

Mechanism of carbon dioxide hydrogenation over copper and nickel catalysts

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Involvement of such stable molecule as CO₂ into chemical transformation allows to produce practical valuable products. Conversion of CO₂ and H₂ mixtures in CO is perspective direction as CO is an initial material for many processes. Besides, one can derive such a composition of CO and H₂ which would be suitable for Fischer-Tropsch-synthesis regulating the reaction conditions. Hydrogenation CO₂ into CH₄ can be used to substitute for natural gas. The direction of CO₂ and H₂ mixture transformation depends on the metal nature in supported catalysts. It was shown [1] that CO formed as main product over Cu- and Fe-supported on carbon fibrous material (CFM) but formation of CH₄ proceeded mainly over Ni and Co on the same support. Cu and Ni catalysts were more active and selective catalysts than Fe and Co ones. In this work we studied the mechanism of CO and CH₄ formation over 10%Cu/CFM and 10%Ni/CFM using isotope, unstationary and stationary kinetics methods. The experiments under unstationary conditions were carried out in special reactor of small volume connected with a flight of time mass-spectrometer. Transient response method was applied in this case. The relaxation curves describing a transition of the system to a new steady state were obtained after a jump change of corresponding concentrations. H₂-D₂ exchange was investigated in the same system. Extent of exchange was determined from HD quantity. The m/e rations employed were as follows: 2 (hydrogen), 15 (methane), 18 (water), 28 (carbon monoxide), 44 (carbon dioxide). Kinetics of the reactions was studied in flow-circulating system at atmospheric pressure. Reaction temperature was 360-460°C for Ni-catalysts and 400-620°C for Cu-ones.

Experiments on H₂ and CO₂ adsorption, replacement of one component by other one and such as (He+H₂)/(H₂+CO₂) and (He+CO₂)/(H₂+CO₂) over Cu-catalysts showed that both components reacted from adsorbed state, CO₂ adsorption was firm and CO₂ replaced H₂. Extent of H₂/D₂ exchange reached 96% at 400°C and was equilibrium. It means that H₂ adsorption in reaction conditions is dissociative because of the reaction of HD formation proceeds from break of H₂ and D₂ bonds.

The responses of (He+H₂)/(H₂+CO₂) and (He+CO₂)/(H₂+CO₂) over Ni – catalysts showed that both components reacted from adsorbed state, CO₂ adsorption was weak and hydrogenation of carbon fragments formed during the reaction was fast. It was stated that the CH₄ formation is consecutive reaction.

The reaction step-scheme of CO and CH₄ formation was proposed over Cu- and Ni-catalysts using isotope, unstationary and stationary data.

1. A.L.Lapidus, A.Yu.Krilova, L.A.Tishkova, N.A.Gaidai, T.N.Myshenkova. *Neftechimia* 45 (2005) 274.

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