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Novel sour water gas shift catalyst (SWGS) for lean steam to gas ratio applications

Bonan Liu [a], Qiuyun Zong [b,*], Xian Du [a], Zhaoxi Zhang [a], Tiancun Xiao [a,*], Hamid AlMegren [c]

[a] Inorganic Chemistry Laboratory, Oxford University, South Parks Road, OX1 3QR, UK
[b] Qindao Lianxin Chemical, Qingdao, Shandong Province, PR China
[c] Petrochemical Research Institute, King Abdulaziz City for Science and Technology, P.O. Box 6086, Riyadh 11442, Saudi Arabia

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ABSTRACT

Dry powder coal gasification is emerging as one of the most energy efficient methods for coal conversion. However, the low steam content, high temperature and high content of CO in the raw syngas make it difficult for a conventional sour water gas shift catalyst to be directly used for syngas conditioning. Conventional sour water gas shift takes place at very high steam to carbon monoxide ratio (H_2O/CO), often 2 or above, but the H_2O/CO ratio from a dry powder coal gasifier is often less than 0.8. To develop a sour water gas shift catalyst suitable for the lean steam raw syngas, we have prepared a series of $MgAl_2O_4$ spinel modified alumina supported $CoMoO_x$ catalysts by changing the content of K_2O in the promoter, and tested them under lean steam to carbon monoxide (H_2O/CO) ratio conditions for sour water gas shift process. Our results show that the addition of potassium into the catalyst increases the catalyst water gas shift activity at a lean steam to gas ratio, and that catalyst activity increases with the K_2O content increase in 0–10 wt.% range; the potassium additive helps to increase the dispersion of MoO_3 and improves catalyst strength and surface area. The increase of K_2O content leads to higher catalyst activity for the CO shift reaction with little methane yield, reducing the hot spot formation in the catalyst bed. This may be due to the high K_2CO_3 content in the catalyst enhancing the surface affinity to steam in the syngas, and the basicity of K_2CO_3 depresses methane formation over the MoS_2 active site. The 10.0 wt.% of K_2O-containing SWGS catalyst showed the highest stability even in the absence of H_2S in the feed gas for up to 90 min, and little H_2S is released from the catalyst (reverse sulfurization) under such conditions. The optimized K_2O-containing SWGS catalyst, e.g., QDB-5-10 has been used in an industrial plant for 2 years in a coal to methanol plant and showed stable and unique performance under the lean steam conditions, allowing the 1st stage SWGS reactor to be well within control. The potassium carbonate included in the catalyst is stable and little leachate occurred even after 2-years of use time on stream.

1. Introduction

Coal is one of the main energy and chemical resources in China; currently 60% of the energy comes from coal, and over 70% of the power supply is generated by burning coal [1,2]. However, the direct combustion for power generation has caused serious environmental pollution and also emitted large amounts of CO_2 into the atmosphere, increasing the threat of global warming [1,3,4]. How to utilize coal resources in a cleaner manner is a challenge worldwide when facing the current and future problems in relation to use of the resources.

Gasification is considered to be a relatively energy efficient technology for coal utilization, and the results syngas can be used to produce various products and chemicals. In addition, CO_2 can be separated and captured from the gasified stream [5–9]. Coal gasification technologies have been developed for several decades and have been commercially used in many industries [10–14]. The currently available gasifiers can be divided into three types; entrained-bed gasifiers, fixed bed gasifiers, and fluidized-bed gasifiers. The entrained-bed gasifier has the feature of fast residence time (typically less than 5 s) in the gasifier as well as high pressure. Fluidized-bed gasifiers have been developed primarily for the application to low-grade coal and wastes that contain lots of impurities. Fixed-bed gasifiers have a long history in industrial application, such as Lurgi slurry gasifier, which is still used extensively in China. Its feature is reliable, but has relatively low efficiency and is not suitable for the single large scale gasifier [10,15–17].

The slurry gasifier has been used in industry for many years and the raw syngas from the slurry gasifier often contains high steam content. This gives a high ratio of H_2O/CO in the feed for water gas shift reaction [18,19]. The gas conditioning for this raw syngas can be easily carried out using typical sour water gas shift catalyst like K8-11 [10,16,20–23]. But the raw syngas from the dry powder coal gasifier (such as Shell GSP) contains up to 70% of CO but very low steam content. Therefore the conventional sour water gas shift catalysts are not suitable for direction application, so often a huge amount of steam has to be added to the raw syngas to increase steam to carbon ratio. This is

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* Corresponding authors.
E-mail addresses: zqy1959@163.com (Q. Zong), xiao.tiancun@chem.ox.ac.uk (T. Xiao).

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because most sour water gas shift catalysts operate at a H_2O/CO ratio above 1, in fact above 2 or 3 [24–26] so as to depress carbon formation and increase the catalyst stability. However, the exothermicity of the water gas shift reaction makes it difficult to control the reactor temperature for the high CO-containing syngas shift process. Thus in industrial operation, to control the temperature under the operating conditions for the 1st stage shift reactor, sometimes high temperature SWGS catalysts were employed with extra steam input into the raw syngas from dry powder gasifier. The adoption of high temperature operation is to limit CO conversion, as predicted by the thermodynamics [27,28], so as to generate less heat. This requires another cooling stage before the follow-up water gas shift process. To make the process simple and allow easy control of the shift reaction stage, a catalyst that can operate at lean steam conditions and especially can work at H_2O/CO (mol. ratio, the same in the following) below 0.5, which is often the composition of the raw dry powder gasified products is highly demanded.

There have been many studies in the development of the SWGS catalysts, mostly based on alumina supported MoS_2 catalysts promoted with Co or Ni [29–31]. As we pointed out before, these developments targeted the slurry gasifier, and often operate at a H_2O/CO ratio above 1 [25,32–34]. A Pt/CeO_2 catalyst has been reported suitable for lean steam condition [27].

In this work we have prepared a series of $MgAl_2O_4$ modified Al_2O_3 supported Co–Mo–S catalysts using potassium carbonate as the promoter. The catalysts showed robust performance for sour water gas shift reaction at low H_2O/CO ratio conditions. The catalyst can even maintain its performance in H_2S-free feed stream for a short period. The catalyst has been used in an industrial plant for 2 years, which reduced steam requirements and energy input significantly compared to the use of the benchmark commercial catalyst.

2. Experimental

The Mg modified alumina support material was prepared by impregnating γ-Al_2O_3 support (China Aluminum Co., Zibo China, chemical grade, surface area, 213 m^2/g) with a proper amount of aqueous solution of magnesium nitrate hexahydrate, which was followed by drying for 4 h at 120 °C in air and calcining for 2 h at 500 °C in air. The content of MgO is 10.5 wt.% and presents in the form of $MgAl_2O_4$, confirmed by X-ray diffraction measurement. This support has been designed and made for the QDB-4 SWGS catalyst, which contains 3.5 wt.% of Co and 8.1 wt.% of MoO_3 in the oxide form catalysts. The proprietary preparation details of this catalyst have been reported in the literature [35–37]. The QDB-04 catalyst has been used for relatively high H_2O/CO conditions for many years, and the industrial operation results have been reported in literature [35, 38]. Here the spinel modified γ-Al_2O_3 is marked as Al_2O_3–$MgAl_2O_4$.

The new K containing SWGS catalysts were prepared by impregnating Al_2O_3–$MgAl_2O_4$ support (extrudate, 3.5 mm in diameter, 20 mm length) with the aqueous solution of Co nitrate, ammonium molybdate and K_2CO_3 solution using our proprietary method, which can effectively bond the potassium carbonate to the support [43,44]. The solubility of the ammonium molybdate was adjusted through the addition of ammonia. The loading of the Co, Mo and K was carried out through incipient impregnation method, which means that the support can absorb all the solutions onto it; the total content of the CoO and MoO_3 in the catalyst oxide form is 3.5 wt.% and 8.1 wt.% respectively. The K_2O content in the catalysts was controlled by K_2CO_3 concentration in the impregnation solution. This novel catalyst series are named as QDB-5-*x* series catalysts, where *x* represents the K_2CO_3 content in the catalyst.

The QDB-5 series catalysts containing nominal K_2O content of 0 wt.%, 2.0 wt.%, 4.0 wt.%, 6.0 wt.%, 8.0 wt.%, 10.0 wt.%, 12.0 wt.%, and 14.0 wt.% are remarked as QDB-5-0 (no K_2O), QDB-5-2 (2 wt.% K_2O), QDB-5-4 (4 wt.% K_2O), QDB-5-6 (6 wt.% K_2O), QDB-5-8 (8 wt.% K_2O), QDB-5-10 (10 wt.% K_2O), QDB-5-12 (12 wt.% K_2O), and QDB-5-14 (14 wt.% K_2O). The ICP analysis of the K_2O content in the QDB-5 series catalyst showed that the K_2O contents in the oxide catalysts are 0.001 wt.%, 1.96 wt.%, 3.92 wt.%, 5.91 wt.%, 7.92 wt.%, 9.88 wt.%, 11.78 wt.% and 13.65 wt.%, which are very close to the nominal value, due to the adoption of the incipient impregnation method. The slightly lower content of the real K_2O may result from the some metal salts contacting the impregnation tank.

2.1. Catalyst test

Catalyst testing was carried out in a fixed bed micro-reactor system, to mimic industrial conditions (3.7 Mpa, 423 °C) in the first conversion reactor of a Shell gasifier [39]. Each time, 10.0 g of the sieved catalyst (20–40 mesh) was loaded into the reactor with a gaseous hourly space velocity (GHSV) of 3000 h^{-1}. The gas feed stock composition is adjusted to be close to the industrial outlet of a Shell gasifier (dry feed coal gasification derived syngas composition, CO 64.9%, CO_2 8.1%, H_2 25.1%, and N_2-1.9% for complement, inlet H_2S concentration 3000 ppm). The inlet temperature is between 200 and 300 °C, with a reactor pressure of 3.7 Mpa. Water is injected into the system using a HPLC pump, passing through a pre-heater operating at 150 °C to feed the steam. The outlet gas is directly transferred into online GC system for analysis (Agilent 7890, with TCD, FID and FPD).

Before the reaction, the gas line was switched to a parallel gas line (3 mol.% H_2S, 47 mol.%H_2 and 50 mol.% N_2), and the catalyst was presulfurized at 250 °C for 3 h, until the gas outlet sulfur composition is constant. The 3 hour-holding time was to completely sulfurize the active phase of Co–Mo–Ox. Afterwards, the catalyst bed was heated to 400 °C at 1 °C/min in the sulfurizing gas to stabilize the active phases. Then the sour syngas was conducted into the reactor and the catalysts were tested under the specific conditions to mimic the lean-steam water gas shift process. The gas analysis was carried out after 4-hour time on stream when the reaction reached steady state. The catalyst activities have been expressed by the CO conversion or the change of CO content in the outlet gas under the same test conditions, and the side reaction is expressed by the CH_4 content in the outlet gas [27,30,45].

The industrial operation results were obtained from Henan Zhongyuan Dahua Fertilizer where a Shell Dry Coal Powder gasifier was used. There were two trains of the gasifiers each with 3 stages SWGS reactor after the gasification. For comparison across the parallel streams, the water gas shift catalyst was initially replaced by QDB-5-10 catalysts in one train, only in the 1st stage SWGS reactor, then gradually replacing the 2nd stage SWGS stage reactor with the QDB-5-10 catalysts. The utility consumption and the exit CH_4 were recorded for comparison in parallel.

When unloading the industrial catalyst after use, the catalyst was purged with flowing N_2 at the reaction temperature under atmosphere pressure and cooled down to room temperature naturally. The reactor containing the SWGS catalyst was placed in static air to passivate the industrial catalysts before collection.

2.2. Catalyst characterization

The phase of the components in the catalyst crystal size and crystalline structure of the prepared CoMo/Al_2O_3–$MgAl_2O_4$ samples was determined using X-ray diffraction (XRD) with an X' PeRT Pro Alpha 1 diffractometer with Cu K_α radiation ($\lambda = 1.5406$ Å), operated at a tube current of 40 kV and a voltage of 40 Ma. Line trace was collected over 2θ values from 20° to 70°, and scanned at a speed of 1°/min.

Fourier transform infra-red (FT-IR) spectra were obtained on Bruker Vertex-70 by diffused reflectance accessory technique. Laser Raman spectra were obtained using a Perkin-Elmer Raman station 400F Raman spectrometer.

3. Results and discussion

3.1. Effect of K_2O content on the SWGS catalyst performance

The K_2O containing sour water gas shift catalyst has been tested in a micro-reactor system to study the effect of K_2O content on the CO