Water gas shift activity of noble metals and promoted noble metals supported on ceria-zirconia oxides

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Water gas shift (WGS) reactors are critical components in fuel processors used in proton exchange membrane (PEM) fuel cells as systems that reduce the amount of CO poison that contaminates the cell stack. The WGS reaction:

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \quad \Delta H = -41.2 \text{ kJ mol}^{-1}$$

is an equilibrium limited, exothermic reaction that requires high activity high selectivity catalysts to maximize CO conversion to CO_2 while minimizing the formation of by products like CH_4. Supported CuO-ZnO catalysts have been the most commonly used WGS catalysts within an operating range of 180 ^oC to 350 ^oC [1, 2]. Ceria based oxide systems are key materials in three way catalysts in automobiles because of their ability to release and uptake oxygen [3]. These oxides have also been identified as promoters for the WGS reaction [4, 5, 6]. Grenoble et al. studied the effect of metal type on WGS activity over Al_2O_3 and SiO_2 supports [7]. There have been limited studies done on the trends in WGS activity of ceria supported precious metal catalysts. These studies have concentrated on Pt [5, 6, 8], Pd [5, 8], Rh [8, 9] and Au [6] catalysts.

The WGS catalyst development effort at UTRC looked at three aspects of catalyst development for ceria-zirconia supported noble metal catalysts. The first part of the work explored the effect of different types of noble metals (Pt, Pd, Ru, Rh, Ir and Au) on WGS activity under fuel processor reformate flow conditions, temperatures and pressures. Pt was identified as the best noble metal for the reaction. Figure 1 shows the effect of noble metal type on WGS activity.

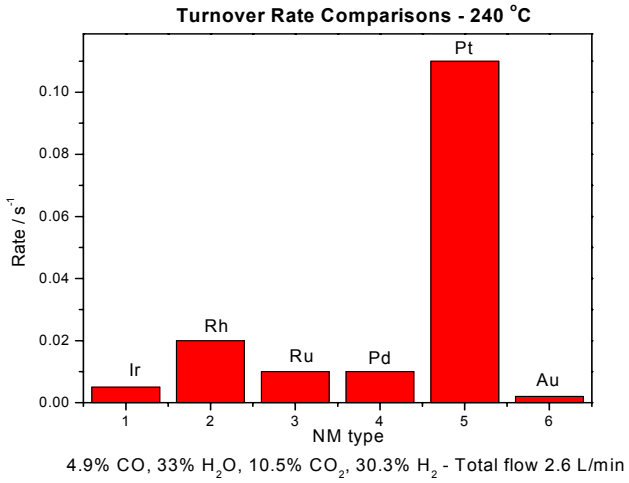

Figure 1. Effect of noble metal type on WGS activity

The second part of the work explored the effect of ceria-zirconia ratio on catalyst activity. The ratio was found to be critical in enhancing catalyst performance under specific reformate conditions. The third part of the studied looked at the effect of Fe on the WGS

activity. It was observed that Fe enhanced the WGS activity for ceria-zirconia supported Pd catalyst in agreement with Gorte[10] while producing an inhibitory effect for ceria-zirconia supported Pt catalyst. An effective metal promoter was identified for enhancing the WGS activity of ceria-zirconia supported Pt catalyst. Integral kinetic data on the promoted and un-promoted catalyst was fit (using Athena software) to a simple model given by:

$$\text{Rate} = A*\exp(-Ea/RT) * [CO]^a * [H_2O]^b * [CO_2]^c * [H_2]^d * (1-\beta) \quad (1)$$

where:

$\beta = ([CO_2] * [H_2]) / (K*[CO]*[H_2O])$ is the approach to equilibrium

A = Pre-exponential, Ea = Activation energy, T = Temperature

a = CO reaction order, b = H_2O reaction order, c = CO_2 reaction order, d = H_2 reaction order

Table I shows that the reason for enhanced performance for the promoted catalyst was due to a fundamental change in three kinetic parameters, the H_2O order, CO_2 order and H_2 order.

Table I. Kinetic Parameters for Catalysts between 240 ^oC – 210 ^oC

Parameter	*Un-promoted*	*Promoted*
CO	0.07	-0.05
H_2O	0.67	0.85
CO_2	-0.16	-0.05
H_2	-0.57	-0.32
Ea / kcal mol^{-1}	17	17
A	$2.5*10^7$	$4.5*10^6$
R^2	0.97	0.93

UTRC also identified a metal dopant for the ceria-zirconia support that enhances the catalyst high temperature (>400 ^oC) stability. The end result of the development work was customized high temperature and low temperature (<300 ^oC) catalysts that have been successfully qualified for commercialization.

References

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