

Abstract

Selective CO methanation (SMET), as an alternative process for cleaning trace CO in reformat gas feed for fuel cell applications, has gained increasing attention recently. This is mostly due to the fact that the technique can circumvent the major setbacks experienced in the preferential oxidation (PROX) reaction of CO to CO₂. The PROX technique is a more established process and has been extensively researched over the years. In this project, we have focused on studying Ru supported on carbon and titania based materials for the selective CO methanation reaction.

A rutile morphology in the form of a novel dandelion like structure was synthesized using TiCl₄. The rutile dandelion like structure was composed on rutile nanorods which were radially arranged and they had fairly high surface area (61 m²g⁻¹). Titania rutile was also synthesized by calcining anatase at 900 °C for 10 h. It was observed that the rutile grains had grown larger after the transformation from anatase to rutile and this was accompanied by a collapsed surface area (from 52 to 9 m²/g). The two rutile morphologies were employed as Ru catalyst supports and applied in both CO and selective CO methanation reactions. The dandelion like supported catalyst demonstrated higher catalytic performance compared to the thermally prepared rutile supports. This was attributed to the smaller Ru particles sizes which were found to be sinter resistant.

Small RuO₂ nanoparticle sizes supported on carbon nanotubes (CNTs) were obtained by the use of a microwave polyol synthesis. Tuning the microwave temperature generated the different RuO₂ sizes without changing the percentage loading or conventionally heat treating the catalyst. The CNTs were synthesized by a chemical vapour deposition (CVD) method using a Fe-Co/CaCO₃ catalyst. The microwave polyol synthesized catalysts were compared to a wet impregnated catalyst. It was noted that the impregnated catalyst preparation method showed little control over the RuO₂ particle size distribution. The catalysts were tested in both selective CO and CO methanation. The catalyst with smaller particle sizes, prepared using a short microwave induction time, performed better when compared to the other catalysts. It was also observed that all the catalysts promoted the undesired reverse water gas shift reaction for all the catalyst at temperatures above 260 °C.

The surface of the CNTs were altered by introducing pyridinic nitrogen in an in situ doping process to give nitrogen doped CNTs (N-CNTs). The doping was confirmed by TEM as the CNTs were seen to show bamboo compartments in the tubular CNT structure. A composite of CNT-TiO₂ was prepared by a facile hydrothermal process and used to modify the CNTs. The TiO₂ (anatase) coated CNTs were synthesized using titanium butoxide as anatase source. A solution containing CNTs and the TiO₂ source was reacted in an autoclave. Images from TEM and SEM revealed partially coated anatase N-CNTs and CNTs. Both the doping and the coating of the CNTs resulted in an improved surface area. The coated samples showed significantly improved thermal stability which was attributed to the shielding effect of the TiO₂. Raman analysis revealed that the N-CNTs had a high defect content compared to the CNTs. When these materials were employed as Ru catalyst supports for methanation reactions, the nitrogen doped CNTs demonstrated superior catalytic activity compared to the CNT supported catalyst. They both promoted the reverse water gas shift reactions. The NCNT-TiO₂ and CNT-TiO₂ catalysts showed higher activity and significantly retarded the reverse water gas shift reaction.

Mesoporous solid carbon spheres (CSs-H) synthesized *via* the hydrothermal route using sugar as carbon source was functionalized by acid treatment. The data were compared to an un-functionalized CSs-H used as a Ru catalyst support. Raman data suggested a high defect content for the functionalized spheres and the carbons had a slightly higher surface area when compared to the un-functionalized spheres. Two catalysts were prepared from the functionalized solid carbon spheres; a microwave irradiation prepared catalyst and a wet impregnation prepared catalyst. The microwave prepared catalyst, with slightly smaller Ru particles, performed slightly better in both CO and selective CO methanation reactions than the impregnated catalyst. In the CO₂ only methanation reaction almost similar activity was obtained for both catalysts which implied the preparation method did not have much effect on the reaction. The un-functionalized supported catalyst performed poorly in both the reactions due to the poorly dispersed Ru nanoparticles which had sintered. Despite the poor performance, the catalyst did not promote the undesired RWGS reaction. This was attributed to the absence of oxygenated functional groups such as OH.