Publishable summary

Silicon carbide is a well-known and widely used material due to its substantial heat conductivity combined with high chemical inertness and mechanical stability. Application in catalysis, nanofiltration or as nanoreactors requires a uniform mesoporosity and high surface area of the SiC. Porous SiC may actually be anticipated to find major applications as catalyst support in reactions with strongly exothermic character, in particular in the Fischer-Tropsch (FT) reaction; the use of more common supports (SiO_2, Al_2O_3, TiO_2, etc) with low heat conductivity may cause local ‘hot spots’, therefore affecting the selectivity and stability of the catalyst through metal sintering or chemical reaction with the support.

To produce porous SiC (pSiC) with well-ordered mesostructure and high surface area, two strategies were applied. The first strategy was based on the electrochemical etching of a bulk 3C-SiC polycrystalline wafer in water-diluted HF (12 % wt.) as electrolyte. Electrochemical pSiC samples were crystalline demonstrating the occurrence of a mesoporous structure (pore size ranging from 40 to 30 nm) with relatively high pore volume (0.85 to 0.68 mL g^{-1}) and surface areas of about 100 m^2 g^{-1}. The pore framework indicated free access of the pores and absence of bottle-necked pores. The samples were stable up to 500 °C in gas flows of either 20% O_2 in Ar or H_2.

A nanocasting synthesis strategy was used and included impregnation of a preceramic polymer (polycarbosilane, PCS) into the pores of a SiO_2 template, annealing of the resulting composite up to 1300 °C, and, finally, removal of the SiO_2 from the SiC pores. A commercially available Ludox® HS-30 colloidal solution, containing 12 nm SiO_2 nanoparticles with narrow size distribution, was proposed as a template for the synthesis of mesoporous SiC with uniform pore size (11 nm). For the larger pore size of 22 nm, a Ludox® TM-40 colloid was used consisting of 22 nm silica spheres. Synthesized pSiC samples were nanocrystalline demonstrating foam-like mesoporous structures (average pore diameters of 11 nm or 22 nm) with high pore volume (1 mL g^{-1}) and surface areas close to 400 m^2 g^{-1}. Modified silicas were also obtained from Ludox using azeotropic distillation with n-BuOH, and toluene for Ludox treated with trimethylchlorsilane (TMS). An improvement in the structural crystallinity was obtained by addition of Ni^{2+} ions to the initial PCS:SiC composite prior to the thermal treatment.

To impregnate porous silicon carbides with active metal for FT reaction studies, colloids of monodisperse cobalt particles were synthesized applying a “hot injection” technique. Accordingly, dicobalt octacarbonyl was used as a precursor and injected into the boiling dichlorobenzene solution. The presence of oleic acid as a capping agent avoided the coalescence of colloidal particles. Typically, 8 nm cobalt particles were used for impregnation into the pSiC. The impregnation was dominated by van der Waals forces in dry (water-free) chloroform. The as-prepared Co/pSiC samples were activated in hydrogen using temperature-programmed reduction (TPR) to remove oleic acid present on the surface of the Co particles.

A second approach to impregnate cobalt metal into pSiC consisted of cobalt salt deposition followed by its thermal decomposition/reduction to the metallic form. Slow cobalt oxalate precipitation from its nitrate salt and oxalic acid in dimethylformamide was used to immobilize cobalt inside the pores of SiC. However, cobalt metal particles showed extremely small sizes (lower than 4 nm) due to the shrinkage of the cobalt oxalate precursor inside the pores. Eventually, 20 wt% metal loading and higher was found as most appropriate to generate particles with sizes larger than 6 nm. The interest in such particles is associated with a particle size effect according to which the methane selectivity at small particle sizes is high (see, for instance den Breejen et al., J. Am. Chem. Soc. 2009, 131, 7197−7203). The use of water-dissolved cobalt citrate as a precursor for pSiC impregnation was also explored. Accordingly, cobalt citrate was activated in TPR up to 450 °C so as to anchor cobalt particles in the pSiC pore framework. The Co metal size distribution according to this method turned out to be relatively broad and centred at 8 nm. A uniform size and shape distribution of the particles similar to the “hot injection” technique was not reached this way.

Co/pSiC samples with 6 nm Co particles were passivated using 2% oxygen in argon flow followed by their transfer to a high-pressure reactor. Catalytic results of the Fischer-Tropsch reaction over these samples showed a suppression in methane formation while the C_{2+} selectivity considerably increased. For instance, a decrease from 23 to 12 % in methane production at 260 °C was obtained on Co NPs impregnated into pSiC as compared to Co NPs deposited on a classical Al_2O_3 support. This effect seems to match the conceptional idea that methane is formed by hydrogenation of surface carbon after CO dissociation while the chain lengthening involves a different mechanism (possibly via CO insertion, as reported by Schweicher et al., J. Am. Chem. Soc. 2012, 134, 16135−16138). For a poorly conducting support the heat removal due to the exothermic CO hydrogenation is inhibited, so it may be anticipated that larger amounts of carbon are formed compared to samples using a pSiC support. Higher methane selectivities of samples prepared via mobilization of cobalt using salt precursors as compared to samples impregnated with cobalt colloidal particles was attributed to a broad particle size distribution.

The use of intimate mixing of Co metal (which has chain-lengthening properties) with Cu (which hardly dissociates CO) provides a suitable combination for the formation of long-chain 1-alcohols via the Fischer-Tropsch process, which is presently under investigation in our laboratory. Long-chain alcohols are an important feedstock for plasticizers, lubricants, detergents, and etc. The selectivity towards 1-alcohol/1-alcene products has reached up to 95% in some cases as was reported by Xiang Y. et al. (J. Am. Chem. Soc. 2013, 135, 7114−7117). However, local hot spot formation may decrease the activity and also the selectivity to alcohols. Impregnation of porous silicon carbide with inorganic heterometallic Co/Cu complexes seems to be an interesting perspective to increase the yield of long-chain 1-alcohols. More generally, it is anticipated that pSiC with well-defined texture will find major applications as a mesoporous support for nanosized metal particles in exothermic catalytic reactions.