Heterogeneous Catalysts from Natural Sources for Tar Removal: A Mini Review

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Abstract: Tar formation in gasifier is a headache problem in biomass gasification process. Catalytic cracking and/or reforming of tar using a catalyst is the most effective way to solve this problem. In order to reduce the cost, some heterogeneous catalysts from natural sources have been found to possess excellent catalytic properties that render them suitable for tar cracking and reforming in biomass gasification process. This article reviews the main natural catalysts such as dolomite, olivine, coal/biomass char and waste scallop shell that have been evaluated for tar removal in biomass gasification till date. Especially, our investigations on waste scallop shell based catalysts are reviewed in more details. The ways to improve the catalytic activity and appropriate options for a practical process are also reviewed and discussed. It is expected to provide the basis for a proposal for the exploitation of heterogeneous catalysts from natural sources to optimize tar removal in biomass gasification.

Keywords: Biomass gasification, Tar removal, Heterogeneous catalyst, Dolomite, Olivines, Waste scallop shell, Coal/biomass char.

1. INTRODUCTION

Gasification of biomass to produce syngas is one of the promising thermo chemical conversion methods to convert low energy density biomass to clean fuel. However, during the gasification process, tar formation is one of the serious problems to deal with since tar generation could decrease the conversion efficiency and tar condenses at reduced temperature could result in some troubles such as filter fouling and pipe blockage [1-6]. Biomass-derived tar consists of a wide range of condensable hydrocarbon and oxygen containing compounds, which are mostly aromatics and complex poly-aromatic hydrocarbons (PAHs) [7]. The reduction of tar content and/or removal of tar are the major challenge for successful operation of gasification.

Considerable efforts have been performed to remove tar from fuel gas. One promising way is to find effective catalysts to reduce tar formation inside the gasifier or hot gas cleaning by cracking or steam reforming of the produced tar into syngas at the exit of the gasifier [8,9]. In the case of no catalyst, due to the endothermic nature of the reactions related to tar reforming or cracking and the high activation energy of over 250-350 kJ/mol, the operation temperature should be over 900^{o}C. In contrast, using a catalyst could reduce the activation energy to 56-123 kJ/mol so that the reaction temperature could be reduced to less than 650-850^{o}C [10-13]. To date, many potential catalysts have been developed for the reforming and/or cracking tar derived from biomass. To reduce the cost and make the process be economically feasible, it is essential to find some low-cost catalysts with high catalytic activity. Some heterogeneous catalysts from natural sources such as dolomite, olivine, coal/biomass char and waste scallop shell have attracted much attention for tar decomposition and cracking since they are cheap and disposable and have high catalytic activity [14-18]. Furthermore, if some metals such as K, Fe, Co, Ni, Mn, and Cu are doped on these natural minerals, the catalytic activity has been found to be greatly promoted for the tar cracking and/or reforming [14-22].

In our group, calcined scallop shell (CS) was investigated for the steam reforming of tar and many interesting results are obtained. In this article, the main natural catalysts that have been evaluated for tar removal in biomass gasification till date are reviewed. The ways to improve the catalytic activity and appropriate options for a practical process are also remarked and discussed. It is expected to provide the basis for a proposal for the exploitation of heterogeneous catalysts from natural sources to optimize tar removal in biomass gasification.

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2. BIOMASS-DERIVED TAR

The quantity and the compositions of tar derived from biomass gasification process depend on various factors such as biomass type, gasifier type, gasifying agent and operating temperature and pressure. More than 100 different compounds exist in the biomass-derived tar. Researchers tried to classify tar in different classes and investigate the characteristics of these classes [23-26]. Milne *et al*. defined biomass-derived tar in 4 groups: (1) primary tars which include levoglucosan and furfurals derived from cellulose, hemicellulose and lignin; (2) secondary tars, which mainly refer to phenolics and olefins such as cresol and xylene; (3) alkyl tertiary tars which are mainly derivatives of aromatic compounds such as toluene; and (4) condensed tertiary tars, which are PAHs without substituent groups such as naphthalene [23]. Corella *et al*. [27] classified biomass-derived tars in 6 lumps: benzene, 1-ring compound, naphthalene, 2-ring compounds, 3- and 4-ring compounds and phenolic compounds. Kiel *et al*. considered the solubility and condensability of different tar compounds rather than the reactivity of the compounds, and classified biomass tar in terms of the tar classes as indicated in Table **1** [24-26]. Herein, the heaviest tar fractions, *i.e*., class 1 and class 5 tars could cause condensation problem as they can condense out even at very low concentration. Class 2 tars always cause severe waste water problems due to their high aqueous solubility. Class 3 tars can only condense at very high concentration. Class 4 tars are either very stable compounds or are getting formed due to breakdown of other higher tars such as class 1 and class 5 tars. In many cases, the simplest way to classify the biomass-derived tar is to mention the tars in two types: “easy to destroy” tar and “hard to destroy tar” or “light tar” and “heavy tar”[28,29]. Tar is also used for representing all organics with a molecular weight greater than that of benzene generated during the biomass gasification. The complex composition of biomass-derived tar make it be difficult to understand the reaction and catalysis mechanism in the removal process using catalyst. In general, the tar molecules should be adsorbed on the catalyst surface, and form radicals or intermediate compounds. At the same time, gasifying agents such as O_2, H_2O, and CO_2 can be also adsorbed on the catalyst surface and dissociated into CO and some free radicals such as O, OH and H, followed by desorption of the free radicals and thus CH_4, CO_2, H_2 and other small molecules are formed [30-35]. The criteria for the selecting of catalysts for the tar removal are summarized as follows [4]:

- The catalyst should be resistant to the deactivation due to carbon deposition and sintering;
- The catalyst should be easily regenerated;
- The catalyst should be strong;
- The catalyst should be cheap;
- The catalyst should have high activity and long-term stability;

3. DOLOMITE CATALYSTS [35-43]

Dolomite is a calcium magnesium ore with general chemical formula $CaMg(CO_3)_2$, and is generally used as raw material in the manufacture of magnesium. It is found that calcined dolomite is a highly efficient catalyst for the removal of tar from the product gases of gasifier. Calcined dolomite is always obtained by calcinations of raw dolomite at high temperatures from 800-1000 ^oC. Table **2** shows the chemical compositions of dolomites produced from different areas. One can see that the main compositions with the catalytic activity for the tar reforming are CaO and MgO. Xie *et al*. [41] investigated alkaline earth metal oxides such as CaO and MgO on the steam gasification of biomass, and found that they improved the quality of gaseous

Table 1: Classification of Tar Components [24-26]

Tar Class	Class Name	Property	Representative Compounds
1	GC-undetectable	Very heavy tars	Unknown
2	Heterocyclic	Containing heteroatoms and highly water soluble	Pyridine; Phenol; Cresols Quinoline; Isoquinoline; Dibenzophenol
3	Light aromatic	Light hydrocarbons with single ring and no Condensability	Toluene; Ethylbenzene Xylenes; Styrene
4	Light polyaromatic	2 and 3 ring compounds and easily condense at low temperatures	Indene; Naphthalene; Methylnaphthalene Biphenyl; Acenaphthanlene; Fluorene; Phenanthrene; Anthracene
5	Heavy polyaromatic	>3 ring componds and easily condense at high temperatures	Fluoranthene; Pyrene Chrysene; Perylene; Coronene

product by promoting the decomposition of tar and light hydrocarbon. Siedlecki *et al*. [40] indicated that magnesite can promote water-gas shift reaction, steam reforming of methane and C_2 hydrocarbons toward their equilibrium, and reducing the tar. Calcined dolomite has been extensively investigated for the tar removal. There are two ways to remove tar using catalysts in the biomass gasification: primary treatment way is addition of catalysts in the gasifier, and secondary treatment way is removal of tar the exit of the gasifier. The catalytic removal of tar in the gasline is commonly known as hot gas cleaning. Corella *et al*. [35] used calcined dolomites as both primary and secondary catalysts for the removal of tar in the biomass gasification, and found that calcined dolomites had equally effectiveness as either a primary or secondary catalyst. Simell *et al*. [42] considered that the presence of CaO in dolomite might be responsible for its activity in tar conversion, and found that the catalytic activities for tar reforming were ranked in the following sequence: CaO>dolomite>MgO. Furthemore, Orio *et al*. [43] demonstrated that the activity of dolomite was increased with the increase in Fe_2O_3 content in the material and its pore diameter. However, when Fe_2O_3 powders were mixed with dolomite to increase its Fe_2O_3 more, the tar conversion was increased only a little at 850 ^oC [30]. Gusta *et al*. [36] also found that iron content in dolomite can promote tar conversion and the water-gas shift reaction, but the effectiveness reached a plateau at 0.9wt% Fe in the dolomite. Although dolomite has been proven to be effective catalyst for tar cracking and reforming in the gasifier, it has some critical limitations. The dolomite catalysts are less effective for removal of PAHs formed in air-blown gasifier. More seriously, dolomite is a kind of soft and fragile materials and easy to be eroded by other bed materials in the gasifier, limiting its use in the fluidized bed gasifiers [5].

4. OLIVINE CATALYSTS [8, 14, 24, 44-51]

An alternative of dolomite is olivine, also a naturally occurring mineral containing magnesium oxide, iron oxide and silica with a general chemical formula of $(Mg,Fe)SiO_4$, as shown in Table **3.** Olivine is advantageous in terms of its attrition resistance over that of dolomite, and some metals can be impregnated into it to enhance steam adsorption, facilitate the reforming of surface carbon and hence hinder carbon deposition. Rapagnà *et al*. [44] found that olivine itself has a good catalytic activity for tar reduction and its activity is comparable to calcined dolomite and can be used as an in-bed catalyst for a gasifier. However, Abu El-Rub *et al*. [8] decomposed naphthalene as a model tar over olivine and observed on significant activity of olivine. In order to make sure how tars behave in the presence of olivine and whether olivine has some activity towards tar destruction, Devi *et al*. [24] added olivine and dolomite to the sand bed to investigate their improvement effect on the conversion of each class of tar shown in Table **1.** They found that thermal treatment (sand bed only) at 900 ^oC is sufficient to remove all the class 2 tars and results in only 48% decrease in heavy PAHs (class 5). The addition of olivine leads to a 71% decrease of the total heavy PAHs while the addition of calcined dolomite causes a

Table 2: Chemical Compositions of Dolomites Produced in Different Areas

Dolomite	Chemical Compositions	Reference
Chinese dolomite	$20.9wt\%MgO-30.9wt\%CaO-1.7wt\%SiO_2-0.6wt\%Al_2O_3$	[30]
Spain Dolomite Norte	$20wt\%MgO-31wt\%CaO-0.7wt\%SiO_2-0.5wt\%Al_2O_3-0.5\%Fe_2O_3$	[38]
Spain Dolomite (PRODOMASA Coin-Malaga)	$21.2wt\%MgO-30.6wt\%CaO-0.4wt\%Al_2O_3-0.1\%Fe_2O_3$	[29]
Netherland Dolomite	$20.3wt\%MgO-31.5wt\%CaO-0.3wt\%SiO_2-0.1wt\%Al_2O_3-0.4\%Fe_2O_3$	[24]
Turkey Dolomite	$16.88wt\%MgO-36.93wt\%CaO-0.08wt\%SiO_2-0.125wt\%Al_2O_3-0.098\%Fe_2O_3$	[58]

Table 3: Chemical Compositions of Olivine's Produced in Different Areas

Dolomite	Chemical compositions	Reference
Netherland Olivine	$49wt\%MgO-41wt\%SiO_2-7wt\%Fe_2O_3-3wt\%Cr_2O_3-0.3wt\%NiO$	[24]
North Carolina Olivine	$31wt\%MgO-19wt\%SiO_2-6wt\%Fe_2O_3$	[14]
Austrian Olivine	$28wt\%MgO-21wt\%SiO_2-7wt\%Fe_2O_3$	[14]
Washington Olivine	$29wt\%MgO-18wt\%SiO_2-6wt\%Fe_2O_3$	[14]

decrease of almost 90% at the same operating conditions. The light PAHs (class 4) also show a considerable decrease in the case of olivine addition. For light aromatic compounds (class 3), olivine shows a slight increase in tar removal when compared to sand whereas the conversion reaches 71% when dolomite is used. It should be noted that class 4 tars are the most difficult to be removed. Apparently, calcined dolomite is more active than olivine with respect to tar decomposition. However, due to its higher attrition resistance property, it is expected that olivine can be a prospective candidate for in-bed use in a fluidized-bed biomass gasifier.

Metal doping on dolomite and olivine has been found to be able to promote their catalytic activities for tar cracking and/or reforming. The addition of nickel to dolomite drastically increased the tar conversion at 650 ^{o}C from 43 to 84% [30]. Moreover, carbon deposition on the Ni/dolomite can be negligible. It is considered that nickel oxide has strong interaction with the dolomite surface. Ni/olivine showed a toluene conversion of about 85% for the reforming of toluene at 750 ^{o}C and good selectivity to H_2, CO and CO_2 whereas olivine alone had almost no activity in the same case [14,49,50]. Ni doped calcinated olivine also remarkably enhanced the conversion of naphthalene, almost 2 times higher than the olivine itself. When Fe/olivine was used for tar removal during biomass gasification in a dual fluidized bed, it is found that Fe/olivine can catalytically promote tar and hydrocarbon reforming and simultaneously act as an oxygen carrier for carrying oxygen from the combustor to the gasifier, and part of the oxygen is applied for the burning of volatile compounds. Furthermore, the addition of more promoters to dolomite and olivine may improve the catalytic activity and long-term stability more. Zhang *et al*. [51] compared the catalytic activity of Ni/olivine, Ni-Ce/olivine and Ni-Ce-Mg/olivine, and found that the addition of Ce can reduce the coking formation on the catalyst and increase toluene conversion. 1% Ce adding to 3% Ni/olivine increased toluene conversion from 59 to 88%. Further addition of 1%Mg to 3%Ni-1%Ce/olivine increased the conversion to 93%. Ni-Ce-Mg/olivine can improve the resistance to carbon deposition, enhance energy gases yield and resist about 10ppm H_2S position at 100cm^{3}min^{-1} for up to 400 min.

5. CHAR COAL SUPPORTED CATALYSTS [52-56]

Char coals derived from biomass or coal have highly porous textural structures and have been widely used as good catalyst support for tar cracking/-reforming. Its macro- and meso-pores could greatly improve the dispersion of metal ions and facilitate reactants transport into its internal surfaces. Li *et al*. [52] prepared a cost-effective and active nickel loaded Loy Young lignite char (Ni/LY) via ion-exchange method and used for tar reforming in woody biomass gasification. They found that nickel particle (dark grains) dispersed very well in coal char with particle sized around 5-10 nm. This kind of catalyst performed high catalytic activity on tar reforming of biomass-derived tar at low temperatures between 450 and 650 ^{o}C. In our study [58], biomass chars were prepared at different conditions and used for the steam reforming of biomass-derived tar. It is found that pyrolysis temperature for the preparation of char had significant effect on the promoting effect of char for the tar reforming since the pyrolysis temperature had obvious influence on the evolution of pore and the change of chemical structure of the char. The BET surface area and the amount of alkaline and alkaline earth metal (AAEM) of the prepared char also had great effect on the steam reforming of char over the biomass char. However, it should be noted that the char itself could be reformed by steam during the removal of tar in this case.

6. CALCINED SCALLOP SHELL CATALYSTS [20-22]

A large amount of scallop shell with main composition of approximately 98 wt% $CaCO_3$, 0.79 wt% $MgCO_3$ and 0.15 wt% $SrCO_3$ is discarded in North Japan area, and how to effectively applied it became an urgent issue. In our studies [20-22], the waste scallop shell was calcined and used for the removal of tar derived from biomass. It is found that tar can be effectively reformed into syngas by using the calcined scallop shell as catalyst. In order to improve the catalytic activity of the calcined scallop shell, some metals such as Fe, Co, Ni, and Cu were deposited on it, and the metal-modified catalysts showed better catalytic activity for the steam reforming of the tar. To understand the improvement effect of potassium (K) on the catalytic activity of Fe-doped calcined scallop shell for the steam reforming of tar, various K precursors were applied for the catalyst preparation. As shown in Figure **1,** a porous structure is clearly observed on the surface of the calcined scallop shell (CS). After deposited by metals, the morphologies of the surface are changed to different states. Interestingly, it is found that pompom-like particle was easy to be formed on the surface of Fe-doped CS when the loading amount of K was between 0.2 and 2.1wt% in the case of K_2CO_3 as the K precursor. These pompom-like particles have microporous structure. Such porous pompom-like

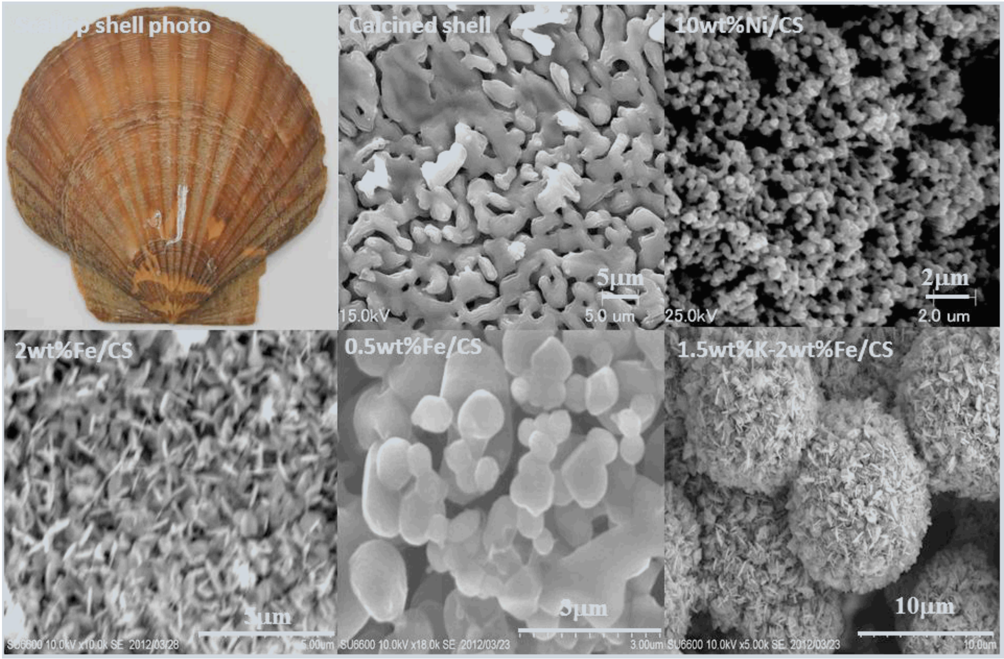

Figure 1: Photo and SEM images of calcined scallop shell and metal doped calcined scallop shells [20-22]. (Adapted with permission from Elsevier).

spheres are expected to have advantages if they are used for the adsorption and decomposition of tar. Figure **2** shows gas production rate at a reaction temperature of 650 °C as a function of the reaction time when CS itself was used as catalyst. Herein, after the catalyst bed in the reactor was heated to 650 °C, the biomass was introduced into it. In this case, gases evolved soon after the biomass was introduced, and reached a peak at 20 min. In the present reforming method, the biomass should be pyrolyzed first, and the generated volatiles moved to the CS surfaces by the carrier gas and reformed by H_2O there. Pyrolysis of wood typically starts at 200-300 °C, and a higher temperature always leads to a higher reaction rate. Hence, the volatiles were produced immediately from the biomass when it was introduced into the reactor. In our experiments, it is found that the accumulated amount of gases during the reaction time (2h) had great relationship with the heating rate, and the higher heating rate resulted in more gas yield [20].

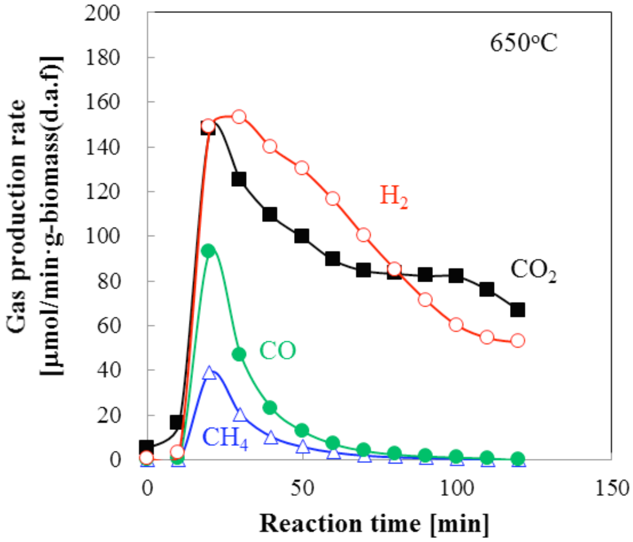

Figure 2: Gas production over CS catalyst at 650°C (CS: calcined scallop shell at 800°C; biomass: pruned apple branch) [20]. (Adapted with permission from Elsevier).

Figure **3** shows the effect of heating rate on the production rates of H_2 over Fe/CS catalyst as a function of reaction time. Comparing with the result shown in Figure **2,** one can see that the doping of Fe on CS promoted the H_2 generation rate greatly. On the other hand, a rapid heating rate is beneficial for the gas production. If the heating rate is too slow (5 °C/min), the volatiles produced at low temperatures (200-500 °C) could adsorb and cover on the surface of Fe/CS. Due to the low catalytic activity of Fe/CS at low temperatures, the H_2 and CO production rates remained low for a relatively long time as shown in the figure. Furthermore, in the case of the slow heating method, the initial tar evolved could be adsorbed on the catalyst, and slowly reformed by steam. The unreacted tar covering on the catalyst could convert into carbon, resulting in the decrease in catalytic activity. In a practical process, it is generally expected that the tar produced is rapidly decomposed and removed from the gas lines. Therefore, the rapid heating method should represent a more realistic approach for steam reforming of the tar.

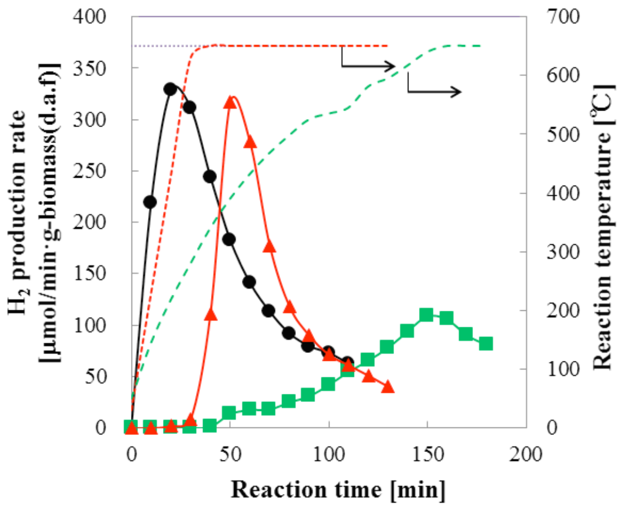

Figure.3: Effect of heating rate on the H_2 production rate over 2.5wt%Fe/CS catalyst at 650 °C (biomass: pruned apple branch) [20]. (Adapted with permission from Elsevier).

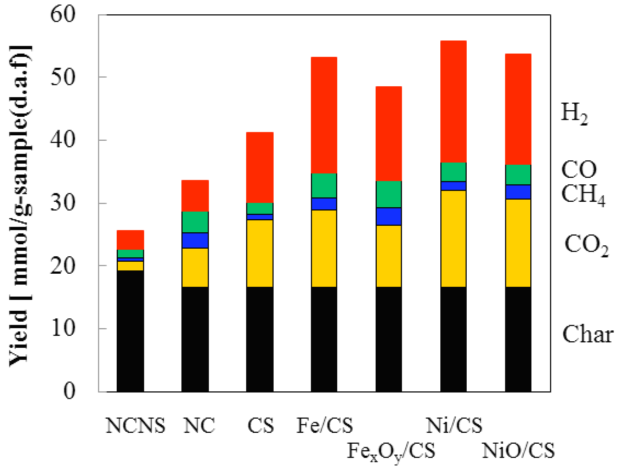

Figure 4: Comparison of gas yields over different catalysts in 2 h at 650°C (NCNS: no catalyst no steam; NC: no catalyst; biomass: pruned apple branch) [20]. (Adapted with permission from Elsevier).

Figure **4** compares gas yields in different conditions [20]. Very low gas yields were obtained in the case of no catalyst and no steam. Approximately 395 mg-tar/g-biomass was produced in this case based on the tar collected by 30ml of isopropanol. H_2 yield was increased by 4.0 times with CS, 6.6 times with Fe/CS, 5.3 times with Fe_xO_y/CS, 6.9 times with Ni/CS, and 6.3 times with NiO/CS at 650 °C for a 2 h reaction. It should be noted that a large amount of gases were also produced when metal oxide loaded catalysts were applied directly. As shown in Figure **5,** a small peak corresponding to metallic iron was clearly seen on the XRD of the catalyst after reaction, suggesting that a part or all of the iron oxides could be converted to metallic iron during the reaction. Similar result was also obtained for NiO/CS [20]. Therefore, although some researchers considered that iron oxide such as Fe_2O_3 could act as catalyst for the reforming or cracking of tar, the catalytic activity should only be present when the iron- or nickel-loaded catalyst is in its metallic state.

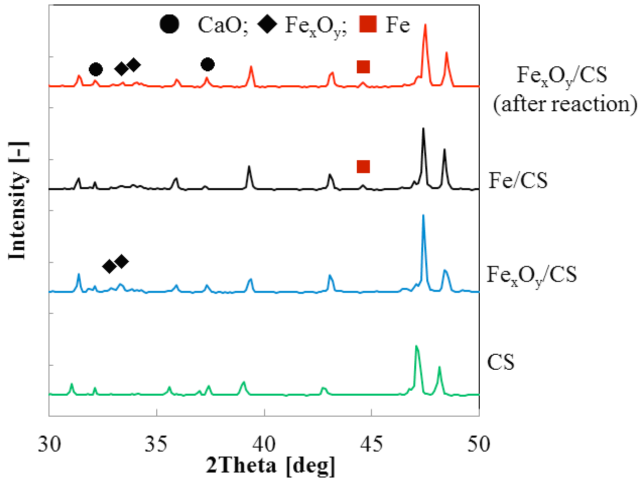

Figure 5: XRD patterns of Fe_xO_y/CS before and after the reaction [20]. (Adapted with permission from Elsevier).

Table **4** shows the gas yields from the steam reforming of tar derived from lignin over the pompom-like potassium-promoted iron-based CS catalysts [21]. One can see that the H_2 yield was increased 76% for 1.5wt%K-2wt%Fe/CS catalyst when it was compared with the result obtained from CS itself, indicating that the pompom-like catalyst has high catalytic activity for the tar reforming.

Table 4: Comparison of Gas Yield from the Catalytic Steam Reforming of Tar Derived from Lignin over Pompom-like Catalysts with other Cases [21]

Catalyst	Gas Yield [mmol/g-lignin]		
	H_2	CO	CH_4
No catalyst	3.67	2.85	0.43
CS	16.95	1.37	0.79
2wt%Fe/CS	21.18	0.78	1.05
0.5wt%K/CS	18.36	0.74	1.09
0.5wt%K-2wt%Fe/CS	26.67	0.89	0.87
1.0wt%K-2wt%Fe/CS	29.07	0.94	1.03
1.5wt%K-2wt%Fe/CS	29.91	1.12	0.88

7. CONCLUSIONS AND REMARKS

The compositions of biomass-derived tar are very complex. During catalytic tar removal process, a matrix of complex reactions among different compositions and gases will occur. The relationship between different reactions is difficult to be known so that it is almost impossible to predict the mechanism of the catalytic processes. Various man-made catalysts such as metal supported catalysts have been successfully developed for the decomposition of model tars such as benzene, toluene, phenol and naphthalene. However, for a practical biomass gasification process, in order to remove the tars using catalysts, heterogeneous catalysts from natural sources attract special attention due to its low cost and disposablility. As reviewed above, calcined dolomites and olivine are active for tar decomposition. Char-coal supported catalysts can work at relatively low temperatures. In our group, steam reforming of the tar derived from biomass over calcined scallop shell (CS) as well as metal-loaded CS was investigated, and the main results can be concluded as follows:

- CS shows alkaline property with porous structure and good catalytic activity for the steam reforming of the tar derived from biomass to produce syngas, and is recyclable.
- Metal doped catalysts show much better activity than CS itself. Larger volumes of gases were produced under the condition of rapid heating rates.
- For metal loaded catalysts in their oxide states, almost no catalytic activity is found at the beginning of the reaction, but good catalytic activity appears after a period of reaction when the metal oxides are reduced to their metallic forms by the syngas (H_2 and CO) initially produced from the pyrolysis of biomass without the aid of the catalyst. Based on these experimental results, a possible catalytic process was proposed to explain the catalysis phenomenon when metal oxide loaded CS was used.
- It is found that pompom-like iron-based particles with a mesoporous structure were easily formed on the surface of calcined scallop shell (CS) when K_2CO_3 was used as K precursor while no such kind of microsphere was formed when other kinds of K precursors such as KOH and KNO_3 were applied. This pompom-like potassium-promoted iron-based catalyst showed a better catalytic activity and reusability for the steam reforming of tar derived from biomass.

Unlike many kinds of man-made catalysts, catalysts from nature could be discarded to the environment directly. Sometimes their catalytic activities are lower than those man-made ones, but they are much cheaper than the man-made ones. To date, most of man-made catalysts also have low reusability and have to regenerate or modified by some noble metals. Therefore, there is strong competitiveness for application of natural catalysts for the tar removal in a practical process. In the future study, the following 3 main points should be considered for such kinds of catalysts:

- Improvement the catalytic activity at lower temperature by modifying the catalyst with low cost elements is needed. In high temperature, these catalysts always show good catalytic activity. However, their strength will become fragile at high temperatures so that they are easily to be broken, and more easily to be carried out of the reactor. If they can work well at lower temperature, waste heat with a temperature of 400-600°C can be effectively used. This is very important for a practical process.
- Larger scale or pilot experiments by using these catalysts are needed. In the lab scale, these catalysts always show good catalytic properties for tar cracking/reforming. However, in a larger scale, the factors related to the activity of the catalyst become complex. We should consider some factors such as gas flow rate, temperature and pressure variations, catalyst broken, the impurities such as HCl, HCN, NOx and SOx in the gas line and so on.
- A chemical looping system design for continuous tar removal with simultaneous catalyst regeneration is needed. In a practical process, the catalyst is easily deactivated due to the complexity of the tar compositions. How to regenerate the natural catalyst is also an important issue although it can be discarded even if it cannot be used again.

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