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Bibliometric study on the application of manganese dioxide in environmental catalysis worldwide from 1991 to 2021

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Since the 21st century, manganese dioxide (MnO_2) has been attracting increasing attention in the environmental and energy fields due to its excellent catalytic oxidation properties. To better grasp the development and trend of MnO_2 in the field of environmental catalysis, the published literature studies in the Science Citation Index Expanded database in the Web of Science Core Collection from 1991 to 2021 with a total of 1133 articles and reviews were analyzed by using visualization software of CiteSpace and VOSviewer. The results show an exponential growth in the number of papers related to MnO_2 in the environmental catalysis field, with China, USA, India, South Korea and Australia providing the main drivers, while China being the most active country, with Applied Catalysis B-Environmental, Environmental Science & Technology, Catalysis Today and Chemical Engineering Journal being the most important sources for publishing relevant research. At present, a more complete theoretical framework and research methods have been formed for MnO_2 environmental catalysis worldwide, but the research network is too centralized and the frontier branches are few. The catalytic research on MnO_2 has been expanded from the macroscopic level to the microscopic scale. Structure–activity relationship, density functional theory, catalytic oxidation and mechanism have become the frontier of research. The present study is of significance for better understanding and supporting further research on the MnO_2 environmental catalytic process.

Environmental significance

As an important environment-benign transition metal oxide, MnO_2 has a wide range of promising applications in electrode materials, electrochromism, catalysis, biosensors, *etc.* To date, there are more than 1000 published papers related to MnO_2 in environmental catalysis according to the Web of Science (WoS), one of the largest databases of peer-reviewed academic literature from Clarivate Analytics. However, there are rarely reports on analyzing the current status of MnO_2 research in the field of environmental catalysis from a bibliometric perspective. As the environmental and energy fields continue to evolve, MnO_2 environmental catalysis has become a new hot research frontier. Therefore, an analysis of the current state of this field is essential, and bibliometrics can provide a new approach to identify the evolution of research hotspots and frontiers in this topic. The results of the present study are of significance for better understanding and supporting further research on MnO_2 catalytic processes, and add new aspects to the field of environmental science.

1. Introduction

Since Antonsson *et al.*[1] selectively formed substituted cyclopentane derivatives in the presence of $Pd(OAc)_2$-MnO_2-benzoquinone as the catalyst in 1986, manganese dioxide (MnO_2) has been capturing more and more attention worldwide. As an important environment-benign transition metal oxide, MnO_2 has the advantages of abundant reserves, diverse morphology, rich crystalline forms and controllable grain sizes, and has a wide range of promising applications in electrode materials,[2–4] electrochromism,[5] catalysis,[6–8] biosensors,[9–11] *etc.*

To date, there are more than 4000 published papers related to MnO_2 in catalysis according to the Web of Science (WoS), one of the largest databases of peer-reviewed academic literature from Clarivate Analytics. Among them, there are more than 1000 papers on the application of MnO_2 in environmental catalysis. As the environmental and energy fields continue to evolve, MnO_2 research in the field of environmental catalysis has become a new hot research frontier. However, there are rarely reports that analyze the current status of MnO_2 research

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in the field of environmental catalysis from a bibliometric perspective. Therefore, an analysis of the current state of this field is essential, and bibliometrics can provide a new approach to identify the evolution of research hotspots and frontiers in this topic.

Bibliometrics is the quantitative analysis of the development of a research topic using mathematical and statistical methods,[12] which has been adopted by many disciplines for its macroscopic research advantages of objectivity, quantification, and modeling.[13] A research field can be analyzed by using visualization methods and mapped knowledge domain analysis to evaluate the current research situations, and evolutionary trajectory and predict the trend of a research field.[12]

In this study, literature data including titles, authors, institutions, journals, keywords, and references are processed by bibliometric methods, and these literature data can directly produce citation networks, co-occurrence networks, and coupling networks for further analysis. Data sources and research methods are described firstly. Following this, publication trends, source journal analysis, author contributions and collaborations, keyword co-occurrence analysis, co-citation analysis, and research frontiers and hotspots are comprehensively analyzed. The present study is significant for providing new insights into further research on MnO_2 environmental catalysis.

2. Data and methods

2.1 Data retrieval

Data were retrieved from the Web of Science Core Collection (WoS CC). The searches are limited to the SCI-Expanded database with strict review criteria and collecting peer-reviewed scientific papers, which ensures the high quality and representativeness of the selected papers used for this study.[14] "MnO_2" and "Manganese Dioxide" as search terms are connected by the Boolean operator "OR", and the search results "cataly*" and "environment*" are connected by the Boolean operator "AND" to filter the documents. In addition, the language is further limited to English, and the document type is restricted to "article" and "review". In order to collect all relevant papers, the time span of the search was set to "all years", from 1950 to the date of the search (December 31, 2021). Finally, the titles and abstracts of all publications were manually reviewed to remove the irrelevant ones, and a total of 1133 relevant papers were obtained, which were written by 5107 authors from 72 countries/regions and spanned 1087 institutions.

2.2 Methods

Bibliometrics has covered structural, dynamic, evaluative, and predictive scientometrics.[15] After data collected from the WoS Core Collection, including the number of publications, authors, institutions, countries/territories, citations, *etc.*, the analysis was performed by tabulation and visual mapping. In addition, knowledge domain maps of author contributions and collaborations, journal co-citations, and keyword co-occurrence were created using the VOSviewer software package.[12,16] Reference co-citation knowledge domain maps and keyword timelines were created using the Citespace software package.[16]

3. Results and discussion

3.1 Yearly quantitative distribution of the literature

Statistical analysis of the publication year provides a clear picture of the trend of scientific output, development and maturity of a research field. Fig. 1 shows the output distribution of MnO_2 in catalysis research based on time series. In general, from 1991, when the first article was published, to 2021, MnO_2 has been active in the field of environmental catalysis, with increased published articles each year, which can be roughly divided into three stages: (1) the initial stage (1991–1999): the total publications (TP) increased slowly with the year, from 1 in 1991 to 7 in 1999, with an average of 6 publications per year. (2) the primary growth stage (2000–2008): the number of total publications in this period peaked in 2007 with 15 papers, and the lowest annual number of publications was 6 in 2002 though. Between 2000 and 2008, the average annual number of papers was 12, which is higher than the average annual publication in the initial phase, but the overall research progress is still relatively slow, and more papers are expected to be published in the following years. (3) The rapid development stage (2009–2021): the number of papers published per year increased sharply during this period, from 23 published in 2009 to 185 published in 2021, with 82.4 average annual publications.

Annual publications from the top 11 countries are also presented in Fig. 1. It can be seen that the research on MnO_2 environmental catalysis in China has been increasing year by year since 1997, while the number of published papers in the USA, India, South Korea, Australia, Germany, Japan, France, England and Spain is showing a fluctuating growth trend. Moreover, the cumulative number of publications showed an exponential growth.

3.2 Source journal analysis

Journals are the most important source of scholarly communication and dissemination of scientific results, and journal analysis can be conducted to identify influential journals in the field. The retrieved results show that 1133 papers have been published in 309 journals, covering research areas such as catalytic chemistry, environmental chemistry, engineering and materials, and energy chemistry. Table 1 lists the top 11 prolific journals that published more than 17 articles related to MnO_2 environmental catalysis, and they are all included in SCI/SCIE. The Applied Catalysis B-Environmental (ACB-E) is a professional journal, which publishes experimental, theoretical and computational research related to new technologies and catalysts for catalytic combustion. With 174 papers, about 15.4% of the total were published in ACB-E, the most prolific journal reflecting the prevalence of catalytic research in the environmental catalysis. The second-ranked journal is Environmental Science & Technology (EST, 57, 5.0%), which focuses on chemical engineering, environmental engineering, and materials synthesis and processing. The third-ranked one is Catalysis

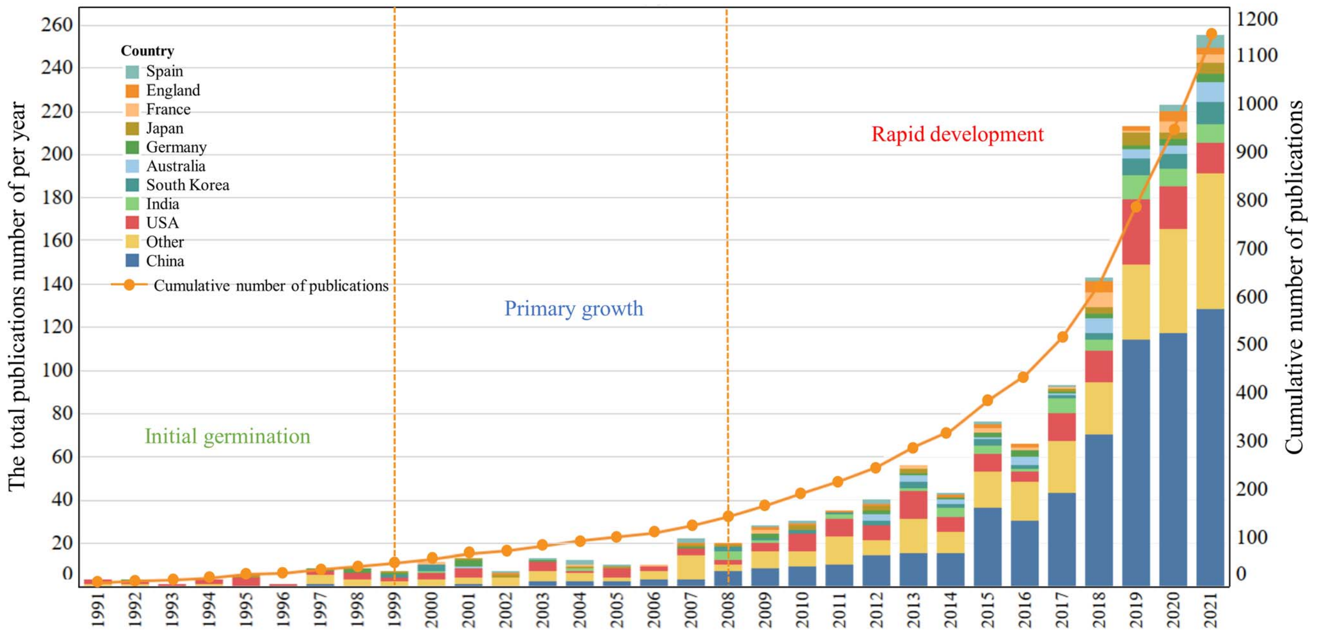

Fig. 1 Annual variation curves for published articles on MnO_2 environmental catalysis.

Table 1 Top 11 source journals ranked by the quantity of publications, 1991–2021

Rank	Source Journal	NP[a]	h[b]	TC[c]	CPP[d]	IF[e]
1	Applied Catalysis B-Environmental	174	274	17 869	102.7	24.319
2	Environmental Science & Technology	57	425	5336	93.6	11.357
3	Catalysis Today	36	221	2053	57.0	6.562
4	Chemical Engineering Journal	31	248	1714	55.3	16.744
5	Environmental Science and Pollution Research	26	132	329	12.7	5.19
6	Journal of Hazardous Materials	21	307	975	46.4	14.224
7	Journal of Environmental Sciences	20	109	673	33.7	6.796
8	Journal of Environmental Chemical Engineering	19	90	313	16.5	7.968
9	ACS Applied Materials & Interfaces	18	255	802	44.6	10.383
10	Science of the Total Environment	18	275	519	28.8	10.753
11	Energy & Environmental Science	17	376	4073	239.6	39.714

[a] Number of papers. [b] h-index. [c] Total citation. [d] Citations per paper. [e] 2021 impact factor.

Today (CT 36, 3.2%), whose broad scope is catalytic chemistry. At the same time, contaminant elimination is one of the hot topics related to MnO_2 environmental catalysis, with the related journals Environmental Science and Pollution Research (ESPR, 26, 2.3%), and Journal of Hazardous Materials (JHM, 21, 1.9%). In addition, research on MnO_2 in the field of environmental catalysis is also closely related to surface and interface reactions, and the related journals include ACS Applied Materials & Interfaces (ACS AMI, 18, 1.6%). In general, the core journals are almost related to this topic, specializing in different aspects of MnO_2 in the field of environmental catalysis.

3.3 Author contribution and collaboration

3.3.1 Author characteristics. Author contribution analysis is a method for studying collaboration patterns.[16] A total of 5107 authors participated in this bibliometric study on MnO_2 environmental catalysis. The top 10 authors with the most publications are listed in Table 2, along with their countries and institutions, number of publications, total citations, h-index and total link strength. Zhang P from Tsinghua University published the most articles with the number of 19. The second one is Li J, also from Tsinghua University. Wang S from Curtin University ranks third, publishing 14 articles. Among these authors, seven of the top ten authors are from China. Prof. Zhang P focuses on environmental pollution control chemistry and nanomaterials science, involving the pollution chemistry of water,[17] wastewater,[18] air and decontamination.[19] And Prof. Li J is specialized in the development of automobile exhaust catalysts,[20] indoor air pollution purification,[21] and flue gas selective catalytic reduction (SCR) technology.[20,22]

Table 2 Top 10 authors with the most publications in the field of manganese dioxide in environmental catalysis research

Rank	Author	Country	Institution	NP[a]	TLS[b]	TC[c]	CPP[d]	h[e]
1	Zhang P	China	Tsinghua University	19	41	1755	92.4	52
2	Li J	China	Tsinghua University	18	44	2464	136.9	74
3	Wang S	Australia	Curtin University	14	25	2710	193.6	131
4	He H	China	Chinese Academy of Sciences	12	24	550	45.8	80
5	Ma J	China	Harbin Institute of Technology	12	24	635	52.9	31
6	Suib, S l	USA	University of Connecticut	12	12	748	62.3	91
7	Sun H	Australia	Edith Cowan University	12	22	2161	180.1	90
8	Wang J	China	Huazhong Normal University	12	22	1098	91.5	24
9	Peng Y	China	Tsinghua University	9	29	435	48.3	55
10	Rong S	China	Nanjing University of Science and Technology	9	16	546	60.7	13

[a] Number of papers. [b] Total link strength. [c] Total citation. [d] Citations per paper. [e] *h*-index.

The total link strength (TLS) obtained from VOSviewer can effectively reveal the relationship between the number and frequency of co-authors. Each node represents an author, and the size of the node represents the number of co-authored papers. The link between two nodes represents the collaboration between them, and a larger link width means a closer collaboration between authors. Different colors represent different author cooperation clusters. The results in Fig. 2 show several clusters of authors working closely together, such as Zhang P (Tsinghua University), Wang S (Curtin University), Li J (Tsinghua University) and Suib S L (University of Connecticut). However, there is no close connection within different clusters, which indicates that the field is currently relatively independent in terms of international collaboration.

3.3.2 The most productive and influential institutions. By analyzing organizational collaboration, information about the most influential and productive institutions can be uncovered.[12] To further identify the major institutions, the top 10 institutions in terms of the number of publications are listed in Table 3. Among these institutions, the top nine are all from China and the fifth is from the USA. Fig. 3 shows the knowledge domain map of the collaborative institution using VOSviewer, presenting the densest TLS. The Chinese Academy of Sciences, with the most publications and ranking first in TLS, indicted its broader collaboration and higher academic impact. Furthermore, from the results in Fig. 3 the two institutions that work most closely together are Chinese Academy of Sciences and University of Chinese Academy of Sciences.

3.3.3 The most productive and influential countries/territories. In order to analyze the cooperation between the countries/regions involved in the study of this topic, the distribution of countries/regions was analyzed (Fig. 4). The theme study involved up to 72 countries/regions, and the top 5 countries/regions were China, USA, India, South Korea, and Australia, with 630 (55.6%), 193 (17.0%), 59 (5.2%), 51 (4.5%), and 37 (3.3%) publications, respectively. The knowledge

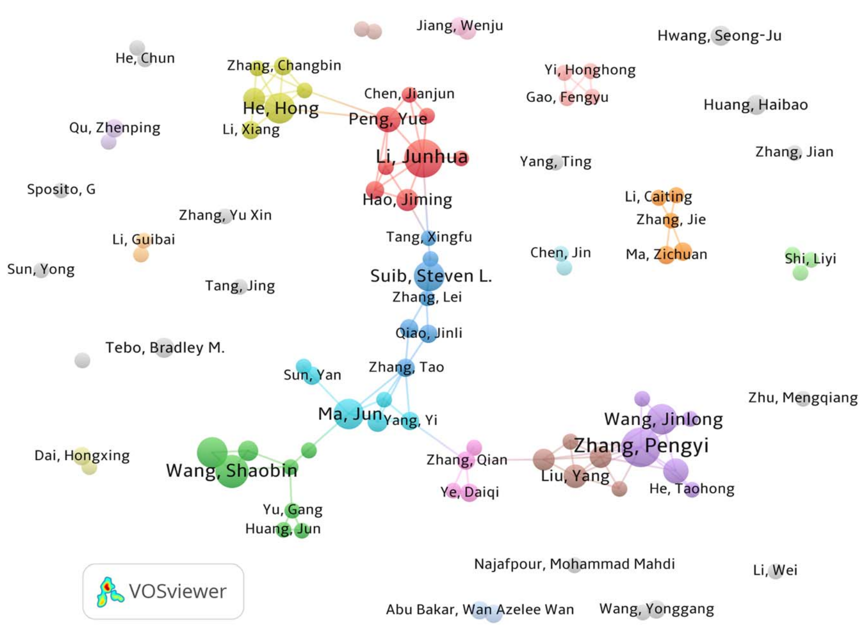

Fig. 2 Mapping knowledge domains of co-authors.

Table 3 Top 10 institutions with the most publications in the field of manganese dioxide in environmental catalysis research

Rank	Institution	Country	NP[a]	P[b]	TLS[c]	TC[d]	CPP[e]
1	Chinese Academy of Sciences	China	94	8.3%	86	5725	60.9
2	Tsinghua University	China	64	5.6%	49	5659	88.4
3	University of Chinese Academy of Sciences	China	32	2.8%	40	1701	53.2
4	Harbin Institute of Technology	China	26	2.3%	6	1830	70.4
5	University of Connecticut	USA	21	1.9%	11	1416	67.4
6	Wuhan University of Technology	China	18	1.6%	17	1079	59.9
7	Dalian University of Technology	China	17	1.5%	6	571	33.6
8	Fudan University	China	17	1.5%	10	2316	136.2
9	Sun Yat-sen University	China	14	1.2%	7	891	63.6
10	University of Science and Technology of China	China	14	1.2%	15	882	63.0

[a] Number of papers. [b] Proportion%. [c] Total link strength. [d] Total citation. [e] Citations per paper.

Fig. 3 Mapping knowledge domain of collaborative institutions of MnO_2 environmental catalysis.

domain map of co-authoring countries/regions is shown in Fig. 5. The nodes on the map represent different countries/regions, and their sizes represent the number of publications. The link between two nodes means that they have a cooperative relationship; the denser the link lines, the closer the cooperation between the two countries/regions. In terms of the number of cooperating countries, a total of 35 nodes are linked to China, 26 nodes are linked to the USA, and 16 nodes are linked to India; the higher the number of linked nodes, the more extensive the international cooperation. As can be seen in Fig. 5, China and the USA cooperate most closely, followed by China–Australia and China–Japan.

3.4 Co-citation analysis

The word co-citation was first proposed by the American intelligence scientist Henry Small, and it refers to the relationship between two papers when they are simultaneously referenced by a later published paper.[23] At the same time, the highly co-cited journals represent the core journals at the forefront of current research. To identify core journals and knowledge bases relevant to this study, co-citation analysis of source journals and publications was performed using the VOSviewer tool.

3.4.1 Journal co-citation analysis. The journal co-citation mapped knowledge domains of MnO_2 in the field of catalysis research are shown in Fig. 6. Two different journals are connected by a connecting line, indicating that two articles published in different journals are cited in the same article (later published). The denser the link, the higher the co-citation intensity of the two journals.

From Fig. 6, ACB-E is the largest node among all journals, indicating that ACB-E is the most cited journal along with other journals. This is not only related to the influence of the journal, but also to the number of articles published in the journal, with ACB-E ranking first among all journals in terms of the number of publications (Table 1). In the green cluster, CT and Journal of Catalysis (JC) are also widely cited, which shows that journals related to environmental catalysis generally have a broader impact. In addition, the connecting lines among ACB-E, JHM and Chemical Engineering Journal (CEJ) are thicker than the other lines, indicating a higher frequency of co-citation among these three journals.

The blue color in Fig. 6 is concentrated in the engineering and technology, with the representative journals of EST and CEJ. In terms of co-citation intensity, EST, JHM and CEJ have a close co-citation relationship with other journals.

The red cluster covers mainly chemical sciences-related journals, including Journal of the American Chemical Society (JACS), Angewandte Chemie-International Edition (ACIE) and Chemical Society Reviews (CSR). The node of links in the green cluster is greater than in the other clusters, suggesting that research on MnO_2 in environmental catalysis is more widespread.

3.4.2 Literature co-citation analysis. To further investigate the distribution of the most influential papers on MnO_2 in the field of environmental catalysis research, the top 20 most cited papers were collected and are listed in Table 4. Fourteen of the top 20 highly cited papers were published after 2010, indicating

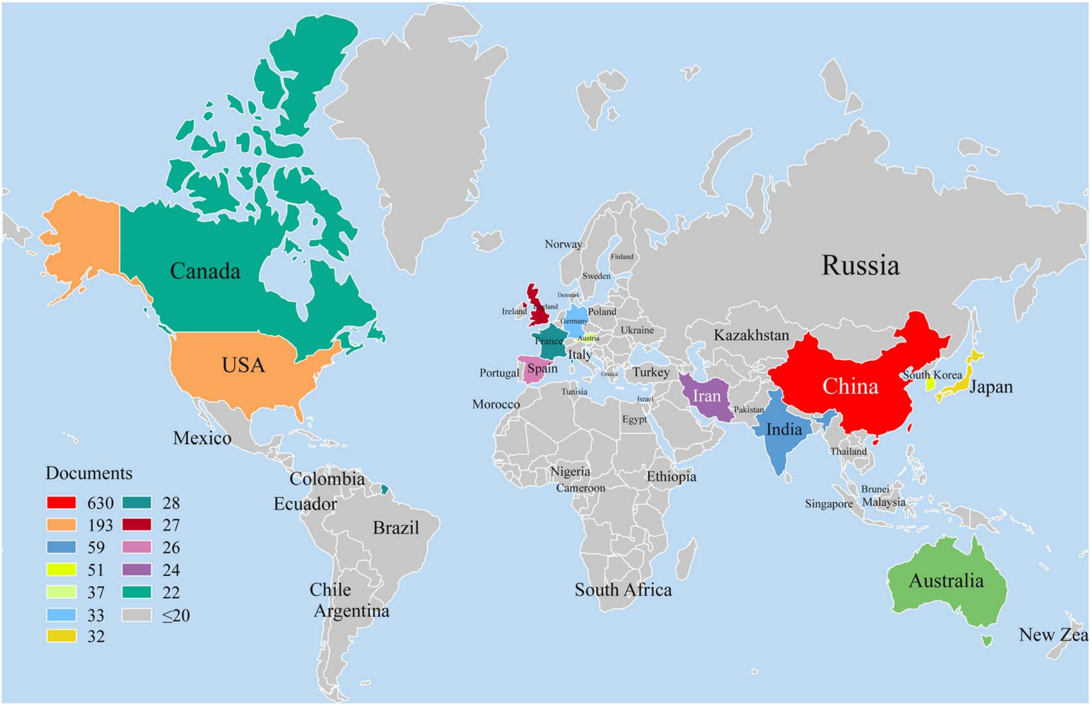

Fig. 4 Country/region distribution of the literature.

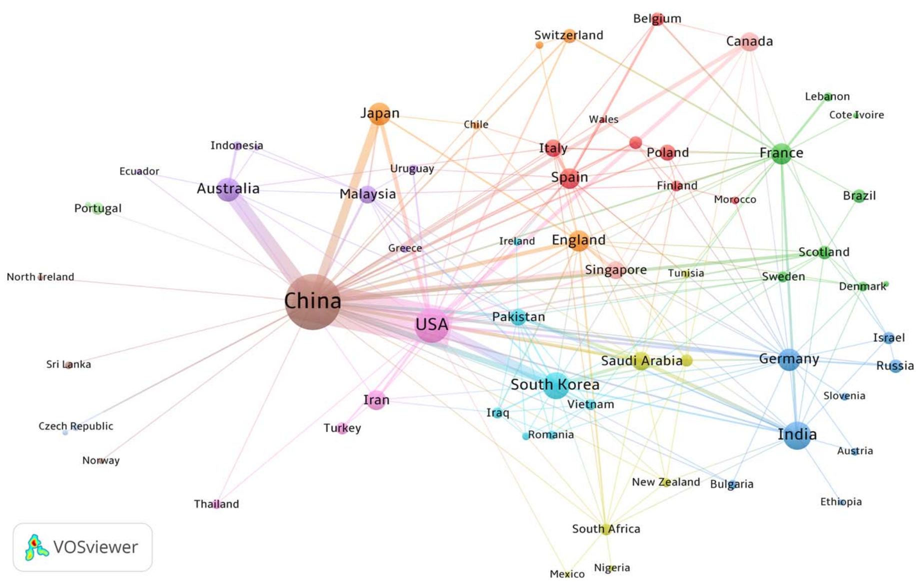

Fig. 5 Mapping knowledge domains of co-authoring countries/regions of MnO_2 environmental catalysis.

that the field has developed rapidly in the last decade or so (Fig. 1). As for the subjects, 10 of the 20 papers are related to catalytic oxidation, 4 papers are on SCR, 3 papers are about electrocatalysis and 2 papers are related to advanced oxidation processes (AOPs). In addition, one paper related to the role of MnO_2 in the global nitrogen cycle is also worthy of attention.

The most cited paper is "Low-temperature selective catalytic reduction of NO_x with NH_3 over metal oxide and zeolite catalysts-A review" written by Li *et al.*, with 772 citations. This study reviews two types of the low-temperature catalyst (LTC), the metal oxide catalyst and metal exchanged zeolite catalyst. For industrial flue gas and exhaust gas of diesel engines, it is of great significance to develop LTC for selective catalytic reduction of NO_x with ammonia (NH_3-SCR). At present, V_2O_5,[24] Fe_2O_3 (ref. 25) and MnO_x (ref. 26) are mainly used as active components in LTC research. Among them, MnO_x are the most active components for NH_3-SCR of NO at low temperatures. MnO_2 exhibited the best catalytic activity in the temperature range of

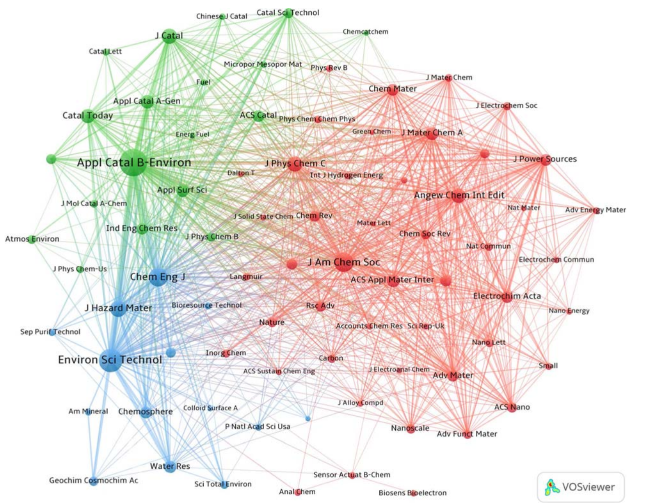

Fig. 6 Mapped knowledge domains for journal co-citation in the field of MnO_2 environmental catalysis.

100–300 °C, but its low N_2 selectivity required further improvement. In addition, efforts need to be made on detailed mechanisms of SO_2 poisoning and H_2O suppression effect on Mn based metal oxides at low temperatures. At the same time, the synergistic effect of composite oxides is also a hot topic in recent years.[27]

Part of the research in the above review has been documented in a paper published in 1994 titled "Activity and selectivity of pure manganese oxides in the selective catalytic reduction of nitric oxide with ammonia", which was the second highly cited article. This study reported that manganese oxides with different crystallinity, oxidation state and specific surface area were used in NH_3-SCR. The highest SCR activity per unit surface area is exhibited by MnO_2, followed by Mn_5O_8, Mn_2O_3, Mn_3O_4 and MnO, in that order. The temperature-programmed reduction (TPR) experiments indicate a relation between the SCR process and surface reactive oxygen species.[28]

The third highly cited paper focuses on catalytic oxidation. The complete oxidation of formaldehyde by MnO_x–CeO_2 mixed oxides prepared by sol–gel, co-precipitation and modified coprecipitation method is reported.[29] It is worth noting that half of the number of the top 20 highly cited articles are on catalytic oxidation, which fully illustrates that catalytic oxidation is a hot area of current research in the complete oxidation of formaldehyde,[29] toluene elimination,[30] phenol degradation,[31] *etc.* Due to the advantages of high catalytic activity, strong stability and low cost, the non-noble metal catalyst MnO_2 has been widely used in Volatile Organic Compound (VOC) elimination. In order to improve its catalytic activity, researchers are now using doping modification and structural modulation to compensate for its weak electron transfer ability and low specific surface area.[32] Although a large number of reports have been conducted for catalytic oxidation of VOCs, there are still some specific areas that need our further attention for the development of industry and the need of environmental protection, for example, the removal of halogenated VOCs and nitrogen-containing VOCs, and the combination of experimental and theoretical calculations to gain insight into the kinetics and mechanism of the catalytic oxidation reaction of VOCs on MnO_2 surfaces. In addition, how to improve the hydrothermal stability of catalysts in industrial applications is also a focus of future research.

As can be seen in Table 4, MnO_2 has also attracted great attention in the electrocatalytic technology due to its excellent hydrogen/oxygen evolution reaction performance. In addition, hydrogen energy is regarded as a green, efficient and renewable new source with the most potential to replace fossil fuels,[33] so MnO_2 catalytic HER technology might be promising to solve the energy crisis. In order to further enhance the electrocatalytic properties of MnO_2, researchers have made many useful explorations, such as doping,[48] construction of defective vacancies[49] and compounding with other active nanomaterials.[50]

3.5 Keyword co-occurrence analysis

The objective of keyword co-occurrence analysis is to study the core content and structure of a specific field and thus to reveal the research frontiers in that field. A total of up to 5330 keywords were extracted from the Web of Science core database for the analysis of MnO_2 environmental catalysis. We selected keywords with a frequency of 22 or more occurrences for visual analysis and obtained a total of 83 keywords, and the results in Fig. 7 show that a total of 4 clusters were obtained, where a node represents a keyword, and the node size represents the frequency of the keyword's occurrence, and the density of the connecting line between the nodes represents the strength of the co-occurrence between the keywords.

Cluster 1 (Blue): the most frequent keyword in the blue cluster is "MnO_2", which is connected to 82 nodes out of 83 nodes in total in Fig. 7. The blue cluster mainly spreads out around the nodes of "Catalytic Oxidation", "Low-Temperature" and "VOCs". VOCs, such as toluene and formaldehyde, are of widespread concern as a major cause of global air pollution.[51] Low-temperature catalytic oxidation technology can convert VOCs into CO_2 and water, which is recognized as one of the blue, efficient and environmentally friendly treatment means.[52] MnO_2 has inherent advantages, such as multiple valence states (Mn^{2+}, Mn^{3+}, and Mn^{4+}) and crystal structures (α-MnO_2, β-MnO_2, γ-MnO_2, and δ-MnO_2). Moreover, MnO_2 is excellent in the significant adsorption of oxygen and low-temperature self-reduction;[30] especially, α-MnO_2 with a $[2 \times 2]$ tunnel structure is considered as one of the ideal catalysts for VOC removal.[53]

Cluster 2 (Red): among the 83 keywords, "Performance" is well correlated with "MnO_2" and is also the largest node in the red cluster. This cluster focuses on the preparation of catalyst materials and their catalytic performance. Zeng *et al.*[54] reviewed the progress of catalytic oxidation of formaldehyde based on materials prepared by different methods, such as MnO_2 loaded noble metals, structural regulation of MnO_2, and MnO_2 and composites of MnO_2 with other non-noble metal materials. The influence of material synthesis methods on the catalytic performance was revealed. In addition, the regulation of interfacial

Table 4 Top 20 publications with the most citations in the field of MnO_2 environmental catalysis

Rank	Title	Journal	Author	Year	Citations	IF (2021)	Reference
1	Low-temperature selective catalytic reduction of NO_x with NH_3 over metal oxide and zeolite catalysts-A review	Catalysis Today	Li *et al.*	2011	772	6.562	27
2	Activity and selectivity of pure manganese oxides in the selective catalytic reduction of nitric oxide with ammonia	Applied Catalysis B: Environmental	Kapteijn, *et al.*	1994	732	24.319	28
3	MnO_x–CeO_2 mixed oxide catalysts for complete oxidation of formaldehyde: effect of preparation method and calcination temperature	Applied Catalysis B: Environmental	Tang, *et al.*	2006	663	24.319	29
4	Manganese oxides with rod-, wire-, tube-, and flower-like morphologies: highly effective catalysts for the removal of toluene	Environmental Science & Technology	Wang *et al.*	2012	571	11.357	30
5	Defect-engineered ultrathin delta-MnO_2 nanosheet arrays as bifunctional electrodes for efficient overall water splitting	Advanced Energy Materials	Zhao *et al.*	2017	568	29.698	34
6	Persulfate activation on crystallographic manganese oxides: mechanism of singlet oxygen evolution for nonradical selective degradation of aqueous contaminants	Environmental Science & Technology	Zhu *et al.*	2019	517	11.357	35
7	The role of lattice oxygen on the activity of manganese oxides towards the oxidation of volatile organic compounds	Applied Catalysis B: Environmental	Santos, *et al.*	2010	504	24.319	36
8	Surface characterization studies of TiO_2 supported manganese oxide catalysts for low temperature SCR of NO with NH_3	Applied Catalysis B: Environmental	Ettireddy, *et al.*	2007	470	24.319	37
9	Gas phase ozone decomposition catalysts	Applied Catalysis B: Environmental	Dhandapani, *et al.*	1997	464	24.319	38
10	*In situ* X-ray absorption spectroscopy investigation of a bifunctional manganese oxide catalyst with high activity for electrochemical water oxidation and oxygen reduction	Journal of the American Chemical Society	Gorlin, *et al.*	2013	417	16.383	39
11	Different crystallographic one-dimensional MnO_2 nanomaterials and their superior performance in catalytic phenol degradation	Environmental Science & Technology	Saputra, *et al.*	2013	363	11.357	31
12	Electrosynthesis, functional, and structural characterization of a water-oxidizing manganese oxide	Energy & Environmental Science	Zaharieva, *et al.*	2012	362	39.714	40
13	Removal of volatile organic compounds by single-stage and two-stage plasma catalysis systems: a review of the performance enhancement mechanisms, current status, and suitable applications	Environmental Science & Technology	Chen *et al.*	2009	350	11.357	41
14	Co-doping a metal (Cr, Fe, Co, Ni, Cu, Zn, Ce, and Zr) on Mn/TiO_2 catalyst and its effect on the selective reduction of NO with NH_3 at low-temperatures	Applied Catalysis B: Environmental	Thirupathi, *et al.*	2011	345	24.319	42
15	Manganese oxides at different oxidation states for heterogeneous activation of peroxymonosulfate for phenol degradation in aqueous solutions	Applied Catalysis B: Environmental	Saputra, *et al.*	2013	339	24.319	43
16	Interactions of manganese with the nitrogen cycle: alternative pathways to dinitrogen	Geochimica et Cosmochimica Acta	Luther, *et al.*	1997	302	5.921	44
17	3D-hierarchically structured MnO_2 for catalytic oxidation of phenol solutions by activation of peroxymonosulfate: structure dependence and mechanism	Applied Catalysis B: Environmental	Wang *et al.*	2015	300	24.319	45

Table 4 (*Contd.*)

Rank	Title	Journal	Author	Year	Citations	IF (2021)	Reference
18	Catalytic decomposition of gaseous ozone over manganese dioxides with different crystal structures	Applied Catalysis B: Environmental	Jia *et al.*	2016	299	24.319	46
19	The effect of manganese vacancy in birnessite-type MnO_2 on room-temperature oxidation of formaldehyde in air	Applied Catalysis B: Environmental	Wang *et al.*	2017	294	24.319	47
20	The role of lattice oxygen on the activity of manganese oxides towards the oxidation of volatile organic compounds	Applied Catalysis B-Environmental	Santos, *et al.*	2010	443	24.319	36

structure is also one of the research hotspots for catalytic activity. Duan *et al.*[55] prepared a bi-component MnO_2 and Mn_3O_4 supported Pt catalyst by interfacial modulation in the *in situ* liquid-phase reduction strategy, which showed excellent catalytic activity for toluene oxidation and could achieve complete mineralization of toluene at 160 °C. This report reveals that the modulation of the interfacial structure in the bi-component manganese oxide supported Pt catalysts is a feasible way to improve the catalytic oxidation performance of toluene.

Cluster 3 (Yellow): the largest node is "Degradation", with 72 nodes connected, including "Oxidation", "Waste water", "Removal", *etc.*, within cluster 3. This cluster mainly reflects the subject of heterogeneous catalysis. He *et al.*[56] investigated the structure–activity relationship of MnO_2 and the mechanism of catalytic ozone oxidation in "Aqueous Solution". Gan *et al.*[57] prepared β-MnO_2/kenaf carbon fiber (KCF) composites for the degradation of "Bisphenol-A" (BPA) in water *via* catalytic oxidation.

Cluster 4 (Green): the largest node is "Density Functional Theory" (DFT), with 48 nodes linked, which indicates that the use of computer simulation techniques to study the catalytic mechanism is becoming an auxiliary research tool. Zhou *et al.*[48] synthesized nano-hybridized MnO_2 catalysts *via* α-MnO_2 nanotubes, and DFT calculations showed that the surface of pristine α-MnO_2 (111) could promote the adsorption and activation of O_2, while the surface of hybridized MnO_2 (111) contributed to the absorption/decomposition of the product H_2O.

3.6 Research frontier identification

The timeline view can clearly reflect the results of the different clusters over time.[12] The *X*-axis is the year of publication and the *Y*-axis represents the different keyword clusters. Fig. 8 shows the entire timeline of MnO_2 environmental catalysis from 2011 to 2021. A keyword represents a node, *i.e.*, the larger node represents the stronger keyword burst, that is to say, the connection between keywords indicates a co-occurrence relationship between each other.[16] A total of eight clusters were obtained with the evolution of representative keywords under each cluster (Fig. 8).

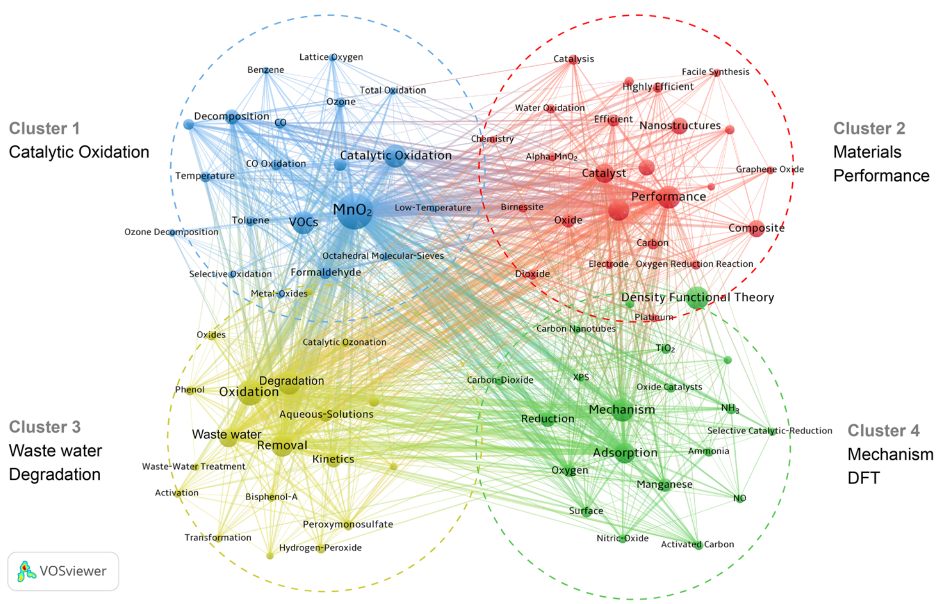

Fig. 7 Keyword co-occurrence knowledge domain map of manganese dioxide in the field of environmental catalytic research.

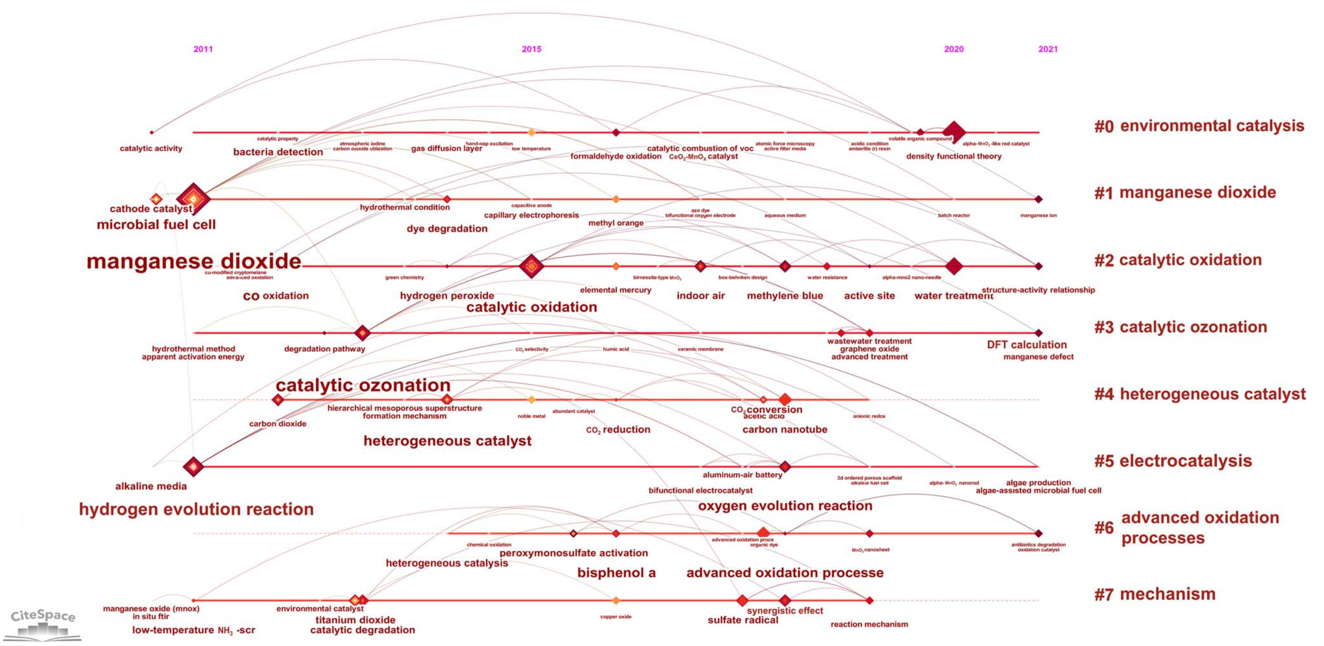

Fig. 8 Keyword timeline view of MnO_2 in the field of environmental catalysis.

From 2011, many keywords appeared in the timeline, including manganese dioxide, hydrogen evolution reaction, and low-temperature NH_3-SCR. By 2015, the keywords, such as catalytic oxidation, low temperature, CO_2 selectivity, and noble metal, appeared. In 2020, the keywords, such as density functional theory and water treatment, appeared. In 2021, structure–activity relationship, DFT calculation, and manganese defect as the three key words emerged.

The top 15 keywords in terms of citation burst strength obtained by CiteSpace software are shown in Table 5. It can be seen that the keyword with the highest citation burst strength is density functional theory. From 2019 to 2021 there were strong citation bursts for the three keywords, *i.e.*, structure–activity relationship, density functional theory and water treatment. Based on the strong citation bursts and the impact of keywords, it can be predicted that overall water splitting, density

Table 5 Top 15 keywords with the strongest citation bursts of MnO_2 in the field of environmental catalysis

No	Keywords	Strength	Begin	End	2011–2021
1	Density functional theory	5.86	2020	2021	
2	Water treatment	4.87	2020	2021	
3	Elemental mercury	4.27	2016	2017	
4	Synthetic humic-like acid	3.48	2018	2018	
5	Carbon nanotube	3.48	2018	2018	
6	Organic dye	3.48	2018	2018	
7	Surface property	3.22	2012	2015	
8	MnO_2 nanoparticle	2.71	2017	2017	
9	Structure–activity relationship	2.71	2019	2019	
10	Inorganic compound	2.68	2015	2015	
11	Low temperature	2.68	2015	2015	
12	Electron microscopy	2.68	2015	2015	
13	Noble metal	2.68	2015	2015	
14	Copper oxide	2.65	2016	2016	
15	Methyl orange	2.65	2016	2016	

functional theory, and water treatment will remain research hot words for MnO_2 environmental catalysis in the future. As shown in Fig. 8, the emerging keywords in 2021, such as DFT calculation and structure–activity relationship, might represent that themes, such as performance, catalytic oxidation and mechanism, are also the research frontier in the field of MnO_2 environmental catalysis (Fig. 7). As is known, the morphology has a crucial influence on the catalytic performance of MnO_2.[30,58–61]

4. Conclusion

A bibliometric analysis of published papers related to MnO_2 environmental catalysis in the WOS core database is conducted to obtain a knowledge map through information visualization analysis. To date, MnO_2 environmental catalysis research shows the following characteristics:

(1) MnO_2 environmental catalysis research can be divided into three stages: the initial stage (1991–1999), the primary growth stage (2000–2008), and the rapid development stage (2009–2021). China is the most active country in this field, and the disciplinary categories indicate that MnO_2 environmental catalysis is a multidisciplinary field based on catalytic chemistry, environmental chemistry, engineering and materials, and energy chemistry. Relevant institutions and authors in China, the USA, India, South Korea, and Australia are the main driving forces of MnO_2 environmental catalysis research. However, from the analysis of author cooperation, the current national cooperation of this field is relatively independent, and global cooperation should be further strengthened.

(2) In terms of co-citation, ACB-E, EST, and JACS have a close co-citation relationship with other journals, which is mainly determined by the annual publication papers and the influence of the journal. According to the literature co-citation analysis, electrocatalysis, catalytic oxidation, AOPs, and SCR are the research spots. In addition, the keyword analysis points out that catalytic oxidation, materials and performance, waste water degradation, mechanism and DFT research themes can also be worthy of attention.

(3) By analyzing the research frontiers, 8 categories are classified, including environmental catalysis, manganese dioxide, catalytic oxidation, catalytic ozonation, heterogeneous catalyst, electrocatalysis, advanced oxidation processes, and mechanism. The themes of structure–activity relationship, density functional theory, catalytic oxidation, and mechanism are also the research frontier in the field of MnO_2 environmental catalysis research.

Author contributions

Yaoguang Guo: investigation, writing original draft, and funding acquisition. Qianqian Chen: investigation, visualization, and writing original draft. Xiaohu Sun: methodology, and investigation. Yujing Liu: methodology, and investigation. Jie Guan: resources, funding acquisition and supervision. Xiaojiao Zhang: software. Nuo Liu: methodology, and investigation. Xiaoyi Lou: writing – review & editing, and supervision. Yingshun Li: methodology. Xiangwen Zhang: editing and supervision.

Conflicts of interest

There are no conflicts to declare.

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