

## CO<sub>2</sub> methanation reaction over Ru doped CeO<sub>2</sub>

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Converting CO<sub>2</sub> into useful products is an important goal in today's world where our daily life contributes a lot towards CO<sub>2</sub> emission. In ideal situation, one would like to make use of energy sources free from carbon, however, the immediate attention can be given to look for the processes where CO<sub>2</sub> can be utilized to make various useful products. Converting CO<sub>2</sub> to methane in some sense is not a viable solution to make use of CO<sub>2</sub> as one of the reactants is expensive hydrogen. But if the hydrogen is cheaply available, this process looks promising because it is possible to achieve high selectivity and good conversion. Moreover, this reaction gives a way to understand the CO<sub>2</sub> interaction in the reducing conditions and giving an important opportunity to learn its catalytic chemistry.

We synthesized Ru doped CeO<sub>2</sub> of the form Ce<sub>0.95</sub>Ru<sub>0.05</sub>O<sub>2</sub> and tested it for CO<sub>2</sub> methanation reaction in presence of hydrogen. The catalyst was fully characterized by XRD, XPS and TEM. XRD showed no peak related to Ru metal or Ru oxide and there was an increase in lattice parameter. Increase in lattice parameter confirmed that there is a possibility of Ce<sup>3+</sup> formation in the bulk which gives rise to the lattice expansion. Further, XPS confirmed that Ru and Ce are in +4 oxidation state. TEM studies showed that the particle sizes are 30-40 nm. When tested for CO<sub>2</sub> methanation reaction in the gas stream of CO<sub>2</sub>, H<sub>2</sub> and Ar with the flow rate of 2, 8 and 12 cc/min, it showed 99% selectivity towards methane formation and 55% of CO<sub>2</sub> conversion. Reaction onset temperature was as low as 200°C. The reaction attains the maximum conversion at 450°C and after that the reaction behavior changes and there are few side reactions happening which hamper the CO<sub>2</sub> conversion towards methane. DRIFT experiments in the *in situ* reaction chamber are also carried out to completely understand the reaction mechanism and reaction intermediates. *In situ* experiments are carried out at 300°C as this temperature is sufficient to proceed the reaction in a reasonable fast rate. *In situ* experiments over Ce<sub>0.95</sub>Ru<sub>0.05</sub>O<sub>2</sub> catalyst in the gas stream having the composition and flow rates similar to that mentioned earlier show that CO<sub>2</sub> forms various kinds of carbonaceous species (carbonates, bicarbonates, adsorbed CO) only in presence of H<sub>2</sub>. In the absence of H<sub>2</sub>, CO<sub>2</sub> does not lead to any visible interaction with the catalyst surface and the spectrum looks almost featureless. The transient experiments have shown that CO<sub>2</sub> does adsorb on the catalyst. Thus, CO<sub>2</sub> is probably physisorbed on the surface but it chemisorbs only when H<sub>2</sub> is present in the gas stream. This gives us information that H<sub>2</sub> first reacts with the surface and makes it suitable for CO<sub>2</sub> chemisorption. It has been shown earlier by us that H<sub>2</sub> reacts with the Ce<sub>0.95</sub>Ru<sub>0.05</sub>O<sub>2</sub> surface and create vacancies and hydroxyls. Clearly, CO<sub>2</sub> chemisorption requires vacancies and/or hydroxyls. This can be further confirmed that when CO is interacted with the surface at the same 300°C, formation of carbonates, bicarbonates, and adsorbed CO are evident even without H<sub>2</sub>. CO reacts with the catalyst surface and makes CO<sub>2</sub> using the lattice oxygen thus creating vacancies. Thus, vacancies play important role in this reaction. Detailed mechanistic studies show the carbonates and CO are important intermediates and the methanation occurs via active 'C' formation which then methanate very fast to give the final product methane. In the last methanation step, directly gas phase H<sub>2</sub> is utilized rather than the hydrogenation via the hydroxyls. In this way, one can say that Ru doped CeO<sub>2</sub> of the form Ce<sub>0.95</sub>Ru<sub>0.05</sub>O<sub>2</sub> is an active CO<sub>2</sub> methanation catalyst and this study gives us insight towards understanding the CO<sub>2</sub> interaction over CeO<sub>2</sub> based materials.

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## Preparation and reactivity of sol-gel titania films on FeCrAl alloys and estimation of adhesion energy of alumina scales

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The sol-gel TiO<sub>2</sub> coatings were applied in order to improve the rapid transformation of alumina scales formed on the FeCrAl alloys during oxidation at high temperatures. The titanium-containing sol-gel coatings were prepared from the precursor tetra-isopropyl-orthotitanate (TIPT).

The preparation conditions such as solvent, concentration and pH were studied. The influence of pH and (solvent/precursor ratio) on gelification time was also studied. The adhesion energy was estimated using the tensile test in the SEM chamber for the samples oxidized in air at 850 and 950°C for 72 h.

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