E2-21: Investigation of active sites responsible for oxidative coupling using H and D labelled methane

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Breaking of C-H bonds over metal oxide catalysts can occur *via* heterolytic or homolytic pathways. To catalyze the heterolytic bond cleavage, strongly basic sites must be present. For the homolytic bond activation, the involvement of oxygen species such as surface peroxides is proposed. It is also known that the hydrogen exchange between simple hydrocarbons occurs *via* heterolytic bond cleavage. Therefore, if oxidative coupling occurs *via* heterolytic C-H bond cleavage, when CH_4 and CD_4 are present, both oxidative coupling and H-D exchange should occur simultaneously.

H-D exchange and oxidative coupling activities of 0.5 mol% Ba/MgO was studied. An equimolar mixture of CH_4 and CD_4 was passed over the catalyst at 850°C and the extent of H and D exchange in methane was measured as a function of CO_2 partial pressure, in the presence and in the absence of O_2. In the absence of oxygen no new products were formed, but exchange of H and D between CD_4 and CH_4 occurred. When CO_2 was added to the reactant stream, H and D exchange activity was markedly decreased. In the presence of oxygen, usual oxidative coupling products were observed, together with a very low H and D exchange in methane. Addition of CO_2 caused the H-D exchange to decrease further, but not the oxidative

coupling activity. These results suggest that, as the CO_2 partial pressure increased, the strongly basic sites were poisoned due to adsorption of CO_2. Therefore, it can be concluded that the heterolytic C-H bond cleavage was not important in oxidative coupling of methane.