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The effect of propane activation over Ga-modified H-ZS M-5 catalysts [a]

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Abstract. *In situ* ^{13}C MAS NMR was used to investigate the influence of total and partial pressure of propane on the initial stages of its conversion over a Ga/H-MFI catalyst (2-^{13}C). Propane was the labelled reactant. Different pressures were achieved by varying the amounts of propane and of nitrogen as diluent in the cell. The nature of primary and secondary labelled reaction products depends on total pressure. High total and partial pressures of propane enhance bimolecular primary formation of *n*-butane and isobutane via a BREST (Bifunctional Reaction Step) mechanism[1]. Low total pressure leads to methane and polymeric fragments as primary products. A reaction pathway including the formation of a polymeric hydrocarbon-chain intermediate is proposed to account for secondary isobutane formation at low pressure. The influence of pressure on reaction equilibria and kinetics and on adsorption and exchange processes is discussed.

Introduction

We have recently[1] demonstrated that activation of propane on Ga/H-MFI catalysts occurs via a bifunctional mechanism involving a Brønsted acidic site and neighbouring (Ga^{3+},O^{2-}) ion pair.

Propane interacting with the (Ga^{3+},O^{2-}) ion pair is converted to a pseudo-cyclopropane entity which is protonated by a neighbouring Brønsted site to form a protonated pseudo-cyclopropane (PPCP) intermediate. The PPCP intermediate model agrees with the activation of propane by dissociative adsorption on Ga species[2–4], the recently disclosed role of gallium as hydrogen "porthole"[5], and the negative reaction order with respect to hydrogen when extra framework Ga species are present[4]. It also rationalizes several earlier mechanistic proposals claiming either propane activation by acidic sites only[6,7] or the dehydrogenation of propane on Ga species[2,8,9]. The PPCP intermediate can decompose in different ways as shown in Figure 1, resulting in the formation of CH_4, C_2H_6, H_2 and CH_3^+, $C_2H_5^+$ and $C_3H_7^+$ carbenium ions.

This paper describes the influence of propane partial pressure and of total pressure on the mechanism of propane activation.

Experimental

Materials

MFI zeolite (Si/Al 35) was prepared as described elsewhere[10]. Gallium was introduced in the H form of the catalyst by aqueous impregnation with $Ga(NO_3)_3 \cdot 9H_2O$ (99.9% from Alfa), followed by drying for 16 h at 393 K and calcination at 823 K for 4 h in air. The resulting catalyst contained 0.95 wt% of gallium. (2-^{13}C) Propane (99.9%-enriched) was obtained from ICON Services Inc. Nitrogen-gas (N-50) (from Alphagas) was used as a diluent.

In situ ^{13}C Mass NMR measurements

In situ ^{13}C MAS NMR measurements were carried out on a MSL-400 Bruker spectrometer operating at 100.6 MHz for ^{13}C. Quantitative conditions were achieved using high-power gated proton decoupling with suppressed NOE effect (90° pulse, recycling delay 4 s). Spinning rate was 3 kHz. Some non-^1H-decoupled spectra were recorded to identify reaction products and intermediates.

Powdered catalysts samples (0.09 ± 0.01 g) were packed into NMR tubes (Wilmad, 5.6 mm o.d. with constrictions) when fitted the double-bearing Bruker zirconia rotors exactly. The catalysts were evacuated to a pressure of $6 \cdot 10^{-6}$ torr after heating for 8 h at 573 K and cooled to 298 K before adsorption. Different partial pressures of propane and total pressures in the system were achieved by varying the amounts of (2-^{13}C) propane and nitrogen in the NMR cells (dosed volumetrically). The concentrations of the gases present in different experiments and the corresponding total and partial pressures in the cells are listed in Table I. After introduction of the reactants, the NMR cells maintained at 77 K to ensure quantitative adsorption were carefully sealed to achieve proper balance and high spinning rates in the MAS NMR probe.

In a typical *in-situ* experiment, the sealed NMR cell is rapidly heated to 573 K and maintained at this temperature for 5 min. The MAS-

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[a] Dedicated to Prof. *Wolfgang M.H. Sachtler* on the occasion of his 70th birthday.

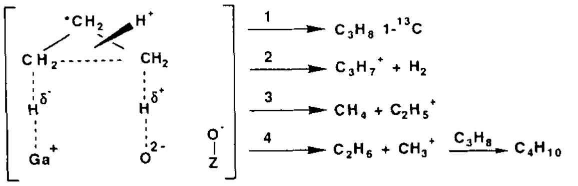

Figure 1. Mechanism for bifunctional activation of propane on Ga / H-MFI catalysts. Initial products and intermediates[1].

NMR spectrum is recorded at 293 K after quenching of the sample cell. After collection of the NMR data, the NMR cell is returned to reaction conditions and heated for progressively longer periods of time.

Definitions

Conversion of reactant r at time t: $X_{r,t} = (1 - I_{r,t}/I_{r,0}) \cdot 100$ [%]; where $I_{r,t}$ is the integral intensity of the resonance of reactant r in the NMR spectrum after heating for t min; $I_{r,0}$ is the integral intensity of the resonance of reactant r in the initial NMR spectrum. Yield of product p at time t: $Y_{p,t} = (I_{p,t}/I_{r,0}) \cdot 100$ [%]; where $I_{p,t}$ is the integral intensity of the resonance of product p in the NMR spectrum after heating for t min.

Results and discussion

Partial pressure of the reactant and total pressure in the NMR cell can affect not only reaction kinetics and equilibria but also adsorption and exchange processes. Reaction kinetics are influenced mostly by partial pressure, whereas the reaction equilibria are influenced mostly by total pressure. Adsorption and exchange processes are influenced by both partial and total pressures when adsorption of the diluent gas competes with that of the reactant.

Samples A, B, and C (Table I) were prepared to study these effects. Sample C corresponds to the low total and partial pressures case. In sample B, total pressure was increased by addition of nitrogen diluent gas, and partial pressure of propane was kept as in C. Finally, sample A corresponds to the high total and partial pressures case.

Figure 2a shows the ^{13}C MAS-NMR spectra of (2-^{13}C) propane adsorbed at 293 K in experiments A, B, and C. The chemical shifts and linewidths of the observed resonances depend strongly on the total pressure in the system. Samples A and B possess a single resonance at 17 ppm which corresponds to the labelled methylene group of propane. The resonance is only slightly shifted relative to gaseous propane (16.1 ppm)[11] and propane in solution (16.3 ppm)[12]. Sample C shows two broad lines shifted towards lower field, indicating that there might be more than one type of centre interacting with propane.

These results indicate that chemical shifts and linewidths of the observed resonances of adsorbed propane are controlled by an exchange process between chemisorbed, physisorbed and gaseous species. According to the exchange model[13,14], the measured resonance is given by a weighted average of the different contributions arising from the molecules adsorbed on sites of stronger and weaker energies. It depends in general on surface coverage and on the rate of molecular exchange between the different sites. Low surface coverage (case C) results in a higher population of strong sites, giving broad resonance shifted relative to the position of propane in solution. With an increasing number of adsorbed molecules (case A) the adsorption sites of weaker energies become populated and the resulting resonance is comparatively narrow and only slightly shifted. Increasing total pressure (case B) enhances the rate of the exchange process, resulting in a narrow and slightly shifted line. It indicates that nitrogen diluent gas can compete with propane for adsorption in the zeolite, which follows from their relatively close adsorption energies[15].

Table I Samples.

Experiment	Loaded reagents (molec./u.c.)[a]		Pressure (torr)[b]	
	C_3H_8 2-^{13}C	N_2	Total	Partial
A	4.0	–	2000	2000
B	0.5	0.7	750	300
C	0.5	–	300	300

[a] u.c. = unit cell [b] Pressures are estimated volumetrically for the empty NMR cell at 298 K; the volume occupied by the catalyst and the adsorption of the reagent are not taken into account for the estimations.

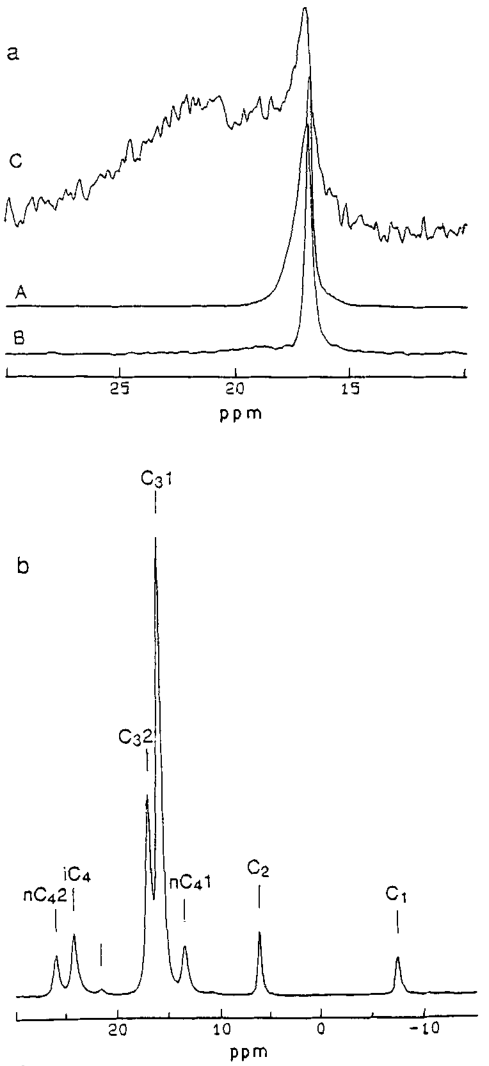

Figure 2. ^{13}C-MAS-NMR spectra of samples A, B and C observed (a) immediately after adsorption and (b) after (2-^{13}C) propane reaction at 573 K for 80 min over sample A.

For all samples, the reaction can be observed at a temperature equal to or above 573 K. Typical spectra observed after (2-^{13}C) propane reaction at 573 K in experiment A are shown in Figure 2b. The main lines correspond to (2-^{13}C)(C_32) propane, (1-^{13}C)(C_31) propane, (^{13}C) ethane (C_2) (^{13}C) methane (C_1), (1-^{13}C) butane (nC_41), (2-^{13}C) butane (nC_42), (1-^{13}C) isobutane and (2-^{13}C) isobutane. The last two resonances are not resolved and will be further considered together as labelled isobutane (iC_4). A more detailed description of these line assignments is given elsewhere[1].

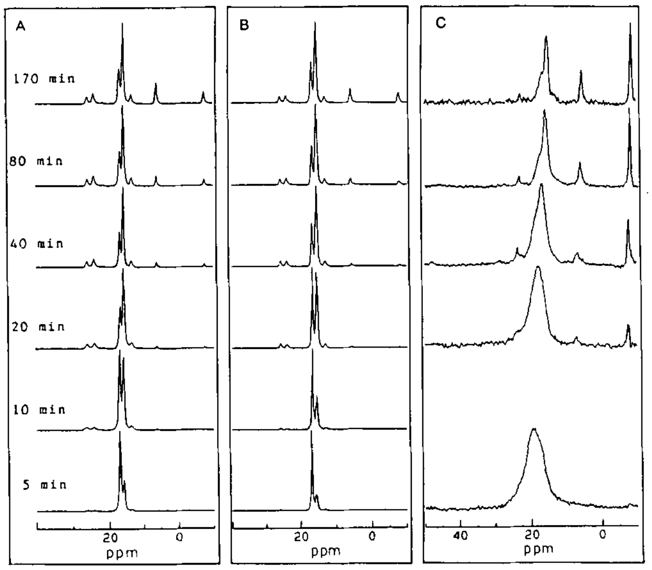

Figure 3. ^{13}C-MAS-NMR spectra observed for (2-^{13}C) propane reaction over samples A, B and C at 573 K as a function of reaction time.

The effect of pressure on propane conversion in batch conditions can be determined from Figure 3, showing the ^{13}C MAS-NMR spectra of (2-^{13}C) propane reacting at 573 K (samples A, B and C).

The following observations are made:

- Samples A and B yield similar spectra with comparable lines, chemical shifts, linewidths, and intensities. This indicates that propane activation is not much affected by propane partial pressure in the batch.
- The resonances of sample C are very broad and shifted to lower field with respect to those of samples A and B. This is due to slower exchange at low pressure between molecules adsorbed on different adsorption centres in the zeolite and the gas phase.
- Decreasing total pressure favours methane formation and restricts formation of *n*-butane.

These results indicate that propane activation is influenced more by total pressure than by partial pressure of propane. The effect of pressure can thus be rationalized in terms of its influence on reaction equilibria, and adsorption and exchange processes.

Identification of primary and secondary labelled reaction products

NMR results were further quantified from the spectra presented in Figure 3. Table 2 lists propane conversions and product yields as a function of reaction time.

^{13}C carbon balances indicate that, at long reaction times, up to 20% of ^{13}C labels is not observed in the NMR spectra (see Table II). The average H/C ratios for non-observed products were calculated using the following equation:

$$(\mathrm{H/C})_{\mathrm{n},t}\cdot Y_{\mathrm{n},t} + (\mathrm{H/C})_{\mathrm{o},t}\cdot(100 - Y_{\mathrm{n},t}) = (\mathrm{H/C})_{\mathrm{o},0}\cdot 100$$

$(\mathrm{H/C})_{\mathrm{n},t}$: average H/C ratio in non-observed products at time t

$(\mathrm{H/C})_{\mathrm{o},t}$: average H/C ratio in observed products at time t

$(\mathrm{H/C})_{\mathrm{o},0}$: H/C ratio in initial propane

$Y_{\mathrm{n},t}$: yield of non-observed products

The estimated values are 2.3 and 2.2 for samples A (t = 170 min) and C (t = 164 min), respectively. Thus, non-observed products are probably long chain oligomers or polymers. Their resonances can be broadened beyond the detection limit. The appearance of weak resonances at 28 and 45 ppm, possibly corresponding to $(\mathrm{C_3})_n$ polymers in the case of sample C, supports this supposition.

Yields of labelled reaction products in runs A, B, and C were plotted against conversion as shown in Figures 4a, b and c, respectively. The selectivity plots can be compared to theoretical selectivity patterns, characteristic for different types of products defined in Ref. 16 (Figure 4d). The labelled products can then be identified as primary or secondary and stable or unstable according to the type of selectivity plot. The initial atomic ^{13}C selectivities for the primary reaction products are determined from the initial slopes of the selectivity plots. The results are summarized in Table III.

The main reaction products are identified as follows:

- $\mathrm{C_3}$1 appears as a major primary unstable reaction product in all runs. ^{13}C scrambling in propane accounts for about 80% of the total initial selectivity.
- Ethane and methane are secondary stable products in experiments A and B performed at a high total pressure. At low pressure, methane appears as a primary stable reaction product.

Table II Conversion of (2-^{13}C) propane yield of initial reaction products as a function of contact time in experiments A, B and C.

Sample/time (min)	Conversion of $\mathrm{C_3}$1 (%)	Yields (%)						
		$\mathrm{C_3}$1	i$\mathrm{C_4}$	n$\mathrm{C_4}$1	n$\mathrm{C_4}$2	$\mathrm{C_2}$	$\mathrm{C_1}$	Others
A								
0	0	–	–	–	–	–	–	–
5	32	23.6	2.8	2.6	2.2	–	–	–
10	53	41.5	3.3	3.6	2.9	1.7	–	–
20	75	53.2	7.2	6.5	4.6	1.9	1.6	–
40	77	54.2	6.8	4.6	3.9	4.2	3.3	–
80	81	47.4	7.2	4.6	3.8	7.8	5.0	5.2
170	85	41.3	6.0	4.4	3.3	14	7.3	8.7
B								
0	0	–	–	–	–	–	–	–
5	23	19.6	0.7	1.5	1.2	–	–	–
10	39	34.2	1.2	1.6	2.0	–	–	–
20	54	45.5	2.3	2.4	2.7	0.8	0.3	–
40	72	58.8	3.6	3.6	3.8	1.6	0.6	–
80	75	52.9	5.8	4.1	5.0	4.1	3.1	–
160	77	48.1	5.7	3.3	4.9	8.7	6.3	
C								
0	0	–	–	–	–	–	–	–
5	24	19.9	–	–	–	–	1.3	2.8
20	49	32.2	2.7	–	–	1.6	3.7	8.8
40	76	48.1	2.7	–	–	3.3	8.4	12
92	82	37.1	3.1	–	–	8.1	19	13
164	86	32.4	2.6	–	–	10	19	22

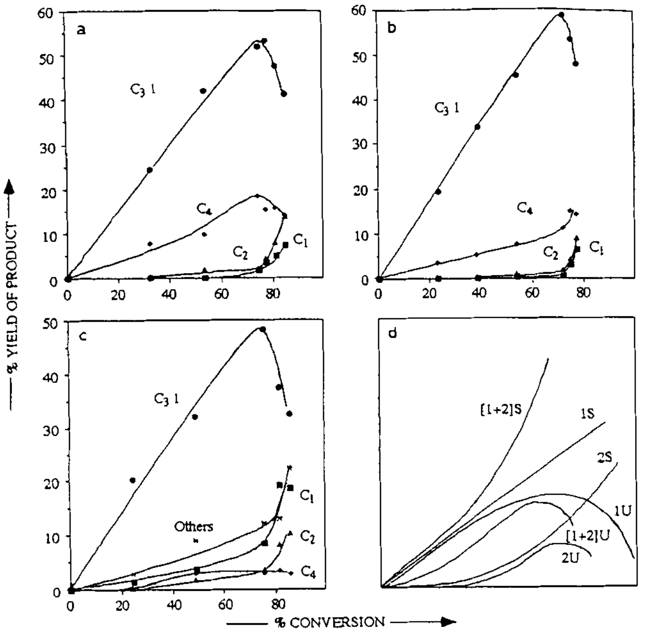

Figure 4. Experimental selectivity patterns observed for different products in experiments A,B,C and theoretical selectivity patterns[16] for stable primary (1S), stable primary plus secondary [(1 + 2)S], unstable primary (1U), unstable primary plus secondary [(1 + 2)U], stable secondary (2S), and unstable secondary (2U) products.

- Non-observed species in experiment C arise from both primary and secondary reactions. Routes 2 and 3 (Figure 1) account for the primary formation of polymeric species which are not observed. At high pressure, the yield of non-observed products is insignificant (Table II).
- The formation of butanes depends on total pressure. Butanes arise from both primary and secondary reactions in runs A and B and only from secondary reactions in run C. The initial selectivity to butanes on sample A is twice higher than on sample B. The selectivity plots for butanes eventually show a decrease in yield, indicating that butanes are transient products.

In conclusion, ^{13}C scrambling in propane (Figure 1, route 1) is the major primary reaction. This pathway does not depend on pressure and confirms the existence of a common PPCP intermediate. Bimolecular reaction 4 (Figure 1) is favoured at high total and partial pressures. This route accounts for primary and secondary formation of butanes in experiments A and B. Ethane which is also expected to be formed in this process, was not observed as a primary product. It may be due to the fact that ethane is unlabelled in the initial stages of the reaction when ^{13}C scrambling in propane is low, considering that CH_3^+ is mainly formed from the labelled methylene group of propane according to the PPCP mechanism. Another possible explanation is the competitive adsorption of reagent and products at high pressure. Indeed, the adsorption energy of alkanes in zeolites increases in the following order[15]: $CH_4 < C_2H_6 < C_3H_8 < C_4H_{10}$. Hence, at high propane pressure, when initial surface coverage is high (4 molec./u.c.), propane and butane are preferentially adsorbed while methane and ethane probably stay in the gas phase and are not detected in our experimental conditions. Similar results were obtained in experiment B when propane was diluted with nitrogen which can compete with methane and ethane as it has a similar adsorption energy[15].

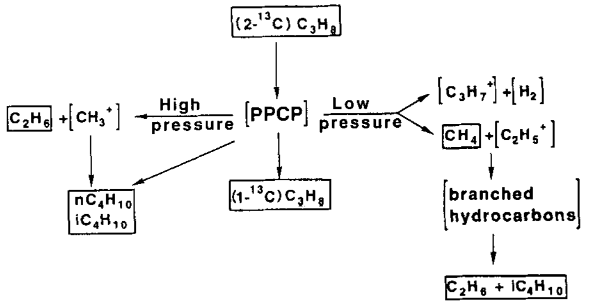

Figure 5. Effect of pressure on the initial products and intermediates in the bifunctional activation of propane on a Ga / H-MFI catalyst.

Low pressure shifts reaction equilibria towards fragmentation. Routes 2 and 3 hence become significant pathways for PPCP decomposition. Secondary butane formation in this case cannot be accounted for by route 4, thus pointing to a different mechanism of butane formation at low pressure.

The effect of pressure on the mechanism of butane formation

Major differences for butane formation at low and high pressures are summarized below:

- Butanes are secondary products at low pressure and primary products at high pressure. The initial selectivity to butanes increases with propane partial pressure.
- Isobutane is the only C_4 product at low pressure while at high pressure all butane isomers are observed. The selectivity to *n*-butane is then about twice that of isobutane (see Table II).

The BREST mechanism[1] provides a satisfactory explanation for the high pressure observations. Butanes are formed by addition of a CH_3^+ carbenium ion (resulting from PPCP decomposition) to propane activated on the Ga site. This mechanism explains the formation of primary and secondary butanes and the observation of both butane isomers. The increase of initial *n*-butane selectivity with propane partial pressure supports this bimolecular pathway.

Table III Initial atomic selectivities for the conversion of (2-^{13}C) propane in experiments A, B and C at 573 K.

Sample	Products						
	C_3l	iC_4	nC_4l	n$C_4$2	C_2	C_1	Others
A product type initial selectivity	1U [a] 0.76	(1+2)U 0.070	(1+2)U 0.070	(1+2)U 0.060	2S 0	2S 0	2S 0
B product type initial selectivity	1U 0.84	(1+2)U 0.030	(1+2)U 0.048	(1+2)U 0.050	2S 0	2S 0	–
C product type initial selectivity	1U 0.71	2U 0	–	–	2S 0	(1+2)S 0.082	(1+2)S 0.16

[a] 1: primary; 2: secondary; S: stable; U: unstable.

To account for the low pressure observations, we propose another mechanistic pathway. It involves the formation of polymeric hydrocarbon chain intermediates by classical cationic polymerization of primary $C_2H_5^+$ or $C_3H_7^+$ carbenium ions formed upon decomposition of the PPCP intermediate. These polymeric intermediates are known to give preferentially isoalkanes[17] by cracking, in our case isobutane. Ethane can be also formed in this way. This pathway could account for secondary formation of butane. It explains the selective formation of isobutane at low pressure.

The model presented in Figure 5 rationalizes further all the above observations. Propane first converts to PPCP via the BREST mechanism[1]. It then decomposes in different ways depending on total pressure. At high pressure, ethane and CH_3^+ carbenium ion are formed, the CH_3^+ reacting further with propane to yield butanes. At low pressure PPCP decomposes into methane, dihydrogen, and $C_2H_5^+$ and $C_3H_7^+$ carbenium fragments. These fragments then polymerize and the polymers eventually crack to yield isobutane and ethane as secondary products.

Conclusion

The PPCP model of propane activation has been further developed to account for the effect of pressure. High total pressure favours a bimolecular reaction, leading to primary formation of butane. Low pressure shifts the reaction equilibria towards fragmentation of PPCP and the primary formation of methane, dihydrogen and carbenium fragments which further polymerize and crack to give isobutane and ethane. The dominant primary ^{13}C scrambling observed in all experiments points to the existence of a common PPCP intermediate for both high- and low-pressure pathways.

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