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Novel Catalysts for Sorption Enhanced Water Gas Shift Reaction

D. Iruretagoyena[1,2*], K. Hellgardt[1], N. Shah[1,2], D. Chadwick[1*]

[1] *Department of Chemical Engineering;* [2] *Centre for Process System Eng., Imperial College London, SW7 2AZ, UK*
**Corresponding author: d.iruretagoyena09@imperial.ac.uk, d.chadwick@imperial.ac.uk*

Highlights

- Activity and selectivity of commercial and novel in-house-synthesised shift catalysts was assessed for SEWGS
- Cu-Zn commercial and
- novel Pt-CeO_2 catalysts display excellent catalytic performance for SEWGS (without methane formation –side product- in the temperature range of interest)
- Cu-Zn commercial and novel Pt-CeO_2 catalysts are remarkably stable for WGS in the presence and absence of a hydrotalcite-based CO_2 adsorbent

1. Introduction

Recently there has been an increasing interest in establishing clean and competitive routes to produce hydrogen. In this regard, sorption enhanced water gas shift reaction (SEWGS) is considered an attractive technology to improve the efficiency of the water gas shift (WGS), which is a key stage in H_2 production by methane steam reforming and coal/biomass gasification. In the sorption assisted process the WGS is performed in the presence of a shift catalyst and a solid adsorbent, which selectively removes CO_2 from the gas phase as it is formed. The in situ capture of CO_2 lifts the thermodynamic constraints of the WGS thereby maximising the production of hydrogen. The SEWGS technology has many potential advantages in comparison to the conventional process including steam usage reduction, improved energy efficiency and capital cost reduction through process simplification. In principle only one reactor stage is required operating at relatively high temperatures, which enhances the catalyst utilisation from more favourable kinetics [1].

The catalysts and adsorbents to be used in SEWGS require a meticulous selection since the kinetics of reaction and adsorption must match under the same operating conditions. In addition, both materials need to be stable during cyclic operation. While many studies have focused on finding suitable CO_2 adsorbents for SEWGS [3,4], so far little attention has been paid to the selection and development of adequate WGS catalysts for the process. In this work, we assess the activity and selectivity of different WGS catalysts under conditions relevant for the sorption enhanced process (473 to 723 K). The catalysts tested include commercial mid/high temperature shift catalysts and a series of novel in-house-synthesised catalysts. The feasibility of using these catalysts and a hydrotalcite-based CO_2 adsorbent in a combined process is explored.

2. Methodology

Commercial mid/high temperature shift catalysts (Cu/ZnO, Fe/Cr, CoMo) and a series of novel in-house-synthesized catalysts (Pt/Al_2O_3, Pt/SiO_2, Pt/CeO_2/SBA15, Pt/CeO_2/ZrO_2 and Pt/CeO_2) were tested. In addition, hydrotalcite based adsorbents (including novel carbon supported hydrotalcites) were prepared via a co-precipitation technique. Full details about the preparation of the CO_2 adsorbents are given elsewhere [2]. The catalytic and adsorption experiments were carried out in a stainless steel fixed bed reactor (ID = 6.9 mm, L=364 mm) and the product evolution was measured by online mass spectrometry. The gases were fed using mass flow controllers and steam was supplied by syringe or HPLC pumps and an electrically heated vaporisation system. All the lines were trace heated to avoid condensation. After the catalysts were activated (573 K, 10% H_2/N_2), they were screened by conducting the forward and reverse water gas shift under a temperature program. Stability tests were carried out at 573 K and 673 K for more than 24h. The CO_2 adsorption capacity and multicycle stability of the hydrotalcite-based adsorbent was assessed by breakthrough curve experiments using an automated 4-way valve. The enhancement of the WGS by CO_2 adsorption was evaluated by comparing the transient H_2 production in the presence and absence of adsorbent. The catalysts and CO_2 adsorbent were characterised by a range of physicochemical techniques including BET, TGA, XRD, XRF, TEM, SEM, EDS, ICP, CO_2-TPD and TPR.

3. Results and discussion

The CO and CH_4 yields obtained at 573 K and 673 K during the TPR-RWGS over the different catalysts tested are presented in Table 1. The mid-temperature Cu-Zn catalyst shows the best performance with conversions close to equilibrium and a negligible methane production. High activities and selectivities towards CO are obtained with the three novel Pt catalysts containing CeO_2, although significant amounts of methane are detected above 773 K. The conversions obtained over the Pt/CeO_2 based catalysts seem to be related to the surface area of the materials but strong metal-support interactions cannot be ruled out. Pt supported on silica and alumina catalysts are highly selective but exhibit poor activities. For the high temperature Fe-Cr catalyst conversions are slightly lower than for the Pt/CeO_2 catalysts but, as expected, its performance improves considerably as the reaction temperature approaches 773 K. Co-Mo is found to be inactive under the conditions assessed. The poor performance of Co/Mo is related to the absence of sulphur-containing molecules in the surrounding gas, which are required in low concentrations to activate the catalyst sites.

Temperature programmed water gas shift (TPR-WGS) experiments were carried out over Cu-Zn and Pt/CeO_2, catalysts, Figure 1. At low temperature Cu-Zn is more active than Pt/CeO_2 but the trend is reversed at ~ 680 K. With the residence time used, the conversion of Cu-Zn is always below equilibrium while Pt/CeO_2 reaches the thermodynamic limit at 770 K and above. The methane concentration measured for both catalysts was very low. The stability of the Cu-Zn and Pt/CeO_2 catalysts was assessed in WGS and SEWGS (in the presence of a hydrotalcite adsorbent) during 48 h. The activity and selectivity of both catalysts remained constant through the tests.

Table 1. CO and CH_4 yields (%).
Conditions: CO_2:H_2 =1:1, GHSV=60299 h^{-1}, 1bar

Catalysts	**573 K**		**673 K**	
	Y_{CO}	**Y_{CH_4}**	**Y_{CO}**	**Y_{CH_4}**
Cu-Zn	13.7	0.2	24.1	0.2
Fe-Cr	3.4	0.7	12.8	0.2
Co-Mo	0.1	0.3	1.1	0.9
1%Pt/Al_2O_3	1.7	0.9	2.8	0.5
1%Pt/SiO_2	0.4	0.2	2.3	0.1
1%Pt/CeO_2	4.9	0.2	15.3	0.5
1%Pt/20%CeO_2/SBA15	5.3	0.2	17.2	0.5
1%Pt/CeO_2/ZrO_2	6.8	0.2	19.1	0.7

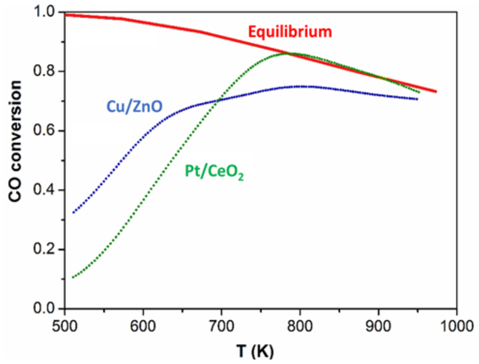

Figure 1. TPR-WGS over Cu-Zn and Pt/CeO_2 catalysts

4. Conclusions

The findings of this study suggest that among different commercial and in-house-synthesised WGS catalysts, Cu-Zn and novel Pt containing CeO_2 are promising candidates for the SEWGS. These catalysts exhibit high activities and selectivities, and are stable under the relevant operating conditions (473 to 723 K) of SEWGS in the presence and absence of a hydrotalcite-based CO_2 adsorbent.

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Keywords

Sorption-enhanced WGS, hydrotalcite-based CO_2 adsorbent, Cu-Zn and Pt-CeO_2 catalysts