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Alkane Activation Initiated by Hydride Transfer: Co-conversion of Propane and Methanol over H-ZSM-5 Zeolite[**]

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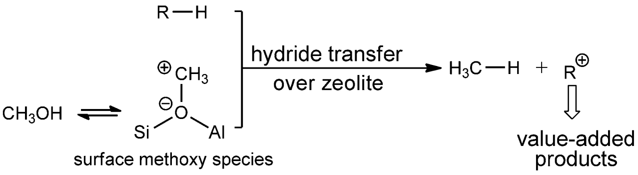
Dedicated to Professor Michael Hunger on the occasion of his 60th birthday

Abstract: *Co-conversion of alkane with another reactant over zeolite catalysts has emerged as a new approach to the long-standing challenge of alkane transformation. With the aid of solid-state NMR spectroscopy and GC-MS analysis, it was found that the co-conversion of propane and methanol can be readily initiated by hydride transfer at temperatures of ≥ 449 K over the acidic zeolite H-ZSM-5. The formation of ^{13}C-labeled methane and singly ^{13}C-labeled n-butanes in selective labeling experiments provided the first evidence for the initial hydride transfer from propane to surface methoxy intermediates. The results not only provide new insight into carbocation chemistry of solid acids, but also shed light on the low-temperature transformation of alkanes for industrial applications.*

Alkanes are the main components in natural gas and crude oil. The conversion of abundant but inert alkanes into high-value-added products has been a long-standing challenge to chemists.[1] The direct transformation of alkanes[2] suffers from the inertness of C–H/C–C bonds and unfavorable thermodynamics which result in high reaction temperature, low product yield/selectivity, and unrealistic cost for industrial applications. Alternatively, the co-conversion of alkanes with reactive hydrocarbons[3] or oxygenates[4] over zeolites has recently been explored to overcome these limitations. Methanol is a key platform chemical produced from various sources and can be readily converted over acidic zeolites through the industrial process.[5] Many efforts have accordingly been attempted to use methanol as the co-reactant[6] for coupling with methane,[6a] ethane,[6b] C_3–C_4 alkanes,[6c] *n*-butane,[6d] *n*-hexane,[6e] and petroleum naphtha.[6f] However, the development of robust catalytic systems for efficient activation and further conversion of alkanes is severely hindered by the lack of mechanistic understanding. In this regard, solid-state NMR spectroscopy has been applied as a powerful tool for monitoring the mechanistic events on heterogeneous catalysts.[7] In addition, GC-MS analysis on the distribution of either ^{13}C or ^{2}H labels in the reaction products may offer the complementary information on many mechanistic details. Through solid-state magic-angle-spinning (MAS) NMR spectroscopy and GC-MS analysis, we found herein, that upon addition of methanol, the C–H bond activation of propane was initiated by hydride transfer to surface methoxy species over zeolite H-ZSM-5 (Scheme 1). Initiated by hydride transfer, even at temperature as low as 449 K, the co-conversion of propane and methanol can be further achieved by secondary reactions, such as propene methylation (Scheme 2). This work not only details the long-pursued evidence for hydride transfer over zeolite catalysts, but also offers insightful information on practical utilization of alkanes through the co-conversion strategy.



Scheme 1. C–H bond activation of alkane (R–H) initiated by hydride transfer to surface methoxy intermediate (denoted as CH_3-ZSM-5 in this work) on acidic zeolites. Once formed by the initial hydride transfer, the carbenium ion (R^+) can be readily converted into value-added products through secondary reactions such as methylation by surface methoxy species (see Scheme 2).

To obtain unambiguous evidence for the initial hydride transfer, we chose ^{13}C-labeled methanol and nonlabeled propane (as the model compound of inert alkane) for the selective labeling experiments. Surface methoxy species (Scheme 1) have been consistently identified as the reactive intermediates in methanol conversion over acidic zeolites,[8] and previous studies have demonstrated its role as an effective methylating agent.[9] Herein, we discovered a new reactivity for suface methoxy species, that is, the hydride abstraction in alkane activation on zeolite H-ZSM-5. The stopped-flow protocol[9] has allowed us to isolate reactive intermediates and study its reactivity by in situ solid-state MAS NMR spectroscopy. By using this protocol, the ^{13}C-

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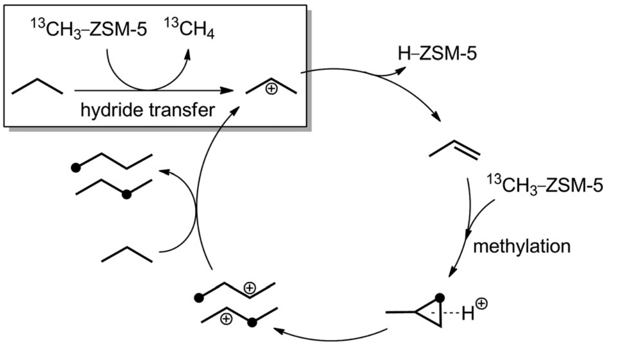

Scheme 2. The role of surface methoxy species in the co-conversion of methanol and propane on zeolite H-ZSM-5: initiation and methylation. The reaction is initiated by hydride transfer from propane to $^{13}CH_3$-ZSM-5, through which $^{13}CH_4$ is formed. The singly ^{13}C-labeled *n*-butanes are formed through propene methylation as one of the secondary reactions depicted herein. The symbol ● denotes the ^{13}C-labeled carbon atoms.

labeled surface methoxy species (denoted as $^{13}CH_3$-ZSM-5) was accordingly prepared[10] from $^{13}CH_3OH$. The reaction between nonlabeled propane (chemical purity of 99.99 %) and $^{13}CH_3$-ZSM-5 could then be monitored by both solid-state ^{13}C MAS NMR spectroscopy and GC-MS analysis.

A key result obtained is that the ^{13}C-labeled methane was formed as the primary product. Figure 1 (left side) shows the ^{13}C high-power proton decoupling (HPDEC) MAS NMR spectra recorded for the reactions occurring at $T = 449$–471 K. The dominant ^{13}C MAS NMR signal at $\delta = 60$ ppm is attributed to $^{13}CH_3$-ZSM-5.[10,11] Meanwhile, the signal at $\delta = 52$ ppm arises from terminal methoxy species or strongly-bonded methanol.[10] The NMR signals at $\delta = 16$ and 17 ppm belong to the methyl and methylene carbon atoms, respectively, of propane. Upon the reaction at 449 K for 5 hours (Figure 1 a), a new NMR signal appeared at $\delta = -7$ ppm and results from the formation of the adsorbed methane [$^{13}CH_4(a)$].[12] The fitted GC-MS data of the isotope distribution patterns (Figure 1 a, right side) showed that methane was almost 100 % ^{13}C-labeled, thus indicating that $^{13}CH_4$ was derived from $^{13}CH_3$-ZSM-5.[13] With the increase of the heating time and temperature (Figure 1 b–d), the formation of methane [$^{13}CH_4(a)$, at $\delta = -7$ ppm] became more evident, and was accompanied by the appearance of free methane [$^{13}CH_4(g)$, at $\delta = 11$ ppm].[12] Again, GC-MS analysis (Figure 1 b–d) indicates that methane was 100 % ^{13}C-labeled. It is worth mentioning that propane or $^{13}CH_3$-ZSM-5 alone on zeolite H-ZSM-5 was not reactive under the same reaction conditions (see the Supporting Information). These results demonstrated that surface methoxy species can abstract a hydride from propane to form methane. This conclusion was further supported by the reaction of deuterated surface methoxy species (CD_3-ZSM-5, prepared from CD_3OH on H-ZSM-5) with propane. The corresponding formation of CD_3H was verified by the GC-MS analysis (see Figure S8 in the Supporting Information).

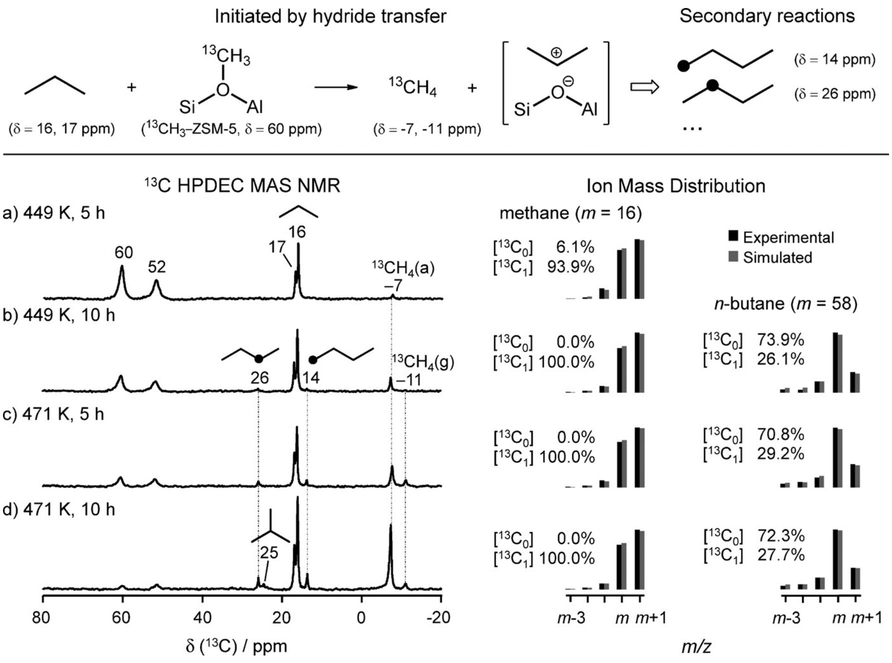

Figure 1. ^{13}C HPDEC MAS NMR spectra (left) and the corresponding bar graphs (right; for methane and *n*-butane products, respectively) of the mass spectra in molecular ion region, recorded upon the reaction of ^{13}C-labeled surface methoxy species ($^{13}CH_3$-ZSM-5, coverage of ca. 13 % Brønsted acid sites on 60 mg of H-ZSM-5) and nonlabeled propane [$n(^{13}CH_3\text{-ZSM-5}):n(\text{propane}) \approx 1:9$] at 449 K for 5 h (a), 449 K for 10 h (b), 471 K for 5 h (c), and 471 K for 10 h (d). Each reaction was conducted in a sealed glass insert to avoid the escape of gaseous products, and the glass insert was directly inserted into a 7 mm rotor for solid-state NMR measurements. The symbol ● denotes the ^{13}C-labeled carbon atoms.

Upon the initial hydride transfer from propane to $^{13}CH_3$-ZSM-5, labeled methane and the adsorbed $C_3H_7^+$ carbenium ion should be simultaneously formed (Scheme 2). Given that it is ^{13}C-unlabeled and readily involved in the secondary reactions, the C_3-species formed initially from propane could not be directly observed by ^{13}C MAS NMR spectroscopy. However, the analysis of secondary reaction products provided the supplemental mechanistic information. As shown in Figure 1, besides methane, *n*-butane was also observed, as evidenced by the ^{13}C NMR signals at $\delta = 26$ (methylene group) and 14 ppm (methyl group).[14] Importantly, GC-MS analysis (Figure 1 b–d) verified that the ^{13}C-labeled *n*-butane products could only have a single ^{13}C label ([$^{13}C_1$]-*n*-butane, see also Table S1), thus indicating that the labeled *n*-butanes came from the ^{13}C-methylation of nonlabeled C_3 species. Meanwhile, the selective formation of [$^{13}C_1$]-*n*-butane rather than isobutane is in excellent agreement with those reported for propene methylation over acidic zeolites.[15] Thus, the observation of singly ^{13}C-labeled *n*-butane indicated one of subsequent transformations after the initial hydride transfer: the adsorbed $C_3H_7^+$ carbenium ion (i.e., surface isopropoxy species) is deprotonated to produce the ^{13}C nonlabeled propene, which can be methylated[15] subsequently by $^{13}CH_3$-ZSM-5 (Scheme 2). Propene methylation on the acidic zeolites involves the protonated methylcyclopropane as the intermediate or transition state.[15] Opening the cyclopropane ring would result in the formation of the singly ^{13}C-labeled *n*-butanes ([$^{13}C_1$]-*n*-butane at either methyl or methylene position), which have also been identified by solid-state NMR and GC-MS. Upon further reaction at 471 K for 10 hours (Figure 1 d), other ^{13}C-labeled products (such as isobutane: $\delta = 25$ ppm and additional propane: $\delta = 16$ and 17 ppm) were produced, thus implying the occurrence of complex secondary reactions (see Figure S5 and Section H in the Supporting Information for detailed discussions).

The experimental observation of $^{13}CH_4$ and singly ^{13}C-labeled *n*-butanes provided direct evidence for the hydride transfer process over acidic zeolite H-ZSM-5 (Scheme 2).[16] To highlight the role of hydride transfer to surface methoxy species for propane activation, we compared the reaction of propane alone (Figure 2 a) with that of propane in the presence of surface methoxy species (Figure 2 b) by GC-MS analysis of the gaseous components. Upon heating at 471 K for 10 hours, propane alone (Figure 2 a) was unreactive over zeolite H-ZSM-5.[13] On the contrary, upon the co-reaction of $^{13}CH_3$-ZSM-5 and propane under the identical reaction conditions (Figure 2 b), 100 % ^{13}C-labeled methane, together with the singly ^{13}C-labeled *n*-butane and isobutane, were formed in a large quantity (see Table S1). Furthermore, we conducted a kinetics investigation on the reaction of $^{13}CH_3$-ZSM-5 and propane by in situ ^{13}C MAS NMR spectroscopy at $T = 449$–471 K (see Figures S9–S11). The apparent activation energy of about 139 kJ mol^{-1} was derived from an Arrhenius plot of methane formation rates against the reaction temperatures.[17] This value is reasonably lower than the apparent activation energy ($E_a = 150$–160 kJ mol^{-1} for ^{13}C-label scrambling of propane over H-ZSM-5.[18] All these data indicate that the C–H bond activation of propane can be indeed initiated by hydride transfer to surface methoxy species.

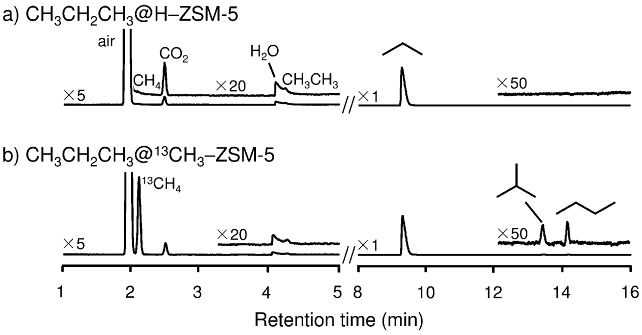

Figure 2. Normalized GC-MS data for the reactions on zeolite H-ZSM-5 of nonlabeled propane alone (a) and of nonlabeled propane together with $^{13}CH_3$-ZSM-5 (b). The reactions were conducted in parallel at 471 K for 10 h, and the samples were measured with the identical GC-MS parameters.

Hydride transfer, as an important step in acid-catalyzed transformation of hydrocarbons, is directly related to the initial C–H bond activation of alkanes and to the formation of the corresponding carbocations.[1b] Once the carbocation is formed, it can be readily converted into the final products by cracking, skeletal isomerization, alkylation, etc. (Scheme 1). In analogy to the classical cases of superacids,[19] hydride transfer has long been proposed to occur between alkanes and surface alkoxy species (as the adsorbed carbenium ions) over acidic zeolites.[20] However, this elementary step[17] has never been experimentally verified because of the complexity of the secondary reactions. Herein, the isolation of surface methoxy intermediates by a stopped-flow protocol and the selective labeling experiments made it possible to verify the initial hydride transfer at low temperatures through a combination of solid-state NMR spectroscopy and GC-MS. This experimental evidence will certainly bridge the gap between the mechanistic studies of alkane activation over liquid and solid acids.

Very similar results were obtained upon the co-conversion of methanol and propane over zeolite H-ZSM-5 (see Figure S12).[21] The practical implication is that methanol may indeed work as an ideal co-reactant for alkane transformation[6] at low temperatures. For example, the CMHC (coupled methanol-hydrocarbon cracking) process over zeolite H-ZSM-5[6g] was initially proposed to achieve energy compensation, but the catalytic results showed that the conversion of hydrocarbon products is also increased.[22] Our mechanistic study not only explains this phenomenon, but also suggests a new possibility for practical conversion of inert alkanes at low temperatures.

In summary, we have used solid-state ^{13}C MAS NMR spectroscopy and GC-MS analysis together to study the initiation mechanism for the co-conversion of propane and methanol over zeolite H-ZSM-5. The formation of ^{13}C-labeled methane and the singly ^{13}C-labeled *n*-butanes was accordingly identified. These results show that, with methanol as the co-reactant, propane conversion can be readily initiated by hydride transfer and followed by methylation on zeolite H-ZSM-5, both of which involve surface methoxy species as the key intermediate (Scheme 2). This research also suggests that co-conversion with methanol may indeed work as an alternative approach to alkane activation. We expect that the in-depth understanding of these elementary steps occurring over acidic zeolites will therefore inspire further investigation on low-temperature conversion of alkanes for industrial utilization.

Keywords: alkanes · hydride transfer · NMR spectroscopy · reaction mechanisms · zeolites

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