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Catalyst properties and direction of selective oxidative transformations of C_1–C_3 paraffins

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Abstract

The mechanism of two major directions for the selective oxidative transformations of lower paraffins; (i) dehydrogenation and coupling; and (ii) oxidation with oxy-product formation are considered. Oxidative dehydrogenation and coupling are 'in temperature reactions', which proceed at the temperature required for effective hydrocarbon activation, with the participation of the lattice oxygen. The reactions with oxy-product formation, due to product instability, proceed at lower temperature ('under-temperature reactions'), when an effective interaction of hydrocarbon with the lattice oxygen cannot take place. For these reactions the participation of active forms of oxygen on the catalyst surface is necessary, this limited the maximum yield of the product due to competition and deep oxidation. For the coupling and dehydrogenation reactions, basic catalysts are more preferable, while for the reactions with oxy-product formations, acid catalysts are necessary.

1. Introduction

The direct oxidative transformation of lower paraffins to valuable products remains one of the more challenging fields of chemistry because it is very attractive to use natural gas as a raw material for the production a number of products traditionally produced from oil [1,2]. Two major group of products can be formed in selective oxidative transformations of lower paraffins: (i) hydrocarbons with the lower contents of hydrogen as a result of oxidative dehydrogenation or oxidative coupling; (ii) oxy-products with an incorporation of oxygen into the hydrocarbon molecules. These two routes require different reaction conditions and different catalysts. The mechanism of these two major pathways for the selective oxidative transformation of low paraffins as well as the catalysts properties needed, for one or other route will be considered in this presentation.

2. C–H bond activation and optimal reaction temperature

For the selective oxidative transformation of hydrocarbons on solid oxides, very important is a specific activation of the C–H bonds. It has been shown for the selective oxidation of olefins that high selectivity is first of all a result of a high rate of selective oxidation due to the specific activation of the hydrocarbon molecule [3]. The stronger the C–H bond which has to be activated, the stronger must be the active centres on the catalysts surface to succeed with the activation process. On the other hand, if we accept that the centres for the activation are basic or acid sites on the catalyst surface, the stronger the active centres used, the higher the temperature that will be required to dehydrate the surface in order to complete the catalytic cycle. This means that a correlation between the strength of the C–H bond which is to

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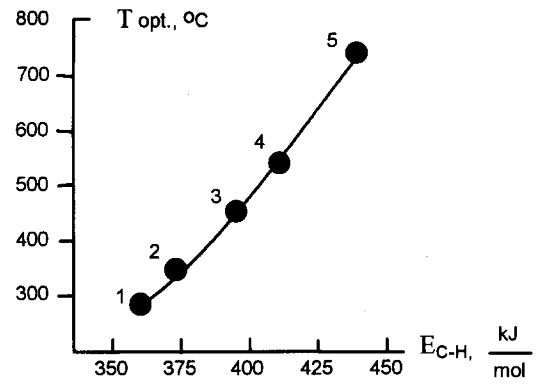

Fig. 1. Dependence of the optimal reaction temperature on the C–H bond energy in the reactions: (1) acrolein-to-acrylic acid, (2) propylene-to-acrolein, (3) butane-to-maleic anhydride, (4) propane-to-acrylonitrile, (5) methane-to-ethylene.

be oxidized and the optimal temperature of a reaction could be expected. In Fig. 1 the energies of the C–H bonds are plotted against the optimal reaction temperatures for a number of reactions, including the industrial processes for conversion of acrolein into acrylic acid, propylene to acrolein, butane to maleic anhydride, as well as the new reactions for the ammoxidation of propane on a gallium-antimonate-based multicomponent catalyst (optimal temperature 550°C) and methane oxidative coupling (optimal reaction temperature according to many papers [1,2] between 700 and 800°C and can be taken about 750°C). One can see that there is quite a clear correlation between these two parameters.

The above correlation shows what temperature of reaction for selective oxidative transformation of organic compounds has to be used to achieve the effective activation of the C–H bonds. At the same time the desirable reaction products must be stable enough in order to obtain a reasonable yield under these conditions. If the stability of product is rather low, the mechanism, which includes the hydrocarbon activation as a crucial step (and, correspondingly, catalysts operating via this mechanism), cannot be used.

3. Mechanism of oxygen participation

One can suppose that at the optimal temperature the hydrocarbon activation step creates intermediates which are active enough to interact with the oxygen of the catalyst in the process of product formation.

The results of investigations of the route of the oxygen participation in the reactions of propane ammoxidation and methane oxidative coupling, both of which proceed at the temperature corresponding to the conditions of their effective activation, are shown in Tables 1 and 2.

Table 1 compares the rates of propane ammoxidation on a number of catalysts with a 'full' reaction mixture 'catalysis' and of the interaction of the same reaction mixture but without oxygen with the surface of a catalyst which had first been treated by the full reaction mixture until steady-state catalysis has been achieved 'reduction' [4].

The data presented indicate clearly that the oxygen of the catalyst can participate in product formation and that the interaction of hydrocarbon

Table 1
Comparison of Catalysis and Reduction rates on the steady-state catalyst in propane ammoxidation (550 °C, 0.5% C_3H_8, 0.6% NH_3, 1.86% O_2, the rest - He).

Catalyst	Rate × 10^{-11} molec C_3H_8/cm^2 × s					
	Catalysis			Reduction		
	C_3H_8	C_3H_3N	CO_2	C_3H_8	C_3H_3N	CO_2
$Ga_1Sb_{19}O_{49}$	5.23	0.56	4.67	4.59	0.56	4.03
$Ga_1Sb_3Ni_{1.5}P_1O_{20.5}$	0.54	0.48	0.06	0.51	0.48	0.04
$Ga_1Sb_{2.5}Ni_{1.5}P_1W_{0.25}O_{12.5}$	0.59	0.33	0.26	0.54	0.32	0.22

Table 2
Comparison of the product amount in the reaction of methane partial oxidation on silica and silica supported catalysts with full and oxygen-free reaction mixtures (550 °C, 20% CH_4, 10% O_2, the rest - He).

Catalyst	Reagents	Product amount, 10^{17} molec/pulse		
		HCHO	CO	CO_2
SiO_2	$CH_4 + O_2$	0.78	0.94	0.53
	CH_4	-	-	-
4% MoO_3/SiO_2	$CH_4 + O_2$	0.37	0.17	0.46
	CH_4	-	-	-
5.3% V_2O_5/SiO_2	$CH_4 + O_2$	2.07	0.88	0.59
	CH_4	-	-	-

with the catalyst surface oxygen occurs with a sufficient rate of the reaction comparable with the rate of reaction in 'catalysis' (i.e. with the full reaction mixture).

Comparable data for the rate of oxidative coupling of methane with a methane–oxygen mixture and the rate of the product formation in the process of methane interaction with the catalyst surface for lead-containing catalysts supported on MgO and alumina at 750°C, obtained by Asami and co-workers [5] provides evidence that methane oxidative coupling under these conditions also proceeds via the involvement of lattice oxygen. The participation of lattice oxygen in methane oxidative coupling over Li/MgO catalyst under steady-state conditions has also been confirmed by isotopic transient kinetic analysis [6].

However, quite a different picture can be observed for reactions of lower paraffins taking place under conditions when effective hydrocarbon activation probably does not occur. The first example to be considered is the reaction of the ammoxidation of ethane to acetonitrile. For this reaction, we have failed to find any catalyst which can operate effectively at high temperature. This is presumably because of product instability (it has been shown that acetonitrile formation proceeds via acetaldehyde as intermediate [7]) at temperature around 600–700°C; all catalysts tested, including effective catalysts for propane ammoxidation, resulted in only total oxidation products. These catalysts which have been found to produce acetonitrile — scandium and chromium molybdates — work effectively at rather low temperatures: 400–450°C. As was pointed out above, we could not expect any effective ethane activation at this temperature. In this case, it is more probable that some active oxygen species must be created with which the hydrocarbon molecule can interact. Results of a study of the mechanism of the participation of the separate components of the reaction mixture for acetonitrile formation using the pulse technique are presented in Fig. 2 [7].

These data indicate that acetonitrile is not formed in any oxygen-free mixture (RN, R, N pulses). This means that lattice oxygen is unable to give the products of selective oxidation. Another oxygen form, presumably partially-reduced active oxygen on the catalyst surface, participates in the reaction.

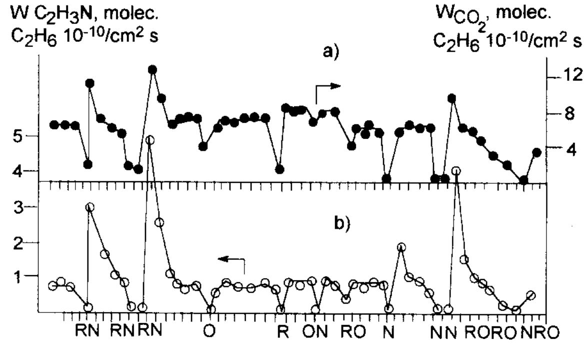

Fig. 2. Rate of the formation of reaction products upon pulsing the components of the reaction mixture on a steady-state catalyst. R, O, N — signify ethane, oxygen and ammonia, unmarked pulses — full reaction mixture — RON. The component concentrations in the mixture were (vol.-%): 0.5, C_2H_6; 0.5, NH_3; 1, O_2; balance He. (Scandium molybdate, T = 500°C). (a) Carbon dioxide, (b) acetonitrile.

A similar situation has been observed recently by Parmaliana and co-workers for the partial oxidation of methane to formaldehyde on silica-supported vanadia and molybdena. The optimal temperature for this reaction has been found to be rather lower than we expected for the temperature of effective methane activation (see Fig. 1). The reason for this may be the instability of formaldehyde at high temperatures. The results of the study of oxygen participation in this reaction are presented in Table 2 [8].

One can see the product formation occurs only in the presence of oxygen in the reaction mixture, showing that lattice oxygen is unreactive under the reaction conditions. As for the ethane ammoxidation reaction considered above, active oxygen species different from lattice oxygen are necessary to participate in this reaction. A similar conclusion has been made recently by Kartheuser et al. [9], who studied the oxidation of methane to formaldehyde on silica-supported vanadia by a temporal analysis technique.

4. Role of acid–base properties

The nature and properties of the intermediate species being formed during the process of hydrocarbon activation depend on the properties of the centres on the catalyst surface. The heterolytic C–H bond cleavage can occurs on either basic or acid centres. If hydrocarbon activation should proceed on a basic centre, a negatively charged carbanion-type intermediate bonded with the surface metal cation is formed. An alkyl anion with a carbon atom number more than one can easily release hydride ions and, as a result, a dehydrogenation reaction will take place. Methyl anion after electron transfer can be desorbed as a methyl radical leading to the formation of coupling products [10]. On an acid site, the formation of positively charged hydrocarbon fragments stabilized on the oxygen anion as alkoxy groups occurs [10]. It has been shown for the methoxy group [10], that this intermediate could be a precursor for both directions: oxy-product formation, as well as coupling reaction. The latter can occur when the methoxy group is stabilized on a centre possessing low acidity which facilitates C–O bond cleavage and methyl radical desorption. If the methoxy group is stabilized on a strong acid centre, the C–O bond must be quite strong and oxy-product formation seems to be preferable. As has been discussed above, because the latter reaction should be carried out at rather low temperature, the reactivity of surface oxygen is not high enough and the active surface oxygen forms must be present for the hydrogen abstraction and oxy-product formation.

5. Conclusion

The reactions of oxidative dehydrogenation and coupling of lower paraffins can be performed at high temperature at which effective activation of the hydrocarbon molecules take place and the lattice oxygen can participate in the reaction, provided that high selectivity is obtained at the rather high level of the initial reagent conversion. These reactions can be named ‘in-temperature reactions’. In contrast, for partial oxidation reactions of lower paraffins with oxy-product formation, the optimal temperature of reaction due to a low product stability must be much lower than the temperature at which effective activation of hydrocarbon occurs. In this case, formation of active oxygen species which can participate in the reaction must take place. This type of reaction could be named ‘under-temperature reactions’. Due to the necessity of the active oxygen to participate in ‘under-temperature’ reactions, we have to expect rather a fast decline of selectivity with increase in conversion and consequently much lower yields of the product in comparison with ‘in-temperature reactions’. The catalysts for these two major directions for selective oxidative transformations C_1–C_3 paraffins must also possess different acid–base properties. The reactions of dehydrogenation and coupling proceed predominantly on basic catalysts, while for the reactions with oxy-product formation is preferable on acid catalysts.

6. Acknowledgement

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7. References

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