

In situ MAS NMR spectroscopy study of catalytic reaction mechanisms[☆]

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Abstract

In situ magic-angle spinning (MAS) NMR spectroscopy has been recently applied successfully to study catalytic reaction mechanisms in batch-like and continuous-flow conditions. The characteristics of both methods are highlighted. Examples taken from our own studies of the activation of propane at low temperature on Ga/H-ZSM-5, the alkylation of benzene with propane on Ga/H-ZSM-5, and the activation of *n*-butane at low temperature on Pt/H-Theta-1 illustrate how batch-like conditions in situ MAS NMR spectroscopy with the help of strategically ¹³C-labelled reagents contributes to the understanding of catalytic reaction mechanisms and of the dynamics and reactivity of surface intermediates and active sites. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recently, there has been increasing interest in the use of in situ techniques to study catalysts and catalytic reactions as such studies can provide a fundamental and molecular understanding of the nature of catalyst behaviour and catalytic transformations. The limited number of in situ analysis tools available today is in constant and rapid growth. Commercial instrumen-

tation is available for IR, Raman, XRD, electron microscopy, and UV investigations. A number of research groups are developing several other techniques, including NMR, EXAFS, and surface spectroscopies.

Heterogeneously catalysed reactions are conventionally followed by analyzing the reactor effluent that contains the reactant(s), the reaction intermediate(s), and the product(s). Reaction mechanisms are indirectly inferred from kinetic equations derived by varying experimental variables such as temperature, pressure, flow rates, contact time, etc. To fully understand and prove reaction mechanisms and to obtain information on the role and dynamics of the active sites, it is necessary to analyse the reactants,

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intermediates and products in the adsorbed state, which for hydrocarbon and other organic reactions are most often in short-range ordered organic molecules in some interaction with the catalyst active sites. Such information can be used to confirm the nature and role of the catalytic sites and to speculate about the nature of transition states and intermediates that are not observed, and serve as a predictive tool for the discovery of novel reactions possibly leading to new catalytic processes.

Except for FT-IR and Raman spectroscopies, commercial in situ spectroscopic instrumentation is still not widely available today. As most heterogeneous catalysts are porous materials, surface electron spectroscopies have limited application to the study of bulk heterogeneous catalysts. Although in situ powder XRD is best suited for the determination of the catalyst structural changes during reaction, it is blind to organic molecules that have no long-range order in the catalyst. IR and Raman spectroscopies detect these organic molecules but, most often, the quantification of the data is complicated by the existence of overlapping absorption peaks and uncertainties in the values of the substrate extinction coefficients. In contrast, ^{13}C NMR spectroscopy enables the differentiation of different organic compounds as almost every organic compound has its individual chemical shift(s) “fingerprints”. NMR is also quantitative as it actually counts nuclear spins and has the ability to investigate a large number of nuclei, enabling the detailed characterisation of catalysts and adsorbates.

NMR resonance lines are much broader for solids than for liquids because of the net anisotropic interaction resulting from chemical shift anisotropy, dipole–dipole, and quadrupolar interactions. The mobility of molecules adsorbed in heterogeneous catalysts is reduced significantly by the interactions between the adsorbed molecules and the catalyst surface and adsorbed molecules themselves. They thus show also broad NMR lines in normal condition. The NMR linewidth is, however, noticeably reduced

when the sample is spun at high speed (thousands of revolution per second) and at an angle of 54.74° relative to the external magnetic field, a technique called magic-angle spinning (MAS) NMR. In addition, nearly all molecules are adsorbed at sufficiently low temperature (this is certainly true for organic compounds in zeolites at ambient temperature), which enables the full quantification of the reaction mixture.

In situ MAS NMR spectroscopy for the study of catalytic reaction mechanisms has been developed for more than 20 years and has been demonstrated to be a very powerful investigation tool [1–31]. This review gives an overview of in situ MAS NMR spectroscopy applications in catalysis and demonstrates, by examples selected from our own work, how in situ MAS NMR spectroscopy can contribute to the detailed understanding of reaction mechanisms and the identification of reaction intermediates, including their interaction with the catalyst active sites.

2. In situ MAS NMR technique

The in situ MAS NMR study of reaction mechanisms is usually made in batch-like conditions, i.e., under controlled atmosphere (CA), and it will be abbreviated as CA MAS NMR [1–7,12–14,21–31]. More recently, flow-through NMR probes (containing cells) operating as microreactors have been designed [8–11,15–17,19,20,32].

In batch-like condition (CA MAS NMR), the catalyst and reactant(s) are sealed in a well-balanced glass cell which perfectly fits in the MAS rotor in order to achieve a sufficiently high spinning rate or are simply sealed in the NMR rotor with special caps [1–7,12–14,21–31]. The NMR cell is exposed to reaction conditions at different pressures, temperatures and time lengths, and the reaction is quenched (e.g., in liquid nitrogen) for MAS NMR observation at room temperature. The difference between using a glass cell [1–3,21–31] and using a NMR

rotor with special caps [4–7] is that the former can be ex situ heated to much higher temperature, whereas the latter can be in situ heated but only up to ca. 600 K. Using a CO₂-laser or radio-frequency as heating sources, the reaction cell can be in situ heated to a much higher temperature (up to ca. 1100 K) and rapid temperature switching can also be achieved [12–14]. This approach enables the study of the time-dependence of fast chemical transformations.

Using strategically ¹³C labelled compounds, CA MAS NMR also enables to study quantitatively the behaviour of specific molecules with some advantage relative to the more conventional GC-MS analysis of downstream vapours (GC-MS usually requires a detailed and sometime tedious analysis of the labelled atom distribution). CA MAS NMR is flexible, quantitative, and rather economical in terms of ¹³C label compounds utilisation.

The reaction conditions in CA MAS NMR measurements are comparable with those in a batch reactor although the NMR observation is made at ambient temperature. Because a closed system is used, this approach is fully quantitative. However, its weakness is that it provides limited information into the chemistry of reactions that are affected by the use of flow conditions (under which heterogeneous catalytic reactors are usually operated).

Over the past 5 years, true in situ MAS NMR in which the NMR cell is exposed to a continuous-flow of reactants, as in a microreactor, has been developed [8–11,15–17,19,20,32]. The flow-MAS probe of Hunger and Horvath [15] is probably the first real MAS NMR catalytic microreactor. It was followed by an independent design of Haw's group [8]. A major problem with these setups is, however, the difficulty to realise a gas-tight seal between the fast-spinning NMR reaction cell and the other gases inlets and outlets (rotor drive, rotor bearings, temperature control) in the NMR probe. This problem appears to have been largely overcome in the recent flow MAS module designed by Isbester et al. [19].

An alternative approach to continuous-flow NMR probes is called magic angle hopping which has been used to design the GRASSHOPPER II probe of Maciel et al. [20,32]. Discrete partial rotation of the sample and a hopping sequence can be performed in a manner that involves no net rotation. Using flexible tubing, it is possible to design hopper probes with gas-tight seals.

Haw's group also introduced recently a pulse-quench reactor for in situ MAS NMR studies in continuous-flow conditions [9]. Using this approach, irreversible reactions can be rapidly stopped by quenching of the sample in liquid nitrogen. The sample is then transferred into a precooled probe and characterised by MAS NMR.

Despite their elegance and advantage to operate in nearly real conditions, the application of such designs is restricted by the high costs of ¹³C-labelled reactants needed in a flow system. Another factor is that fluctuations in gas flow that are not easily avoided can affect the quantification of the results. Finally, it is not clear as yet that such sophisticated MAS NMR probes will be soon commercially available and fully compatible with various MAS NMR instrumentation.

In contrast, no hardware modification is needed to apply the CA MAS NMR technique except for the use of special glass cells which are nowadays commercially available. In addition, the utilisation of ¹³C label compounds is economical. Therefore, it is likely that the CA MAS NMR technique will still be the most common method to study catalytic reaction mechanisms in the near future.

In the remaining part of this review, we give examples of applications of the CA MAS NMR technique, combined with the strategic ¹³C-labelling of the reactants, to study the mechanistic details of various catalytic transformations. We will show that the information gathered in such experiments can have a predictive character and lead to the proposal of new catalytic reactions. The examples selected are from our own work.

This selection indicates by no means that work performed by other groups active in this field is less relevant than ours.

3. CA MAS NMR studies of catalytic reaction mechanisms

3.1. Low temperature activation of propane on Ga/H-ZSM-5

The activation and functionalisation of light alkanes in rather mild and non-oxidative conditions are receiving increasing attention. Using economical and abundant alkanes feeds to replace other more costly reactants such as olefinic or aromatic compounds is indeed commercially attractive.

The aromatisation of propane on acidic zeolite catalysts has been widely discussed. The attention was focused mainly on zeolite H-ZSM-5, usually modified by the addition of a dehydrogenation component involving elements such as Ga and Zn as oxides. Ga/H-ZSM-5 is the preferred catalyst [33–45] used in a commercial process, CYCLAR, which is now jointly developed commercially by UOP and BP. Aromatisation is generally achieved at a temperature in the range 773–823 K and its pathway has been extensively described in the literature. In contrast, the mechanism responsible for the activation of propane at low temperature, i.e., 523–673 K, on the same type of catalysts has received much less attention. This was at the origin of our investigations. We have addressed this problem by using ^{13}C CA MAS NMR using strategically labelled propane-2- ^{13}C as reactant.

Three catalysts, Ga/silicalite (H-ZSM-5 with Si/Al = 480), Ga/H-ZSM-5 (Si/Al = 35) and H/ZSM-5 (Si/Al = 35), were used to investigate the synergistic action of the dehydrogenation function provided by the gallium species and the acidic function from the Brønsted sites of the zeolite. The first two catalysts contained ca. 1 wt.% of Ga modifier (impregnation by gallium nitrate, followed by drying and calcina-

tion). All catalysts were first calcined in air at 773 K and then evacuated at 573 K prior to adsorption of propane-2- ^{13}C (4 molecules per unit cell) on the samples in the NMR cell. Details of the catalysts preparation for the NMR experiments are reported elsewhere [23].

The reaction of propane on Ga/H-ZSM-5 begins at 573 K. Typical spectra showing its progressive transformation on a Ga/H-ZSM-5 (Si/Al = 35) are shown in Fig. 1. The initial spectrum shows only a resonance at ca. 17 ppm, corresponding to the labelled methylene group of propane-2- ^{13}C . After 5 min at 573 K, a resonance is observed at ca. 16 ppm corresponding to the methyl group of propane. No other resonances were observed in the spectrum at this stage, indicating the absence of other products. Complete scrambling of the ^{13}C label, leading to the expected 2:1 ratio of the methyl and methylene resonances, is observed after ca. 20 min. As scrambling of the ^{13}C label in propane can occur without the formation of other products, it is most likely to take place via a cyclic intermediate.

In the above spectra, the resonances at ca. –9 and 6 ppm correspond to methane and ethane, respectively. *n*-Butane is characterised by resonances at 13.5 and 26 ppm whereas resonances at 22 and 24.5 ppm are typical of *i*-butane.

Compared to Ga/H-ZSM-5, extremely low activity is observed for Ga/silicalite (Si/Al = 480), as shown in Fig. 2. Scrambling only occurs at ca. 723 K. It demonstrates that Brønsted acidity is necessary to activate propane at 573 K on Ga/H-ZSM-5 catalysts. Lower activity is also observed for H-ZSM-5 (Fig. 3). Scrambling is only detected after 20 min at 573 K and completed after ca. 80 min. Thus, Ga-sites and Brønsted acid sites act in synergy. It is further noticed that identical spectra are observed for the Ga/H-ZSM-5 and H-ZSM-5 catalysts at longer reaction times (Figs. 1 and 3), from which we conclude that the major role of the Ga species in Ga/H-ZSM-5 is to promote the initial activation of propane.

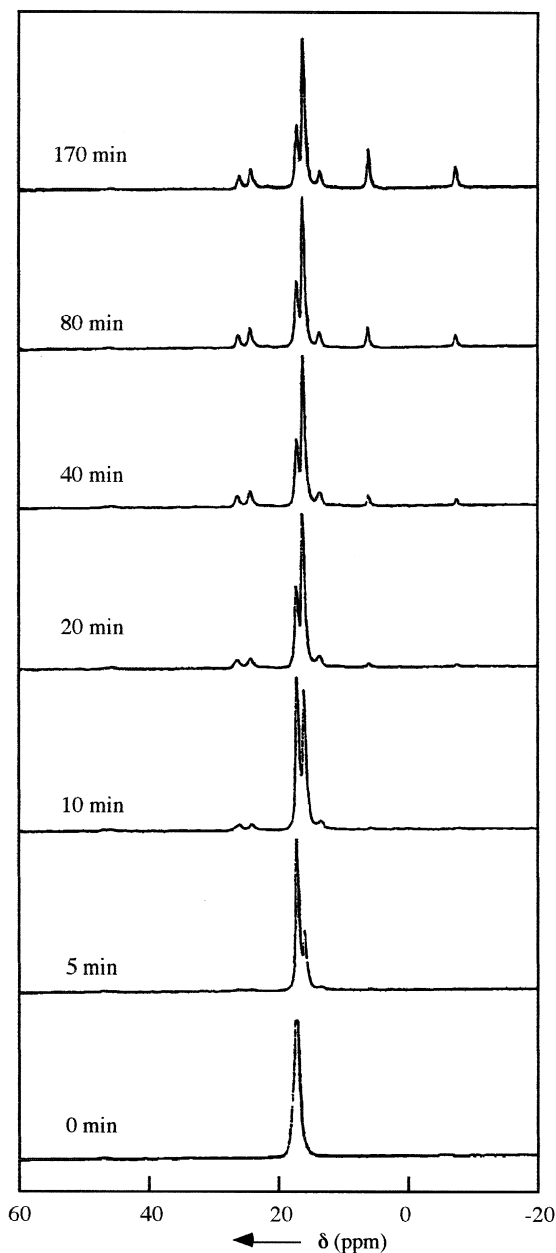


Fig. 1. ^{13}C MAS NMR spectra observed after reaction of propane- $2\text{-}^{13}\text{C}$ (4 molecules/u.c) at 573 K on Ga/H-ZSM-5 (Si/Al = 35) (adapted from Ref. [23]).

It was further demonstrated that dihydrogen inhibits the activation of propane. This effect may be due to competitive adsorption of H_2 on the Ga species or even to reduction of Ga^{3+} to Ga^+ . The reduction of Ga_2O_3 to Ga_2O in such

conditions has been reported by several authors [46–48].

All these observations can be rationalized by the proposal of a bifunctional reaction step (BREST) mechanism (Fig. 4) [23,27]. The active site responsible for the activation of propane consists of a $(\text{Ga}^{3+}, \text{O}^{2-})$ ion pair closely associated with an acidic Brønsted site of the zeo-

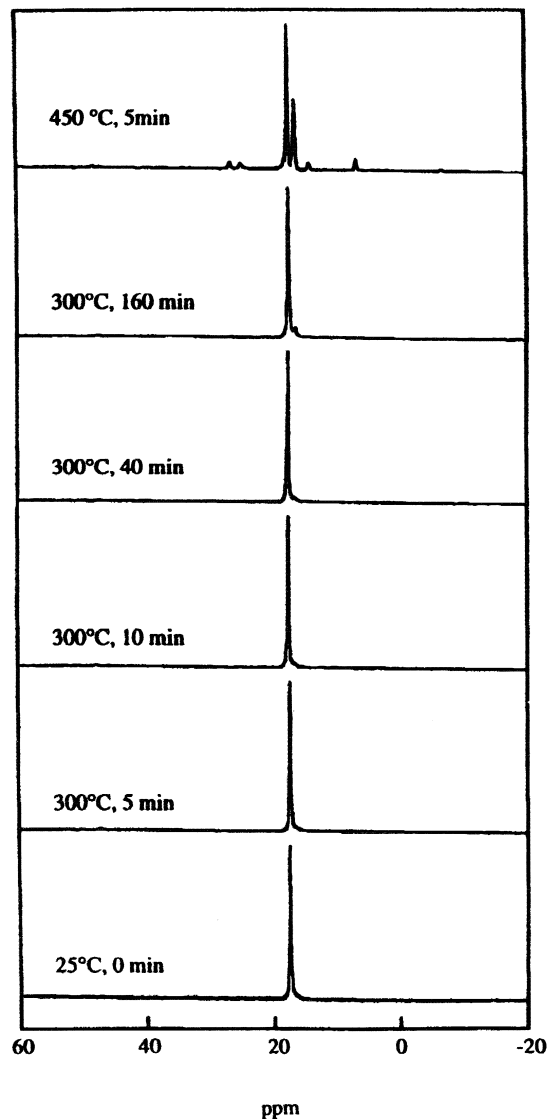


Fig. 2. ^{13}C MAS NMR spectra observed after reaction of propane- $2\text{-}^{13}\text{C}$ (4 molecules/u.c) at 573 and 723 K on Ga/H-ZSM-5 (silicalite: Si/Al = 480) (adapted from Ref. [23]).

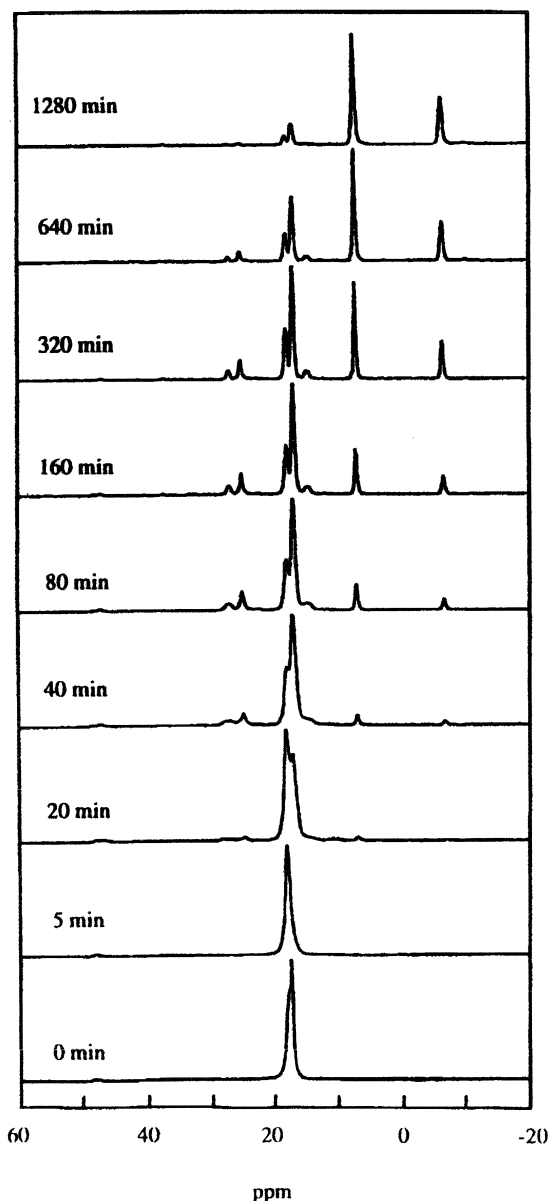


Fig. 3. ^{13}C MAS NMR spectra observed after reaction of propane-2- ^{13}C (4 molecules/u.c) at 573 K on H-ZSM-5 (Si/Al = 35) (adapted from Ref. [23]).

lite. The $(\text{Ga}^{3+}, \text{O}^{2-})$ ion pair involves either ion-exchanged gallium (Ga_{ionex}) and an oxygen anion from the zeolite lattice, or dispersed extra-framework Ga species (Ga_{D}) which may contain oxygen if they are (hydroxy)-cations or neutral species, or are associated to zeolite oxygen anions otherwise. In this scheme, propane

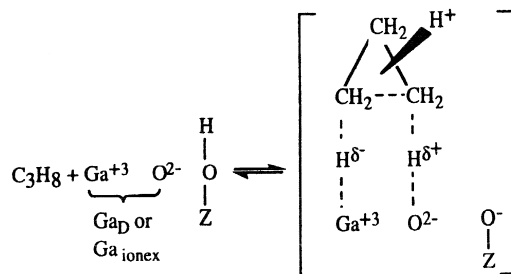


Fig. 4. Bifunctional reaction step (BREST) mechanism for the bifunctional activation of propane on Ga-containing H-ZSM-5 catalyst: the protonated pseudo-cyclopropane (PPCP) intermediate (adapted from Ref. [23]).

interacts heterolytically with the $(\text{Ga}^{3+}, \text{O}^{2-})$ ion pair via a positively and a negatively charged hydrogen atom, respectively, and it is further converted into a pseudo-cyclopropane entity which is protonated by the Brønsted site (Fig. 4). This scheme agrees with the heterolytic activation/dissociation of propane as $(\text{C}_3\text{H}_7^+, \text{H}^-)$ on an oxidic Ga component which was proposed previously [49,50]. However, the specific role of the Ga sites was only claimed in our work and the existence of a cyclic intermediate was not identified previously.

The BREST scheme explains the ^{13}C scrambling in propane without formation of other products and the synergistic action of Ga species and Brønsted sites.

The protonated pseudo-cyclopropane (PPCP) intermediate can also evolve in different ways as shown in Fig. 5. Dehydrogenation produces a C_3H_7^+ carbenium ion (route 1) which can lead to propene or oligomerize by reaction with olefinic intermediates. The PPCP intermediate can also decompose into methane and a C_2H_5^+

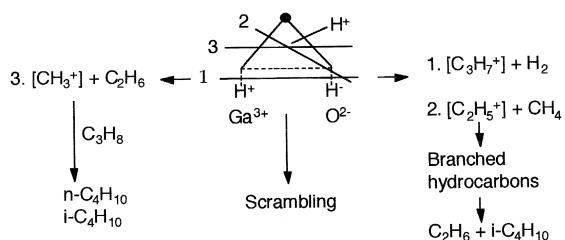


Fig. 5. Initial products and intermediates resulting from the bifunctional activation of propane on Ga-containing H-ZSM-5 catalysts (adapted from Ref. [23]).

carbenium ion (route 2) or ethane and a CH_3^+ carbocation (route 3). The CH_3^+ carbocation and the C_2H_5^+ carbenium ion can react further with olefins and alkanes. The reaction of CH_3^+ (stabilized on a basic zeolite oxygen anion) with propane (activated on the Ga site) may yield either *n*-butane or *i*-butane. These products are indeed observed in the initial reaction stages.

The PPCP intermediate model and the BREST reaction scheme are in agreement with the observed activation of propane by dissociative adsorption on Ga species [49–51], the proposed role of Ga species as hydrogen “portholes” [52], and the negative reaction order observed with respect to dihydrogen when extra-framework Ga species are present [52]. It also rationalises several earlier mechanistic proposals claiming the activation of propane by acidic sites only [34,53] and the dehydrogenation of propane on Ga species [32,49,54].

Obviously, the PPCP model should not only be restricted to the activation of propane but could also apply to the activation of other light alkanes such as *n*-butane, which we will demonstrate later. It suggests further that carbocation or carbenium ions species generated by the decomposition of PPCP-type complexes may lead to some unexpected reactions with other nucleophiles such as aromatics, water, carbon dioxide, or ammonia.

3.2. Alkylation of benzene with propane on Ga/H-ZSM-5

The alkylation of benzene with alkanes occurs in superacidic media [55,56]. Two competitive mechanisms were suggested to account for cumene formation from benzene and propane [57]. However, these mechanisms cannot readily be extended to the benzene alkylation of propane using zeolite catalysts as different reaction products are observed [57–59]. ^{13}C CA MAS NMR was used to clarify the mechanism of the benzene alkylation with propane using Ga/H-ZSM-5 (Si/Al = 35) catalysts. Table 1 lists the various experiments that were performed. De-

Table 1
Description of the experiments for benzene alkylation with propane

Experiment	Catalysts	Loaded reactants (molecule/u.c.)		
		Propane-2- ^{13}C	Benzene	H_2
A	Ga/H-ZSM-5	–	9	3
B	Ga/H-ZSM-5	3	9	–
C	Ga/H-ZSM-5	1	9	–
D	Ga/H-ZSM-5	3	–	–

tails of the catalysts preparation for the NMR experiments are reported elsewhere [28].

When benzene is adsorbed in the presence of hydrogen (experiment A in Table 1), the NMR resonance of adsorbed benzene is shifted significantly to higher field relative to solution data, indicating some distortion of benzene upon adsorption.

Co-adsorption of propane (experiments B and C in Table 1) results in a shift of the benzene resonance to lower field. The presence of benzene, in turn, affects the resonance corresponding to the labelled methylene group of propane appearing then as two lines, narrow and broad lines, centered at ca. 17 ppm. The narrow line, identical to the resonance observed when propane alone is adsorbed (experiment D in Table 1), is attributed to propane molecules which have some mobility. The broad line corresponds to propane molecules with restricted mobility as evidenced by cross-polarization experiments. Restricted propane mobility in the presence of benzene may be due to the decreased space available within the zeolite channels following benzene adsorption or to a specific interaction of the propane methylene group with adsorbed benzene.

The reaction of propane with benzene begins at 573 K, as also observed when propane only is adsorbed. However, an induction period (40–160 min) whose duration increases with the benzene/propane ratio is observed. During this induction period, the broad resonance line at ca. 17 ppm, corresponding to propane molecules with restricted mobility shifts to lower field and becomes more pronounced. It then disappears

when the first reaction products are formed. It suggests that the stronger adsorption of benzene relative to propane and/or the interaction between adsorbed benzene and the propane methylene group retard the direct activation of propane on the zeolite active sites, leading to an induction period, and that the propane molecules with restricted mobility are those reacting initially with benzene.

Benzene alkylation with propane can be initiated in the following two different ways (Fig. 6) [60].

- Benzene activation by H-ZSM-5 was reported to occur by benzene protonation on strong acid sites to form a benzenium ion [61]. The benzenium ion can abstract a hydride ion from the nearest propane molecule leading to an isopropenium ion. The latter can alkylate benzene to yield cumene which in turn can convert to toluene and ethylbenzene via secondary reactions [25,62].

- Propane activation by Ga/H-ZSM-5 may occur via a bifunctional mechanism involving the cyclic PPCP intermediate, as discussed above. The latter can decompose in various

ways resulting in the formation of CH_4 , C_2H_6 , H_2 and methyl, ethyl and propyl carbenium ions (Fig. 5). These carbenium ions can lead to the corresponding alkylbenzenes: toluene, ethylbenzene, cumene and *n*-propylbenzene when the reaction is carried out in the presence of benzene.

^{13}C CA MAS NMR results indicate that both activation pathways probably operate in our reaction conditions.

The appearance of the small but distinct NMR line at ca. 124.4 ppm in the very early stage of the reaction, which disappears at longer reaction times, shows the formation of cyclohexadienes. Weak resonances at ca. 23.5 and 34 ppm also evidence the formation of small amount of cumene with ^{13}C labelled in the alkyl chain, respectively. These observations favour the first activation pathway.

The progressive shift of the methylene resonance line at 17 ppm to higher field, in the early stages of the reaction, indicates that the resonance corresponding to the propane methylene group appears at ca. 16 ppm. The resonances of the methylene and methyl groups of propane are not well resolved in the presence of benzene because of significant line broadening. The scrambling of the ^{13}C label in propane implies the existence of a PPCP-type intermediate and points to the second activation pathway.

Although evidence for both routes exists, the observation of an induction period suggests that the activation pathway involving the preliminary activation of propane is dominant.

In the initial stages of the reaction (experiments B and C in Table 1), major resonances corresponding to toluene (21 ppm), ethylbenzene (29 ppm), ethane (7 ppm), and methane (−6 and −11 ppm) are observed together with weak resonances attributed to cyclohexadienes (124.4 ppm), cumene (23.5 and 34 ppm) and *n*-propylbenzene (14 and 25 ppm). After heating at 573 K, the lines corresponding to cyclohexadiene and cumene disappear, and toluene and methane become the major reaction products. Longer reaction times cause ethylbenzene and

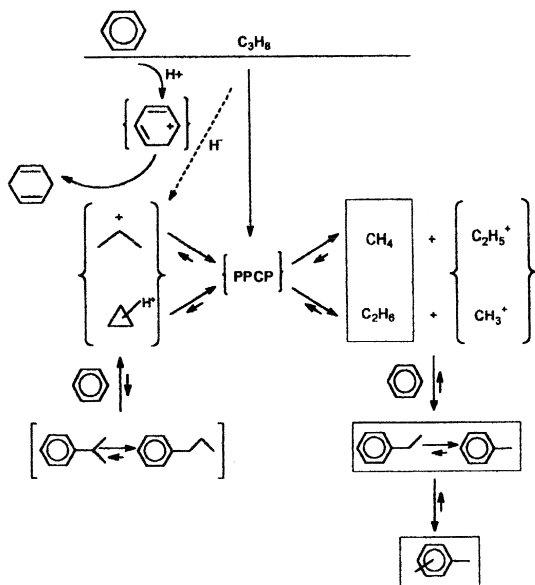


Fig. 6. Proposed mechanism for the benzene alkylation with propane over Ga/H-ZSM-5 (adapted from Ref. [28]).

n-propylbenzene to disappear while the amounts of toluene, xylenes, ethane and methane increase. Eventually, toluene and xylenes are converted into condensed aromatics.

The following conclusions are drawn from the above observations.

(1) When benzene and propane are co-adsorbed on Ga/H-ZSM-5, benzene is preferentially adsorbed on the acidic and Ga sites of the zeolite, and two types of propane species co-exist, characterised by different mobilities.

(2) The stronger adsorption of benzene and the interaction of adsorbed benzene with the methylene group of propane, preventing the direct activation of propane via the BREST mechanism and the PPCP intermediate, lead to an induction period which becomes longer when the benzene/propane ratio is increased.

(3) The dominant reaction mechanism includes the formation of the PPCP intermediate, its evolution towards CH_3^+ , C_2H_5^+ and C_3H_7^+ carbenium ions, and their subsequent reaction with benzene to give toluene, ethylbenzene, cumene and *n*-propylbenzene, respectively.

(4) The alkylation products are mainly toluene, xylenes, and ethylbenzene as cumene and *n*-propylbenzene eventually undergo cracking at 573 K.

3.3. Low temperature activation of *n*-butane on Pt/H-Theta-1

The PPCP model discussed above is obviously not only restricted to the activation of propane as it can also apply to other light alkanes, as shown below in a study of the low temperature activation of *n*-butane over a Pt/H-Theta-1 catalyst [69].

The catalyst was Pt/H-Theta-1 (Si/Al = 29). The zeolite was ion-exchanged with NH_4^+ (70%) and K^+ (30%) to decrease its acidity (in order to minimise cracking) and was calcined under a flow of air (50 ml/min) at 823 K for 4 h before it was impregnated with 1 wt.% platinum (aqueous solution of H_2PtCl_6) using incipient wet-

ness technique. The solid was dried at 383 K overnight and the temperature was then increased to 673 K at a rate of 2 K/min for 2 h while the reduction was performed at 773 K for 2 h under a flow of pure H_2 (50 ml/min). For the CA MAS NMR investigation, the catalyst was evacuated at 723 K prior to adsorption of *n*-butane-1- ^{13}C (1 molecule per unit cell) in a NMR cell.

The ^{13}C MAS NMR spectrum observed after adsorption of *n*-butane-1- ^{13}C at 293 K shows resonances at ca. 12.3 and 15.0 ppm (Fig. 7) which are close to the chemical shift of methyl group of *n*-butane at 13.1 ppm. When the temperature of NMR cell increases to 323 K during the NMR measurements, the resonance at 12.3 ppm grows at the expense of that at 15.0 ppm. The former also shows a weaker cross-polarisation signal than the latter. The resonances at 12.3 and 15.0 ppm, therefore, may be assigned to methyl group of adsorbed *n*-butane-1- ^{13}C molecules with weak and strong interactions with the zeolite surface and/or platinum species, respectively.

The NMR spectra remained unchanged after the NMR cell was heated progressively at 423, 473, and 523 K, for 5 min each time. Two more

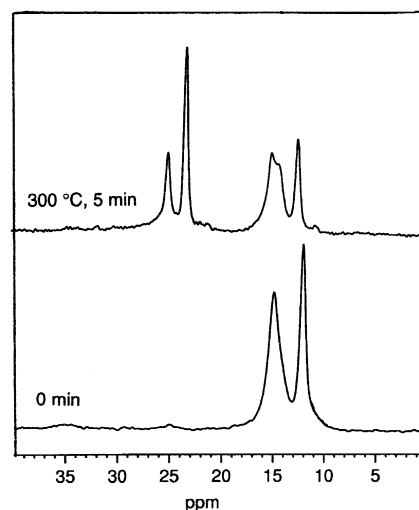


Fig. 7. ^{13}C MAS NMR spectra observed before and after reaction of *n*-butane-1- ^{13}C at 573 K on Pt/H-Theta-1 [69].

resonances at ca. 23.3 and 25.0 ppm were observed after the NMR cell was further heated at 573 K for 5 min (Fig. 7). The spectra then remained identical after the NMR cell was further heated twice at 573 K for 5 min (total reaction time of 15 min at 573 K).

The chemical shifts of the peaks at 23.3 and 25.0 ppm could correspond to those of the methylene group of *n*-butane (24.9 ppm) and of the methyl (24.6 ppm) and methenyl (23.3 ppm) groups of *i*-butane. Further NMR investigation was carried out to check these assignments. The ^{13}C MAS NMR spectrum without ^1H decoupling, which may reveal the C–H J-coupling, shows that the peaks at 23.3 and 25.0 ppm are indeed a quadruplet and a triplet, respectively, indicating the carbon atoms corresponding to the resonance at 23.3 and 25.0 ppm are bonded to three and two hydrogen atoms, respectively. Therefore, the resonance at 23.3 ppm and 25.0 ppm are assigned unambiguously to the methyl group of *iso*-butane and to the methylene group of *n*-butane. These assignments are further supported by cross-polarisation experiments, which reveals that the resonances at 23.3 ppm is then much weaker than that at 25.0 ppm, in accordance with the fact that the cross-polarisation signal of the methyl group should be less because of its rapid rotation. CA MAS NMR investigations thus show that the activation of *n*-butane-1- ^{13}C occurs at 573 K over the Pt/H-Theta-1 catalyst and leads to *n*-butane-2- ^{13}C and *i*-butane-1- ^{13}C without any other side products.

Several mechanisms have been reported to explain the activation of *n*-butane in its isomerisation to *iso*-butane. Adeeva et al. [63–65] studied its transformation at low temperature over sulphated ZrO_2 catalysts, using mass spectroscopy analysis and *n*-butane-1,4- ^{13}C . These authors found that extensive intermolecular scrambling occurs and suggested that the reaction mechanism involves a bimolecular reaction whereby a C_4^+ carbenium ion interacts with C_4^- to form a C_8^+ intermediate which further undergoes isomerisation and β -fission, leading to *i*-

butane. This bimolecular route is usually preferred as it does not involve the formation of a thermodynamically unfavourable primary carbenium ion. Via this mechanism, no labelled *i*-butane is formed by intramolecular scrambling.

DelGallo et al. [66], using carbided MoO_3 catalysts, proposed a mechanism whereby *i*-butane can be formed by a methyl group shift via a metallacyclobutane intermediate. According to this mechanism, when *n*-butane-1- ^{13}C is the reactant, *i*-butane-1- ^{13}C should be the only main product along with some other minor by-products, such as methane, propane and larger alkanes.

Olah et al. [67] suggested a monomolecular mechanism involving a protio-*tert*-butyl dication. This intermediate allows the interconversion of a *sec*- and a *tert*-butyl cations via bond-to-bond migration of CH_3 and H. With *n*-butane-1- ^{13}C as reactant, only *i*-butane-1- ^{13}C and no *n*-butane-2- ^{13}C can be formed.

Another skeletal rearrangement of *n*-butane was also proposed on solid superacid catalysts [68]. *n*-Butane-2- ^{13}C , *i*-butane-1- ^{13}C and *iso*-butane-2- ^{13}C products were observed when *n*-butane-1- ^{13}C was used as reactant. This monomolecular process does not account for the absence of *i*-butane-2- ^{13}C in our work. Also, this model fails to justify the high amount of *i*-butane-2- ^{13}C observed.

Consequently, no published model explains our observations, i.e., the appearance of only two new resonances corresponding to the methyl group of *i*-butane-1- ^{13}C and to the methylene group of *n*-butane-2- ^{13}C following the activation of *n*-butane-1- ^{13}C , without the formation of other products.

We, therefore, propose a new route for the initial activation of butane on Pt/H-Theta-1, i.e., bifunctional catalysts, in general, involving a protonated pseudo-methylcyclopropane (PPMCP) intermediate (Fig. 8) that is principally analogous to the PPCP intermediate discussed above.

The PPMCP intermediate, which is formed on the surface of zeolite modified by the dehy-

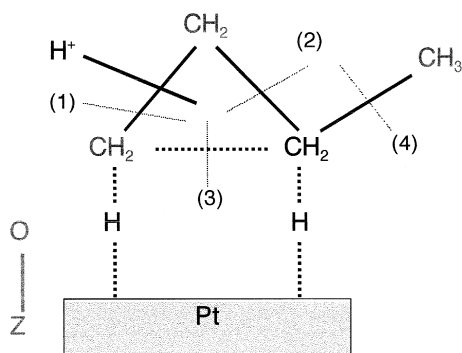


Fig. 8. *n*-Butane on Pt/H-Theta-1 catalyst: the protonated pseudo-methylcyclopropane (PPMCP) intermediate [69]. The CH₃ and CH₂ groups in grey are positions where the ¹³C label may be located, depending on how *n*-butane-1-¹³C adsorption occurs on the active sites.

drogenation component, can evolve in several ways similar to those previously observed for the PPCP intermediate. The scrambling of the ¹³C label of *n*-butane-1-¹³C and the formation of *i*-butane-1-¹³C and *n*-butane-2-¹³C result from the breakage of C–C bonds at positions 1, 2, and 3 (Fig. 8), leading to *n*-butane-1-¹³C, *n*-butane-2-¹³C and *i*-butane-1-¹³C in a ratio of 3:1:2.

The intensity ratio of *n*-butane-2-¹³C to *iso*-butane-1-¹³C observed in Fig. 7 is close to 1:2 as predicted by the evolution of the PPMCP intermediate and the *n*-butane/*i*-butane ratio is equal to 2 in agreement with thermodynamic calculations (573 K). As no methane was observed, bond breaking does not occur at position (4) which also agrees with the fact that only bonds 1–3 in the cyclopropane ring of PPMCP are activated. These observations substantiate the proposed mechanism and show that the redistribution of the ¹³C label of *n*-butane-1-¹³C in *n*-butane and *i*-butane as the only reaction product is governed by both kinetics (C–C bond activation) and thermodynamics, as it should be expected.

At higher temperature, other products are formed as other reactions proceed: cracking, dimerisation, alkylations, etc., as observed previously for the conversion of propane [23].

4. General conclusions

The development and application of in situ MAS NMR spectroscopy have witnessed tremendous progress in the recent years. Several designs of continuous-flow NMR probe have been proposed. In situ CA MAS NMR spectroscopy, combined with the strategic ¹³C-labelling of organic reactants, has been shown to be a powerful technique for the detailed investigation of catalytic transformations. The main advantages of CA MAS NMR relative to other spectroscopies that could also provide molecular and mechanistic information are the ease with which it can identify species present in the NMR cell, the possibility to fully quantitate those, and the economical utilisation of ¹³C-labelled compounds.

Using some examples from our own work, we have showed in this review that CA MAS NMR can unveil the mechanistic detail of complex reactions relating to the activation of light alkanes, including some detailed insight into the nature and evolution of surface species. Novel mechanisms for the activation of light alkanes that have been identified should lead to their broader utilisation as primary reactants in bi-functional catalytic processes.

While CA MAS NMR can undoubtedly identify the intermediates and products of a catalytic transformation, using their ¹³C labelled carbon atom chemical shifts as fingerprints, its rational application to mechanistic studies and the derivation of a reaction mechanism require a close interaction of the NMR expert with organic and catalytic chemists possessing a broad view and a good understanding of reaction mechanisms.

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