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A Kinetic Study of Oxidative Dehydrogenation of Isobutane to Isobutylene over Chromium Oxide Supported on Lanthanum Carbonate[1]

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Abstract—Kinetics of oxidative dehydrogenation of isobutane to isobutylene over chromium oxide supported on lanthanum carbonate was studied. The formation rate of isobutylene was found to be first order in isobutane and zero order in oxygen concentration and the rate limiting step was the regeneration of active sites by the gas phase oxygen. The formation of CO_2 was due to the consecutive oxidation of isobutylene which occurred on the same active sites used for isobutylene formation, not by the parallel oxidation of isobutane.

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Oxidative dehydrogenation of isobutane to isobutylene has received considerable attention in recent years. Many supported and unsupported metal oxides have been found to yield good conversion and selectivity in oxidative dehydrogenation of isobutane to isobutylene [1–18]. Among the large number of metal oxide catalysts being studied, supported chromium oxide was proven to be a promising catalyst for the oxidative dehydrogenation of isobutane to isobutylene. Chromium oxide catalysts on different supports (Al_2O_3, SiO_2, TiO_2, CeO_2, and $La_2(CO_3)_3$) were found to be active and selective at temperatures lower than 300°C [4, 5, 7, 9–13, 16]. Grabowski et al. [11] have studied the oxidative dehydrogenation of isobutane over chromium oxide supported on various metal oxides at temperatures between 200–400°C and reported selectivities to isobutylene of up to 73% at 5% of isobutane conversion. An isobutylene yield of 9% has been obtained on CrO_x/TiO_2 and K-promoted CrO_x/Al_2O_3. Moriceau et al. [9] reported 57% isobutylene selectivity at 10% of the isobutane conversion on a binary catalyst of Cr–Ce–O at 270°C, Elbashir et al. [16] have shown that alumina supported chromium oxide exhibited isobutane conversion of 10% and isobutylene yield of 6% at 250°C.

Supported chromium oxide is well known to possess high activity for the selective oxidation of hydrocarbons [1, 7, 19–21]. The catalytic performance of supported chromium catalysts are strongly affected by the acidity/basicity of the oxide support [22] and the nature of the support [11]. The reactivities of the surface chromium oxide species are controlled primarily by metal-support interactions as the bulk oxides such as CrO_3 or Cr_2O_3 are believed to be inactive phases [23]. Moriceau et al. [18] have studied the oxidative dehydrogenation of isobutane on Cr–Ce–O oxide catalyst and also found that agglomerates of Cr_2O_3 did not contribute to the reaction. It was found the activity of the catalyst was due to the well dispersed $Cr^{6+}O_x$ species on the ceria surface.

Chromium-manganese catalyst supported on silica has been studied by Mirzabekova and Mamedov for dehydrogenation of isobutane in the presence of carbon dioxide [24]. Over this catalyst, the reaction of isobutane with carbon dioxide proceeds mainly through the dehydrogenation pathway with subsequent oxidation of hydrogen. Grzybowska et al. [8] found that the main reaction of isobutane with oxygen is the oxidative dehydrogenation to isobutylene in the presence of chromium oxide supported on alumina catalyst, with the selectivity at 10% and conversion higher than 50%.

The oxidative dehydrogenation of isobutane to isobutylene over chromium oxide supported on lanthanum carbonate has been previously reported [12–15]. This catalyst has been found active and selective for this reaction. In pulse reactor, selectivity of greater than 95% at reasonable activities has been achieved at temperatures below 250°C. Water and carbon dioxide are the only other reaction products observed. The performance of the catalyst was found to be a function of chromium oxide loading and activation conditions. There is no detectable coke formation and carbon balances were routinely found to be better than 98%.

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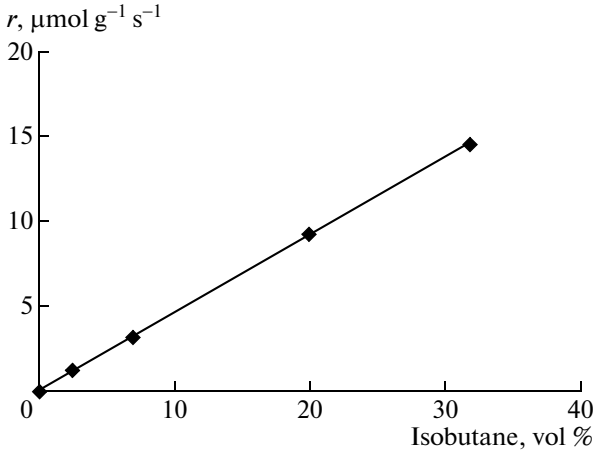

Fig. 1. Rate of isobutylene formation as a function of isobutane content (temperature 195°C, GHSV = 30000 h^{-1}).

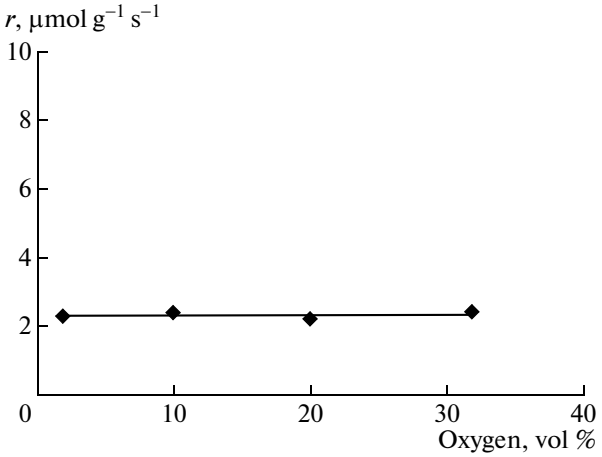

Fig. 2. Rate of isobutylene formation as a function of oxygen content (temperature 195°C, GHSV = 30000 h^{-1}).

Reaction kinetics is an important aspect of catalysis. It can contribute to the understanding of reaction mechanisms, and thereby spark ideas for formulation of new catalytic systems. Despite great attention to the oxidative dehydrogenation of isobutane to isobutylene, only limited research has been conducted on the kinetic study of this reaction [10, 25–28]. Madeira et al. [26, 27] studied the kinetics and mechanisms of the *n*-butane oxidative dehydrogenation over a 3% Cs-doped α-$NiMoO_4$ catalyst and proposed a kinetic model based on a redox (Mars–van Krevelen) mechanism.

This paper presents a study of the kinetics of oxidative dehydrogenation of isobutane over chromium oxide supported on lanthanum carbonate.

EXPERIMENTAL

Catalyst Preparation

The mixed carbonate precursor was prepared by the drop-wise addition of a mixed solution of $La(NO_3)_3 \cdot 6H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$, in a predetermined mole ratios, to a stirred solution of NH_4HCO_3. The resultant hydro gel was separated by centrifugation, washed with water and then with acetone. The product was first dried at room temperature in an air stream and then at 110°C in air for 4 h. The final catalyst was obtained by calcination at 300°C in air for 2 h.

Kinetics Measurement

Kinetic studies were carried out in a differential-mode reactor. Details of the testing reactor have been previously reported [12]. In order to eliminate mass and heat transfer effects, catalyst testing was carried out at a very short residence time (0.12 s) which was achieved by working at a space velocity of 3×10^4 h^{-1}. The feed stream was also diluted with He.

The catalytic activity is expressed as the rate of product formation (isobutylene for the oxidative dehydrogenation and CO_2 for the combustion).

RESULTS AND DISCUSSION

Rate Dependency on Isobutane

The formation rate of isobutylene as a function of isobutane concentration in feed gas is shown in Fig. 1. Oxidative dehydrogenation of isobutane is a two electron process, consuming only 0.5 oxygen molecules. Thus in this experiment, the oxygen concentration was kept constant at 20 vol % and the oxygen/isobutane ratio was >0.5. As can be seen from Fig. 1, the formation rate of isobutylene is first order in isobutane.

Rate Dependency on Oxygen

The influence of oxygen concentration on the formation rate of isobutylene is illustrated in Fig. 2. In this experiment, the isobutane concentration was kept constant at 2.9 vol %. Again, the oxygen/isobutane mole ratio was maintained >0.5. At oxygen concentrations >2 vol %, and within the experimental error of <10%, the reaction was found to be zero order in oxygen. However, the non-zero intercept of the rate as a function of oxygen concentration is observed indicating a contribution of lattice oxygen from the catalyst surface to the reaction.

The reaction mechanism involving a paraffinic hydrocarbon at the catalyst surface involves an electron donating/accepting mechanism in which the hydrocarbon acts as an electron donor. In principle, the basic nature of the surface of the catalyst promotes hydrogen abstraction from hydrocarbons.

Oxidative dehydrogenation of isobutane possibly proceeds by the following path:

$$i\text{-}C_4 \longrightarrow i\text{-}C_4[S] \longrightarrow CO_2$$
$$\searrow \quad \nearrow$$
$$i\text{-}C_4^{=}$$

Here [S] denotes a site for chemisorption.

Considering only the selective reaction for the formation of isobutylene, firstly an initialising reaction step takes place, assumed to be the formation of an adsorbed isobutane intermediate. The reduction of the active site [S] by isobutane is followed by the formation of isobutylene:

$$i\text{-}C_4H_{10} + [S] \xrightarrow{k_r} i\text{-}C_4H_8 + [S^*] + H_2O.$$

The reduced site [S*] is then regenerated by oxygen supplied from the gas phase:

$$[S^*] + 0.5O_2 \xrightarrow{k_o} [S].$$

The overall reaction is

$$i\text{-}C_4H_{10} + 0.5O_2 \rightarrow i\text{-}C_4H_8 + H_2O.$$

In this equations k_r and k_o are the rate constants of the reduction and oxidation of active site respectively. This redox reaction seems to be the key for the oxidative dehydrogenation mechanism.

At steady-state the overall rate of reaction can be expressed as:

$$r = \frac{k_r P_{C_4} k_o P_{O_2}}{k_r P_{C_4} + k_o P_{O_2}}$$

or

$$\frac{1}{r} = \frac{1}{k_o P_{O_2}} + \frac{1}{k_r P_{C_4}}.$$

As suggested previously, at oxygen concentrations more than 2%, the reaction rate is independent of the oxygen partial pressure in the gas phase. From the experimental data, at 468 K,

$$k_o = 1.4 \times 10^{-7}\ \text{mol s}^{-1}\,\text{g}^{-1}\,\text{kPa}^{-1}$$

and

$$k_r = 2.3 \times 10^{-6}\ \text{mol s}^{-1}\,\text{g}^{-1}\,\text{kPa}^{-1}.$$

From this analysis, the limiting step of the oxidative dehydrogenation of isobutane over supported chromium oxide/lanthanum carbonate catalyst appears to be the regeneration of active sites by gas phase oxygen.

In alkane oxidation, it is well known that the first step of the reaction involves the formation of a radical intermediate. It is reasonable to assume the same activation step for isobutane. Thus, isobutane is first activated by a catalyst that abstracts an H atom from the molecule to form an adsorbed isobutyl radical intermediate. This step requires the presence of a very reactive surface oxygen species such as Cr=O, and the catalytic activity can be related to the amount of this species at the catalyst surface. In a previous study [15], we reported the presence of Cr=O species on the catalyst surface. The catalytic property of supported chromium oxide/lanthanum carbonate is due to the surface Cr(VI) oxide species, rather than to bulk oxide or $LaCrO_3$. The reaction rate is also inversely dependent on the strength of the C–H bond. The bond energy of tertiary C–H is 375 kJ/mol compared to 395 and 410 kJ/mol for secondary and primary C–H bonds respectively [25]. This makes the hydrogen abstraction from isobutane much easier.

In the lower hydrocarbons, the primary radicals are generally active; they often react with surface oxygen from the catalyst or oxygen in the gas phase to form precursors for combustion products. In contrast the tertiary radical in H-abstracted isobutane is more stable. The most likely reaction of this radical becomes the loss of second hydrogen to form isobutylene. It is reasonable to suggest that the most important function of the catalyst is to facilitate the activation of the isobutane molecule by providing a sufficient number of suitable active sites for the reaction. The activity and selectivity of the catalyst are possibly influenced by the ionic strength of the Cr–O bond.

Although the regeneration of active sites is the limiting step, it appears that adsorbed oxygen from the gas phase and lattice oxygen in the catalyst attain equilibrium fairly rapidly even at low reaction temperatures. The performance of this catalyst has been reported in previous publications [13, 15]. In a pulse reactor operated at 150 kPa and at 240°C with a pulse size of 4.25 μmol, the catalytic activity decreased by about 54% over the first six pulses. However it could be restored by exposure to two pulses of oxygen at the reaction temperature. The catalyst has been tested for up to twenty reduction-oxidation cycles without loss of catalytic activity.

Activation Energies

Change in isobutylene formation rate as a function of inverse temperature is shown in Fig. 3. Arrhenius analysis for isobutane conversions below 5% yields apparent activation energy for the formation of isobutylene of 76 kJ/mol. Activation energies of 92 and 113 kJ/mol for oxidative dehydrogenation of *n*-butane to 1-butene and isobutane to isobutylene respectively on Mg-vanadate has been reported by Kung et al. [25].

It has been observed from the gas phase analysis that the reaction occurs at 100% selectivity to isobutylene at temperatures below 215°C. The reaction rates in this region therefore represent the rate of isobutylene formation. At temperatures higher than 215°C, CO_2 starts to form and increases as the temperature was increased. However it can be seen from Fig. 3 that the same activation energy was observed for this region. This suggests that the formation of CO_2 was possibly due to the consecutive oxidation of isobutylene, not by the oxidation of isobutane (parallel path). It is well understood that hydrocarbons and oxygen (either gas phase or lattice) can participate in a network of competing parallel and consecutive reactions.

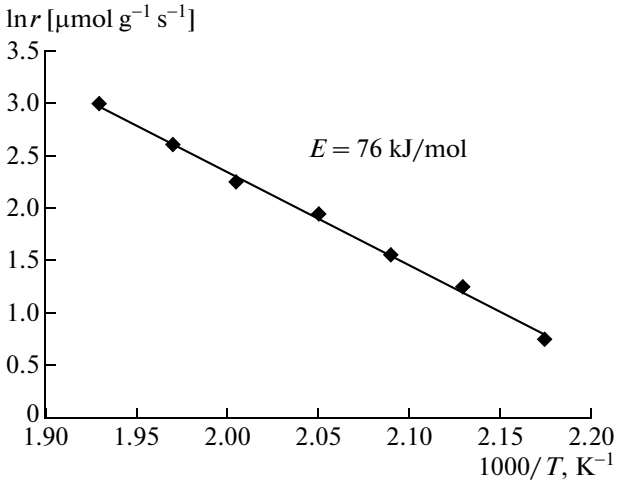

Fig. 3. Arrhenius plot for isobutylene formation on 10% $Cr_2O_3/La_2(CO_3)_3$.

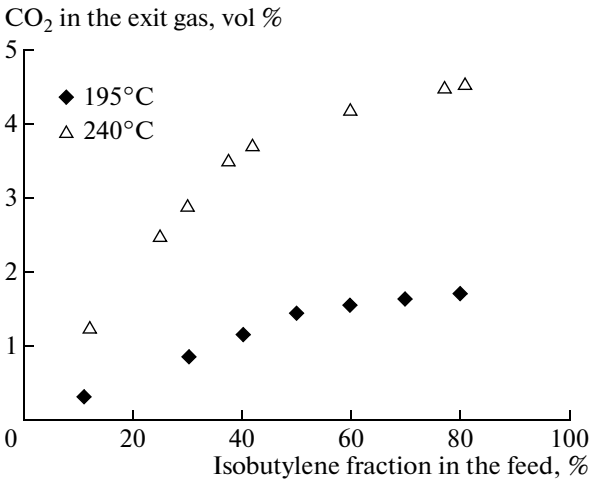

Fig. 4. Effect of isobutylene addition on the formation of CO_2.

Carbon Dioxide Formation

To further support the above suggestion, another set of experiments was carried out in which isobutylene was added to the oxygen/isobutane mixture and an analysis for CO_2 in the exit gas was made. Figure 4 shows the formation of additional CO_2 as a function of isobutylene fraction in the feed gas at 195 and 240°C. At 195°C and with premixed oxygen/isobutane used as the reaction feed, the selectivity of isobutylene formation was 100%. Upon addition of isobutylene to the feed stream, CO_2 was detected in the exit gas. Analysis of the data from Fig. 4 shows that over the isobutylene fraction range of 10–50%, the additional CO_2 in the exit gas varies linearly with isobutylene concentration. The formation of CO_2 then falls away from the linear extrapolation as the isobutylene fractions reach 50%. This is probably due to the limitation of active sites in the catalyst. At 240°C, and with premixed oxygen/isobutane used as the reaction feed, the selectivity to CO_2 was 30%. Upon addition of isobutylene to the reaction feed, the concentration of CO_2 in the exit gas increased significantly. Over the isobutylene fraction range of 10–30%, a straight line was observed; the plot then again deviates from linearity at the end. On extrapolating the experimental data of the low isobutylene fraction region to origin, results obtained at 195 and 240°C both fall onto a straight line. This result provides more evidence that CO_2 is produced by a consecutive step.

Reactivity of Isobutylene on the Catalyst Surface

The problems in the oxidative dehydrogenation of alkanes are not only the alkanes activation but also the stability of the reaction products. Olefins often participate in total oxidation by further reacting with surface oxygen or oxygen available from the gas phase. The formation of CO_2 from isobutylene has been further investigated by using oxygen/isobutylene mixture as a feed gas. At 240°C the oxidation of isobutylene gave 100% selectivity to CO_2. No evidence of any formation of CO and oxygenates was found.

The isobutylene combustion appears to be of first order in isobutylene, as can be seen in Fig. 5. In this experiment, the oxygen concentration was kept constant at 25 vol % so that the oxygen/isobutylene ratio >6.

In contrast to the rate of isobutylene formation, the rate of isobutylene combustion appears to be first order in oxygen (Fig. 6). Again, a non-zero intercept of the rate as a function of oxygen concentration indicates the contribution of lattice oxygen to the reaction. An intercept value of 3.2×10^{-5} mol g^{-1} s^{-1} was obtain by extrapolating the experimental data to $[O_2] = 0$.

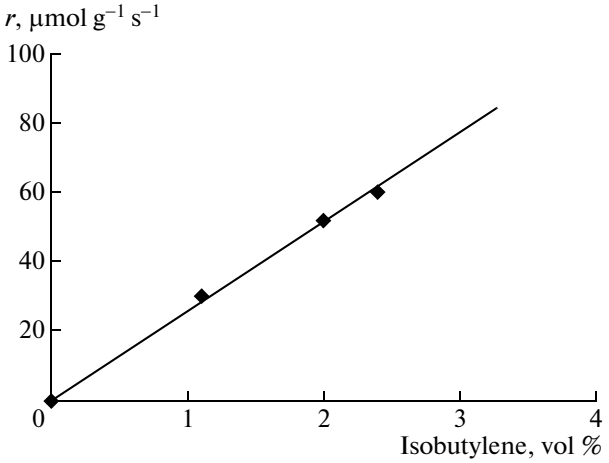

Fig. 5. Rate of isobutylene combustion as a function of isobutylene content (temperature 240°C, $[O_2] = 25$ vol %).

Isobutylene combustion kinetics over chromium oxide/lanthanum carbonate catalyst may involve parallel oxidation mechanism utilising two different sources of surface oxygen: (*i*) lattice oxygen, which depends on the nature of the catalyst, and (*ii*) chemisorbed oxygen, which is strongly dependent on both the catalyst surface property and the oxygen partial pressure in the gas phase. Both oxygen sources are formed reversibly on the surface of the catalyst. The rate of isobutylene combustion thus can be expressed as follows:

$$r_{com} = k_1 P_{i\text{-}C_4} + k_2 P_{O_2} P_{i\text{-}C_4}.$$

Here k_1 is the rate constant for reaction involved with lattice oxygen and k_2 is the rate constant for reaction involved with chemisorbed oxygen.

Accordingly, the contribution of both lattice and chemisorbed oxygen to the reaction can be derived from data plotted in Fig. 6. The contribution of chemisorbed oxygen can be evaluated from the slope and the intercept represents the contribution of lattice oxygen. At 240°C the major contribution to the formation of CO_2 is that of lattice oxygen (3.2×10^{-5} mol × g^{-1} s^{-1} for lattice oxygen vs. 0.9×10^{-6} mol g^{-1} s^{-1} for chemisorbed oxygen). Depending on the nature of the catalyst and specially the reaction temperature, the contribution of these two oxygen sources will be changed. It was observed that the contribution of lattice oxygen to the combustion of isobutylene was significantly increased with temperature.

The formation of CO_2 from the oxidation of isobutylene has been studied by Nieto et al. [29] over silica-supported multicomponent oxides. The rate of CO_2 formation in the temperature range between 315–340°C is reported to be independent of isobutylene concentration and half order dependent on oxygen. In contrast, a first order dependent on both isobutylene and oxygen over supported chromium oxide/lanthanum carbonate catalyst was observed. This difference is attributed to the differences in the nature of the catalyst and working conditions. The result [29] is based on a reaction network involving the formation of methacrolein, acetone, CO and CO_2, as well as acetic acid. The CO_2 is formed directly from both isobutylene and further combustion of other products.

Thus the formation of isobutylene from isobutane over supported chromium/lanthanum catalyst was found to be first order in isobutane and zero order in oxygen. Although the adsorbed oxygen from the gas phase and lattice oxygen in the catalyst attain equilibrium fairly rapidly, the rate limiting step was found to be the regeneration of active sites by gas phase oxygen. The formation of CO_2 was due to the consecutive oxidation of isobutylene not by the direct oxidation of isobutane. Being a basic compound, isobutylene can only desorb from the surface more quickly on a less acidic or basic type of catalyst. Since the lattice oxygen from the catalyst is limited, a necessary condition of an effective catalyst is the possession of sufficient basicity.

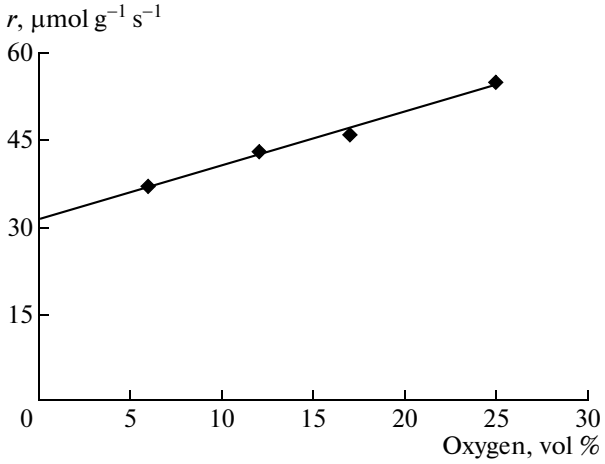

Fig. 6. Rate of isobutylene combustion as a function of oxygen content (temperature 240°C, [isobutylene] = 1 vol %).

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