

CO₂ reduction reactions in heterogeneous oxidation and catalytic cracking processes

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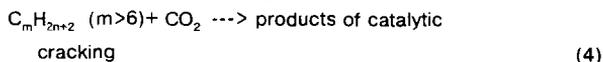
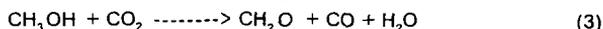
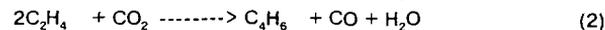
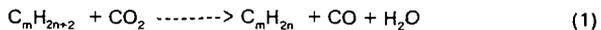
Abstract - The paper contains the results of heterogeneous catalytic activation of CO₂ by various organic substances, generalizes main scientific aspects of the new direction - "Oxidative Catalysis by Carbon Dioxide " ,and develop the petrochemical oxidative processes using carbon dioxide as an oxidant.

I.INTRODUCTION

Catalytic processes of oxidation of organic substances are realized mainly in the presence of oxygen. Low selectivity is characteristic of them due to partial conversion of crude product into CO₂.

In this connection the elaboration of new classes of oxidative processes, based on the nontraditional oxidant -carbon dioxide, is of great importance both to theory and practice and to environmental protection.

We aim to reduce CO₂ by hydrogen evolved from organic compounds IN SITU reaction,i.e. to realize the reduction of carbon dioxide with simultaneous selective oxidation of organic compounds. The reduction of carbon dioxide with alkanes, olefins, alcohols and highmolecular parafins were studied as examples of these reactions:



2.EXPERIMENTAL

Experiments were carried out in a flow vibro-fluidized catalyst bed reactor atatmosphere pressure.Catalysts were prepared by usual impregnation method on SiO₂ and Al₂O₃ usingappropriate metal salts.As metal salts Mn,Cr,Fe,K,Mo,V,W,Ca and Ni were used.These catalysts were dried at 120 °C and calcined at 700-800 °C for 5 hours.

3.RESULTS AND DISCUSSION

Model example of the specified reactions is the oxidation of methane by carbon dioxide. Investigation of CH₄ interaction with CO₂ showed that the traditional regularities of this reaction, known for nickel catalysts, are not valid in the case of manganese system, where there is no formation of carbon even during the reaction of CO₂ in equimolar mixture with CH₄. At 930 °C full conversion of CO₂ and CH₄ was observed, yielding the equimolar mixture of CO+H₂ [1].

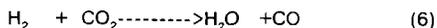
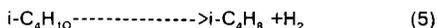
In the reaction of ethane with CO₂ the regularities of alkane oxidation with CO₂ change a little. The reduction of C-H bond energy in the case of ethane leads to the decrease of CO₂ activation temperature.

Reaction of C₂H₆ takes place at 800-830 °C. For simultaneous activation of CO₂ and dehydrogenation of ethane the catalyst has to combine reduction-oxidation and basic functions. K-Cr-Mn-O/SiO₂ system meets these requirements, in its presence the conversion of CO₂ satisfies to 52,3%, that of ethane was -82,6% with ethylene selectivity of 76,8 % [2]. Contents of ethylene and carbon monoxide in the reaction mixture are similar, thus making it possible to use this mixture without separation for carbonylation of ethylene.

The main tendency of propane oxidation with CO₂ is similar to those observed one in ethane conversion. During oxidation of propane by carbon dioxide the products are C₃H₆, C₂H₄, CO. In the presence of K-Cr-Mn-O/SiO₂ catalyst at 830°C olefins yield was 73% with the olefins selectivity of 78%. [3].

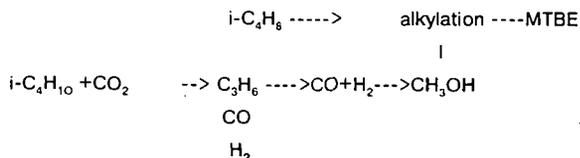
Another regularity is characteristic for isobutane rehydrogenation. The reaction of isobutane with carbon dioxide proceeds mostly by dehydrogenation mechanism followed by hydrogen oxidation. Apparently this is the result of quick decreasing of C-H bond energy in the row from methane to isobutane.

Stoichiometric equations of isobutane conversion can be represented as follows:



The yield of isobutylene in this reaction amounts to 45%, and its concentration was 20% in gas volume. The ratio of CO to H₂ is close to 1 with the high isobutylene selectivity (82 %).

Propylene in this case is by-product. The gas composition allows to recommend the new alternative process of isobutane oxidation by carbon dioxide with production of MTBE:



Combination of endothermic reaction of isobutane dehydrogenation with exothermic one of methanol production from CO+H₂ makes it possible to decrease twice energy consumption of the process and carry it out partially by thermoneutral scheme.

One of the new reactions with CO_2 participation is ethylene oxidation, which is characterized by ethylene dehydrodimerization into butadiene. Cleavage of the C-H bond in ethylene with formation and dimerization of vinyl radicals in the presence of mild oxidant - carbon dioxide, unlike molecular oxygen, proceeds selectively. Conversion of C_2H_4 in this process is not yet high, butadiene yield is 8-10% [4].

During CO_2 reaction with methanol takes place the partial oxidation reaction. On Mo-Mn-O/ SiO_2 catalyst high selectivity of CH_2O formation (90%) takes place [5].

Mechanism of CO_2 reduction during oxidation of organic substances have been established and showed that the properties and reactivity of surface oxygen, generated by carbon dioxide is different essentially from the properties of oxygen, generated from molecular oxygen.

The surface oxygen, generated by carbon dioxide, is homogeneous, but the content of the oxygen, generated by CO_2 , in catalyst, is 5-6 times lower, than in the case of reoxidation by molecular oxygen.

The study of the conversion of various organic substances under the condition of stages separation showed that the rate of CO formation during CO_2 reduction in catalyst reoxidation stage is much lower, than the rate of CO formation under stationary conditions. Besides CO_2 reduction and catalyst reoxidation proceed with high rate only at higher temperatures than 700°C . At the same time under stationary conditions CO_2 reduction up to CO occurs mainly from 620°C . In order to elucidate this phenomenon, we carried out experiments with addition of 1-2% H_2 into CO_2 . It has been established, that the addition of 1% H_2 into CO_2 leads to abnormally sharp increase of CO_2 reduction rate to CO.

The observed phenomenon and the initiating effect of H_2 is probably connected with CO_2 reduction proceeding in the presence of hydrogen by new chain mechanism.

This mechanism of CO_2 activation allows to carry out in its presence not only the reactions of reduction-oxidation type, but also of acidic basic ones. Such possibility has been discovered in new reactions of oxidative cracking. Thus, destructive conversion of heptane, which was chosen as a cracking model hydrocarbon in the presence of CO_2 proceeds more efficiently than in its absence [6].

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