected. Its aim is choosing the best one from all alternatives by finding an alternative that is characterised by the shortest distance from the positive ideal solution and, at the same time, the farthest distance from the negative ideal solution. The main feature of this mathematical model is possibility of combining many different criteria into a single score, which in consequence allows to obtain ranking of available options in a reference to analysis assumptions. It is done due to definition of parameter, the value of similarity to ideal solution, for each alternative, which ranged between 0 and 1. In brief, the value 0 is assigned to completely non-ideal alternative (the worst values for all criteria), in opposite value 1 indicates an ideal solution (the best values for all criteria). These are basics of TOPSIS theory, however its mathematical algorithm are presented below.

The input data for TOPSIS analysis are the matrix consisting of *n* alternatives which are described by *m* criteria. The algorithm can be described in several steps as follows:

- Construction of normalised decision matrix
    - $r_{ij} = x_{ij} \div \sqrt{\sum x_{ij}^2}, i = 1,2,\dots,m \wedge j = 1,2,\dots,n(1)$
    - Where x_{ij} and r_{ij} are original and normalised scores in decision matrix, respectively.
- Construction of the weighted normalised decision matrix
    - $v_{ij} = r_{ij} \times w_j, i = 1,2,\dots,m \wedge j = 1,2,..,n(2)$
    - Where w_j is the weight of the criterion j and $\sum_{j=1}^{n} w_j = 1$
- Determination of positive ideal (A^*) and negative ideal (A^-) solutions
    - $A^* = \{(max_i v_{ij} \vee j \in C_b),(min_i v_{ij} \vee j \in C_c)\} = \{v_i^* \vee j = 1,2,\dots,m\}(3)$
    - $A^- = \{(min_i v_{ij} \vee j \in C_b),(max_i v_{ij} \vee j \in C_c)\} = \{v_j^* \vee j = 1,2,\dots,m\}(4)$
- Calculation of the separation measures for each alternative
    - $S_i^* = \sqrt{\sum_{j=1}^{m} \left(v_{ij} - v_j^*\right)^2} j = 1,2,\dots,m \quad (5)$
    - $S_i^- = \sqrt{\sum_{\mathrm{j}=1}^{\mathrm{m}} \left(v_{ij} - v_j^-\right)^2 j} = 1,2,\dots,m \quad (6)$

- Calculation of the relative closeness to the ideal solution
    - $C_i^* = \frac{S_i^-}{S_i^* + S_i^-}, \quad i = 1,2,\dots,m \wedge 0 < C_i^* < 1 \quad (7)$
- Arrangement of scenarios in order of closest to ideal to furthest from ideal - creation of a ranking

  The alternative with C_i^* closest to 1 is the best preference among the possible options.

Only basic information about TOPSIS algorithm are presented above. More details may be found in the articles describing its fundamentals [56, 57]. The calculations involving TOPSIS are performed in Excel program (Microsoft 2016).

Weights and confidence rankings

The undisputed advantage of MCDA methods is possibility of assessing weights to criteria. Its aim is to distinguish relative importance of criteria and, hence, their influence on final ranking results. To provide a comprehensive rankings all eleven criteria are simultaneously taken into evaluation, but with different importance. Toxicity of pure metals and metal salts towards fish as well as toxicity towards rats via ingestion are considered to have higher influence on the greenness character of catalysts. This is reflected by “Toxicity” scenario of assessment. Information about carcinogenicity class according to IARC is found to be a little less important, mainly because it carries little variability. Next places are arranged by toxicity of pure metals and metal salts towards *Daphnia magna* as well as towards algae/plants and information about the degree of endangerment of metals. Then lower weights are assessed for issues connected with LCA assessment. Parameters concern with physical properties as boiling point and energy for atom detachment affect less the green nature of the catalysts. As in certain cases the toxicological criteria may be of secondary importance, the scenario “Endangered elements” is introduced, with very high weight (0.40) assigned to this criterion. More often, LCA is also included in environmental risk assessments. Therefore, we add third evaluation scenario with priority weight values (0.11) to each of five LCA criteria. Their weights applied in mentioned above three rankings are presented in **Table 1.**

Sensitivity Analysis

Uncertainty of the values of input data, as well as obtained results is obvious and widely accepted fact. However, the most important question is: How small changes in input data may influence the final ranking? To find it out, we apply sensitivity analysis, which allows to consider errors of measured or predicted data, and additionally to assure that transformation of descriptive criteria into points does not influences final result or indicate the extent of impact. In other words, more mathematically, it allows to determine how possible changes or errors in parameters values affect model outputs [58]. We include randomly changed values in the dataset for 10% or -10% and 25% or -25% and then performed the analysis once more. The changes in secondary obtained ranking results were carefully checked and compared with original ones.

Moreover, not only changes of input data may influence on final ranking but also the weights [59]. Of course, if the weight ratio will change, then position of alternatives in the assessment may be different in the final ranking. To show how rankings are changing due to differences in applied weights then we prepared some additional analyses with weights changes for 50% or -50%.

Results and discussion

Results of TOPSIS analysis

The results of TOPSIS analysis including proposed criteria weight values are presented in **Table 1**. The outcomes are defined by the score of similarity to ideal solution, which may range between 0 and 1. If the value equals 0 (completely non-ideal alternative), it means that the option is characterised by the worst values for every single criterion and, oppositely, if the value equals 1 (an ideal solution), then it is characterised by the best values for all criteria.

Table 2. Ranking of heterogeneous catalysts with a respect to assessed weights

"Toxicity" scenario			**"Endangered elements" scenario**			**"Life cycle assessment" scenario**		
Rank	**Chemical**	**Similarity to ideal solution**	**Rank**	**Chemical**	**Similarity to ideal solution**	**Rank**	**Chemical**	**Similarity to ideal solution**
1	Ru	0.536	1	Fe	0.871	1	Ru	0.986
2	Mo	0.387	2	Mo	0.748	2	Mo	0.985
3	Pt	0.068	3	Ru	0.564	3	Fe	0.955
4	Mn	0.054	4	Sn	0.540	4	Sn	0.953
5	Ir	0.019	5	Mn	0.517	5	Zr	0.949
6	Sn	0.017	6	Zr	0.508	6	Mn	0.948
7	Fe	0.011	7	V	0.488	7	V	0.945
8	Ag	0.009	8	Cu	0.482	8	Cu	0.940
9	Zn	0.006	9	Pd	0.461	9	Ag	0.940

10	Zr	0.005	10	Co	0.437	10	Zn	0.938
11	Rh	0.004	11	Ni	0.434	11	Co	0.938
12	Cu	0.003	12	Au	0.422	12	Ni	0.937
13	V	0.003	13	Cd	0.390	13	Cd	0.935
14	Cd	0.002	14	Ir	0.068	14	Pd	0.887
15	Pd	0.002	15	Pt	0.067	15	Pt	0.752
16	Au	0.002	16	Rh	0.031	16	Ir	0.736
17	Co	0.001	17	Ag	0.012	17	Au	0.248
18	Ni	0.001	18	Zn	0.011	18	Rh	0.004

Table 2. shows ranking results within above-described criteria and weights according to three scenarios. According to “Toxicity” scenario the best alternative was found to be ruthenium catalyst. This alternative was characterised by good performance in terms of carcinogenicity and first of all toxicity. The second rank was reached by molybdenum catalyst due to low hazard, carcinogenicity and also toxicity. Then the values of similarities to ideal solution of next two catalyst (platinum and manganese) decrease significantly. The reason may be relatively high score for precautionary statements, as well as lower values for toxicity. Moreover, manganese catalyst is characterised by very low value of energy for atom detachment, what is unfavourable since it can be more easily emitted. The score for latter ten heterogeneous metal catalysts drastically changes its value from 0.019 to 0.001, mostly due to low values of parameters as LC50, EC50, LD50 and values of rest criteria in the middle range. Final three positions on the list belong to gold, cobalt and nickel, where two last are classified by IARC as certainly or potentially carcinogenic to humans. Interestingly, cadmium catalyst, which supposed to be the most dangerous due to its negative properties is placed not last. However, it is worth to notice that last five metals (Cd, Pd, Au, Co and Ni) have comparable values of similarity to ideal solution. Therefore basing on their poor scores for hazard and precautionary statements, carcinogenic character, high toxicity potential towards algae/plants and living organisms as *Daphnia magna* and fish, as well as low value of energy for atom detachment they may be evaluated as one group of metal catalysts with environmentally problematic nature. The results according to “Endangered elements” scenario are quite different. The first rank is obtained by iron, which is the only one element in the dataset that is not defined as of “limited availability” nor “rising threat from increased use”. Moreover, iron and its compounds are not very much toxic in comparison to some of other elements. The last ranks are for elements with “rising threat from increased use” and “serious threat in the next 100 years” labels – rhodium, silver and zinc. Ruthenium, another element with this label, is ranked third, mainly due to favourable toxicological endpoints

values. The another metal that performs well in assessments according to both scenarios is molybdenum. It is characterized by “limited availability” label and relatively low toxicity. In “Life cycle assessment” scenario values of similarity to ideal solution for majority of metals are similar. They only drastically change for two last metals, gold and rhodium. These metals are characterised by the highest values of LCA factors, four, and five, respectively. First place belongs to ruthenium, however it is not the most favourable metals bearing in mind all five factors` values (GWP, CED, etc.), as for instance Mo, Fe, Sn have. The reason may be fact that all the other criteria (as some toxicity endpoints) taken into evaluation are more beneficial in case of ruthenium than for molybdenum or iron.

Results of sensitivity analysis and comprehensive ranking

Sensitivity analysis allows to assess the reliability of conducted analysis based on collected data. Results of sensitivity analysis rankings are presented in **Table 3**.

Table 3. Summarized TOPSIS results combined with sensitivity analysis for changes in range of ±10% and ±25%

"Toxicity" scenario					**"Endangered elements" scenario**					**"Life cycle assessment" scenario**				
Metal	**Similarity to ideal solution**	**Original rank**	**Ranking difference for 10% or -10% changes**	**Ranking difference for 25% or -25% changes**	**Metal**	**Similarity to ideal solution**	**Original rank**	**Ranking difference for 10% or -10% changes**	**Ranking difference for 25% or -25% changes**	**Metal**	**Similarity to ideal solution**	**Original rank**	**Ranking difference for 10% or -10% changes**	**Ranking difference for 25% or -25% changes**
Ru	0.536	1	0	1	Fe	0.871	1	0	0	Ru	0.986	1	0	0
Mo	0.387	2	0	-1	Mo	0.748	2	1	0	Mo	0.985	2	0	0
Pt	0.068	3	0	0	Ru	0.564	3	-1	0	Fe	0.955	3	0	0
Mn	0.054	4	0	1	Sn	0.540	4	0	0	Sn	0.953	4	0	0
Ir	0.019	5	0	-1	Mn	0.517	5	4	2	Zr	0.949	5	0	1
Sn	0.017	6	0	2	Zr	0.508	6	4	2	Mn	0.948	6	0	-1
Fe	0.011	7	0	0	V	0.488	7	-2	2	V	0.945	7	0	0
Ag	0.009	8	0	-2	Cu	0.482	8	-2	4	Cu	0.940	8	1	2
Zn	0.006	9	0	1	Pd	0.461	9	4	4	Ag	0.940	9	-1	-1
Zr	0.005	10	1	-1	Co	0.437	10	-3	-5	Zn	0.938	10	0	1
Rh	0.004	11	-1	2	Ni	0.434	11	-3	-5	Co	0.938	11	0	1
Cu	0.003	12	0	-1	Au	0.422	12	-1	-2	Ni	0.937	12	0	1
V	0.003	13	0	-1	Cd	0.390	13	-1	-2	Cd	0.935	13	0	-4
Cd	0.002	14	0	0	Ir	0.068	14	2	0	Pd	0.887	14	0	0
Pd	0.002	15	0	1	Pt	0.067	15	-1	0	Pt	0.752	15	0	1
Au	0.002	16	0	-1	Rh	0.031	16	-1	0	Ir	0.736	16	0	-1
Co	0.001	17	0	0	Ag	0.012	17	0	0	Au	0.248	17	0	0
Ni	0.001	18	0	0	Zn	0.011	18	0	0	Rh	0.004	18	0	0

In this case study, potential errors or changes of a given data within ±10% and ±25% of original values are insignificant, due to fact that these changes do not affect the ranking of possible alternatives. Therefore, the ranking results can be considered as reliable.

Additionally, we consider changes in the final ranking in case of some shift of criteria weight values to assess the sensitivity of assigned weights. The values are the either plus or minus 50 % in respect to initial ones. The outcomes of TOPSIS analysis are presented below in **Table 4**.

Table 4. The results of rankings for changing weights of criteria (for 50%) obtained by TOPSIS algorithm for **"Toxicity" scenario*** as an example

Metal	**Similarity to ideal solution**	**Original rank**	**Ranking difference for 50% or -50% changes**
Mo	0.891	2	1
Mn	0.200	4	2
Pt	0.099	3	0
Ru	0.040	1	-3
Sn	0.033	6	1
Fe	0.019	7	1
Zn	0.009	9	2
Zr	0.009	10	2
Cu	0.006	12	3
Rh	0.005	11	1
V	0.005	13	2
Ir	0.004	5	-7
Ag	0.004	8	-5
Au	0.003	16	2
Pd	0.003	15	0
Cd	0.003	14	-2
Co	0.002	17	0
Ni	0.002	18	0

* The weights sensitivity analysis for "Endangered elements" scenario is not performed as +50 % change of endangered elements criterion would in fact result in uni-criterion decision analysis.

According to the above, it could be seen that the 50 % changes of criteria weight values do not significantly affect the ranking of catalysts. Thus, also in this case, the ranking results should be considered as reliable. However, these changes are more visible than in case of sensitivity analysis of input data involving all the scenarios for changes in range of ±10% and ±25% (Table 3.). This results underline the importance of criteria` weighting stage in MCDA algorithms, and thus in environmental evaluations. Therefore, the selection of appropriate weight values to each criterion should be carried out with great consideration by specialists with extensive, interdisciplinary knowledge in the field of chemistry, the environment and modelling/statistical methods. Moreover, it is necessary to have a clearly defined purpose of the analysis (for instance in terms of toxicity, renewable materials, waste management, manufacturing, special application etc.) to give the adequate priorities for each elements in a reference to specified scenario of assessment.

Comparison of obtained results

Bearing in mind, reliability of the analysis, sensitivity analysis have been performed, with ±10% and ±25% changes of initial data set. Moreover, the same analysis is conducted for the inputs with modified weight values for each criterion in a range ±50%. From **Tables 3 and 4** it may be seen that the performed greenness assessment of heterogeneous metal catalysts is reliable. In general, according to both scenarios, there are no significant shifts within ±10% and ±25% changes of original values. However, in the latter case, the differences are obviously more noticeable. In spite of that, probable mistakes, errors or changes of a given data may be considered as irrelevant. The most visible modifications occur while weights` values of criteria are switched, for instance on ±50% (in case of "Toxicity" scenario). Therefore, the positions of available alternatives in the ranking is slightly different.

How the ranking results correspond to practice in green catalysis? The articles in which authors claim that heterogeneous catalysis are green processes are presented in **Table S1.** The most commonly used metals in green catalysis is silver, followed by zinc and tin. Silver in form of nanoparticles (AgNPs) is used mainly in oxidation/dehydrogenation/epoxydation reactions (industrial application: ethylene oxide or formaldehyde production). It is due to fact that it is not affected by the reaction, thus it is easy to be recovered and reused. Moreover, 1/3 of summarized papers concerning environmentally friendly Ag catalysts application are based on their biogenic synthesis using for instance the peel extract of *Punica granatum* [60], the *Simarouba glauca* leaf extract [61] and the *Valeriana officinalis L.* root extract [62].However, nanoparticle size and shape are expected to play a significant role in the toxicity due to their influences on the uptake mechanisms and distribution in tissue, which is not considered in this study. There are some studies describing correlation of AuNPs and its particle size, stating that the smaller diameter, the greater toxicity effect [63, 64]. In case of AgNPs similar observations are conducted, but mechanism of its speciation is much more complicated. This toxicity potential of silver is also visible in out result of environmental evaluation, where according to "Toxicity" scenario, this metal is eight in the ranking. The next group with high number of applications is palladium, manganese and cooper. Less common are cobalt, iron, gold and molybdenum. Surprisingly, the application of cadmium is also used, i.e. for oxidation of primary and secondary alcohols [65] and synthesis of a variety of dihydropyrimidinone derivatives through the Biginelli reaction [66]. In the first case, the green label is assigned due to the possible seven-time reuse of the catalyst without significant loss of performance, as well as manner of catalyst preparation by thermal decomposition and calcinations. The other one is favored by its stability under the reaction conditions, short reaction time with high yields of the desired products simultaneously and organic solvent less reaction. However, it is important that the green character here refers to the whole catalysis process and not to the catalyst as a material, which was not stated. Therefore, cadmium may possibly offer an eco-friendly catalytic process, even if this metal catalyst as a material is not a good choice. Moreover, there are other metals, such as palladium or copper, which application is common, although their properties indicate they are not green. The results of our analysis are similar to toxicity evaluation based on available data on selected metals biological activities presented by Egorova and Ananikov [67]. Accordingly, the analysis of the metals environmental profiles suggests that the concept of toxic heavy metals and safe nontoxic alternatives based on lighter metals could be improper. They indicated that widely considered heavy and toxic metals as palladium, platinum, and gold compounds, may not be so dangerous, while complexes of nickel and copper, generally assumed as a green and sustainable options, may be significantly toxic (i.a. due to their solubility in water and biological fluids). The reason may be, fact that nickel, copper, and iron are usually treated as essential trace nutrients for living organisms [68, 69, 70, 71], whereas gold, palladium, platinum, and rhodium are discussed more often in terms of toxicity [72, 73]. The difference between toxic heavy metals and eco-friendly alternatives has been taken for granted in a such manner that it has turned into a motivation for the development of nickel, iron, and copper catalysts as replacements for more toxic metals. The widespread belief in toxic/non-toxic metal compounds as catalysts should not be straight-lined. Especially, that the presence of a metals in the environment does not go along with their toxicity. To enter the living organism, the metal must be in an appropriate bioavailable form. The main factors, which influence the environmental dangers of chemical compounds is their solubility in water (including valence state, particle size, and coordination sphere of metal) and its transformation within the environment. Additionally, the solubility of a compound in pure water may differ from that in biological fluids [74, 75], and the substance bioavailability also depends on mechanisms of its uptake and clearance from the organism [76]. Therefore, many different criteria should be taken into environmentally targeted evaluation, not only that based on toxicity. Especially, if we consider using inexpensive catalysts, where their subsequent use may be related to toxic waste and some additional procedural steps, which in turn may affect the overall cost efficiency and underestimate their potential for green character.

It seems to be obvious that for given case study not all 18 heterogeneous catalysts could be available. The results of rankings are still valuable to select greener options from those available. For specific reactions additional criteria can be included, such as reaction efficiency, selectivity of reaction or formation of (toxic, problematic) byproducts, mild catalytic reaction conditions, etc.

Conclusions

In this study, the TOPSIS algorithm is applied for heterogeneous metal catalysts ranking by their greenness. The greenest catalysts are ruthenium and molybdenum and iron, while the less environmentally desired are nickel, cobalt, gold, iridium, silver and rhodium - depending on scenario of assessment (“Toxicity”, “Endangered elements” and “Life cycle assessment” scenario). The reliability of the results has been provided by sensitivity analysis. Obtained data are compared with literature concerning heterogeneous metal catalysts application. The most commonly used catalysts are silver, tin and zinc, followed by to palladium, cooper and manganese. The first one, although of slight toxicity, is characterized by antibacterial properties and the catalyst may be synthesized via green, biogenic methods. The palladium and cooper are widely used in laboratory practice, although their properties indicate their environmentally problematic character. One the other hand, there are some examples of cadmium application in the reaction as a green alternative. However, it should be highlighted, that its green nature refers to the catalysis as a reaction, not to the material itself.

This is the first time, where catalysts as a materials has been evaluated from the environmental point of view, including great variety of criteria. It has to be clearly stated that this study is the first approximation as heterogeneous catalysts can be present different forms of metal catalysts, as pure metals, metal oxides, metal complexes, with support of different materials, in nanosized particles, etc. Hence, a more detailed studies considering metals chemical species are needed but due to lack of data are probably not yet possible.

Nevertheless, the presented approach based on MCDA can be successfully applied to assess the greenness of specific catalysis reaction in particular case studies. MCDA algorithms allow for a comprehensive evaluation, bearing in mind technological (selectivity, reaction yield, formation of by-products, possible catalyst recycling and re-use, reaction time, etc.) and environmental points of view at the same time.

Supporting Information. Summary of different authors claims on catalytic processes being green with different heterogeneous metal catalysts, transformation of hazards and precautionary statements into numerical values.

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