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Oxidative Dehydrogenation of 1-Butene to 1,3-Butadiene over a Multicomponent Bismuth Molybdate Catalyst: Influence of C_3–C_4 Hydrocarbons

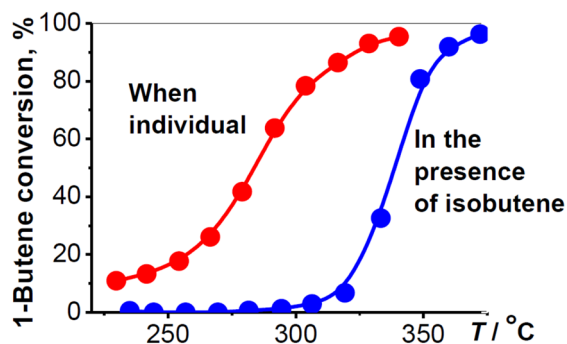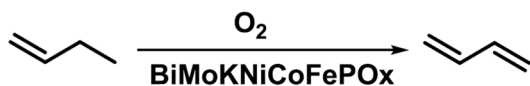Vladimir I. Sobolev[1,2] · Konstantin Yu. Koltunov[1,3] · Galina A. Zenkovets[1,3]

Abstract The influence of light hydrocarbons, such as n-butane, isobutane, propylene, *cis-* and *trans-*2-butenes, and isobutene on the oxidative dehydrogenation of 1-butene to 1,3-butadiene over BiMoKNi-CoFePO$_x$/SiO$_2$ catalyst has been studied using a gas flow reactor. The inhibition effect of the listed hydrocarbons on the target reaction increased in the order of n-butane ~ isobutane < propylene < 2-butenes < isobutene. In addition, in contrast to 1-butene, isobutene has shown significant contribution to coke formation. It was suggested, that the coke formation and therefore the rate of the catalyst regeneration exercise a significant influence on the efficiency of 1-butene transformation into 1,3-butadiene in the concurrent presence of other hydrocarbons.

Graphical Abstract

Oxidative dehydrogenation (ODH) of 1-butene in the presence of C_3-C_4 hydrocarbons

$$\xrightarrow[\text{BiMoKNiCoFePOx}]{O_2}$$

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1 Introduction

1,3-Butadiene (BD) is an important bulk chemical which is mainly produced as a byproduct in ethylene and propylene manufacturing through a naphtha cracking process [1]. As an additional method, catalytic dehydrogenation of normal butane is employed to obtain BD (the Houdry process) [2].

On the other hand, catalytic oxidative dehydrogenation (ODH) of isomeric n-butenes (1-butene, *cis-* and

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trans-2-butenes) has attracted much attention as a promising alternative approach to produce BD [3–6]. Indeed, ODH reactions are thermodynamically favorable and offer significant savings of energy and cost [7–10]. Therefore, considerable efforts have been made to find an appropriate catalyst for the ODH of n-butenes. To date, bismuth molybdates with various metal components have proved to be the most efficient catalysts for this reaction [11–18].

Furthermore, it is important that, commercial value of the BD production through the ODH reaction can be much enhanced on condition that mixtures of light hydrocarbons, such as BBF (butane-butene fraction), C_4-raffinates, and other available row materials are used as a significant and cheap source of n-butenes [19]. In that case, however, the accompanying hydrocarbons can affect negatively the target reaction. Moreover, even though only n-butenes are present in the feed gas, their integral reactivity may not be the same as the sum of the original reactivities of the three isomers. In fact, *cis*- and *trans*-2-butenes are noticeably less inclined to ODH than 1-butene [15, 20, 21]. Therefore, it is not improbable that 2-butenes will exert a suppressing effect on the reactivity of 1-butene and vice versa. It should be noted also that the promotion or inhibition effects of isomeric 2-butenes, BD and water on the ODH of 1-butene have been studied earlier, but the conclusions drawn by the authors were controversial [20, 22, 23].

In view of these considerations, we decided to investigate the influence of selected light hydrocarbons, such as n-butane, isobutane, propylene, 2-butenes, and isobutene on the ODH of 1-butene over a typical multicomponent Bi-Mo catalyst. Also, the main aim of this study was to elucidate the possible reasons of such a potential influence.

2 Experimental

The multicomponent 50% $K_{0.1}Ni_{3.5}Co_{5.0}Fe_{2.0}Bi_{2.0}P_{0.5}Mo_{12}O_x$/50% SiO_2 catalyst denoted as MCC was prepared by mixing the aqueous solution of ammonium paramolybdate $[(NH_4)_6Mo_7O_{24} \cdot 7H_2O]$ with 40% silica sol (particle size of 20 nm, Nalco 2327, US) under vigorous stirring at room temperature followed by successive introduction of aqueous solutions of KNO_3, $Fe(NO_3)_3 \cdot 9H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Bi(NO_3)_2 \cdot 5H_2O$ and H_3PO_4 (reagent grade materials purchased from Aldrich or Merck). All the solutions had a concentration of 90–150 g/L counting on the corresponding metal. The suspension obtained was spray dried on the Spay Drier (Buchi B-290, Germany), then dried in the dry-box at 110 °C for 12 h and calcined in air at 550 °C for 4 h.

Atomic adsorption spectrometry was used to determine the concentrations of the chemical elements in the catalyst with an Optima 4300 DV spectrometer (Perkin Elmer, US) with an accuracy of 0.01–0.05%.

XRD studies were conducted using a D8 diffractometer (Bruker, Germany) with monochromatic Cu*K*α radiation in 0.05° steps with a counting time of 5 s per data point in the 2θ = 15°–90° range. According to XRD data, the catalyst consisted of multiphase system of iron, cobalt, nickel, and bismuth molybdates ($Fe_2Mo_3O_{12}$, α,β-$CoMoO_4$, α,β-$NiMoO_4$ α-$Bi_2Mo_3O_{12}$) and phase of MoO_3.

The specific surface area of the catalyst (S_{BET}) was determined by argon thermal desorption at 77 K on a SORBI-M instrument (META, Russia) using four points of the sorption equilibrium. The measured BET surface area was 29 m²/g.

1-Butene (Sigma-Aldrich Inc., 99%), isobutene (Sigma-Aldrich Inc., 99%), 2-butenes (a ~1:2 mixture of cis- and trans-isomers, ABCR GmbH & Co. KG, 99%), propylene, butane, isobutane, oxygen and He were used for preparation of gas mixtures by using mass flow controllers.

The temperature programmed gas-phase reactions were performed in a quartz tube flow reactor with an internal diameter of 6 mm using shaped catalyst granules (d = 0.25–0.5 mm; 1.64 g, ca. 2 mL). The reactive gas mixtures were fed (30 mL min⁻¹) into the reactor filled with the catalyst; the reactor was operated under atmospheric pressure. The reaction temperature (±1 °C) was measured inside the reactor using a thermocouple inserted into the catalyst bed. The heating rate was 0.5 °C min⁻¹. During the catalytic runs, gas samples were analyzed periodically by integrated online gas chromatography (GC, gas chromatograph Tsvet-500; 30 m × 0.32 mm monolithic poly(divinylbenzene) capillary column; 170 °C) with a flame-ionization detector for determination of organics. For determination of CO and CO_2, they were preliminarily separated on a 1.5 m × 3 mm steel column filled with Porapak Q at 20 °C followed by methanation and analysis with a flame-ionization detector.

Prior to the kinetic measurements, the catalyst was activated in the reactor at 400 °C in a flow of O_2/He (1:3) for 1 h. The reactor was then cooled to 200 °C and the feed was switched at this temperature to the reactive gas mixture for 20–30 min in order to reach steady state initial conditions.

The catalytic reactions of 1-butene and isobutene under reduced pressure were carried out in a vacuum static setup. The setup was made of stainless steel with a small quartz reactor and was described elsewhere [24]. The setup was equipped with an on-line mass-spectrometer (SRS RGA 200) to analyze the gas phase composition. The reactor loaded with the catalyst sample (0.5 g) can be isolated from the rest of the setup. This ensures substitution of the gas phase in the setup at a closed reactor. Prior to the experiments, the catalyst was subjected to a standard pretreatment in vacuum, then in oxygen (1 Torr) at 500 °C for 1 h and

then again in vacuum at 500 °C for 1 h. After cooling to reaction temperature under vacuum, the mixture of 0.2 Torr of 1-butene (or iso-butene) and 0.4 Torr of O_2 was introduced into the system. The *m/e* values used in the experiments were 18 (H_2O), 32 (O_2), 28 (CO), 44 (CO_2), 54 (BD), 56 (1-butene or isobutene), 70 (methacrolein).

3 Results and Discussion

3.1 Gas-Phase Catalytic Reactions in a Flow Reactor

Figure 1 demonstrates temperature-dependent behavior of individual 1-butene over the obtained multicomponent catalyst (MCC) in a single-pass flow reaction in the presence of oxygen. As expected, BD is the main reaction product, and the major by-products are *cis-* and *trans*-2-butenes. The isomeric 2-butenes can be produced through various pathways including acid-catalyzed isomerization [8, 17, 21–25]. The latter possibility is in accordance with a substantial surface acidity of the modified Bi–Mo oxides [23, 26, 27]. The complete conversion of 1-butene is achieved at 300 °C, while the temperature around 320 °C allows a maximum BD production to be attained. The further increase in temperature leads to overoxidation of the produced BD to CO and CO_2. Thus, the main catalytic transformations of 1-butene include two types of reactions. The first one is the reversible isomerization of 1-butene to 2-butenes; the second reaction is the ODH of 1-butene and 2-butenes to BD:
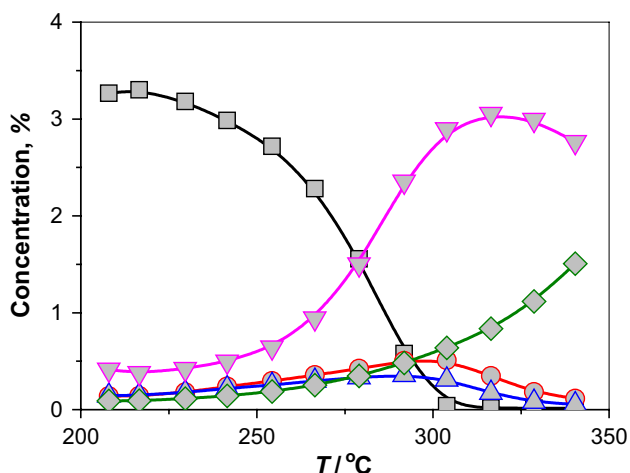
$$1\text{-butene} \rightleftarrows 2\text{-butenes} \tag{1}$$

$$n\text{-butenes} \rightarrow BD \tag{2}$$

Figure 2 illustrates the relative contribution of the oxidation and isomerization reaction pathways as a function of temperature. The conversion of 1-butene to the oxidation products, BD and CO_x, was estimated as the sum of concentrations of BD and ¼ of CO_x divided by the starting concentration of 1-butene. The conversion, related to isomerization was calculated as the sum of concentrations of 2-butenes divided by the starting concentration of 1-butene. Although the relative contribution of both reaction pathways is comparable until 260 °C, further increasing the temperature decreases contribution of isomerization. This is obviously due to the growing rate of oxidation of 2-butenes produced.

In the absence of oxygen, conversion of 1-butene to 2-butenes becomes predominant (Fig. 3). Despite this reaction is reversible, it occurs far from equilibrium under conditions used. Indeed, we have shown that the ratio of n-butenes depends strongly on the contact time of the reaction (at the same temperatures). Notably, in the absence of oxygen in the feed gas, BD is nevertheless produced in a small amount. This may be due to ODH of n-butenes by the metal oxide. Alternatively, BD can be formed via nonoxidative dehydrogenation pathway.

Figure 4 shows the reactivity of 2-butenes under aerobic conditions. The major reaction product is again BD. However, in contrast to a similar reaction of 1-butene, total conversion of 2-butenes is practically due to oxidation reactions only. On the other hand, isomerization of 2-butenes into 1-butene can be masked by a comparatively rapid ODH of 1-butene. In fact, we have found that in the absence of oxygen, isomerization of 2-butenes into 1-butene over MCC is well-marked.
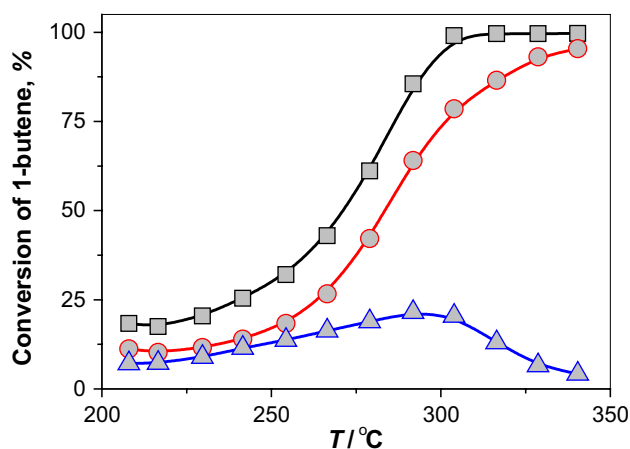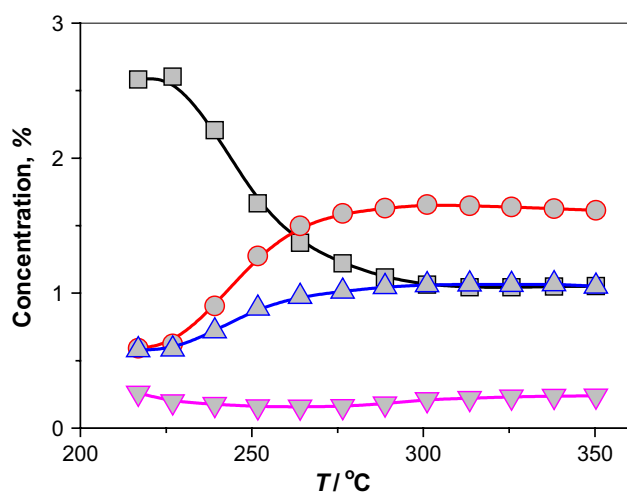

Fig. 1 Reactivity of 1-butene over MCC in the presence of oxygen: concentrations of 1-butene (filled square), BD (filled inverted triangle), *cis*-2-butene (filled triangle), *trans*-2-butene (filled circle), and CO_x (filled diamond). Feed composition: 4 vol% 1-butene, 20 vol% O_2 and He balance; S.V. = 1100 mL h^{-1} g^{-1}

Fig. 2 Oxidation vs. isomerization of 1-butene over MCC: total conversion of 1-butene (filled square), conversion of 1-butene to BD + CO_x (filled circle), and conversion of 1-butene to 2-butenes (filled triangle). Feed composition: 4 vol% 1-butene, 20 vol% O_2 and He balance; S.V. = 1100 mL h^{-1} g^{-1}

Fig. 3 Reactivity of 1-butene over MCC in the absence of oxygen: concentrations of 1-butene (filled square), BD (filled inverted triangle), *cis*-2-butene (filled triangle), and *trans*-2-butene (filled circle). Feed composition: 4 vol% 1-butene and He balance; S.V. = 1100 mL h^{-1} g^{-1}
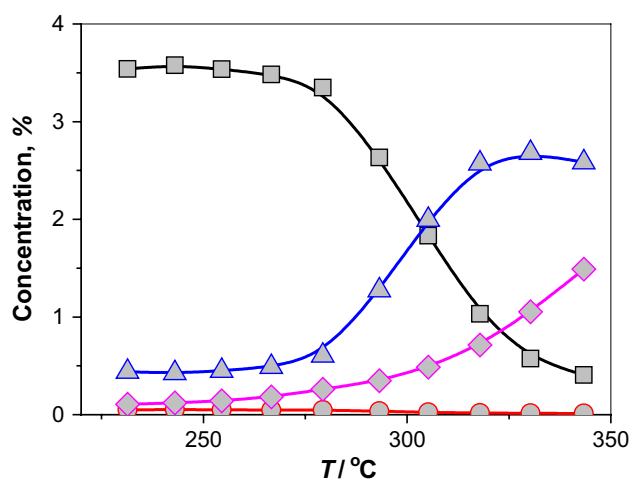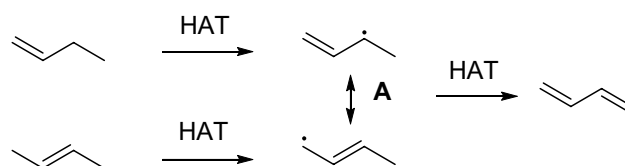

Fig. 4 Reactivity of 2-butenes over MCC in the presence of oxygen: concentrations of 2-butenes (filled square), BD (filled triangle), 1-butene (filled circle), and CO_x (filled diamond). Feed composition: 4 vol% 2-butenes, 20 vol% O_2 and He balance; S.V. = 1100 mL h^{-1} g^{-1}

It is widely accepted that hydrogen atom transfer (HAT) to a metal oxide is the key reaction step in the ODH of n-butenes [17]. Notably, both 1-butene and 2-butenes transform initially to the same allylic radical **A**, represented by two resonance structures (Scheme 1). However, activation energy of the allylic H abstraction from 2-butenes is higher compared to that from 1-butene [28]. Intermediate **A** can further undergo a second hydrogen abstraction step to give BD [17].

Scheme 1 Proposed mechanism for the ODH of n-butenes to BD over Bi–Mo oxides (general pattern) [17]
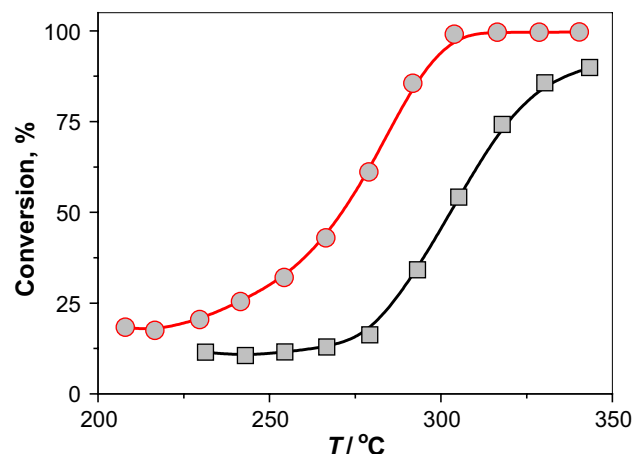

Fig. 5 The relative reactivity of 1- and 2-butenes over MCC in the presence of oxygen: conversions of 1-butene (filled circle), 2-butenes (filled square). Feed composition: 4 vol% 1- or 2-butenes, 20 vol% O_2 and He balance; S.V. = 1100 mL h^{-1} g^{-1}

In agreement with earlier observations [15, 20, 21], 2-butenes appeared to be less reactive (with respect to ODH) than 1-butene. Figure 5 allows a comparison of the reactivity of individual 1-butene and 2-butenes in the presence of oxygen as a function of temperature. The high temperature shift in the ODH of 2-butenes is definitely seen. The diminished reactivity of 2-butenes can be explained by relatively higher activation energy of the allylic H abstraction from 2-butenes [28]. In addition, conversion of 2-butenes to BD may proceed via preliminary isomerization of 2-butenes into more reactive 1-butene followed by ODH. Obviously, the rate of reaction in that case will be limited by the rate of the isomerization.

Figure 6 compares the oxidation results of individual 1-butene and 1-butene in the presence of an equimolar amount of 2-butenes. Although reactivity of 2-butenes is not influenced by the presence of 1-butene, it is apparent that reactivity of 1-butene decreases in the presence of 2-butenes. However, 2-butenes seem to suppress only the contribution of isomeriszation of 1-butene to 2-butenes (compare Figs. 2, 6). Consequently, the oxidation reactions of 1-butene are practically not influenced by the presence of 2-butenes.
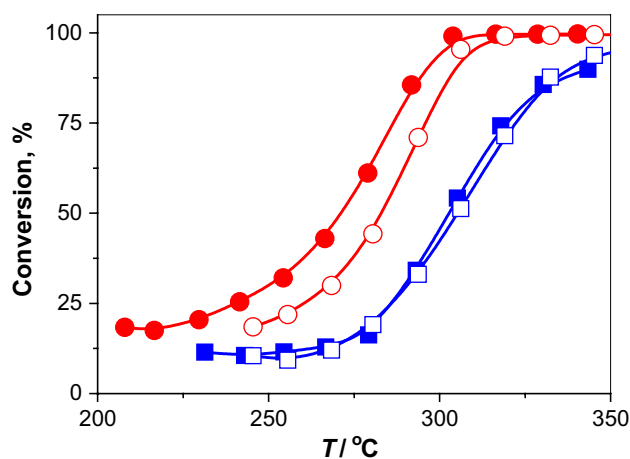
Fig. 6 Conversions of 1-butene (*circle symbols*) and 2-butenes (*square symbols*) over MCC in the presence of oxygen for different feed compositions: 4 vol% 1- or 2-butenes, 20 vol% O_2 and He balance (*shaded symbols*); 4 vol% 1-butene, 4 vol% 2-butenes, 20 vol% O_2 and He balance (*empty symbols*); S.V. = 1100 mL h^{-1} g^{-1}
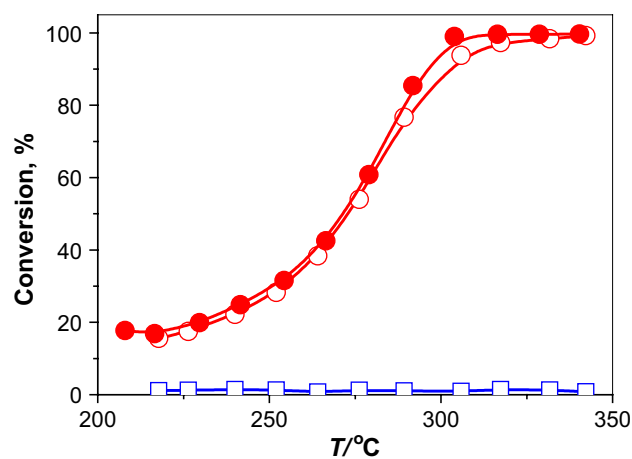

Fig. 7 Conversions of 1-butene (*circle symbols*) and n-butane (*square symbols*) over MCC in the presence of oxygen for different feed compositions: 4 vol% 1-butenes, 20 vol% O_2 and He balance (*shaded symbols*); 4 vol% 1-butene, 4 vol% n-butane, 20 vol% O_2 and He balance (*empty symbols*); S.V. = 1100 mL h^{-1} g^{-1}

As was mentioned above, the main commercial source of n-butenes is the C_4-fraction from steam cracking of hydrocarbons. This fraction, after extraction of BD, consists mainly of n-butane, 1-butene, 2-butenes, and isobutene (the C_4 raffinates). Butane and butene mixtures are also obtained from natural gas and refinery waste gases from catalytic dehydrogenization of n-butane. Thus, the raw materials apart from n-butenes contain significant amounts of butane, isobutane, isobutene, and other light hydrocarbons. Since a preliminary isolation of n-butenes from the mixtures is not advantageous, it remains to carry out ODH of n-butenes in the presence of these hydrocarbons. Below we consider the influence of four selected hydrocarbons on the ODH of 1-butene.

Firstly, it was studied reaction of 1-butene in the presence of n-butane. Figure 7 compares the reactivity of individual 1-butene and 1-butene when mixed with n-butane. As it can be seen, n-butane does not practically influence the reaction of 1-butene, which is in accord with earlier findings [19]. It should be noted also that n-butane itself does not react under conditions applied; its conversion is close to zero (Fig. 7). The same inertness and no influence on the reactivity of 1-butene have shown isobutane.

In contrast to alkanes, which do not react themselves and do not influence the oxidation of 1-butene over MCC, propylene and isobutene revealed the opposed properties. Figure 8 compares behavior of individual and mixed 1-butene and propylene under oxidation conditions. The conversion of propylene over MCC is exclusively due to its oxidation to acrolein and CO_x. In order to compare reactivities of 1-butene and propylene properly, conversion of 1-butene in Fig. 8 is represented by the oxidation

component only. In that case, the curves of conversions of individual 1-butene and propylene seem very close. It could therefore be proposed that the concurrent oxidation of 1-butene and propylene will be synchronic. Indeed, the reactivity of 1-butene does not practically change in the presence of propylene; the curves of conversion of pure 1-butene and 1-butene mixed with propylene remain very close, especially at low values of conversion (below 40%). However, 1-butene appears to exert dramatic influence on the reactivity of propylene. Thus, conversion of individual propylene attains 70% at 305 °C, while
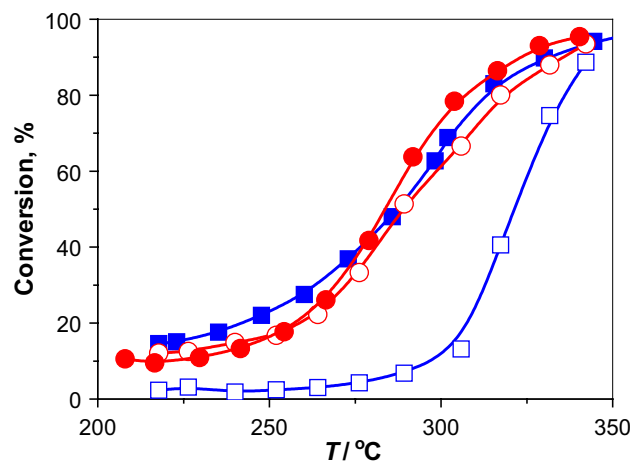

Fig. 8 Oxidation of 1-butene (*circle symbols*) and propylene (*square symbols*) over MCC in the presence of oxygen for different feed compositions: 4 vol% 1-butene or propylene, 20 vol% O_2 and He balance (*shaded symbols*); 4 vol% 1-butene, 4 vol% propylene, 20 vol% O_2 and He balance (*empty symbols*); S.V. = 1100 mL h^{-1} g^{-1}

conversion of propylene mixed with 1-butene is only 10% at the same temperature (Fig. 8). The observed detrimental influence of 1-butene on the propylene oxidation is in accord with the known inhibiting action of C2–C5 unsaturated hydrocarbons present in the raw material on propylene oxidation to acrolein [29]. The reason is the poisoning effect by variety of impurities, such as terephthalic acid and other aromatic oxygenates formed in trace amounts as a result of combination of Diels–Alder and oxidative reactions [30].

Figure 9 compares reactivity of individual 1-butene, isobutene and their concurrent reactivity under oxidation conditions. Taking into account that isobutene undergoes oxidation reactions only (to give methacrolein and CO_x), conversion of 1-butene is also represented by the oxidation component part. As it can be seen, reactivities of pure 1-butene and isobutene are very different, and 1-butene is notably more reactive. However, reactivity of 1-butene decreases sharply in the presence of an equimolar amount of isobutene. Indeed, a notable oxidation of 1-butene occurs only at temperature above 320 °C, whereas individual 1-butene is converted almost completely at this temperature. It is noteworthy that 1-butene, in its turn, seems to exert no influence on the reaction of isobutene: the curves of conversion of pure isobutene and isobutene mixed with 1-butene are practically coincident.

Thus, the inhibition effect of hydrocarbons on the producing of BD decreases in the order of isobutene > 2-butenes > propylene > isobutane ~ n-butane (no influence). The strongest effect shows isobutene shifting the curve of 1-butene conversion horizontally along the temperature axis by about 50 °C.
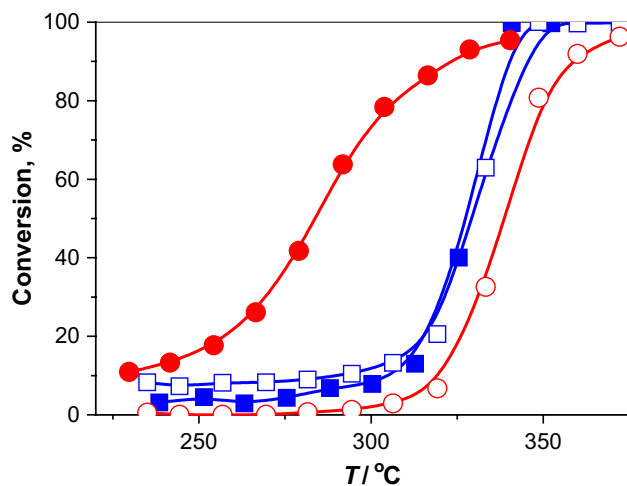
3.2 Catalytic Reactions of 1-Butene, Isobutene and Their Mixture in a Static Setup

In order to understand the reason of the strong influence of isobutene on the ODH of 1-butene, we have studied reactivity of these compounds over MCC using a vacuum static setup equipped with an on-line mass-spectrometer. This allowed measuring the gas composition both qualitatively and quantitatively at low pressures of reagents. The initial pressure of butenes and oxygen was 0.2 Torr (~8 μmol) and 0.4 Torr, respectively. This provided a quick monitoring of 'undistorted' reactions induced by the catalyst.

Figure 10 shows the catalytic reaction of isobutene with oxygen at 300 °C. In addition to deep oxidation products (CO_2 and H_2O), only methacrolein is formed. It is noteworthy a delay of methacrolein evolution during the first 2 min of reaction. This may be due to a partial accumulation (adsorption) of methacrolein on the catalyst surface. On the other hand, it can be related to coke formation at the catalyst. In agreement with the latter assumption, a negative balance of carbon atoms is notably seen. Moreover, oxidative regeneration of the used catalyst confirms a significant accumulation of coke consisted mainly of carbon and, in less extent, hydrogen (Fig. 11).

In contrast to the reaction of isobutene, 1-butene reacts with oxygen more selectively to give BD along with comparatively low amounts of CO_2 and H_2O (Fig. 12). No delay in BD evolution is observed. Moreover, only negligible amount of organics is "burned" during oxidative regeneration of the catalyst after oxidation of 1-butene (Fig. 13). This means that MCC sample does not induce significant coking upon the ODH of 1-butene.
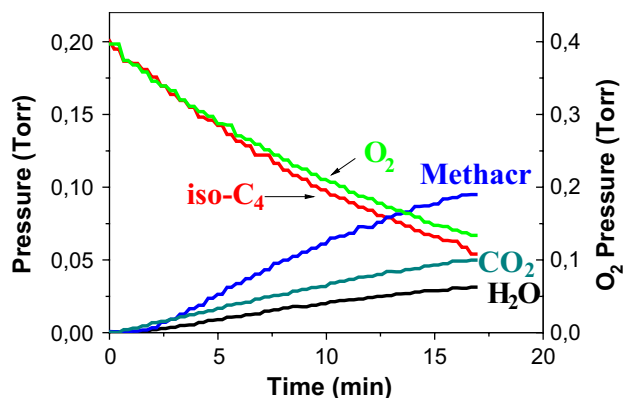

Fig. 9 Conversions of 1-butene (*circle symbols*) and isobutene (*square symbols*) over MCC in the presence of oxygen for different feed compositions: 4 vol% 1-butene or isobutene, 20 vol% O_2 and He balance (*shaded symbols*); 4 vol% 1-butene, 4 vol% isobutene, 20 vol% O_2 and He balance (*empty symbols*); S.V. = 1100 mL h^{-1} g^{-1}

Fig. 10 Oxidation of isobutene (iso-C_4, 0.2 Torr) with O_2 (0.4 Torr) at 300 °C over MCC
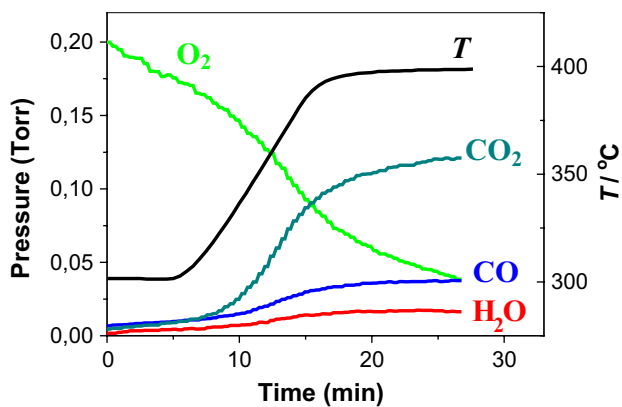
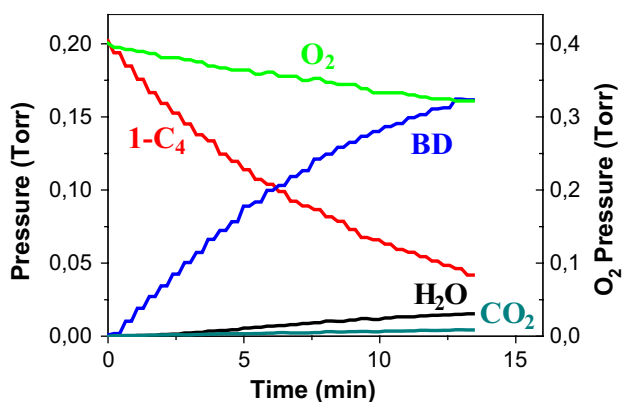**Fig. 11** Oxidative regeneration of MCC after oxidation of isobutene

Fig. 12 Oxidation of 1-butene (1-C_4, 0.2 Torr) with O_2 (0.4 Torr) at 300 °C over MCC
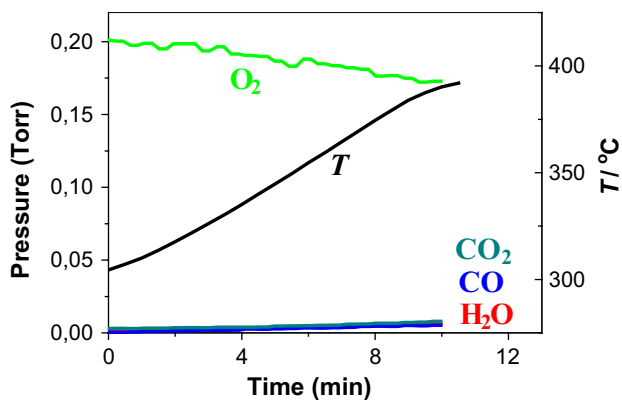

Fig. 13 Oxidative regeneration of MCC after oxidation of 1-butene

Therefore, the influence of isobutene on the ODH of 1-butene under a flow reactor conditions can be explained not only by the competitive formation or difficult desorption

of methacrolein. It seems also probable that in the flow-gas/fixed bed reaction conditions isobutene deactivates significant part of the catalyst surface due to coke formation. This leads to a decrease in the number of active sites involved in the oxidative reactions. As a result, the rate of 1-butene reaction in the presence of isobutene is limited by the rate of the catalyst regeneration.

4 Conclusion

The influence of concurrent C_3–C_4 hydrocarbons on the ODH of 1-butene to BD over a typical multicomponent Bi–Mo–O catalyst has been studied. Although alkanes (butane, isobutane), as well as propylene practically did not exert influence on the reaction, 2-butenes, and especially isobutene exhibited significant suppressive effect. In addition, isobutene (in contrast to 1-butene) has shown significant contribution to coke formation. Taking these facts into account, it can be concluded that the coke formation, along with competitive catalytic reactions can be a notable factor influencing the efficiency of 1-butene transformation into BD in the presence of other hydrocarbons.

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