

申 报	系列：教师系列 科研为主型
	专业：工业催化
	职 称： 副 教 授 (科研型)

业绩成果材料

(申报人的业绩成果材料包括论文、科研项目、获奖以及其他成果等)

单 位 (二级单位) 生物质工程研究院

姓 名 钟家伟

材料核对人：

单位盖章：

核对时间：

华南农业大学制

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项目批准号	22478143
申请代码	B0815
归口管理部门	
依托单位代码	51064208A0499-0932



22478143 1004574

国家自然科学基金 资助项目计划书 (预算制项目)

资助类别: 面上项目

亚类说明:

附注说明:

项目名称: 多活性位协同Ni基纳米催化剂的构建及催化甲烷双重重整反应的抗失活机制

直接费用: 50万元 执行年限: 2025.01-2028.12

负责人: 钟家伟 BRID: 08099.00.12117

通讯地址: 广东省广州市天河区五山街五山路483号华南农业大学生物质工程研究院

邮政编码: 510642 电话: 15521303982

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依托单位: 华南农业大学

联系人: 唐家林 电话: 020-85280070

填表日期: 2024年08月26日

国家自然科学基金委员会制

Version: 1.004.574



简表

项目负责人信息	姓 名	钟家伟	性 别	男	出生年月	1988年06月	民 族	汉族
	学 位	博士			职称	副教授		
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	电 话	15521303982		个人网页	https://www.researchgate.net/profile/Jiawei-Zhong-2			
	工 作 单 位	华南农业大学						
	所 在 院 系 所	生物质工程研究院						
依托单位信息	名 称	华南农业大学					代码	51064208A0499
	联 系 人	唐家林		电子邮件	kycjkh@scau.edu.cn			
	电 话	020-85280070		网站地址	http://kjc.scau.edu.cn/			
合作单位信息	单 位 名 称							
	中国科学院上海高等研究院							
项目基本信息	项 目 名 称	多活性位协同Ni基纳米催化剂的构建及催化甲烷双重重整反应的抗失活机制						
	资 助 类 别	面上项目			亚 类 说 明			
	附 注 说 明							
	申 请 代 码	B0815:能源化工			B0803:反应工程			
	基 地 类 别							
	执 行 年 限	2025.01-2028.12						
	直 接 费 用	50万元						

项目编号：2023YFC3905800

密 级：公开

国家重点研发计划 项目任务书

项目名称：	种养产业集聚区多源种养废物耦合利用集成技术及示范	
所属专项：	循环经济关键技术与装备	
指南方向(榜单任务)：	8.1 种养产业集聚区多源种养废物耦合利用集成技术及示范（应用示范类）	
创新分类：	应用示范	
项目管理专业机构：	中国 21 世纪议程管理中心	
推荐单位：	广东省科学技术厅	
项目牵头承担单位：	华南农业大学	（公章）
项目负责人：	仇荣亮	
执行期限：	2023 年 12 月 至 2027 年 11 月	

中华人民共和国科学技术部制

2023 年 11 月 26 日

0002YF 2023YFC3905800 2023-11-26 17:56:27



课题编号：2023YFC3905802

密 级：公开

国家重点研发计划 课题任务书

课题名称：	菌群结构定向调控高效制备生物天然气技术及装备 种养产业集聚区多源种养废物耦合利用集成技术及示范
所属项目：	范
所属专项：	循环经济关键技术与装备
项目牵头承担单位：	华南农业大学
课题承担单位：	中国科学院广州能源研究所
课题负责人：	李颖
执行期限：	2023 年 12 月 至 2027 年 11 月

中华人民共和国科学技术部制

2023 年 11 月 24 日

0003YF 2023YFC3905802 2023-11-24 17:25:57



关于国家重点研发计划“循环经济关键技术与装备”重点专项

“8.1 种养产业集聚区多源种养废物耦合利用集成技术及示范

(应用示范类)”组织实施协议

甲方：中国科学院广州能源研究所

法定地址：广东省广州市天河区能源路 2 号

乙方：华南农业大学

法定地址：广东省广州市天河区五山路 483 号

依据《中华人民共和国科技进步法》、《中华人民共和国民法典》、《中华人民共和国著作权法》、《中华人民共和国专利法》、《中华人民共和国促进科技成果转化法》、《关于改进加强中央财科研项目和资金管理若干的意见》等法律和管理办法，经甲、乙双方协商一致，为按时高质量完成双方联合承担的国家重点专项“8.1 种养产业集聚区多源种养废物耦合利用集成技术及示范（应用示范类）”（项目编号：2023YFC3905800）之课题 2：菌群结构定向调控高效制备生物天然气技术及装备，经过平等协商，在真实、充分地表达各自意愿的基础上，达成如下协议。由签约双方共同进守。

一、甲、乙双方承诺按课题要求，团结协作，按期，保质完成课题各阶段任务。

为本课题研究工作做出贡献。

二、甲方的责任：

1. 甲方为本课题牵头单位，负责本课题的组织与实施，为乙方完成本课题任务提供必要的支持。
2. 根据科技部的相关管理办法及政策，为保证整个课题的成功实施，甲方对乙方科研活动，完成任务的进度情况等负有监督和建议的责任。

三、乙方的责任：

1. 乙方承诺按照课题要求配备满足要求的资源，确保按要求完成研究任务和目标。
2. 乙方采取的研究方法，技术路线。实施进度等应按照国家科技部审批的课题任务书执行。

3. 乙方按课题任务书要求完成自己所承担课题主要考核指标(包括示范工程,应达到的主要技术指标,应发表的论文、获得的发明专利等知识产权,以及其他应考核的指标)。

4. 乙方应提供有关资料,并积极配合甲方完成本课题的年度报告、中期检查、课题结题验收、审计等各项工作。

5. 乙方承诺与甲方及其他参与课题工作的单位密切合作,相互支持,在课题工作中接受甲方的统一安排和协调。乙方相关工作出现于课题规定不相符情况下,乙方承诺按规定接受科技部管理部门、专家、甲方、审计部门等相关部门的要求,改进工作,并承担相关责任。

四、经费与财务

甲乙双方按照科技部批准的经费预算书进行经费(包括国拨经费和配套经费)的管理、分配和使用,并遵照国家科研项目资金管理规定建立相应的财务管理制度。乙方必须根据任务分工和课题任务书约定,将获得的经费全部用于所承担的课题研发工作。双方承诺无条件接受科技部项目或课题管理方要求的财务审计,并根据审计要求进行整改,直至符合国家相关规定。

五、双方本着相互合作的精神,在课题执行过程中涉及的知识产权按以下方式处理:

1. 双方在执行本课题之前各自所获得的知识产权及相关权益均归各自所有,不因共同执行本课题而改变。

2. 因执行本课题的需要,各自向对方提供的相关信息,不构成向对方授予任何关于专利、著作权、商标权等知识产权的许可行为,且提供的资料不得用于本合作课题外的任何活动。

3. 在课题执行过程中,双方应对课题执行过程中产生的科技成果按下列方式及时采取知识产权保护措施:

(1) 根据课题任务分工情况,在双方的工作范围内独立完成的科技成果及其形成的知识产权归各自独自所有。一方转让其专利申请权时,另一方有以同等条件优先受让的权利。

(2) 在课题执行过程中,由双方共同完成的科技成果及其形成的知识产权归双方共有,并共同进行维护。一方转让其共有的专利申请权的,另一方有以同等

条件优先受让的权利。一方声明放弃其共有的专利申请权的,可以由另一方单独申请或者由其他各方共同申请。有一方不同意申请专利的,另一方不得申请专利。

(3)由双方共同完成的技术秘密成果,双方均有独自使用的权利。未经另一方同意,任何一方不得向第三方转让技术秘密。

(4)共同完成的科技成果的精神权利,如身份权、依法取得的荣誉称号、奖章、奖励证书和奖金等荣誉权归完成方共有,成果排名方法应另行约定。

(5)双方对共有科技成果实施许可、转让专利技术,非专利技术而获得的经济收益由双方共享。收益共享方式应在行为实施前另行约定。

六、任何一方不履行本协议约定的义务或履行义务不符合本协议约定的,视为违约,应停止违约行为,并承担继续履行,采取补救措施或赔偿损失等违约责任。任何一方未按本协议约定为对方提供相应的支持或未按时提供支持的,应承担相应的违约责任以及双方由于进度延误等原因所遭受的损失。任何一方未按计划实施或不实施研究工作的,为违约行为。守约方有权要求违约方实施研究计划并采取补救措施。

七、利用国拨专项经费或购置的设备、器材、资料按国家相关法规处理。利用配套经费研制或购置的设备、器材、资料,按配套经费提供方与使用方之间的协议处理。

八、本协议适用中华人民共和国法律。本协议在执行过程中发生的任何争议,双方应协商解决,也可以请求主管部门进行调解;若双方不愿协商、调解解决或者协商、调解不成的,任何一方有权将争议提交甲方所在地仲裁委员会,按照申请仲裁时现行有效的仲裁规则在甲方所在地进行仲裁。

九、本协议一式六份,甲乙双方各持贰份,其余贰份用作课题管理部门备案。加盖单位公章后生效,各份具有同等法律效力。

十、附表

表1 乙方具体任务、成果指标、负责人及经费表

课题名称	任务内容	成果指标	负责人	国拨经费 (万元)	自筹经费 (万元)
课题 2: 菌群结构定向调控高效制备生物天然气技术及装备	任务四: 沼气净化提纯及高值利用技术	1. 净化提纯副产物(二氧化碳)转化利用率 $\geq 90\%$, 提供现场核查报告和专家论证; 2. 提供示范矿区土壤修复材料的 50%; 3. 申请发明专利 ≥ 1 项; 4. 发表高水平论文 ≥ 2 篇; 5. 培养研究生 ≥ 2 名	钟家伟	50	0
	任务五: 沼气高值利用系统与装备	1. 开发沼气高值利用装备 1 套, 完成沼气高值利用系统装备集成及调试运维, 提供现场核查报告; 2. 申请发明专利 ≥ 1 项	张止戈	90	0
		1. 协助开发沼气高值利用装备、集成运维、数据收集、建模寻优; 2. 发表高水平论文 ≥ 1 篇	陈毓暑	30	0
	任务六: 沼气高值利用过程元素流分析与优化	1. 完成沼气高值利用路径对比和技术优化报告 1 份; 2. 形成技术标准及规范 1 项;	谭涛	55	0

甲方(公章):

法定代表人(签章):

课题负责人签字:

日期:

2023.11.17

乙方(公章):

法定代表人(签章):

子课题负责人签字:

日期:

2023.11.17

受理编号: c222019102400001033

项目编号: 2022A1515110028

文件编号: 粤基金字(2022)18号

广东省基础与应用基础研究基金项目

任务书

项目名称: 高熵铈基氧化物负载Ni基亚纳米/单原子催化剂的宏量制备及其多功能协同催化甲烷双重重整反应的研究

项目类别: 区域联合基金-青年基金项目

项目起止时间: 2022-10-01 至 2025-09-30

管理单位(甲方): 广东省基础与应用基础研究基金委员会

依托单位(乙方): 华南农业大学

通讯地址: 广东省广州市天河区五山路483号

邮政编码: 510642

单位电话: 020-85283435

项目负责人: 钟家伟

联系电话: 15521303982



(广东科技微信公众号)



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(受理纸质材料二维码)

广东省基础与应用基础研究
基金委员会
二〇二〇年制

五、人员信息

项目负责人								
姓名	证件号码	年龄	性别	职称	学历	在项目中承担的任务	所在单位	签名
钟家伟	44138119880604471X	35	男	副研究员	博士研究生	项目负责人	华南农业大学	钟家伟

任务书编号：2023A04J0058

广州市科技计划项目 任务书

项目名称：	二氧化铈纳米棒负载镍基合金核壳型催化剂的构建及其多功能协同催化甲烷双重重整反应的研究
承担单位：	华南农业大学
项目负责人：	钟家伟
计划类别：	基础研究计划
专题名称：	基础与应用基础研究专题
支持方向：	一般项目（博士青年科技人员类）
组织单位：	华南农业大学
起止时间：	2023-04-01 至 2025-03-31
主管处室：	基础研究处

广州市科学技术局制

二〇二三年

三、项目组成员信息

项目负责人	姓名	钟家伟	证件类型	身份证
	证件号码	44138119880604471X	性别	男
	出生年月	1988-06-04	民族	汉族
	国籍	中国	学历	博士研究生
	学位	博士	学位授予国家 (或地区)	中国
	职务	首聘副教授	职称	副高级
	所学专业	工业催化	手机号码	15521303982
	办公电话	020-85280319	电子邮箱	zhongjiaweiv@163.com



项目批准号	52276192
申请代码	E0607
归口管理部门	
依托单位代码	51064208A0499-0932



国家自然科学基金 资助项目计划书 (预算制项目)

资助类别: 面上项目

亚类说明:

附注说明:

项目名称: 酸碱双功能低共熔溶剂对原生木质素制备高密度航油组分的增效机制

直接费用: 54万元 执行年限: 2023.01-2026.12

负责人: 余强

通讯地址: 广州市天河区五山路483号

邮政编码: 510642 电 话: 13650805645

电子邮件: yuqiang@scau.edu.cn

依托单位: 华南农业大学

联系人: 唐家林 电 话: 020-85280070

填表日期: 2022年09月19日

国家自然科学基金委员会制

Version: 1.002.818



项目组主要成员

编号	姓名	出生年月	性别	职称	学位	单位名称	电话	证件号码	项目分工	每年工作时间（月）
1	余强	1983.12	男	研究员	博士	华南农业大学	13650805645	140225198312263711	项目负责人	9
2	吕杰	1984.12	女	副研究员	硕士	中国科学院广州能源研究所	020-87048514	411503198412256329	传热传质数值模拟	8
3	钟家伟	1988.06	男	副教授	博士	华南农业大学	15521303982	44138119880604471X	量子化学计算与催化	8
4	毕桂灿	1983.11	男	实验师	博士	华南农业大学	13826012528	440182198311221213	结构表征与产物分析	8
5	姜华彬	1993.04	男	研究实习员	硕士	华南农业大学	15517639396	412822199304200855	加氢脱氧实验	9
6	王志男	1993.05	男	无	博士	华南农业大学	13560217092	210213199305146012	原位氧化解聚实验	8
7	周海洋	1994.10	女	无	博士	华南农业大学	13936330340	232321199410191529	定向增碳实验	8
总人数		高级		中级		初级		博士后	博士生	硕士生
13		3		1		1		2	2	4

检索证明

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序号	论文名称	发表刊物及发表的年月卷期/页码等	作者排名	论文等级	作者文中单位	收录情况	影响因子	中科院大类分区
1	Upgrading renewable biogas into syngas via bi-reforming over high-entropy spinel-type catalysts derived from layered double hydroxides	FUEL 出版年: 2024 出版日期: FEB 15 卷期: 358 页码: - 文献号: 130155 文献类型: Article	共同通讯作者	A类	华南农业大学 生物质工程研究院	SCI	IF2-year=7.5 IF5-year=7.1 (2024)	工程技术 2 区 Top 期刊: 是 (2025)
2	Bi-reforming of model biogas into syngas over layered double hydroxides-derived bimetallic Ni-Ga catalysts	FUEL 出版年: 2024 出版日期: AUG 1 卷期: 369 页码: - 文献号: 131792 文献类型: Article	共同通讯作者 (倒数第一)	A类	华南农业大学 生物质工程研究院	SCI	IF2-year=7.5 IF5-year=7.1 (2024)	工程技术 2 区 Top 期刊: 是 (2025)
3	Bi-reforming of model biogas to syngas over Ru nano-catalysts supported on Mg-Al oxide derived from layered double hydroxides	FUEL 出版年: 2023 出版日期: JUL 1 卷期: 343 页码: - 文献号: 127941 文献类型: Article	第一作者	T2类	华南农业大学 生物质工程研究院	SCI	IF2-year=6.7 IF5-year=6.5 (2023)	工程技术 1 区 Top 期刊: 是 (2023)

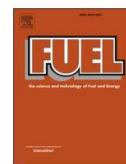
4	Key properties of Ni/CeAlO ₃ -Al ₂ O ₃ /SiC-foam catalysts for biogas reforming: Enhanced stability and CO ₂ activation	FUEL 出版年: 2022 出版日期: JAN 1 卷期: 307 页码: - 文献号: 121799 文献类型: Article	共同通讯作者	T2 类	华南农业大学 生物质工程院	SCI	IF2-year=7.4 IF5-year=7.0 (2022)	工程技术 1 区 Top 期刊: 是 (2022)
5	Upgrading biogas into syngas via bi-reforming of model biogas over ruthenium-based nano-catalysts synthesized via mechanochemical method	INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 出版年: 2023 出版日期: MAY 26 卷期: 48 45 页码: 16958-16970 文献类型: Article	共同通讯作者 (倒数第一)	A 类	华南农业大学 生物质工程院	SCI	IF2-year=8.1 IF5-year=7.3 (2023)	工程技术 2 区 Top 期刊: 否 (2023)
6	Key features of nano Ni _{0.5} Mg _{1-x} Al ₂ O ₄ spinel for biogas bi-reforming: CO ₂ activation and coke elimination	INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 出版年: 2024 出版日期: JAN 31 卷期: 53 页码: 383-393 文献类型: Article	共同通讯作者	A 类	华南农业大学 生物质工程院	SCI	IF2-year=8.3 IF5-year=7.7 (2024)	材料科学 2 区 Top 期刊: 否 (2025)
7	SiC-foam structured Ni-based catalyst derived from perovskites for methane value-added application: Enhanced resistance to Ni sintering and stability	MOLECULAR CATALYSIS 出版年: 2021 出版日期: AUG 卷期: 513 页码: -	共同通讯作者	A 类	华南农业大学 生物质工程院	SCI	IF2-year=5.089 IF5-year=4.788 (2021)	化学 2 区 Top 期刊: 否 (2021)

		文献号: 111831 文献类型: Article							
8	The promotional role of β -cyclodextrin on Ni-Mo2C/MgO catalyst for biogas reforming	MOLECULAR CATALYSIS 出版年: 2021 出版日期: OCT 卷期: 515 页码: - 文献号: 111897 文献类型: Article	共同通讯作者	A类	华南农业大学 生物质工程院	SCI	IF2-year=5.089 IF5-year=4.788 (2021)	化学 2 区 Top 期刊: 否 (2021)	

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Full Length Article

Bi-reforming of model biogas to syngas over Ru nano-catalysts supported on Mg-Al oxide derived from layered double hydroxides

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ABSTRACT

A series of Ru/Mg_x(Al)O (x=3, 4, 5) nano-catalysts, derived from Ru/MgAl layered double hydroxide, were facilely synthesized. The properties of Ru/Mg_x(Al)O catalysts, before and after stability tests, were comprehensively characterized via N₂ physisorption, XRD, ICP-OES, XRF, SEM, H₂-TPR, CO₂-TPD, XPS, TEM, TGA, Raman spectroscopy. In the bi-reforming of model biogas, at 800 °C, CH₄/CO₂/N₂/H₂O = 3/2/1/2.6, WHSV = 30960 mL g⁻¹ h⁻¹, 0.7Ru/Mg₄(Al)O and 0.9Ru/Mg₅(Al)O catalysts display high catalytic activity and stability without obvious deactivation within 100 h time-on-stream. The basic Mg_x(Al)O mixed oxides facilitate the CO₂ activation and generation of active O* species, contributed to prompt removal of coke precursor and effective coke-resistance behavior. The highly-dispersed Ru ultrafine NPs also contributed to the inhibited coke deposition due to size effect. In addition, the strong interaction between Ru NPs and Mg_x(Al)O mixed oxides, result in the satisfying anti-sintering performance. The combined support effect, size effect as well as metal-support interaction over Ru/Mg_x(Al)O (x=4, 5) catalyst result in excellent catalytic performance.

1. Introduction

The amount of anthropogenic CO₂ has dramatically increased and result in severe greenhouse effect since the industrial revolution, thus the concept of "methanol economy" [1] proposed by Nobel laureate George A. Olah have attracted worldwide attention. Methanol can be employed in fuel cells and internal combustion engines, as well as feedstock for the production of value-added chemicals (e.g., olefin, aromatics) and fuels (e.g., gasoline) [2–3]. Currently, methanol is mainly produced via the syngas (CO+H₂) conversion route. Methane reforming is the most widely used process for syngas production [4], which can be classified into steam reforming of methane (CH₄+H₂O=CO+3H₂), dry reforming of methane (CH₄+CO₂=CO+H₂), bi-reforming of methane (combined steam and dry reforming of methane, 3CH₄+CO₂+2H₂O=4CO+8H₂), and so on. In particular, the bi-reforming of methane generate intermediate syngas with H₂/CO molar ratio of approximately 2, which is suitable for the subsequent methanol synthesis [5]. Biogas, with CH₄ (~50–65%) and CO₂ (~30–40%) as the major composition, is one of the renewable carbon resource from the viewpoint of "green carbon science", thus it is of great importance to

convert biogas to syngas with particular molar ratio of H₂/CO via the bi-reforming of biogas, and bio-methanol ultimately [6]. Table 1

For methane reforming reaction, by contrast with non-noble metal-based catalysts (e.g. Ni-based) [7–8–9–10–11–12], noble metal-based catalysts (e.g. Rh, Ru-based) usually exhibit higher catalytic activity and excellent coking-resistance capability under the harsh reaction conditions (generally higher than 650 °C) [13]. For example, Ru/MgAl₂O₄ catalyst prepared by physical vapor deposition [14], Ru catalysts supported on Mg-Al layered double hydroxides (LDHs) derived Mg-Al oxides [15], Sm₂Ru_{0.2}Ce_{1.8}O₇ solid solution derived Ru based nano-catalyst [16], Ru/La₂O₃CO₃ [17], have been applied in the DRM reaction or combined DRM and partial oxidation of methane. However, the industrial application of noble metal-based catalysts in methane reforming reaction is severely hindered by their high prices and limited reserves. Thus, the rational design and preparation of noble metal-based catalysts with relatively low cost sites (e.g. Ru) and low-amount of metal loading is of great significance. LDHs are a typical class of 2D anionic compounds consist of positively charged host layers (brucite-like M(OH)₆ octahedra) and interlayer anions, in the general formula of [M₁²⁺_{1-x}M₂³⁺(OH)₂]^{z+}A_n^{z-}·mH₂O, have attracted

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Full Length Article

Upgrading renewable biogas into syngas via bi-reforming over high-entropy spinel-type catalysts derived from layered double hydroxides

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ABSTRACT

The bi-reforming of biogas is of great significance for the consumption of greenhouse gases and the generation of valuable syngas. In this study, porous high-entropy spinel-type HE-MgAlO (up to quinary metals: Ni, Co, Zn, Ga, Mn,) catalysts derived from layered double hydroxide were prepared by the one-step co-precipitation method. The catalysts were characterized comprehensively via XRD, XRF, H₂-TPR, CO₂-TPD, XPS, SEM, HR-TEM, STEM-EDS, CH₄-TPSR/CO₂-TPO, TG-DSC, Raman, and so on. Compared to the monometallic Ni/MgAlO and binary NiCo/MgAlO catalysts, the HE-MgAlO catalyst exhibits higher initial CH₄ (~98 %) and CO₂ (~55 %) conversion and high stability up to 100 h under certain reaction conditions. The homogeneously-dispersed and electronically-enriched Ni sites, the oxophilic property and medium-strong basic sites of HE-MgAlO catalyst, lead to efficient activation of CH₄ and CO₂ (H₂O), respectively, and high catalytic activity ultimately. The generation of reactive O* from CO₂ (H₂O) over oxophilic and medium-strong alkaline sites of HE-MgAlO catalyst prompts the rapid removal of coke precursors, leads to satisfying coke-resistant behavior. The spinel structure and strong metal-support interaction in HE-MgAlO catalyst enhances the thermal stability and results in satisfying anti-sintering performance.

1. Introduction

Since the industrial revolution in the mid-18th century, fossil fuels such as coal, petroleum, and natural gas have contributed significantly to the development of the global economy. However, excessive consumption of fossil fuels has inevitably led to serious consequences including climate change and environmental degradation. Thus, the concept of “green carbon science” has gained increasing attention as a promising strategy to solve the problems mentioned above [1]. In particular, the conversion of syngas (CO + H₂) is one of the significant aspects in the green carbon science. Methane reforming, as the most widely adopted process for syngas generation, can be mainly classified into steam reforming of methane (SRM), carbon dioxide reforming of methane (CRM), and bi-reforming of methane (i.e., combined steam and dry reforming of methane) [2]. Among the reforming process mentioned above, syngas with an H₂/CO molar ratio of approximately two that are suitable for the synthesis of high value-added alcohol (e.g., methanol) can be produced by bi-reforming of methane [3]. In particular, methanol functions as critical raw material for the manufacture of value-added

chemicals such as light olefins [4,5]. In addition, from the perspective of “green carbon science”, biogas that mainly consists of CH₄ (60–75 %) and CO₂ (25–40 %), as a renewable carbon resource, can be converted into syngas with H₂/CO molar ratio of about 2, via the bi-reforming of biogas, and environmentally friendly bio-methanol ultimately [6].

The catalytic systems applied in the methane reforming can be mainly classified into noble-metal-based catalysts (e.g., Pd, Pt, and Ru) and non-noble-based catalysts (e.g., Ni and Co) metals [7]. In general, noble-based catalysts display relatively higher stability and less tendency of coke formation compared to non-noble metal-based counterparts [8,9]. However, to date, most studies have focused on non-noble metal-based catalysts, mainly Ni-based catalysts, owing to the shortage of and high cost of noble-metal-based catalysts [10]. In particular, Ni-containing bimetallic catalytic systems including NiCo [11]/NiZn [12]/NiGa [13]/NiMn [14,15] based catalysts have been applied in the methane reforming reaction, and satisfying catalytic performance was obtained. Recently, high-entropy (HE) materials with multiple elements (usually ≥ 5) have attracted significant attention and been extensively explored in a variety of applications (e.g., carbon dioxide conversion),

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Full Length Article

Bi-reforming of model biogas into syngas over layered double hydroxides-derived bimetallic Ni-Ga catalysts

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ABSTRACT

The upgrading of biogas to value-added syngas through bi-reforming is of enormous significance. The mechanochemical method was adopted to prepare a range of layered double hydroxide-derived bimetallic Ni-Ga catalysts, and the as-prepared catalysts were employed in the bi-reforming of biogas. Comprehensive characterization was carried out to analyze the fresh or spent catalysts. 10Ni10Ga/MgAlO catalyst exhibits high initial catalytic activity in terms of CH₄/CO₂ conversion (~96%/66%) and satisfying stability up to 120 h without significant deactivation, at 800 °C and WHSV = 30,960 mL/g/h. 10Ni10Ga/MgAlO catalyst with direct-reduction pretreatment of catalyst precursor exhibits more homogeneously dispersed active metal sites, which facilitates the dissociation of CH₄. Meanwhile, 10Ni10Ga/MgAlO catalyst with electron-rich Ni species, as well as moderately strong and strong basic sites, promotes the CO₂ activation, the combined effects result in high initial catalytic activity. In addition, the interaction between active metal site and MgAlO composite oxide, combined with the potential reversible phase transition between Ni₃Ga and Ni₃GaC_x, result into satisfying anti-sintering and anti-coking performance of 10Ni10Ga/MgAlO catalyst, respectively.

1. Introduction

To date, most of the worldwide energy supply comes from fossil fuels, including coal, petroleum, and natural gas. However, the overconsumption of fossil fuels has dramatically increased anthropogenic CO₂ emissions, leading to a severe greenhouse effect [1,2]. As a result, the “green carbon science” concept has attracted worldwide attention [3,4]. The generation and utilization of syngas has been widely accepted as one of the most vital parts of the field of green carbon science [5]. Methane reforming, mainly divided into methane steam reforming, CO₂ reforming of methane, methane bi-reforming (e.g., combined steam and dry reforming of methane), methane tri-reforming, and so on, is the typical route for syngas production [6,7]. The bi-reforming of methane produces synthesis gas with a molar ratio of H₂/CO of about 2 that appropriate for the further production of important and critical intermediate chemicals such as methanol [6], and methanol acts as an essential material for the generation of a variety of chemicals (e.g., gasoline, aromatic, light olefins [8]). Furthermore, biogas, a renewable carbon resource mainly consisting of CH₄ (~60–75%) and CO₂ (~25–40%), usually produced from a wide variety of

residue or waste, can be converted into green chemicals or fuels (bio-natural gas, bio-methanol, etc.). In particular, biogas can be turned into syngas by combined steam and dry reforming of methane, and subsequently into bio-methanol [9]. This process of “biogas-syngas-bio-methanol” meets the requirements of both “green carbon science” [3,4] and “methanol economy” [10].

Currently, the catalytic systems for methane reforming are composed of noble metal-based and non-noble metal-based catalytic systems. In general, noble metal-based catalysts show better performance in resisting coke deposition than non-noble metal-based catalysts [11]. However, the majority of investigations have focused on Ni-based catalysts due to the low cost and satisfying catalytic activity of Ni-based catalysts. For example, Ni-based bimetallic catalytic systems including Ni-transition metal catalysts (NiCo [12]/NiCu [13]/NiFe [14]/NiZn [15]/NiGa [16]/NiIn [17], etc.) and Ni-noble metal catalyst (NiPt [18,19]/NiRu [20]/NiIr [21–23], etc.) have been employed in the methane reforming, and the synergistic effect (electronic and/or geometric effect) between Ni and the second metal has been demonstrated to effectively enhance the carbon resistance and sintering resistance of the catalysts [24,25]. In particular, Ni-based monometallic catalysts (e.

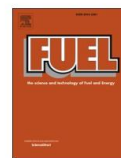
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Full Length Article

Key properties of Ni/CeAlO₃-Al₂O₃/SiC-foam catalysts for biogas reforming: Enhanced stability and CO₂ activationZhige Zhang^{a,1}, Guofeng Zhao^{b,1}, Wenyang Li^a, Jiawei Zhong^{a,*}, Jun Xie^{a,*}^a Institute of Biomass Engineering, Key Laboratory of Energy Plants Resource and Utilization, Ministry of Agriculture and Rural Affairs, Guangdong Engineering Technology Research Center of Agricultural and Forestry Biomass, South China Agricultural University, Guangzhou 510642, PR China^b Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200062, PR China

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ABSTRACT

The efficient conversion of renewable biogas has attracted ever-increasing interest in past decades. Ni-CeO₂-Al₂O₃ supported on monolithic SiC-foam (denoted as Ni/CeO₂-Al₂O₃/SCF) is designed and applied in biogas reforming. The monolithic Ni/CeO₂-Al₂O₃/SCF catalysts were deeply characterized by XRD, ICP-AES, SEM, HR-TEM, CO₂-TPD, etc. The cycle between CeO₂-Al₂O₃ and CeAlO₃ was verified by *in-situ* CH₄/CO₂-TPSR, and the catalytic role of CeAlO₃ in coke elimination and CO₂ activation was further confirmed. Due to the uniform distribution of Ni nanoparticles (NPs) and the activation of CO₂ by CeAlO₃, Ni/CeAlO₃-Al₂O₃/SCF shows excellent catalytic stability to inhibit sintering and eliminate carbon deposition. At 900 °C and a gas hourly space velocity (GSHV) of 24000 mL g_{Cat}⁻¹h⁻¹, excellent CH₄/CO₂ conversion of 86/99% are initially achieved over Ni/CeAlO₃-Al₂O₃/SCF catalyst, followed by slight decrease after 140 h, and remain basically stable for the next 260 h.

1. Introduction

Currently, research in the field of energy consumption indicates that fossil fuels must be replaced by renewable green energy, in order to achieve the goal of limiting greenhouse gas emissions [1]. Biogas is a kind of representative green energy produced by biomass decomposition under anaerobic conditions [2]. Its main components are methane (CH₄) (40–60%) and carbon dioxide (CO₂) (30–60%). The most common way of biogas utilization is to provide heat and power [3]. In addition, a variety of chemical can be obtained from biogas, including syngas (CO + H₂), bio-methanol [4] and higher hydrocarbons [5]. In particular, the dry reforming of biogas can convert the main components of biogas, CH₄ and CO₂, into syngas at the same time, greatly improving the utilization of biogas [6]. However, the dry reforming of biogas is mainly endothermic reaction (Eq. (1)), so the design and construction of appropriate catalyst system is very important [7].



There is no doubt that noble metals show excellent activity and resistance to sintering in dry reforming of biogas, but their

commercialization is limited by the high cost and abundance problems [8]. Fortunately, nickel (Ni), as a non-precious metal, has great commercial potential in reforming reactions due to its similar activity, high abundance and low cost as precious metals [9]. It should be noted that the Ni-based catalyst has the defects of easy sintering and carbon deposition. The main reason for the easy sintering of nickel-based catalyst is that the Ni particles tend to move and aggregate into large NPs in the reaction process without the limit of external force [10,11]. The size of Ni NPs becomes larger after sintering during the reaction process, which promotes carbon diffusion in Ni crystals and leads to the ultimate carbon deposition [12,13]. Thus it is very important to rationally design the composition of the Ni-based catalyst [14].

To date, a variety of methods have been employed to enhance the resistance to carbon deposition and aggregation of nickel-based catalysts, one of which is the incorporation of a metal additive such as alkaline earth and rare earth elements. Among the reported elements, cerium has found to exert positive impact on inhibiting the aggregation of active components and carbon deposition [15]. CeO₂ displays high oxygen storage capacity attributed to the redox couple Ce⁴⁺→Ce³⁺ [16]. During the DRM process, oxygen species formed by CO₂ dissociation

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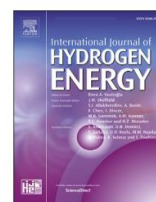
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Upgrading biogas into syngas via bi-reforming of model biogas over ruthenium-based nano-catalysts synthesized via mechanochemical method

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HIGHLIGHTS

- A series of Ru-based catalysts supported on MgO, La₂O₂CO₃ and CeO₂ were prepared by mechanochemical method.
- Ru/MgO show excellent catalytic performance in bi-reforming of model biogas.
- The small Ru NPs, basic MgO, and interaction between Ru NPs and MgO result in satisfying catalytic performance.

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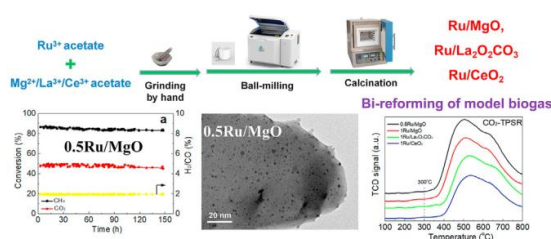
Model biogas

Mechanochemical synthesis

Ru-based catalysts

MgO

GRAPHICAL ABSTRACT



ABSTRACT

The upgrading of biogas to value-added syngas via reforming of biogas is of great significance from the perspective of green carbon science. A series of Ru based nano-catalysts (Ru/MgO, Ru/La₂O₂CO₃, Ru/CeO₂) with relatively low Ru loading and high dispersion were successfully prepared by mechanochemical method, and applied in the bi-reforming of model biogas reaction. The representative catalysts were comprehensively characterized by XRD, N₂ physical adsorption, ICP-OES, SEM, XPS, H₂-TPR, CO₂-TPD, HRTEM, FTIR of CO adsorption, TPSR, TG, and Raman spectroscopy, etc. Ascribed to the appropriate basicity of MgO, homogeneous Ru dispersion with ultra-small particle size, and strong interaction between Ru ultra-small nano particles and MgO support, Ru/MgO exhibit higher CO₂ adsorption and activation, higher CH₄ activation and dissociation, compared with Ru/La₂O₂CO₃, Ru/CeO₂, which facilitate the formation of active oxygen species and intermediate coke removal, thus enhance the resistance to coke deposition and sintering. At reaction conditions of T = 750 °C and weight hourly space velocity = 32,400 mLg_{Cat}⁻¹ h⁻¹,

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journal homepage: www.elsevier.com/locate/heKey features of nano $\text{Ni}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$ spinel for biogas bi-reforming: CO_2 activation and coke eliminationZhige Zhang¹, Guican Bi¹, Jiawei Zhong^{**}, Jun Xie^{*}

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ABSTRACT

Using green and sustainable biogas as raw material to produce syngas ($\text{H}_2/\text{CO} \approx 2$) suitable for direct synthesis of green methanol has attracted wide attention, but developing efficient catalysts with high activity/stability remains a big challenge. A series of MgAl_2O_4 spinel catalysts (denoted as $\text{Ni}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$) is designed and applied in biogas bi-reforming. The nano $\text{Ni}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$ catalysts were comprehensively characterized by Raman, SEM, HR-TEM, H_2 -TPR, CO_2 -TPD, etc. The CO_2 activation was verified by in situ CH_4 -TPSR/ CO_2 -TPO, and the key role of $\text{Ni}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$ in coke removal behavior mechanism was further confirmed. Due to the efficient CO_2 adsorption/activation and strong metal-support interaction, nano $\text{Ni}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$ shows excellent catalytic stability to inhibit sintering and carbon deposition. At reforming conditions of 750 °C, a weight hourly space velocity (WHSV) of 32,400 $\text{mL g}^{-1} \text{h}^{-1}$, the $\text{Ni}_{0.4}\text{Mg}_{0.6}\text{Al}_2\text{O}_4$ catalyst exhibits excellent CH_4/CO_2 conversion of 91/51 % are achieved, followed by slight decrease after 40 h, and remain basically stable for the next 40 h.

1. Introduction

The extensive use of dwindling fossil fuel reserves has been accompanied by the release of large amounts of active carbon dioxide (CO_2), which has disrupted the natural balance of CO_2 , resulting in significant environmental hazards [1]. To enhance the natural carbon cycle, an active chemical CO_2 cycle, the so-called “methanol economy” [2], has been developed, which involves the capture of carbon sources into fuels for chemical synthesis of high value products such as methanol and dimethyl ether. Methanol, the most basic C1 liquid product, is readily available from a variety of carbon sources, such as biomass and CO_2 , and is considered a key component of the externally driven carbon cycle and the methanol economy [3]. Methanol can be used to produce high-demand chemical commodities such as hydrocarbons, i.e., olefins including ethylene and propylene and gasoline [4]. Consequently, methanol has been the focus of intensive academic and industrial research [5]. Methanol can be obtained through the selective oxidation of methane (CH_4), from syngas [6,7], and via CO_2 hydrogenation, which combines solar energy, CO_2 , and water to produce a green liquid fuel also known as liquid sunlight [8]. However, with the exception of

methanol synthesis from syngas, these methods are still in the laboratory stage. Therefore, syngas is currently essential for the chemical production of methanol.

The most widespread source of syngas is CH_4 reforming, which is also an important application of C1 chemistry. C1 catalysis involves the conversion of simple molecules with one carbon atom, such as CH_4 , into a variety of high value-added liquid fuels and chemicals [9]. This process is essential in the context of “green carbon science” [10], that is, the efficient use of carbon resources toward carbon neutrality for the sustainable development of our society. The most common methods of CH_4 reforming to syngas are dry reforming (DRM) of CH_4 [11,12], steam reforming, and auto-thermal reforming. Methanol can be prepared from syngas, for which a syngas with an H_2/CO ratio of 2 is required. However, the H_2/CO ratio of the syngas produced by DRM and steam reforming is 1 and 3, respectively. The suitable H_2/CO ratio of 2 for the methanol synthesis can be obtained via the so-called “bi-reforming,” i.e., the combination of DRM and steam reforming [13]. Importantly, the composition of the biogas derived from sustainable biomass (CH_4 , CO_2 , and a small amount of steam) perfectly conforms to the raw material ratio required for the bi-reforming process to obtain syngas suitable for

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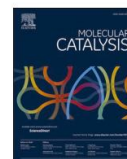
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SiC-foam structured Ni-based catalyst derived from perovskites for methane value-added application: Enhanced resistance to Ni sintering and stability

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ABSTRACT

Sustainable transformation of methane into methanol feedstock syngas is a promising direction in future energy generation. A monolithic SiC-foam (SiC-foam, denoted as SCF) supported structured Ni-SrO composite nano-material was prepared via reducing the SrNiO₃ perovskite. The Ni-SrO/SCF displays a stronger resistance to Ni-sintering/coke-deposition than the unmodified Ni/SCF due to its uniform Ni distribution as well as the strong Ni-SrO interaction. In the presence of Ni-SrO/SCF sample at a gas hourly space velocity (GHSV) of 24,000 mL_{CH₄-CO₂} g_{Cat}⁻¹ h⁻¹ and an operating temperature of 850 °C, the initial conversion rate of biogas (CH₄/CO₂) was 70/94%, which gradually dropped to 55/72% within 40 h, but its activity remained stable for the next 60 h. By contrast, the conversion rate of biogas (CH₄/CO₂) in the presence of Ni/SCF sample was decreased rapidly from 60/80 to 50/65% within 20 h, due to the severe coke deposition and Ni-sintering.

1. Introduction

Biogas, with main components of methane (CH₄, 50–60 vol%) and carbon dioxide (CO₂, 40–50 vol%), is an attractive alternative to natural gas, and can be produced continuously from biomass through anaerobic respiration [1–3]. Unfortunately, most of the biogas is currently utilized through being burned, an inefficient process for heat or electricity generation [4,5]. A more appealing technology has been recently proposed, namely, through conversion of biogas to syngas, a mixture of hydrogen (H₂) and carbon monoxide (CO), with further transformations to methanol as well as other high-value chemicals [6,7]. Considering the high CO₂ content in biogas, it is preferred to reform methane-CO₂ mixture, through a process known as dry reforming of methane (DRM) than other reforming procedures for the methane gas such as reforming CH₄-O₂ or CH₄-H₂O mixtures [7,8]. For facilitation of the DRM reaction, various metals have been found advantageous such as noble metals as well as transition metals. However, the application of the noble metals is restricted due to their high cost and low abundance [9, 10]. Transition metals such as nickel (Ni), on the other hand, have been

widely used due to their high activity and low cost. However, there are some issues associated with the use of the transition metals such as rapid deactivation of the sample due to the serious sintering and carbon deposition of Ni [11,12]. As a result, enhancing the resistance to Ni sintering as well as carbon deposition is of utmost importance for Ni-based catalysts [13,14].

It has been generally recognized that diameter of Ni particles plays an important role in preventing carbon deposition [15]. The carbon deposition on the surface of highly dispersed Ni nanoparticles is minimal [16,17]. Therefore, it is intended to obtain and maintain small Ni particles by selecting appropriate support, preparation method, and promoter [18]. Perovskite oxides have a unique ordered cellular structure, and after going through the reduction process, the reducible metal ions can be reduced into highly dispersed nanoparticles which strongly interact with the simultaneously formed irreducible oxides (acting as supporter and/or promoter) [19,20]. Accordingly, the perovskite oxides have been presented as promising precursors to fabricate high-performance DRM samples. For example, Rabelo-Neto et al. [21] reported a LaNiO₃-derived Ni-La₂O₃ sample with small Ni particles

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The promotional role of β -cyclodextrin on Ni-Mo₂C/MgO catalyst for biogas reforming

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ABSTRACT

In this work, Ni-Mo₂C/MgO catalysts were prepared by sol-gel method with β -cyclodextrin (β -CD) as the carbon source and dispersant, and applied in the dry reforming of biogas. The roles of ratio of Ni/Mo as well as β -CD on the catalytic activity and stability were analyzed. Systematic characterizations analysis such as XRD, XPS, and TEM confirm that Mo₂C can only form under the condition of pre-reduction and carburization, confirming that metallic Ni nanoparticles promote the carbonization process of Mo₂C, and that β -CD as a carbon source is of great necessity for the formation of Mo₂C. In the dry reforming of biogas, the formation of Mo₂C significantly impacts the catalytic activity and stability, which is beneficial for CO₂ activation and coke removal via the redox cycle. Ni-Mo₂C/MgO catalysts with optimized Ni and Mo contents of 7 and 15 wt%, respectively, exhibit the best catalytic activity and stability for the dry reforming of biogas. The CH₄ and CO₂ conversion rates remained above 90% and 85%, respectively, for 200 h at 850 °C and WHSV = 30,000 ml. g⁻¹. h⁻¹.

1. Introduction

Energy consumption has been increasing in the past decades [1]. At present, the dependence on fossil fuels to meet energy demand has caused great environmental problems through anthropogenic greenhouse gas emissions [2]. Methane and carbon dioxides are the most notorious gasses contributing to global warming [3,4]. The biogas, with CH₄ and CO₂ as the major components, can be utilized to generate syngas through the reforming process [5,6]. The generated syngas can be further converted into hydrocarbons via the Fischer-Tropsch process [7–9]. It is well known that the C–H bond in CH₄ is difficult to be activated, and CO₂ is the upmost oxidized state of carbon, which is also very stable [10]. Therefore, the simultaneous activation of both C–O bond in CO₂ and C–H bond in CH₄ is a great challenge. The dry reforming of biogas is usually conducted at high temperature (~800 °C), and the presence of catalysts could significantly lower the required activation energy for the C–O bond in CO₂ as well as the C–H bond in CH₄. The noble metal-based catalysts display satisfying catalytic activity and stability in the dry reforming of biogas [11]. However, the applications of noble metal-based catalysts at the industrial scale are restricted by their high prices. The Ni-based catalysts exhibit similar activity to noble metal in dry reforming of the biogas, but suffer from

easy deactivation due to the sintering as well as coke deposition caused by methane decomposition (i.e., CH₄ → C + 2H₂) as well as CO disproportionation (i.e., 2CO → CO₂ + C) [12]. A variety of strategies have been explored to enhance the stability of the Ni-based catalysts, including adoption of suitable supports (e.g., metal oxides with basic sites or rich oxygen vacancy to activate CO₂) [13,14], and bimetallic catalysts [15].

The alkaline-earth oxide (e.g., MgO) positively impacts the coking inhibition due to its strong CO₂ adsorption property [13]. In recent years, transition metal carbides such as molybdenum carbide, with noble metal-like properties, have attracted great interest in dry reforming of biogas [16–18]. Shi et al. mentioned that metal carbides and oxides can circulate in the alternating flow of CO₂ and CH₄ s, and that metal carbides exhibit stable catalytic activity at atmospheric pressure in the dry reforming of biogas [19]. Yao et al. also demonstrated that CO₂ activation can occur on Mo₂C with oxidation-re carburization cycle [20]. Ni-Mo₂C/MgO have been demonstrated to exhibit great activity for the dry reforming of biogas, due to the presence of dual active-site and the corresponding catalytic redox cycle in the following manner, Mo₂C activates CO₂, then oxygen species in CO₂ replace the carbon of Mo₂C, while Ni dissociates CH₄ and promotes the reduction of molybdenum oxides to molybdenum carbide [13,19]. It is worth noting that the contents of Ni and Mo are very

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