Technology Disclosure Form:

RI File Ref:

This form should be completed by the lead scientist and a copy of the completed form should be submitted each to the RI director and the tech transfer officer.

The Technology Disclosure (TD) form is designed to capture all types of inventions. It provides some pointers towards determination of patentability, market potential and also basic information needed by various parties involved in exploiting inventions, including RI staff, ETPL, patent agents and legal advisers.

Name of Lead Scientist: Chen Luwei

Lab Note Book Ref No: KCHO001002

Lab Note Book Page Numbers: 5

Title of Project TD Derived From:
Project Code: ICES/11-313A01

1. PROPOSED SHORT TITLE OF INVENTION

Ni-based Methanation Catalyst with Improved S Resistance II

2. TECHNOLOGY KEY WORDS

Methanation, Nickel, dopant, Cerium, Hydrogen sulphides

3. DESCRIPTION OF INVENTION

{Please attach draft manuscript, if available. In describing the invention, you should clearly state what the invention is, how the invention works (including experimental results, simulation results and diagrams, where applicable) and answer the question "what problem does the invention solve? "}

The use of Substitute Natural Gas (SNG) was proposed during the energy crisis in the 1970's. Today SNG is becoming important since SNG production can potentially mitigate the greenhouse gas emissions and enhance the diversity of energy and chemical resources. Combination of the gasification and the catalytic methanation technologies can produce SNG from variety types of feedstocks such as coal, biomass and waste.

Currently, several commercial SNG plants are being built all over the world. -In particular, coal-to-SNG technologies are becoming the new focus in China's coal-based chemical industry. About 15 coal-to-SNG projects are being considered in China. It is -estimated that China will have around 20 billion Nm^3/a SNG capacity in 2015.

A simplified SNG production process is shown below:



IHI (Japan) has recently developed a proprietary gasification technology. Currently, ICES is collaborating with IHI to develop a robust catalyst which can be used in the methanation step. The key challenge of the development is to ensure high methane yield and stability. Particularly, sulphur poisoning on catalyst surfaces is one of the major challenges.

This invention discloses a Ni-based methanation catalysts, i.e., Ni/CeO_2-M (M=Ca, Gd, Y etc) for methanation reaction with improved S resistance. The Ni/CeO_2-M catalysts were prepared by conventional wet impregnation method using $Ni(NO_3)_3$ $6H_2O$ as Ni precursor and commercially available CeO_2-M (Sigma Aldrich).

2.1 Catalytic results:

Cerium oxide is well known for its oxygen storage and redox properties. The partial replacement of - Ce with some other components such as Zr, Gd, Sm etc is believed to increase the stability, oxygen storage ability and reducibility. Therefore, various nano-size cerium

oxides with dopants of Y, Sm, Gd and Ca, nano- and micro- size CeO_2 were used as catalyst supports. Fig. 1 shows the results of the performance of 5%Ni supported on Al_2O_3, $Ce_{0.9}Ca_{0.1}O_2$ and $Ce_{0.9}Gd_{0.1}O_2$ in the gas stream containing 20 ppm of H_2S at 500 °C and 1 bar. The concentration of CH_4 over 5%Ni/Al_2O_3 decreases from the 22% (dry based) at the beginning of the reaction to the initial 4.4% which indicates the complete deactivation of catalyst at around 150 min. It takes about 350 min to deactivate 5%Ni/ $Ce_{0.9}Gd_{0.1}O_2$. However, some activity still remains over the 5%Ni/ $Ce_{0.9}Ca_{0.1}O_2$ catalyst at 470 minute.

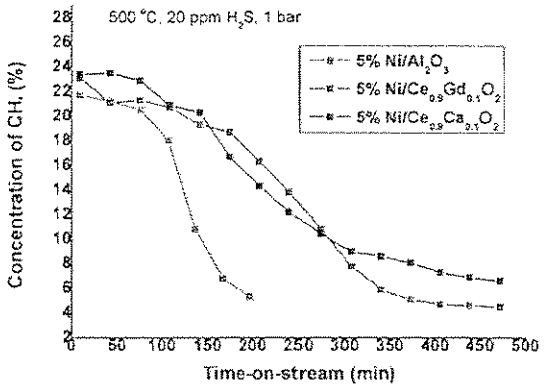


Fig. 1 Long-term stability test of catalysts: Alterations of the methane concentrations with time-on-stream. Feed composition: 10%H_2O, 10%N_2, 40%H_2, 20% CO, 16% CO_2, 4% CH_4, 20 ppm H_2S; T= 500 °C; SV= 20,000 h^{-1}.

The spent catalysts were analyzed by XPS, TPH, S analyzer and TOF-SIMS. Taking into account of the Ni dispersion measured by H_2 adsorption (Table 1), the ratios of the exposed number of Ni to the total number of sulfur on the spent catalysts are calculated and listed in Table 2.

Table 1 Ni dispersion (*Micromeritics ASAP 2020* Surface Area and Porosity Analyzer**)**

Samples	Nominal metal loading	Metal dispersion	Metallic surface area (m²/g cat)	Metallic surface area (m²/g metal)
5% Ni/Al_2O_3	5%	1.5 %	0.51	10.2
5% Ni/$Ce_{0.9}Gd_{0.1}O_2$	5%	5.9 %	1.96	39.2

Table 2: The ratio of surface Ni to total sulfur on the spent catalysts.

Reaction Conditions	Sample Name	S on spent catalysis	Metal Dispersion	Ni : S
20 ppm, 500 °C 180 min	5% Ni/Al_2O_3	352.2 ppm	1.5 %	1: 0.83
20 ppm, 500 °C 900 min	5% $Ni/Ce_{0.9}Gd_{0.1}O_2$	1900 ppm	5.90 %	1: 1.25

According to the following reaction (eq (1)), one Ni is supposed to adsorb one S. However, probably owing to the size of the sulfide ion, the sulfur capacity is less than one sulfur atom per nickel atom. [1] The Ni:S ratio is 1: 0.83 on the 5%Ni/Al_2O_3, which is consistent with the observation of ROSTRUP-NIELSEN in the study of H_2S adsorption on 10wt% Ni supported on $MgAl_2O_4$ at 550°C.

$$H_2S\ (gas) + Ni == Ni\text{-}S + H_2\ (gas) \quad \text{----- } eq\ (1)$$

Unusual Ni:S ratio of 1:1.25 is observed on 5% $Ni/Ce_{0.9}Gd_{0.1}O_2$ indicating that - other adsorption sites for H_2S must exist besides Ni. Ma *et al.* reported that Ceria can be an adsorbent of H_2S to form Ce_2O_2S [2]. The results obtained from TOF-SIMS may shed some light. The SIMS spectrum in Fig. 2 show NiS is easier to be detected on 5%Ni /Al_2O_3 than on 5% $Ni/Ce_{0.9}Gd_{0.1}O_2$ despite that there are much more surface active Ni sites (metal dispersion 5.9% vs 1.5%) and S content (0.19% vs 352 ppm) on 5% $Ni/Ce_{0.9}Gd_{0.1}O_2$ than on 5% Ni/Al_2O_3. Therefore, it is reasonable to propose that S is more strongly bonded to Ni on Al_2O_3 than on $Ce_{0.9}Gd_{0.1}O_2$. Ceria is reported to be able to react with H_2S and form Ce_2O_2S according to eq. (2). Indeed, peaks attributed to Ce_2O_2S and respective fragments can be observed from the SIMS spectrum of spent 5%$Ni/Ce_{0.9}Gd_{0.1}O_2$ in Fig.3.

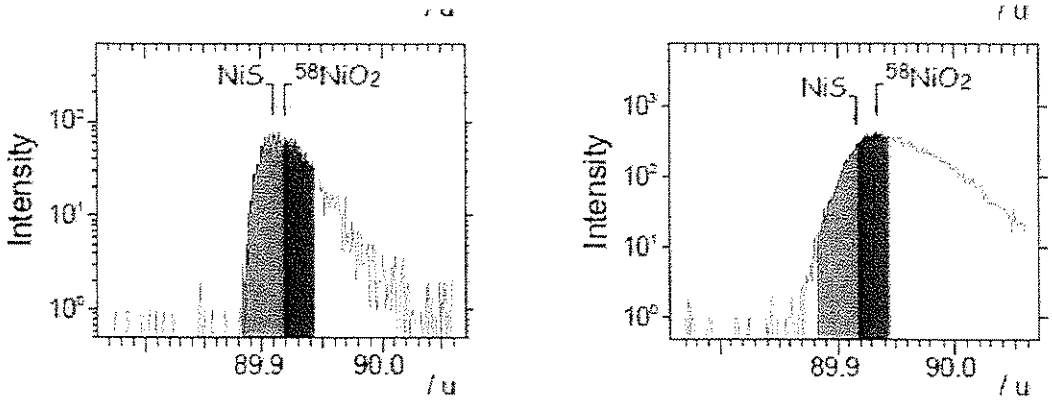


Fig. 2 Positive SIMS spectrum of spent 5%Ni/Al_2O_3 (left) and 5%$Ni/Ce_{0.9}Gd_{0.1}O_2$ (right).

$$2CeO_2 + H_2S == Ce_2O_2S + H_2O + 0.5\ O_2 \quad \text{..... } eq\ (2)$$

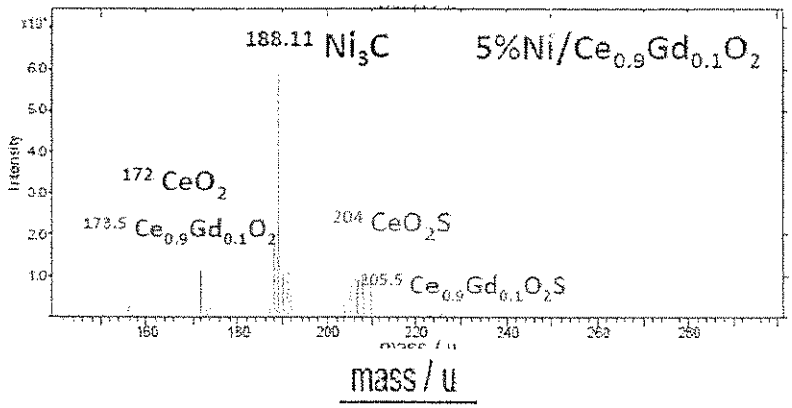
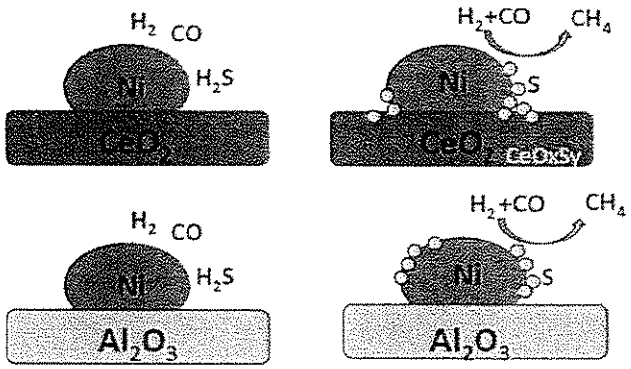


Fig. 3 Positive SIMS spectrum of spent 5%Ni/$Ce_{0.9}Gd_{0.1}O_2$.

A reaction mechanism based on the above experimental results is proposed in scheme 1. Methanation reaction of syngas is catalyzed by Ni. Ni sites are also prone to be poisoned by H_2S which decomposed into S + H_2. The remaining S is strongly attached to Ni. NiS is more stable when Ni is supported on Al_2O_3 since Al_2O_3 is inert to S. Hence Ni/Al_2O_3 deactivates quickly when surface Ni is covered by Ni. However, when Ni is supported on Ceria, some oxygen vacancies are generated during the reaction. Hence, some of the S will react/transfer into Ceria, and as such the S tolerance of Ni/CeO_2 is enhanced compared to that of Ni/Al_2O_3.



Scheme 1: Proposed reaction mechanism of methanation of syngas in the presence of H_2S over Ni/CeO_2 (top) and Ni/Al_2O_3 (bottom).

References:

1. JENS R. ROSTRUP-NIELSEN, Chemisorption of Hydrogen Sulfide on a Supported Nickel Catalyst, JOURNAL OF C4TALYSIS 11, (1968) 220-227.

2. Yuchun Ma, Qingjie Ge, Wenzhao Li and Hengyong Xu, Methanol synthesis from sulfur-containing syngas over Pd/CeO_2 catalyst, Appl. Catal. B: 90 (2009) 99 -104.
3. S. Elangovan et al, Sulfur Tolerant Anode For Solid Oxide Fuel Cell, Application number: 12/240,725, Publication number: US 2010/0279194 A1, Filing date: Sep 29, 2008

4. ADVANTAGE AND IMPROVEMENT OVER EXISTING TECHNOLOGY

4(i) Are you aware of similar developments or research in this direct field?
NO : *(Attach separate sheets if necessary)*

The details are elucidated in our manuscript.

4(ii) What practical advantage does the invention provide over existing technology?

The Ni catalyst supported on CeO_2 and M (M= Gd, Ca, Y) doped CeO_2 in this invention has shown significant improvement in the catalytic performance of methanation reaction in the gas stream containing sulfur .

4(iii) Please provide references to what you consider to be the closest published work (inc. your own) to the new invention.

1. Yuchun Ma, Qingjie Ge, Wenzhao Li, Hengyong Xu, A sulfur-tolerant Pd/CeO_2 catalyst for methanol synthesis from syngas, Journal of Natural Gas Chemistry 17(2008)387–390

2. Yuchun Ma, Qingjie Ge , Wenzhao Li , Hengyong Xu, Methanol synthesis from sulfur-containing syngas over Pd/CeO_2 catalyst, Applied Catalysis B: Environmental 90 (2009) 99–104

3. Rajesh Shivanahalli Kempegowda, Navadol Laosiripojana† and Suttichai Assabumrungrat, High temperature desulfurization over nano-scale high surface area ceria for application in SOFC , Korean J. Chem. Eng., 25(2), 223-230 (2008)

4. S. Elangovan et al, Sulfur Tolerant Anode For Solid Oxide Fuel Cell, Application number: 12/240,725, Publication number: US 2010/0279194 A1, Filing date: Sep 29, 2008

5. EXPLOITATION STRATEGY: Potential Commercial Applications

Indicate the possible commercial applications of the invention, either in the short or long term and who potentially would be interested in the invention.

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technologies can provide SNG from variety types of feedstocks such as coal, biomass and waste.

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IHI (Japan) has recently developed a proprietary gasification technology. Currently, ICES is collaborating with IHI to develop the methanation step. IHI would be the potential user of this invention.

6. PUBLICATION, PUBLIC USE, DISCLOSURE

Valid patent protection depends upon the invention not having been previously disclosed to the public in any way, therefore the following questions should be carefully considered.

6(i) the following is a list of potential disclosures, please indicate the type of disclosure and the date when it occurred, together with details of any planned disclosures including expected date of disclosure.

TYPE OF DISCLOSURE	DATE OF DISCLOSURE	DATE OF PROPOSED DISCLOSURE
Abstract	None	
Poster	None	
Paper	None	
Thesis	None	
Media	None	
Lecture / Seminar	None	
Sample / Material Supply	None	
Discussion with other colleagues	None	
Discussion with others outside of unit / institute	None	
Internet	None	
Others	None	

6(ii) Please provide details of specific disclosures indicated above, including where appropriate, copies of written disclosures.

CLAIMS

1. A catalyst, comprising metallic nickel disposed on a substrate, wherein said substrate has formula $Ce_{1-x}M_xO_2$, wherein x is between about 0 and about 0.3, optionally between about 0.01 and about 0.3, and wherein M, if present, is a metallic element other than Ce, when used for catalysing a methanation reaction.

2. The catalyst of claim 1 wherein the substrate is particulate.

3. The catalyst of claim 2 wherein particles of the substrate have a mean particle diameter of less than about 0.5 μm.

4. The catalyst of claim 2 wherein particles of the substrate have a mean particle diameter of less than about 100 nm.

5. The catalyst of any one of claims 1 to 4 wherein x is between about 0.01 and about 0.25.

6. The catalyst of any one of claims 1 to 5 wherein x is between about 0.1 and about 0.2.

7. The catalyst of any one of claims 1 to 6 wherein the metallic element is a lanthanoid, a transition metal, or an alkaline earth metal.

8. The catalyst of claim 7 wherein the metallic element is a transition metal.

9. The catalyst of claim 8 wherein the transition metal is Y.

10. The catalyst of claim 7 wherein the metallic element is a lanthanoid.

11. The catalyst of claim 10 wherein the lanthanoid is selected from the group consisting of Sm and Gd.

12. The catalyst of claim 7 wherein the metallic element is an alkaline earth.

13. The catalyst of claim 12 wherein the alkaline earth is Ca.

14. The catalyst of any one of claims 1 to 13 wherein the metallic element has a greater affinity for sulfur than for oxygen.

15. The catalyst of any one of claims 1 to 14 wherein the catalyst comprises regions of metallic nickel dispersed on a surface of the substrate.

16. The catalyst of any one of claims 1 to 15 wherein the catalyst comprises between about 5% and about 20% metallic nickel by weight.

17. The catalyst of any one of claims 1 to 16 wherein the surface area of the substrate is between about 50 and about 300 m^2/g.

18. Use of a catalyst as described in any one of claims 1 to 17 for catalysing a methanation reaction.

19. Use of a catalyst as described in any one of claims 1 to 17, said use being for reducing the carbon monoxide content of a gas mixture comprising carbon monoxide and hydrogen.

20. A method for methanation of a feedstock comprising carbon monoxide and hydrogen, said method comprising contacting the feedstock with a catalyst as described in any one of claims 1 to 17.

21. The method of claim 20 wherein the feedstock additionally comprises carbon dioxide gas.

22. The method of claim 20 or 21 wherein the feedstock additionally comprises steam.

23. The method of any one of claims 20 to 22 wherein the feedstock comprises coal gasification effluent and/or biomass gasification effluent.

24. The method of any one of claims 20 to 23 wherein the feedstock additionally comprises a sulfur-containing gas or vapour.

25. The method of claim 24 wherein the sulfur-containing gas or vapour is present at a concentration of about 0.1 to about 5000 ppm.

26. The method of claim 24 or 25 wherein the sulfur-containing gas or vapour comprises any one or more of hydrogen sulfide, carbonyl sulfide, sulfur dioxide and an organic thiol.

27. The method of any one of claims 20 to 26 wherein the molar ratio of hydrogen to carbon monoxide in the feedstock is between about 4:1 and about 1:1.

28. The method of any one of claims 20 to 27 wherein contacting comprises passing the feedstock through a packed bed reactor comprising the catalyst.

29. The method of any one of claims 20 to 28 wherein the pressure of the feedstock during said contacting is between about 1 bar and about 40 bar.

30. The method of any one of claims 20 to 29 wherein said contacting is conducted at a temperature of at least about 250 °C, or between about 250 and about 750 °C.

31. The method of any one of claims 20 to 30 wherein the temperature and feedstock flow rate during said contacting are sufficient to achieve equilibrium conversion of carbon oxides to methane.

32. The method of any one of claims 20 to 31 wherein the flow rate of the feedstock is between about 1000 h^{-1} and about 100 000 h^{-1}.