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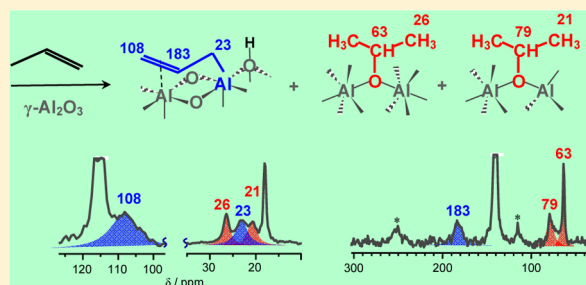
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Solid-State NMR Characterization of the Structure of Intermediates Formed from Olefins on Metal Oxides (Al_2O_3 and Ga_2O_3)

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ABSTRACT: The interaction of olefins with metal oxides affords surface species which are considered to be the intermediates in olefin isomerization reactions. The nature and the structure of these intermediates after earlier characterization by IR spectroscopy still remain debatable. In this paper by using ^{13}C solid-state NMR spectroscopy we have characterized the surface intermediates formed from propene, *n*-butene, and isobutene on $\gamma\text{-Al}_2\text{O}_3$ and $\alpha\text{-Ga}_2\text{O}_3$, based on analysis of specific chemical shifts expected for similar organometallic or oxygenated compounds. NMR clearly shows that both allylic and alkoxy intermediates are simultaneously formed on two studied metal oxides. Propene affords isopropoxy and allylic intermediates on both oxides. Allyl formed on alumina is bound to the Al^{3+} cations of metal oxide surface in a η^1, η^2 -like fashion, whereas allyl on $\alpha\text{-Ga}_2\text{O}_3$ is bound to the Ga^{3+} cation exclusively in a η^1 -like fashion. *n*-Butene gives 2-butoxy species for both metal oxides, whereas allylic species (σ -allyl) was identified for this olefin only for $\gamma\text{-Al}_2\text{O}_3$. Adsorption of isobutene results to the formation of *tert*-butoxy and allylic species on both metal oxides. π -Allyl with η^3 -like fashion of allyl bonding to the oxide surface is formed in the case of $\gamma\text{-Al}_2\text{O}_3$, whereas σ -allyl is formed in the case $\alpha\text{-Ga}_2\text{O}_3$. Both allylic and alkoxy species can be involved as intermediates in a double bond shift reaction of olefins on metal oxide surfaces.



1. INTRODUCTION

It is well-known that metal oxides such as zinc oxide, aluminas, and gallium oxides are catalytically active in a broad variety of reactions, including olefin isomerization^{1–7} and hydrogenation,^{8–11} alkane dehydrogenation and aromatization,^{12–15} water gas-shift reaction,¹⁶ carbon dioxide hydrogenation/methanol synthesis,^{17,18} etc.

Because of a wide application of these oxides in catalysis there is an interest for identification and characterization of the intermediates formed at hydrocarbon interaction with metal oxides surfaces. After the first suggestion on a possible formation of transient carbanions as intermediates in olefin isomerization on alumina by Peri,¹⁹ persistent carbanion intermediates as π -allyl complexes were identified for propene and *n*-butene on ZnO with IR spectroscopy by Dent and Kokes.^{2,20} Further, allylic intermediate as π -allyl was also identified for propene on γ -alumina by Davydov, et al.^{21–23} However, the nature and the structure of the intermediates formed from olefins on oxides^{2,22,24} or from alkanes on metal oxide modified zeolites^{25,26} still remain debatable. Contrary to conclusions on the formation of π -allyls on ZnO,^{2,20} Corrado, et al.¹ and Guisnet, et al.,⁴ postulated and, later on, based on IR spectroscopic studies, Busca et al.²⁴ concluded that allyl species formed from propene and butenes were σ -bonded to the alumina surface. It was also claimed that the allyl species was the intermediate only for a double bond isomerization, whereas skeletal isomerization occurred with the intermediate formation of alkoxy species,²⁷ albeit this species was not identified. Recent NMR studies by Gabrienko and Stepanov²⁸ have shown that allyl complexes of

propene and *n*-butene on ZnO are indeed σ, π -allyls rather than exclusively π -allyl as formerly concluded by Dent and Kokes.^{2,20,29} σ -Allyl species was also identified at propane dehydrogenation on Zn/H-BEA zeolite.²⁶

Ambiguity in determination of the nature and the structure of the surface intermediates based on IR, UV,^{2,20,22,24,27} and kinetic studies^{1,4} prompted us to use NMR spectroscopy to analyze the structure of the surface species formed at the interaction of olefins with the metal oxides. In this paper we characterize the surface species formed at the interaction of propene, *n*-butene, and isobutene with Al_2O_3 and Ga_2O_3 by ^{13}C solid-state NMR. This allows us to unravel both the diversity of the nature of the surface intermediates and the modes of bonding of a hydrocarbon with the metal oxide surface. The exact structure of the intermediates in olefin transformation on metal oxide catalysts can thus be clarified more thoroughly. This provides the basis to follow the fate of the identified intermediates at higher temperature in catalytic conversion of the olefins on the metal oxide catalysts.

2. EXPERIMENTAL SECTION

Gallium(III) oxide (α -modification, $\alpha\text{-Ga}_2\text{O}_3$) was prepared from amorphous $\text{Ga}(\text{OH})_3$ by calcination at 793 K for 5 h by the method described in ref 30, and the structure of synthesized α -

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Ga₂O₃ was confirmed by XRD analysis. The surface area was $S_{\text{BET}} = 70 \text{ m}^2 \text{ g}^{-1}$. A commercial γ -alumina (γ -Al₂O₃) powder (surface area $214 \text{ m}^2 \text{ g}^{-1}$, pore volume $0.85 \text{ cm}^3 \text{ g}^{-1}$, medium pore radius 158 \AA , sodium contents $<0.036\%$, Si $<0.13\%$) was used for olefin adsorption.

Propene-1-¹³C (99% ¹³C), propene-3-¹³C (99% ¹³C), both from ICON Isotope Inc., propene-2-¹³C (99% ¹³C) from ACC Inc., *n*-butene-1-1-¹³C (99% ¹³C) and *n*-butene-1-2-¹³C (99% ¹³C), from MSD isotope Inc., and 2-methylpropene-2-¹³C (99% ¹³C) from Cambridge Isotope Laboratories, Inc. (CIL) were used for adsorption on the activated metal oxides.

The NMR analyses of the products of olefin interaction with metal oxide surface were performed in a glass closed batch microreactor of 0.05 cm^3 . It represents an axially high symmetrical sealed glass tube of 3 mm outer diameter and 10 mm length with olefin adsorbed on oxide powder. This reactor could be tightly inserted into a NMR zirconia rotor for in situ analysis of the reaction products.

The samples of γ -Al₂O₃ or α -Ga₂O₃ (ca. 60–80 mg) in a glass tube were activated at 673 K for 8 h under vacuum with the residual pressure less than 10^{-3} Pa . A total of $80 \mu\text{mol g}^{-1}$ of olefin was adsorbed on the sample under vacuum at the temperature of liquid nitrogen, and then the glass tube with adsorbed olefin was sealed with a flame. On the eve of NMR analysis the sealed glass tube with the sample was taken out of the liquid nitrogen and transferred to 4 mm zirconia rotor, and ¹³C MAS NMR analysis was performed at 296 K. For some cases the sample was additionally heated at 373–523 K to follow the fate of the surface intermediate at higher temperature.

NMR spectra were recorded at 9.4 T on a Bruker Avance-400 spectrometer at room temperature. ¹³C NMR spectra with magic angle spinning and high-power proton decoupling (during the acquisition time) were recorded with (¹³C CP/MAS NMR) and without (¹³C MAS NMR) cross-polarization (CP) technique. The following conditions were used for recording the spectra with CP: the proton high power decoupling field strength was 11.7 G ($5.0 \mu\text{s}$ length of $90^\circ \text{ } ^1\text{H}$ pulse), the contact time was 1–2 ms at the Hartmann–Hahn matching condition of 50 kHz, and the delay time between scans was 3 s. Several tens of thousands of scans were collected for each ¹³C NMR spectrum. The spinning rate was 5–8 kHz. ¹³C chemical shifts of adsorbed organic species were measured with respect to TMS as an external reference with accuracy $\pm 0.5 \text{ ppm}$.

3. RESULTS

The interaction of olefin with the surface of alumina could offer either π -allyl complex (η^3 -like fashion of allyl ligand bonding to aluminum) or σ -allyl complex (η^1 -like fashion of allyl bonding to aluminum). The main argument for the formation of π -allyl was the observation of the IR band at 1570 cm^{-1} from the C=C stretch ($\nu_{\text{C=C}}$), shifted by 65 cm^{-1} from $\nu_{\text{C=C}}$ of gaseous propene at 1635 cm^{-1} due to π bonding of the olefin double bond with surface Al³⁺ cation.²² The evidence for the σ -allyl complex²⁴ was thought to be an observed similarity of the overall IR spectrum of the allyl complex of propene on γ -Al₂O₃ with that reported for propylmagnesium bromide ($\text{H}_2\text{C}=\text{CHCH}_2\text{MgBr}$),³¹ containing a nearly covalently bonded, partly anionic allyl species. In contrast to IR, NMR spectroscopy could provide more exact information about the nature and structure of the surface intermediates. Specific chemical shifts of the carbon atoms bound either to metal cation or oxygen surface atoms can unequivocally differentiate between alkoxy and allylic nature of

the surface intermediate. Moreover, the mode of allyl bonding to the surface metal cation is easily ascertained based on the specific chemical shifts of C₁, C₂, and C₃ carbons of the allyl ligand (formed, e.g., from propene), since η^1 - and η^3 -like fashions of bonding to a metal cation provide difference in both the number of the ¹³C NMR signals and their position in the spectrum.³² The allyl ligand η^1 -bound to metal cation should exhibit three signals, whereas only two signals exist for the η^3 -bound allyl ligand.³² Furthermore, the use of olefin molecules with selective ¹³C-labels for adsorption on metal oxide provides an unambiguous assignment of the observed NMR signals to the certain hydrocarbon fragments of the surface intermediates, since only the labeled signal is mainly observed in the spectrum.

3.1. Surface Species Formed from Olefins on γ -Al₂O₃.

3.1.1. Propene. Figure 1 shows ¹³C CP/MAS NMR spectra of

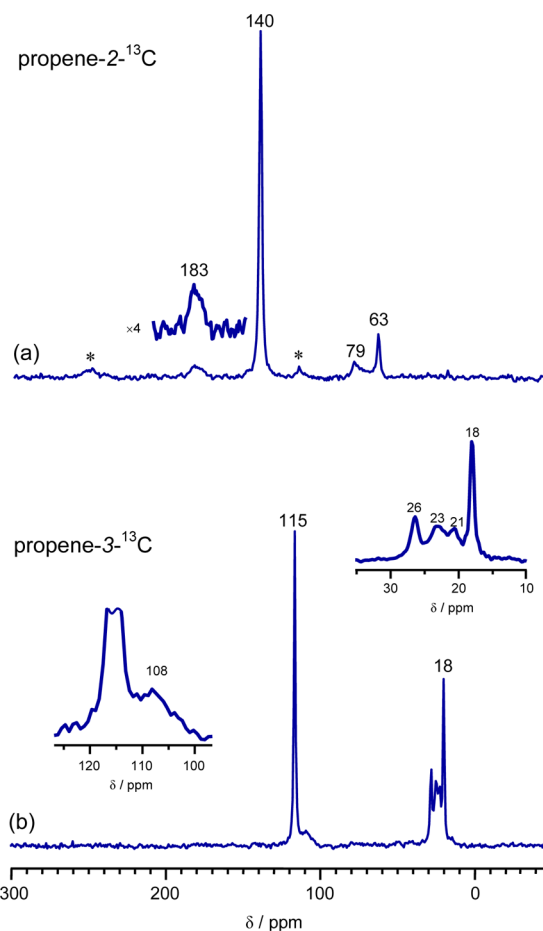
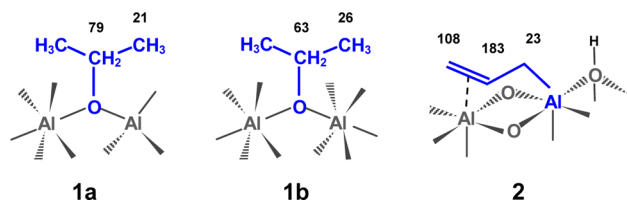


Figure 1. ¹³C CP/MAS NMR spectra of the products of propene interaction with surface of γ -alumina at room temperature: (a) adsorption of propene-2-¹³C on γ -Al₂O₃; (b) adsorption of propene-3-¹³C on γ -Al₂O₃. Asterisks (*) denote the spinning side-bands.

two propenes, labeled with ¹³C isotope either in the CH= group (propene-2-¹³C) or the CH₃– group (propene-3-¹³C), adsorbed on γ -Al₂O₃ at room temperature. In case of propene-2-¹³C, three weak signals from the reaction products are identified at 183, 79, and 63 ppm, besides the signal at 140 ppm from the initially labeled CH= group of the propene (Figure 1a). At the same time, adsorbed propene-3-¹³C exhibits four signals, arising from the initially labeled CH₃– group at 108, 26, 23, and 21 ppm, which should belong to the reaction products (Figure 1b). The narrow intense signal at 18 ppm is from the initially labeled

methyl group of propene-3- ^{13}C , and the signal at 115 ppm is from the $\text{CH}_2=\text{}$ group of the propene. The signal at 115 ppm appears as a result of the ^{13}C -label transfer from the methyl group into the $\text{CH}_2=\text{}$ group by a double bond shift reaction occurred with propene on this catalysts.

Two signals at 79 and 63 ppm are in the region of chemical shifts, typical for carbons bound to the oxygen atoms.³³ This evidences for the formation of alkoxy species from the adsorbed propene. Observation of two signals indicates that two types of surface alkoxy species are formed. We conclude that two types of isopropoxy species (**1a** and **1b**) are formed with the corresponding signals of their methyl groups at 21 and 26 ppm, identified in the spectrum of adsorbed propene-3- ^{13}C . It is reasonable to assume that the alkoxy species are formed by a transfer of a proton from the acidic surface AlOH groups to the adsorbed olefin molecule.³⁴ The ratio between intensities of the signals at 79 and 63 ppm corresponds to the ratio of the different isopropoxy species, which could be formed on the surface bridged AlOHAl groups with Al in the tetrahedral–octahedral-like and octahedral–octahedral-like environments, respectively.^{34,35}



For the expected allyl complex, formed on the alumina surface, there should be observed one signal in NMR spectrum at adsorption of propene-2- ^{13}C and one signal at adsorption of propene-3- ^{13}C in the case of η^3 -like fashions of bonding of allyl ligand.^{32,36–38} If allyl complex with a η^1 -like fashion of bonding to a surface Al^{3+} cation is formed, then two signals from the adsorbed propene-3- ^{13}C and one signal from propene-2- ^{13}C should be detected in the spectrum.^{32,36–38} The expected two signals from propene-3- ^{13}C in the allyl with a η^1 -like fashion of bonding is obliged to the ^{13}C -label scrambling between C_1 and C_3 carbons by a double bond shift (isomerization) reaction in the olefin on this oxide catalyst.

Observation of two signals at 108 and 23 ppm for propene-3- ^{13}C and one signal at 183 ppm from propene-2- ^{13}C (Figure 1a,b) is indicative of the formation of allyl complex (**2**) with a η^1 -like fashion of bonding to aluminum and the following assignment of the signals of the allyl ligand: 23 (C_1), 183 (C_2), and 108 ppm (C_3). The position of the C_1 – C_3 signals for the surface allyl is in the range of the signals typical for σ -allyl compounds of Al, Li, Mg, and Zn.^{32,36–39} Note, however, that there is a strong deshielding of the central allyl C_2 atom ($\Delta\delta(\text{C}_2) \approx 20\text{--}45$ ppm) with respect to position of C_2 in the known σ -allyl compounds.^{32,36–39} We interpret this fact in terms of an additional interaction of the double bond to the surface aluminum cations in such a way that the allylic C-atoms in **2** are unsymmetrically bound in a η^1, η^2 -like fashion. Additional interaction of a double bond of the surface σ -allyl with the other surface aluminum cation by π bonding (σ, π -allyl) could rationalize the observed shift by 65 cm^{-1} of the $\text{C}=\text{C}$ stretch from $\nu_{\text{C}=\text{C}}$ of gaseous propene at 1635 cm^{-1} at the formation of σ, π -allylic species on γ -alumina.²²

3.1.2. *n*-Butene-1. Adsorption of *n*-butene-1 on $\gamma\text{-Al}_2\text{O}_3$ results in a fast isomerization of the olefin to *n*-butene-2. Indeed, adsorbed *n*-butene-1-1- ^{13}C exhibits two signals at 17 and 11 ppm arising from the ^{13}C -labeled methyl groups of trans and cis

isomers of the formed *n*-butene-2-1- ^{13}C (Figure 2a). Adsorbed *n*-butene-1-2- ^{13}C shows the signal at 128 ppm from the ^{13}C -labeled

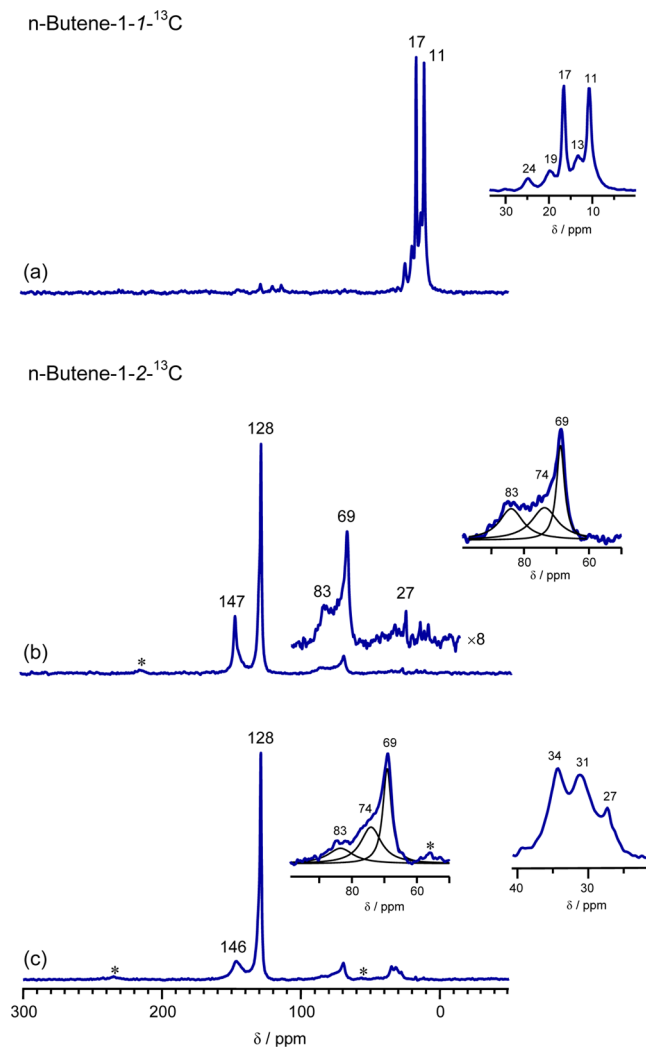
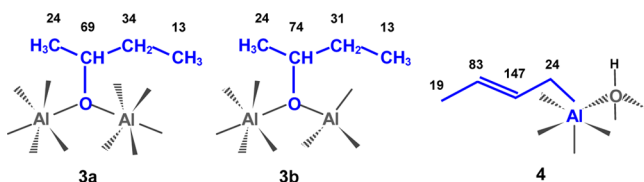


Figure 2. ^{13}C CP/MAS NMR spectra of the products of *n*-butene-1 interaction with surface of $\gamma\text{-Al}_2\text{O}_3$ at room temperature: (a) 20 h after adsorption of *n*-butene-1-1- ^{13}C on $\gamma\text{-Al}_2\text{O}_3$; (b) 2 h and (c) 20 h after adsorption of *n*-butene-1-2- ^{13}C on $\gamma\text{-Al}_2\text{O}_3$. Asterisks (*) denote the spinning side-bands.

— $\text{CH}=\text{}$ group of both trans and cis isomers of the formed *n*-butene-2-2- ^{13}C (Figure 2b). Besides the signals from the product of *n*-butene-1 isomerization, several signals arising from the ^{13}C -labeled carbon atoms of the other reaction products are detected. *n*-Butene-1-2- ^{13}C affords the signals at 147, 83, 74, 69, 34, 31, and 27 ppm arising from the labeled internal $=\text{CH}-$ group, whereas *n*-butene-1-1- ^{13}C gives the signals at 24, 19, and 13 ppm from the methyl groups of the reaction products. Two couples of the signals at 69, 34 and 74, 31 ppm point to the formation of the 2-butoxy species (**3a** and **3b**) bound to the surface of alumina. Indeed, the position of the signals from **3** is very close to position of those of *sec*-butyl (2-butyl) alcohol [23 ppm (CH_3), 69 ppm (CHOH), 32 ppm (CH_2), and 10 ppm (CH_3)].³³ The signals from the methyl groups of species **3** could be found at 24 and 13 ppm in the spectrum of the products formed at *n*-butene-1-1- ^{13}C adsorption. These signals are in the region of the signals of the methyl groups of *sec*-butyl alcohol.³³ Observation of only two,

rather than expected four signals in this region evidence that the chemical shifts for the methyl groups of **3a** and **3b** coincide.

Similar to the case with propene adsorption on γ - Al_2O_3 , the formation of two types of alkoxy species is obliged to the interaction of *n*-butene with protons of bridged AlOHAl groups, in which Al is disposed in the octahedral–octahedral-like (**3a**) and tetrahedral–octahedral-like (**3b**) environments.^{34,35}



The broad signals at 147, 83, and 19 ppm might be indicative of the formation of the σ -allyl complex (**4**) with η^1 -like fashion of bonding to aluminum and the following assignment of the signals of the allyl ligand: 19 (C_4), 83 (C_3), and 147 (C_2) ppm. The signal at the C_1 position of the allyl species **4** seems to coincide with the signal at 24 ppm from the 2-butoxy species **3**. The position of the signals from **4** is in the range of the signals typical for σ -allyl compounds of Al, Li, Mg, and Zn.^{32,36–39} One more signal at 27 ppm, detected among the signals of the reaction products, formed from *n*-butene-1-2- ^{13}C is assigned to the signal of the CH_2 group of the unreacted *n*-butene-1, and the other signals of this butene are not detected either because of low intensity and large width or due to overlapping with more intense signals from the reaction products.

3.1.3. Isobutene. Isobutene, labeled with ^{13}C isotope in the $>\text{C}=\text{C}$ group (isobutene-2- ^{13}C or 2-methylpropene-2- ^{13}C) adsorbed on γ - Al_2O_3 , exhibits seven signals in the ^{13}C CP/MAS NMR spectrum (Figure 3). The signal at 153 ppm arises

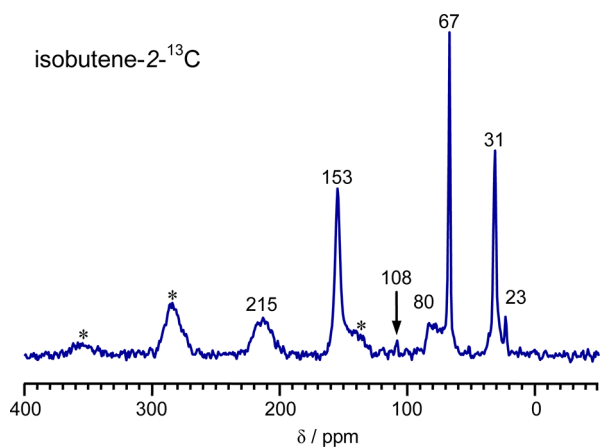
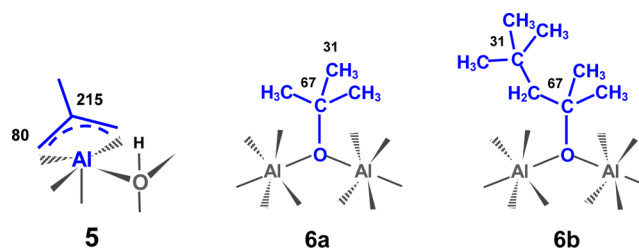


Figure 3. ^{13}C CP/MAS NMR spectrum of the products of formed at 2-methylpropene-2- ^{13}C (isobutene-2- ^{13}C) adsorption on γ - Al_2O_3 at room temperature. Asterisks (*) denote the spinning side-bands.

from the labeled carbon atom of the initial olefin, and the weak signals at 108 and 23 ppm belong to the $\text{H}_2\text{C}=\text{C}$ and the methyl groups with natural ^{13}C isotope abundance. The signals at 215 and 67 ppm are from the ^{13}C -labeled carbon atoms of the surface intermediates. Based on the position of the signals in the spectrum, the signal appearing at 215 ppm gives evidence for the formation of π -allylic intermediate (**5**). The position of this signal is typical for C_2 carbon atom of (2-methylallyl)ZnCl in solid state³² or π -allylic intermediate formed from isobutene on ZnO ⁴⁰ with a η^3 -like fashion of allyl bonding to zinc cation. The weak

signal at 80 ppm is presumably assigned to the C_1 carbon of species **5** with natural ^{13}C -isotope abundance, since the $\text{H}_2\text{C}=\text{C}$ or methyl groups were not enriched with ^{13}C -label in the initial isobutene. The signal at 67 ppm is indicative of the formation of *tert*-butoxy species (**6a**) with ^{13}C -labeled quaternary carbon atom. Its unlabeled methyl groups could display the weak signal at 31 ppm, like in *tert*-butyl alcohol [69 ppm (C) and 31 ppm (CH_3)].³³ Note, however, that the observed signal at 31 ppm is of rather notable intensity and could not correspond to a carbon atom with natural ^{13}C isotope abundance. This signal gives evidence for a partial isobutene dimerization and the formation of dimeric alkoxy species **6b**. Alkoxy species **6b** should display two signals from the ^{13}C -labeled carbon atoms: one from the quaternary carbon atom bonded to the terminal methyl groups with the chemical shift of 31 ppm and the other ^{13}C -labeled quaternary carbon atom attached to the surface oxygen. Its chemical shift evidently coincides with the chemical shift of the corresponding carbon atom of species **6a**.



3.2. Surface Species Formed from Olefins on α - Ga_2O_3 .

3.2.1. Propene. ^{13}C MAS NMR spectra of propene-3- ^{13}C and propene-2- ^{13}C (Figure 4a,c) adsorbed on gallium oxide exhibit two broad and weak signals from the reaction product at 26 ppm (C_1 and C_3 labeled atoms) and at 69 ppm (C_2 labeled atom), whereas the signals from the initial (unreacted) olefin are observed at 115 (C_1), 138 (C_2), and 18 ppm (C_3). The corresponding ^{13}C CP/MAS NMR spectra (Figure 4b,d), which emphasize the signals from the adsorbed species strongly bound to the oxide surface, show the same but of enhanced intensity signals at 26 and 69 ppm from the reaction products. Additionally two broad signals at 109 and 143 ppm (a left-hand shoulder to the signal 138 ppm) in the vicinity of the signals from the initial propene are observed. The signals at 26 and 69 ppm could be interpreted in terms of formation of *iso*-propoxy species on Ga_2O_3 (**7**) by a transfer of a proton of the acidic GaOH group to an olefin molecule. Two signals in the vicinity of 69 ppm (the second weak one at 75 ppm is displayed as a shoulder to the intense signal at 69 ppm) point to the formation of two types of *iso*-propoxy species **7a** and **7b**, presumably formed on the surface oxygens bridging two gallium cations either in the octahedral–octahedral-like environments or in tetrahedral–octahedral-like environments. The broad signals of notable intensity at 109 and 26 ppm resulted from propene-3- ^{13}C , and the signal at 143 ppm originated from propene-2- ^{13}C , which is evidence for the formation of σ -allyl complex from propene on Ga_2O_3 (**8**). The position of the signal at 143 from C_2 of σ -allyl, which is in the region of chemical shifts typical for the known σ -allyl compounds,^{32,36–39} may indicate that, contrary to allyl species **2**, there is no an additional interaction of a double bond of **7** with surface gallium cations. The analysis of the lineshapes of the signals in vicinity of signals 18, 115, and 138 ppm from initial propene (see the additional inserts of Figure 4) indicates that there are some additional weak signals at 15, 112, and 135 ppm. They are reasonably assigned to a π complex of the olefin with

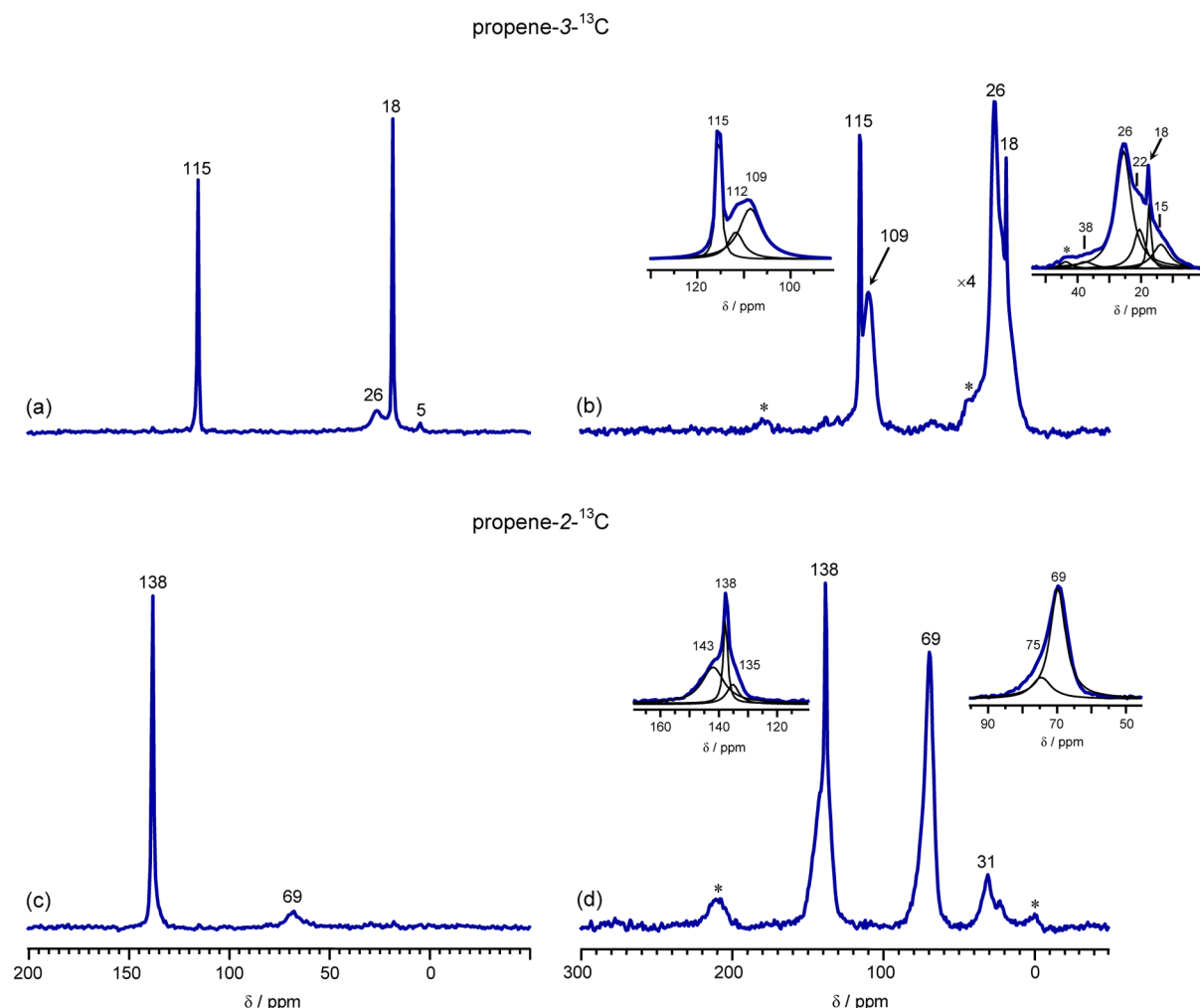
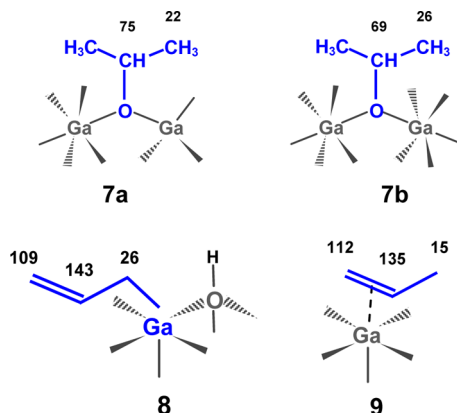


Figure 4. NMR spectra of the products of propene interaction with surface of α -Ga₂O₃ at room temperature: (a and c) ^{13}C MAS NMR and (b and d) ^{13}C CP/MAS NMR. (a and b) Adsorption of propene-3- ^{13}C on α -Ga₂O₃; (c and d) adsorption of propene-2- ^{13}C on α -Ga₂O₃. Asterisks (*) denote the spinning side-bands.

Ga³⁺ surface cations (9). There are also some weak signals at 31 ppm that could be assigned to some dimers of propene.



3.2.2. *n*-Butene-1. Adsorption of *n*-butene-1 on Ga₂O₃ results in the fast isomerization of the olefin to *n*-butene-2. Therefore, adsorbed *n*-butene-1-1- ^{13}C shows (Figure 5a) two signals at 17 and 11 ppm arising from the ^{13}C -labeled methyl groups of *trans* and *cis* isomers of the formed *n*-butene-2-1- ^{13}C . Adsorbed *n*-butene-1-2- ^{13}C (Figure 5b) shows a signal at 127 ppm from the ^{13}C -labeled $-\text{CH}=\text{}$ group of both the *trans* and *cis* isomers of

the formed *n*-butene-2-2- ^{13}C . The reaction product formed from the initially adsorbed *n*-butene-1-2- ^{13}C exhibits two signals at 75 and 34 ppm from the ^{13}C -labeled carbons. These two signals unequivocally point to the formation of the 2-butoxy species (10) bound to the surface of gallium oxide. Indeed, the position of the signals from 10 is very close to that of the signals of *sec*-butyl alcohol (vide supra).³³ The methyl groups of species 10 could be found in the spectrum of adsorbed *n*-butene-1-1- ^{13}C . This spectrum (see Figure 5a) exhibits a superposition of several broad signals at 10–30 ppm, and they are seen as a background for the narrow signals 17 and 11 ppm from the weakly adsorbed *trans*- and *cis*-*n*-butene-2. Among these broad signals at 10–30 ppm, the signals at 13 and 27 ppm might be assigned to methyl groups of the species 10, whereas the signals at 9, 21 ppm and at 135, 120 ppm could be assigned to the CH_3- and $-\text{CH}=\text{}$ groups of π complexes of *cis*- (11b) and *trans*-butene-2 (11a) with the surface gallium cations.

3.2.3. Isobutene. The interaction of isobutene-2- ^{13}C with the Ga₂O₃ surface gives rise to the appearance of four signals in the ^{13}C CP/MAS NMR spectrum from the labeled carbon at 151, 147, 74, and 31 ppm (Figure 6). The signal at 74 ppm is indicative of the formation of *tert*-butoxy species (12) formed from the olefin. The signal at 31 ppm is in the region of chemical shifts typical for the quaternary carbon atoms of alkanes.³³ This

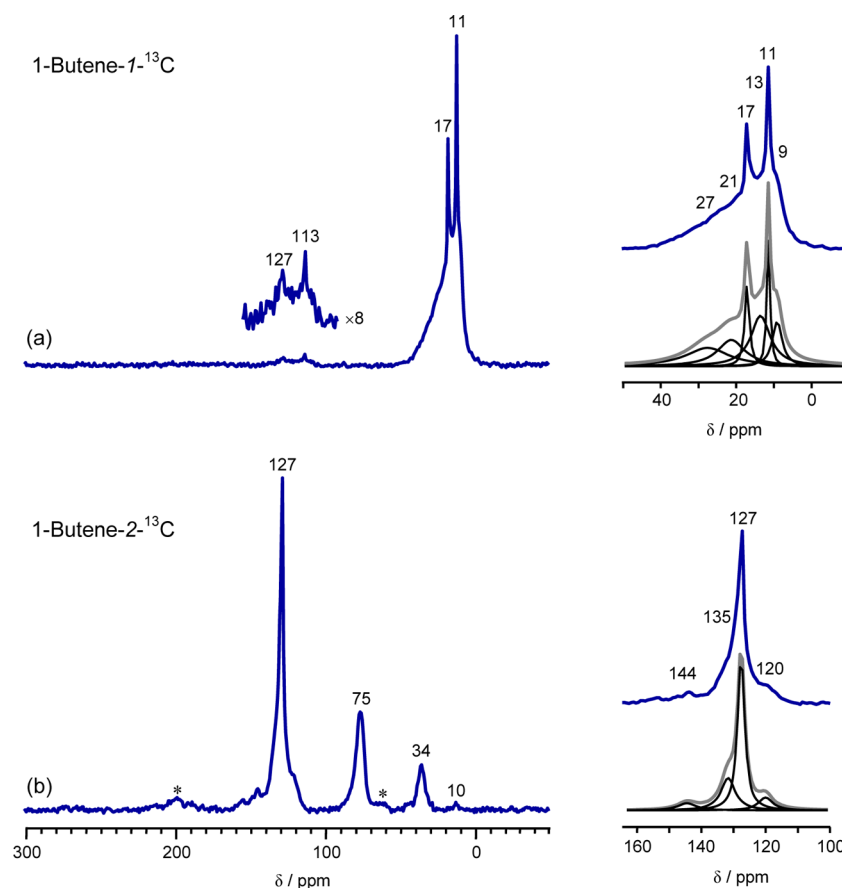


Figure 5. ^{13}C CP/MAS NMR spectra of the products of *n*-butene-1 interaction with surface of $\alpha\text{-Ga}_2\text{O}_3$ at room temperature: (a) adsorption of *n*-butene-1-1- ^{13}C on $\alpha\text{-Ga}_2\text{O}_3$; (b) adsorption of *n*-butene-1-2- ^{13}C on $\alpha\text{-Ga}_2\text{O}_3$. Asterisks (*) denote the spinning side-bands.

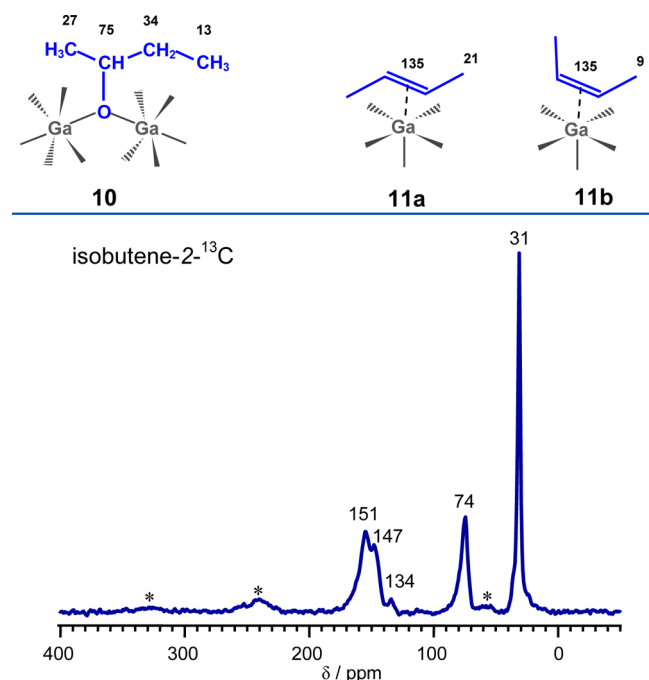


Figure 6. ^{13}C CP/MAS NMR spectra of the products formed at 2-methylpropene-2- ^{13}C (isobutene-2- ^{13}C) adsorption on $\alpha\text{-Ga}_2\text{O}_3$ at room temperature. Asterisks (*) denote the spinning side-bands.

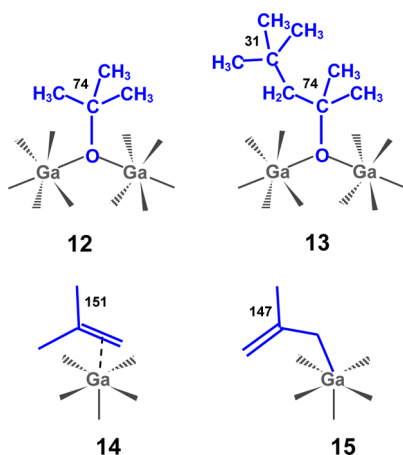
signal from the quaternary labeled carbon atom can be produced at isobutene dimerization to offer 2,4,4-trimethyl-pentene-2. If a

dimer formed, the second labeled carbon atom of this dimer with intensity comparable to that of the signal at 31 ppm should be detected at a chemical shift slightly higher than 130 ppm.³³ The small intensity signal at 134 ppm could substantiate the formation of an isobutene dimer but in small quantity and evidently not corresponding to some product with the intense signal at 31 ppm. Most probably, the signal at 31 ppm belongs mainly to the isobutene dimer, bound to the surface oxygen of gallium oxide to form a dimer alkoxy species (13). In this case, a second labeled carbon atom should exhibit the signal in vicinity of 70 ppm. So, the observed signal at 74 ppm, which we assign to the species 12, contributes also to the alkoxy species 13.

The broad signals at 151 and 147 ppm exhibiting spinning side bands point to the formation of strongly adsorbed species of isobutene. The position of the broad signal at 151 coincides with that of the signal from the initial isobutene. This signal should be ascribed to the π complex of isobutene with surface gallium cations 14. The other broad signal at 147 ppm can indicate on the formation of σ -allyl complex 15 from isobutene on Ga_2O_3 . If π -allyl were formed, the signal from the expected labeled carbon atom would be expected above 170 ppm.^{28,32,40}

4. DISCUSSION

NMR analysis of the species formed at the interaction of olefins with alumina and gallium oxide at room temperature demonstrates a formation of a variety of the surface species different in the structure and the nature of olefin interaction with the oxide surface (Table 1). Both surface allyl species formed at dissociative adsorption of olefin on metal oxides by the



interaction of the C–H bonds of the terminal methyl groups with strongly polarized $\text{Al}^{3+}\text{--O}^{2-}$ ($\text{Ga}^{3+}\text{--O}^{2-}$) couples, and alkoxy species, formed by a protonation of olefin double bond with acidic surface AlOHAl (GaOHGa) groups, exist on the oxide surface. Conclusions on the allylic nature of the surface species formed at olefin adsorption on Al_2O_3 were earlier made with IR spectroscopy.^{23,24,27,41} However, a formation of alkoxy species from olefins was not earlier detected with IR spectroscopy at room temperature.²⁷ Based on the relative intensities of the signals from allyl and alkoxy species, NMR shows that alkoxy and allyl species are formed in comparable quantities. The formation of alkoxy species from the olefins indicates that alumina and gallium oxide possess Brønsted acid sites, which are sufficiently strong to protonate the adsorbed olefins already at room temperature, rather than at higher temperature as was postulated earlier.²⁷

NMR offers more exact information with respect to IR data about the structure of allyl intermediates. For example, IR spectroscopy identified the formation of π -allyl^{22,23,41} or σ -allyl^{24,27} complexes formed from propene on Al_2O_3 , whereas NMR shows the formation of σ , π -allyl complex 2, rather than the σ -allyl complex. According to IR data,^{24,27} *n*-butene affords 1-methylallyl complex (σ bonding of C_2 carbon atom to aluminum cation) on Al_2O_3 , whereas NMR unambiguously points to the formation of 3-methylallyl complex 4, based on observation of

the specific NMR signals in the allyl formed from *n*-butene-1 with selective ^{13}C labels at the certain carbon atoms. IR spectroscopy identified 2-methylallyl complex with σ bonding of the C_1 carbon atom to the aluminum cation, formed from isobutene on alumina,^{24,27} whereas NMR unequivocally shows that it is indeed 2-methylallyl complex 5 with η^3 -like fashions of allyl ligand bonding to a metal cation (π -allyl).

Since alkoxy and allyl species are formed in comparable quantities on the metal oxides studied, the mechanism of a double bond isomerization may be reconsidered, because each intermediate can contribute to the isomerization process. A possible role of alkoxy and allyl species as intermediate in olefin double bond isomerization reaction deserves discussion.

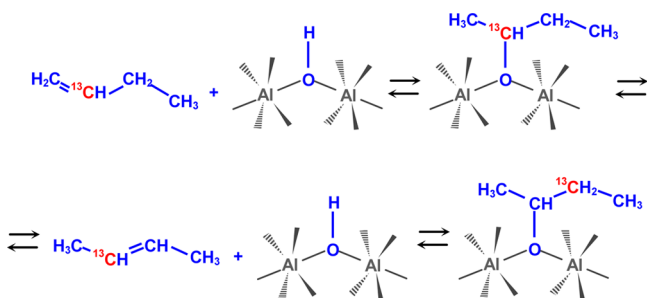
It is widely discussed and assumed that allyl species could contribute to a double bond isomerization on metal oxides.^{1,4,24,27,42} There is no doubt that allyl species represents the intermediate in a double bond isomerization reaction of propene on ZnO , as far as the allyl species was identified as the only intermediate at propene adsorption on ZnO .^{20,43–45} For the same reason, it is considered that *n*-butene-1 to *n*-butene-2 isomerization on ZnO occurs with involvement of allyl intermediate.^{2,3,29}

At the same time, the evolution of the intensities of the signals from ^{13}C labels (C_2 and C_3 atoms) in 2-butoxy species 3 and 10, formed from *n*-butene-1-2- ^{13}C , is evidence for the involvement of these butoxy species and Brønsted acid sites of Al_2O_3 and Ga_2O_3 in the reaction of a double bond isomerization of *n*-butene. Indeed, within 2 h after adsorption of *n*-butene-1-2- ^{13}C on Al_2O_3 , the formed alkoxy species 3 exhibits solely the signals at 69–74 ppm from the $>\text{HC--OAl}$ fragment, i.e., the signals from the carbons attached to the surface oxygen (Figure 2b). This points to a transfer of a proton from the acidic AlOHAl group to the *n*-butene-1-2- ^{13}C molecule by the Markovnikov rule to afford the alkoxy species 3 with the ^{13}C label at the $>\text{CH--OAl}$ fragment (Scheme 1). So, despite a notable amount of *n*-butene-2-2- ^{13}C (the signal at 128 ppm in Figure 2 b) formed by this time and therefore a possibility of the acidic OH group of oxide to protonate both *n*-butenes, the primary object for olefin protonation represents *n*-butene-1-2- ^{13}C . Otherwise, a protonation of *n*-butene-2-2- ^{13}C would give the alkoxy species 3 with equal intensities of the signals at 69–74 and 31–34 ppm from

Table 1. Chemical Shifts (δ , ppm) of the Surface Species 1–15 Formed on Interaction of Olefins with γ - Al_2O_3 and α - Ga_2O_3

olefin	surface species	surface species number	γ - Al_2O_3				α - Ga_2O_3			
			C_1	C_2	C_3	C_4	surface species number	C_1	C_2	C_3
propene	<i>iso</i> -propoxy	1a	79	21			7a	75	22	
		1b	63	26			7b	69	26	
	σ , π -allyl	2	23	183		108				
	σ -allyl						8	26	143	109
<i>n</i> -butene	π complex						9	112	135	15
	2-butoxy	3a	69	24 (CH_3) 34 (CH_2)	13		10	75	27 (CH_3) 34 (CH_2)	13
		3b	74	24 (CH_3) 31 (CH_2)	13					
	3-methyl- σ -allyl	4	24	147		83 19				
	π complex						11a	135	21	
isobutene	2-methyl- π -allyl	5	80	215			11b	135	9	
		6a	67	31			12	74		
		6b	67		31		13	74		31
	π complex						14		151	
							15		147	
	2-methyl- σ -allyl									

Scheme 1. Possible Pathway of *n*-Butene Double Bond Isomerization with 2-Butoxy Species Formation As the Intermediate on Alumina^a



^aThe scheme rationalizes the evolution with time of ¹³C label from the >CH–OAl fragment into the –CH₂– group of 2-butoxy species. The scheme is also valid for gallium oxide.

both >HC–OAl and –CH₂– fragments. Twenty hours after olefin adsorption, the signals at 31–34 ppm from the –CH₂– fragment indeed appeared in the spectrum (Figure 2c). This is accounted for by a transfer of the ¹³C label from the >CH–OAl fragment to the –CH₂– group with time. This label transfer can occur by a deprotonation of species 3 to form *n*-butene-2-2-¹³C and further reprotonation of *n*-butene-2-2-¹³C to give alkoxy species 3 with the label at the –CH₂– group (Scheme 1). Thus, NMR data show evidence for the involvement of alkoxy species 3 in *n*-butene-1/*n*-butene-2 double bond isomerization on Al₂O₃, including the steps of *n*-butene-1 protonation and alkoxy species deprotonation to give *n*-butene-2. Note however, that reversible process of alkoxy species 3 deprotonation and *n*-butene-2-2-¹³C reprotonation occurs slowly with the rate corresponding to the increase with time of the intensities of the signals from the –CH₂– groups at 31–34 ppm. Taking into account that a notable amount of *n*-butene-2 is already formed within the first 2 h after olefin adsorption on Al₂O₃, and a reversible process of *n*-butene-2 formation from alkoxy species is essentially slower process (20 h of reaction at room temperature), the formation of *n*-butene-2 from *n*-butene-1 by Scheme 1 could not be the only process, providing a double bond isomerization reaction in *n*-butene-1. The process in Scheme 1 contributes to the total process of *n*-butene-1/*n*-butene-2 isomerization, occurring mainly with involvement of allylic intermediate species as was claimed earlier.^{2,4,27}

A similar mechanism involving the protonation of *n*-butene-1 and deprotonation of alkoxy species 10 to give *n*-butene-2 and further *n*-butene-2 reprotonation to afford again species 10 is realized on gallium oxide. The greater intensity of the signal at 75 ppm compared to that at 34 ppm (Figure 5b) indicates that alkoxy species 10 is primarily formed by protonation of *n*-butene-1 rather than by *n*-butene-2. Therefore, similar to the case of Al₂O₃, two mechanisms with intermediate formation of allylic and alkoxy species can contribute to the *n*-butene double bond isomerization on Ga₂O₃.

5. CONCLUSIONS

Interaction of olefins (propene, *n*-butene, isobutene) with the surface of alumina (γ-Al₂O₃) and gallium oxide (α-Ga₂O₃) results to a formation of a variety of intermediates different in the structure and the nature of olefin interaction with oxide surface at room temperature. NMR clearly shows that both allylic and alkoxy species are simultaneously formed on these oxides. Alkoxides, i.e., hydrocarbon fragments bound to the surface

oxygens, are formed by a transfer of acidic proton from the oxide surface to olefin molecule. Dissociative adsorption of olefin on metal oxides by the interaction of the C–H bonds of the terminal methyl groups with strongly polarized surface M³⁺–O^{2–} (M = Al and Ga) couples gives rise to allyl species bonded to aluminum or gallium ions.

Propene affords *iso*-propoxy and allylic intermediates on both oxides. Allyl formed on alumina is bound to the Al³⁺ cations of oxide surface in a η¹,η²-like fashion, i.e., σ-allyl is formed with additional interaction of a double bond with the other surface aluminum cation by π bonding (σ,π-allyl). Allyl formed on α-Ga₂O₃ is bound to the Ga³⁺ cation of surface oxide exclusively in a η¹-like fashion (σ-allyl).

n-Butene gives 2-butoxy species for both oxides, whereas allylic species (σ-allyl) was identified for this olefin only for γ-Al₂O₃. Adsorption of isobutene results in the formation of *tert*-butoxy species (and alkoxide of dimeric isobutene) on both oxides. Allylic species are also produced from isobutene. π-Allyl with η³-like fashion of allyl bonding to oxide surface is formed in the case of γ-Al₂O₃, whereas σ-allyl is formed in the case α-Ga₂O₃.

Both allylic and alkoxy species can be involved in the reaction of a double bond shift reaction of olefins on oxide surfaces as intermediates. Analysis of characteristic time for a double bond shift reaction in adsorbed *n*-butene and ¹³C-label scrambling in the internal (CH₂ and CH) groups of 2-butoxy species evidence that the allyl rather than alkoxy pathway contributes preferentially to the olefin double bond isomerization.

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Notes

The authors declare no competing financial interest.

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