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A Study into the γ -Al₂O₃ Binder Influence on Nano-H-ZSM-5 via Scaled-Up Laboratory Methanol-to-Hydrocarbon Reaction

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Abstract: Development of a laboratory selected zeolite into an industrial zeolite-based catalyst faces many challenges due to the scaling-up of reaction which requires many upgrades of the as-prepared catalyst such as an enhanced physical strength. To meet this requirement zeolite powders are normally mixed with various binders and then shaped into bulky bodies. Despite the fact there are a lot of reports on the positive features brought by the shaping treatment, there is still a great need to further explore the zeolite properties after the binder introduction. In this case, a lot of studies have been continuously conducted, however, many results were limited due to the usage of much smaller laboratory samples rather than a real factory plant, and more importantly, the maximal/minimal proportion of zeolites in the shaped catalyst. In this research, our shaped catalysts are based on nano-H-ZSM-5 zeolites and alumina (γ -Al₂O₃) binder while keeping the zeolite content to a maximum. H-ZSM-5 samples and Al-H-ZSM-5 samples are compared in the designed methanolto-hydrocarbons reaction. With a reduced weight-hourly-space-velocity (WHSV = 1.5 h^{-1}) and a higher reaction pressure (6 bar) favorable for aromatization, together with the tailored instruments for catalyst volume scale-up (20 g samples are tested each time), our tests focus on the early period catalytic performance (during the first 5 h). Unlike a normal laboratory test, the results from the scaled-up experiments provide important guidance for a potential industrial application. The role of the γ -Al₂O₃ introduced, not only as binder, but also performing as co-catalyst, on tailoring the early time product distribution, and the corresponding coke deposition is systematically investigated and discussed in details. Notably, the Si/Al ratio of H-ZSM-5 still has a decisive influence on the reaction performance of the Al-H-ZSM-5 samples.

Keywords: methanol-to-hydrocarbons; scaling-up; H-ZSM-5; alumina; catalyst

1. Introduction

Methanol-to-hydrocarbon (MTH) reactions represent an important route to produce valuable petrochemicals from the non-oil fossil resources, e.g., coal, natural gas and sustainable biomass [1–3]. Since the last century, many successful MTH studies were carried out using acidic ZSM-5 zeolite (H-ZSM-5) as catalyst due to its excellent catalytic properties [4,5]. In this context important scientific findings have been continuously announced, including the prevailing 'hydrocarbon pool' mechanism [6], and the very important discovery that ethylene production seems to be different from that of other light olefins in an H-ZSM-5-catalysed MTH reactions [7].

In the recent years, nano-H-ZSM-5 zeolites have gradually taken a major role in MTH studies. Their particle size is controlled to several hundred nanometers or smaller, which brings in many advantages such as a larger surface area, potential hierarchical pores, easier access to reactants, shorter diffusion distance and better coke tolerance [8–10]. However, for a harsh plant application many zeolite-based industrial catalysts must be shaped into solid



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). bodies of a much larger size, from a few millimetres to several centimetres. The shaped zeolite-based catalysts could be beads, pellets, tablets and extrudates, which normally consist of active phases (parent zeolite), binders or supports, and promoters or other additives. In the above case, the intrinsic catalytic properties of nano H-ZSM-5 zeolite will be inevitably changed in the shaped catalysts [11,12].

The catalytic difference between a shaped nano-H-ZSM-5 zeolite-based catalyst and the parent nano-H-ZSM-5 zeolite could be compared in a laboratory, however, the obtained results may not be readily transferrable to real industrial applications. The limited catalyst dosage (typically less than 1 g or just XX mg) fatally reduces the value of such experimental observations, particularly, because sometimes the already shaped catalysts have to be ground back and tested in powder status [13–15]. To overcome the above difficulties, pilot tests and factory experiments enable the loading of shaped catalysts in a much larger volume, but greatly increase the cost, and therefore are very difficult to be employed by researchers in academic environments.

By scaling-up the laboratory MTH test with a customized fixed-bed reactor we managed to test a group of shaped nano-H-ZSM-5 zeolite-based catalysts (parent nanozeolites were bonded with alumina and shaped into a cylindrical industrial extrudate; H-ZSM- $5/Al_2O_3 = 7.3$ in weight; zeolite contents were kept in maximum while retaining good mechanical strength) with the catalyst loading (20 g) increased to many times that normal used in the laboratory (0.5–1 g). With the enlarged reactor volume shaped samples could be tested in their 'as prepared' status, while for comparison the parent zeolite powders were also tested in the same experimental set. Compared with other commonly used zeolite binders, our selected alumina, γ -Al₂O₃ (the preparation steps are described in Section 6), possesses many merits, as it well binds the zeolite particles with good mechanical strength for the later reactions, and it could also provide some extra catalytic features; more importantly, alumina-bonded zeolite catalysts are easier to be prepared in both the laboratory and the factory [16–21].

Most previous scaled-up MTH tests were carried out with shaped conventional microsize zeolites [13,21,22]. Our study focuses on the utilization of nano-H-ZSM-5 zeolite and more importantly, the potential influence of catalyst 'shaping', e.g., the influence of the alumina binder, on the parent zeolites' intrinsic properties. The 5 h reaction time length employed by our experiments is much shorter than the real time period of a normal industrial run-cycle which usually runs for thousands/hundreds of hours/days. This is because we are particularly interested in the early time behavior of catalysts (which occurs in the first several hours/days in industry and by the end of which a stable product yield normally appears) as it significantly affects the subsequent product yields as well as the catalyst coke formation. The 450 °C reaction temperature and 6 bar reactor pressure used also favored more aromatic product formation, and particularly a reduced methanol feeding rate (weight-hourly-space-velocity, 'WHSV' = $1.5 h^{-1}$, every one hour 1.5 g of methanol were sent to 1 g catalyst) the gas yields over most catalysts gradually increased and had been observed to reach a fairly stable level just by the end of the 5 h reaction; therefore, the early time catalytic behavior of samples could be well studied [2,19,22,23].

In the following sections, parent zeolites (nano-H-ZSM-5) are named according to their Si/Al ratio, i.e., H-ZSM-5 20, and their sample shapes are indicated with 'Al', i.e., Al-H-ZSM-5 20 (*20 is the original Si/Al ratio of parent zeolite, Al means alumina binder, H-ZSM-5/Al₂O₃ = 7:3 in weight).

2. Catalytic Performance

All samples were tested in MTH reactions under the above experimental conditions. Each sample showed ~100% methanol conversion as no methanol was detected in the reactor outflow. Gas hydrocarbons were mainly C_1 – C_4 (Figures S1–S6), which showed a steadily increasing yield from the beginning to the end of the 5 h MTH reaction. The observed increasing gas yield is not like a normal small-scale laboratory MTH reaction in which the initial reaction gas yield is often the highest. A possible reason is the apparently

increased catalyst usage, as a result of which the initially generated gas products have more chances to be further converted into heavier products, e.g., aromatics, as they pass through the enlarged catalyst bed. The consumed gas products might also contribute to the formation of catalytic hydrocarbon pools which are supposed to accelerate the later MTH reaction. Therefore, in our tests a reaction induction period is supposed to exist, which is commonly seen and very important to the situation that the catalyst usage is greatly increased [4,19,24]. The restricted methanol feeding rate (WHSV = 1.5 h^{-1}) might also extend the time for such induction as reflected by the gradually increased gas yields; however, it shows better the early time catalytic properties of each sample and further slows the coke deposition.

Not surprisingly, the two catalyst groups were quite different in their gas hydrocarbon yields. While propane and C_4 yields always represented a large portion, which was observed on all tested samples in time-on-stream (TOS), apparently enhanced yields of propylene and ethylene were exclusively achieved by the Al-H-ZSM-5 samples (Figure 1). All observations clearly point to the fact that the intrinsic zeolite catalytic properties have been modified as a result of the alumina introduction, which is presumed to lead to the observed higher gas olefin yields. Here the propylene yield showed a more significant difference between the two sample groups. There was always a less than 6% propylene yield in TOS over all H-ZSM-5 samples, whereas over Al-H-ZSM-5 120, a ~14% yield of propylene could be achieved by the end of the 5 h reaction period. A similar phenomenon was also observed for the ethylene yield; the highest ethylene yield was again achieved by the Al-H-ZSM-5 120 sample, which was \sim 7% at the end of the 5 h reaction. The C₄ mixtures were not successfully separated during a total 30 min GC running time, thus, no apparent difference was shown among the tested samples; however, based on the C_2 and C_3 yield results, we can still propose that a transformation from butane to butylene in the C₄ mixtures over the Al-H-ZSM-5 samples potentially existed.



Figure 1. Cont.



Figure 1. (a) Propylene yield and (b) Ethylene yield over different samples.

Among all tested samples, the H-ZSM-5 60 sample achieved the highest total benzenetoluene-xylenes (BTX) yield after the 5 h MTH reaction (Figure 2). The reactions over H-ZSM-5 120 generated more trimethylbenzenes, thus, it exhibited a yield of the major C_6 - C_9 aromatics close to that seen with the H-ZSM-5 60 sample. The aromatics yield was apparently repressed in the three Al-H-ZSM-5 samples, where the Al-H-ZSM-5 60 sample showed slightly higher BTX and greater C_6 - C_9 aromatic yields than the other two samples.



Figure 2. Aromatic yields of different samples.

3. Catalyst Characterizations

3.1. NH₃-TPD

In Figure 3, temperature programmed desorption of ammonia (TPDA) plots are used to show the acid distribution of the different samples.



Figure 3. TPDA plots of different samples.

Compared with their parent zeolites, Al-H-ZSM-5 60 and Al-H-ZSM-5 120 show some notable changes in their lower temperature NH₃ desorption peaks (LTNDP) in terms of the slightly reduced peak intensity as well as the visible shifts from 230–245 °C to 270–275 °C. For the above case, a possible reason could be the partial loss of parent zeolite weak acid sites caused by the introduced alumina binders. Here one would argue that the introduced Al³⁺, if possible, could also bring in some extra acidity, i.e., Lewis acid sites (LAS); however, if additional LAS adsorb NH₃, the desorption peaks should exhibit higher intensity-which is not the case for Al-H-ZSM-5 60 and Al-H-ZSM-5 120. Interestingly, the LTNDP of Al-H-ZSM-5 20 sample shows a clear broadening effect in the plot, which is in a sharp contrast to the other two Al-H-ZSM-5 samples. In this case, the introduced Al³⁺ might have contributed to the sample acidity with more weak acid sites formed. To some extent, the above TPDA results reveals that the resulting acid change caused by the introduced alumina is somehow related to the Si/Al ratio of parent zeolites when the parent zeolite/binder ratio is fixed. As compared with their parent zeolites, the higher temperature NH₃ desorption peaks (HTNDP) of Al-H-ZSM-5 samples are slightly reduced. HTNDP changes are possibly caused by the partial neutralization of zeolite Brønsted acid sites by the introduced alumina. A similar phenomenon has been reported in previous studies on methanol-butene cracking and paraffin conversion, which also leads to an improved coke tolerance [4,18,25,26].

3.2. SEM

In the captured scanning electron microscope (SEM) images (Figure 4), for each parent H-ZSM-5 we have selectively shown their post reaction, Al-H-ZSM-5, and post reaction Al-H-ZSM-5 morphologies. In the SEM images, carbon deposits are not well shown on the post-reaction samples. Particles of post-reaction H-ZSM-5 samples are againated, but still have very clear and sharp edges even after the 5 h MTH reaction. As reported in many relevant studies, it is often very difficult to distinguish the morphological differences between zeolite and their lightly-coked samples with SEM [27–29].



Figure 4. SEM images of post-reaction H-ZSM-5, Al-H-ZSM-5, and post-reaction Al-H-ZSM-5.

There is no doubt that the alumina binder has changed the morphology and porosity of the parent H-ZSM-5 samples. Zeolite particles of Al-H-ZSM-5 60 and Al-H-ZSM-5 120 are still clearly shown in the SEM images, but their profiles become fairly fuzzy. Zeolite particles of Al-H-ZSM-5 20 are notably bonded with a lot inter-crystalline spaces occupied by the alumina binders; such 'binding effect' is very clearly seen by SEM. Strikingly, this sample even becomes more severely bonded after the MTH reaction, and its zeolite particles are visually surrounded by some 'gel-like' structures in SEM. Although more inter-crystalline spaces have been lost after the MTH reaction, there are still some edgeclear nanoparticles in the post-reaction Al-H-ZSM-5 60 and post-reaction Al-H-ZSM-5 120 samples. According to our Brunauer-Emmett-Teller (BET) results (Table S1), most Al-H-ZSM-5 samples have lost ~10% surface area as compared with their parent H-ZSM-5 samples. For an accurate judgment, comparisons between extrudates and their ground powders were also made. The loss of surface area is mainly attributed to the introduction of alumina binders, and particularly their coverage over the zeolite particles. The surface areas of binder precursor (pseudo-Boehmite, uncalcined) and individually prepared alumina $(\gamma-Al_2O_3)$ under the same preparation conditions are also analyzed, and are apparently smaller than the parent H-ZSM-5 samples, thus supporting our explanation above. For those post-reaction Al-H-ZSM-5 samples, their surface areas have been further decreased as a result of many reasons, such as coke formation.

3.3. TEM

In Figure 5, we have selectively shown the TEM images of post-reaction Al-H-ZSM-5 samples, and another coked H-ZSM-5 20 sample for comparison.



In Figure 5, the alumina binders bonded to zeolite can be clearly identified and are marked with red circles. They are amorphously distributed surrounding the zeolite body but do not appear in the post-reaction H-ZSM-5 20 samples. As reported in many previous studies, the black zones on the zeolite bodies are very likely due to the deposition of coke species or their precursors, as more obviously shown in other works [27–30] in images of post-reaction H-ZSM-5 20 which was severely coked. The alumina binders may have either positive or negative effects on the zeolite coke tolerance, as they could adsorb the reaction formed coke species and prevent their accumulation on the zeolite surface; however, as seen in the above images, the alumina binders may have also partially blocked the zeolite pore openings thus leading to a worse inner coke formation. From the TEMs, one could only conclude that Al_2O_3 helped to attract coke species, but the preference of coke distribution between zeolite and Al_2O_3 is not clear.

Figure 5. TEM images of post reaction Al-H-ZSM-5.

3.4. XRD

XRD analysis (Figure 6) was used to further investigate any possible phase or crystal change of the H-ZSM-5 caused by the catalyst preparation and subsequent MTH reactions. Al-H-ZSM-5 samples before and after the 5 h MTH reaction are compared. Peaks characteristic of the γ -Al₂O₃ crystal structure (JCPDS reference no. 00-010-0425) could hardly be seen, in fact, the obtained diffractograms are very similar to the parent H-ZSM-5 60 [31,32]. The fairly weak signal reveals that the existence of γ -Al₂O₃ is more likely in an amorphous state. To confirm our assumption, a reference γ -Al₂O₃ was prepared from the same boehmite (AlOOH) and under the same conditions used for the Al-H-ZSM-5 samples, which shows two clear diffraction peaks at ~45° (400) and ~67° (440) proving that γ -Al₂O₃



could be well formed in our Al-H-ZSM-5 samples. No apparent difference in XRD is found between Al-H-ZSM-5 and post reaction Al-H-ZSM-5 samples.

Figure 6. XRD pattern of Al-H-ZSM-5 samples before and after the 5 h MTH reaction in comparison with ref. γ -Al₂O₃ and H-ZSM-5 60.

3.5. ²⁷Al and ²⁹Si MAS NMR

²⁷Al MAS NMR spectra (Figure 7a,b) are used to investigate the Al distribution in different samples before and after the 5 h MTH reaction. All H-ZSM-5 samples show peaks representing the tetrahedrally-coordinated zeolite framework Al (55 ppm) and the octahedrally-coordinated extra-framework Al (0 ppm), where the 55 ppm peak intensity is obviously stronger than the one at 0 ppm [33]. For H-ZSM-5 samples, the 5 h MTH reaction causes a certain weakening and loss of the signal at 55 ppm while broadening the peak at 0 ppm. This effect is more obviously visible in the post-reaction H-ZSM-5 20 sample, as the 0 ppm peak is almost flattened.

In the spectra of Al-H-ZSM-5 samples, the 55 ppm peaks are apparently reduced, which is more obviously seen in the Al-H-ZSM-5 120 sample. Here the reduced signals are only reflected by the lowered peak height representing a weaker NMR intensity; by contrast, no apparent broadening is observed. The 55 ppm peaks of post-reaction Al-H-ZSM-5 samples are further reduced, but they are fairly close. The above reduced 55 ppm peaks all possess a new shoulder at 70 ppm which is assigned to the tetrahedrally coordinated extra-framework Al sites normally seen in the γ -Al₂O₃ structure [31]. The formation of γ -Al₂O₃ in Al-H-ZSM-5 samples is better evidenced by a suddenly emerged, much stronger peak centered at 12 ppm, which is assigned to the chemical shift of γ -Al₂O₃ framework Al sites. At the same time, the peak at 0 ppm related to the zeolite extra-framework Al is overlapped.



Figure 7. (a) (left) ²⁷Al-NMR spectra of H-ZSM-5 samples (before and after MTH reaction); (b) (right) ²⁷Al-NMR spectra of Al-H-ZSM-5 samples (before and after the MTH reaction).

One could question how uniformly those newly formed γ -Al₂O₃ phases could have been dispersed in the prepared catalyst. For those Al-H-ZSM-5 samples, it is noticed that their XRD response of γ -Al₂O₃ is so poor that it is in a strong contrast with the corresponding ²⁷Al-NMR signal. Therefore, as we proposed in the above discussions, the newly formed γ -Al₂O₃ phases could hardly coagulate into bulked crystals; in fact, they are more likely to effectively bind with the zeolite nanoparticles, filling the interconnecting inter-crystalline spaces, and homogenously spread over the zeolite surfaces.

The ²⁹Si-NMR spectra of different samples are quite similar (Figure 8a,b). In detailed deconvolutions (Figures S7–S9), either three or four lines in an unconstrained fit have been obtained. While each simulation represents the overall bandshape very well, the results of different samples are quite variable. Particularly, the higher frequency part of the bandshape (-115 to -100 ppm) has shown some noticeable differences.

All H-ZSM-5 samples possess a deconvoluted peak at -106 ppm, related to the Brønsted acid sites in the zeolite framework [34]. This peak disappeared after the MTH reaction in most post-reaction H-ZSM-5 samples; at the same time, a new peak near -111 ppm emerged. Here we attribute the newly found -111 ppm peak to those Brønsted acid sites covered by the reaction formed coke species. The signal intensity of this peak ('%' in the total peak area integration, shown in Table 1) could somehow reflect the level of coke formation for a particular sample, which has been noted to increase from the post reaction H-ZSM-5 120 sample to the post reaction H-ZSM-5 20 sample. Smaller Si/Al ratio indicates more Brønsted acid sites in a zeolite, so as the corresponding Al-H-ZSM-5 sample (this is also confirmed by our NH₃-TPD results in Figure 3), which often leads to a faster coke formation [4,19].



Figure 8. (a) (left) ²⁹Si_NMR spectra of H-ZSM-5 samples (before and after MTH reaction); (b) (right) ²⁹Si_NMR spectra of Al-H-ZSM-5 samples (before and after MTH reaction).

Table 1. Signal intensity of chemical shifts near -106 ppm, and -111 ppm.

Samples	Near –106 ppm	Near –111 ppm				
H-ZSM-5 20	29.8% (-108.7 ppm)	no signal				
H-ZSM-5 60	20.0% (-106.8 ppm)	no signal				
H-ZSM-5 120	16.9% (-107.1 ppm)	no signal				
Al-H-ZSM-5 20	23.3% (-106.5 ppm)	no signal				
Al-H-ZSM-5 60	18.9% (-106.2 ppm)	no signal				
Al-H-ZSM-5 120	16.5% (-106.4 ppm)	no signal				
post reaction H-ZSM-5 20	no signal	38.6% (-111.9 ppm)				
post reaction H-ZSM-5 60	no signal	23.3% (-110.5 ppm)				
post reaction H-ZSM-5 120	no signal	22.8% (-109.4 ppm)				
post reaction Al-H-ZSM-5 20	no signal	32.7% (-111.9 ppm)				
post reaction Al-H-ZSM-5 60	16.4% (-108.1 ppm)	no signal				
post reaction Al-H-ZSM-5 120	12.0% (-107.1 ppm)	no signal				

Interestingly, only the post-reaction Al-H-ZSM-5 20 sample presents a -111 ppm peak. For the post-reaction Al-H-ZSM-5 60 sample and post-reaction Al-H-ZSM-5 120 samples, only slight shifts of the -106 ppm peak to -108 ppm and -107 ppm, respectively, noticed, implying only very limited changes on the chemical environment of the zeolite Brønsted acid sites caused by the reaction coke formation.

4. Coke Characterization

Coke species formed on different samples are analysed based on the results from ¹³C-NMR (Figure 9), FT-IR (Figures 10 and 11), and laser-Raman (Figure 12). At the same time, Thermogravimetric Analysis (TGA) data gives a total coke amount (Figure 13). Here the coke species are mainly polymerized, condensed, and partially dehydrogenated organic residues formed in the MTH reactions and could be further dehydrogenated through



sub-reactions such as aromatization and hydrogen transfer, which is commonly seen in the zeolite catalyst studies [27].

Figure 9. CP ¹³C-NMR spectra of coked samples after MTH reaction.



Figure 10. FT-IR spectra of all coked samples $(3500-2000 \text{ cm}^{-1})$.







Figure 12. Laser Raman spectra of coked samples.



Figure 13. Thermogravimetric analysis (TGA) plot of the post-reaction samples (**down**), and corresponding derivative thermogravimetry (DTG) curves (**up**).

4.1. ¹³C-NMR

Regarding ¹³C-NMR, the only limitation, i.e., the very low natural abundance of the ¹³C isotope (only 1.1%), can be avoided by using ¹³C enriched reactants (a costly way) and/or cross-polarization (CP) techniques to enhance the carbon responses [27]. In this study, signals from coke species are successfully boosted with CP ¹³C-NMR. The strongest signal is attributed to aromatic coke species (a broad region highlighted at ~126 ppm, which is commonly attributed to monocyclic aromatics, e.g., benzene, toluene, xylenes, trimethylbenzenes, etc.), for which post-reaction H-ZSM-5 samples have shown apparently stronger intensities (notably, post-reaction H-ZSM-5 20 samples even have a sharp peak at ~126 ppm in the spectra) [35]. In each case, the aromatic coke species also possess weak spinning sidebands at ~70 ppm and ~190 ppm, respectively; and again, these signals are more clearly seen on the post-reaction H-ZSM-5 samples. The band at ~17 ppm could be related to some aliphatic structures, and only-post reaction H-ZSM-5 samples and post-reaction Al-H-ZSM-5 20 have a sharp peak [36]. The obtained ¹³C-NMR results reveal that more coke species are adsorbed on the H-ZSM-5 samples, which have included both aromatic and less dehydrogenated aliphatic compounds.

4.2. FT-IR

A general scan on all post-reaction samples is presented in Figure S10, showing the well-maintained zeolite structure of each sample. Among all post-reaction samples, post-reaction H-ZSM-5 20 exhibits the strongest carbonaceous signals.

Our study focuses on the specification of various coke species. In Figure 10, complex IR signals are shown in the region of 3100–2800 cm⁻¹, in many cases these can be assigned to aromatic and aliphatic rings [37]. A very weak signal of aromatic CH stretching could be seen at ~3038 cm⁻¹; post-reaction H-ZSM-5 20 has a fairly week response at this band (marked with a red cycle), not well visible but still stronger than in other samples [38]. The bands at ~2920 cm⁻¹ and ~2880 cm⁻¹ could be ascribed to the stretching of methyl groups on aromatic rings, very similar to those of methylbenzenes (toluene and xylenes) adsorbed

on zeolites [20,39,40]. The band at ~2980 cm⁻¹ could be related to the CH stretching of olefinic species [41].

CC stretching of unsaturated hydrocarbons and CH bending of paraffinic groups can be observed in the 1300–1700 cm⁻¹ region, as shown in Figure 11 [27,30]. Again, the spectra of post-reaction H-ZSM-5 20 has the most obvious signals for these bands (a strong IR peak near 1600 cm⁻¹ with a shoulder moving towards smaller wavenumbers) in strong contrast to other post-reaction samples. The band just below 1400 cm⁻¹ could be related to ethylene type (olefinic) polymers which is better shown in post-reaction Al-H-ZSM-5 20 and post-reaction Al-H-ZSM-5 120 samples. Those non-aromatic precursors are also important components of coke species [37]. Our FT-IR results suggest a potential weaker coke deposition occurred on those Al-H-ZSM-5 samples. All the findings can be related to and are well supported by some previous pioneering works [4,19,27,28].

4.3. Laser-Raman

Post-reaction samples were also characterized by laser-Raman, where in the 1400–1650 cm⁻¹ region coke species on the zeolite surface are well presented (the exact band positions may vary in different studies) [42]. The 1605–1615 cm⁻¹ bands (graphite band or 'G-band') associated to the ring stretches of aromatic structure are clearly observed on those post-reaction H-ZSM-5 samples [29,43]. The signal highlighted at 1605 cm⁻¹ produces a sharp peak in the spectra of post-reaction H-ZSM-5 60 and post-reaction H-ZSM-5 120, although for post-reaction H-ZSM-5 20, the desired peak at the same position is unexpectedly covered (shown in a more flat shape, but the ¹³C-NMR spectra of this sample shows a sharp aromatic peak) by the greatly enhanced overlapping signal (this also demonstrates much severer coke deposition in this sample).On the other hand, post-reaction H-ZSM-5 samples also show detectable signals in the region of 1200–1210 cm⁻¹, associated to the CC stretching of polyaromatics [43].

The above figure implies more aromatic coke species are formed on those post-reaction H-ZSM-5 samples, matching with our FT-IR (Figures 10 and 11) and ¹³C-NMR (Figure 9) results. For the post-reaction Al-H-ZSM-5 samples we have seen enhanced signals in the 1480–1550 cm⁻¹ region, as reflected by the rising peak at ~1480 cm⁻¹ in the Raman spectra. This peak (more obviously seen in the post-reaction Al H-ZSM-5 20 and post-reaction Al H-ZSM-5 60 spactra) has been assigned to the C=C stretching vibration of conjugated olefins (or polyenes), with an extended tail shifting towards the larger wavenumbers also considered as an evidence for the deposited olefinic compounds [27,43]. Here the distribution of coke species seems to vary between H-ZSM-5 and Al-H-ZSM-5 samples, where coke species in post-reaction H-ZSM-5 samples are more aromatic while the coke species in post-reaction Al-H-ZSM-5 samples are more olefinic.

4.4. Thermogravimetric and Derivative Thermogravimetry

Our thermogravimetric (TGA) results (Figure 13) describe a total coke amount (shown in weight loss by the analysis) for each sample. The most obvious changes at ~600 °C, also clearly shown by the peaks in derivative thermogravimetry (DTG) curves, are due to the coke species formed at higher temperatures (450 °C and higher), with large portion of aromatics [27]. The obtained results reveal that most Al H-ZSM-5 samples have less coke formation than the H-ZSM-5 samples. Alumina binder may have a positive effect on reducing the coke formation; however, the Si/Al ratio of zeolite is still a determinant factor.

Sample porosity properties are examined by BET analysis (Table S1). Here we note the introduction of alumina binders has reduced both the sample surface area and the pore volume when we compare a H-ZSM-5 sample with its corresponding Al-H-ZSM-5 sample. Surprisingly, the mechanical shape (of extrudates), only possesses a very limited influence, as there is nearly no difference between the results of a shaped catalyst and its ground powders. It seems that the loss of porosity properties would be primarily caused by the combination of alumina binders with the zeolite particles (this is also discussed in Section 3.2). On the other hand, it is noted that although a certain porosity is lost, all

Al-H-ZSM-5 samples retained more surface area and pore volumes after the MTH reaction than the H-ZSM-5 samples. It seems that the alumina binders firstly reduced, but later effectively maintained the sample porosity. Here the Al/Si ratio of zeolite still has an important impact on the loss of sample porosity for all post-reaction samples.

5. Conclusions

Based on the above observations, we believe that the major catalytic activity, for an efficient methanol conversion, and higher yield of aromatic hydrocarbon products, are mainly dependent upon the intrinsic amount of Brønsted acid sites in the parent zeolite (H-ZSM-5). However, the introduced alumina binders do have unique impacts on the MTH product selectivity, related to the adjusted zeolite Brønsted acidity, or the potential co-catalytic functions by introduced Al³⁺. The alumina binders also help to prevent coke accumulation on zeolite body, which contributes to a more stable catalytic performance.

The customized experiments for a larger-scale catalyst test better represented actual industrial implementation, as well as the future application of nano-zeolites, with detailed comprehensive study on coked catalysts, have completed some blanking areas in the MTH research, and as we expected, contributed to a coming flourishing 'methanol chemistry', which is uniquely important for the 'post-oil' century.

6. Experimental

Powdered nano-H-ZSM-5 (Si/Al = 20, 60 and 120, precalcined to remove the ammonium, supplied by Qingdao Lianxin Chemical Co. Ltd., Qingdao, China) was mixed with peptized boehmite (AlOOH) to form the first-step paste (63.6 wt% H-ZSM-5, mixed with 36.4 wt% boehmite spread in distilled water, 100 g total solid mixture/25 mL water). Before the extrusion process, sesbania powder (herbal plant seeds, the major component is galactomannan, removed by calcination) was added as shaping promoter (sesbania power weight to clean zeolite weight = 1:12). A mini-industrial screw extruder (designed and manufactured by Lianxin Chemical, Qingdao, China) was used for shaping the catalysts (the shaped catalyst extrudates possess a uniform diameter of 2.0 mm and are cut into 0.3–0.5 cm in length pieces). The prepared catalysts (zeolite powders and shaped extrudates) and instruments for the extrusion are shown in the Figure S11. The fresh extrudates were dried in air for 24 h before calcination in a conventional oven for 5 h (550 $^{\circ}$ C). The shaped Al-H-ZSM-5 samples possesses 70 wt% of zeolite and 30 wt% of Al₂O₃ (expected result), in case of a 25 wt% weight loss for the boehmite after calcination. The applied zeolite/alumina ratio is to preserve the zeolite properties at a maximum with satisfactory binding effects. The major preparation steps are similar to those described in other studies [14], only a pre-calcination step to activate the NH₄-ZSM-5 into H-ZSM-5 before the all the preparation steps is employed to explore the direct interactions between the zeolite acid sites and the introduced alumina. Before characterizations, all extrudates were ground into particles smaller than 0.074 mm in diameter.

The scanning electron microscopy (SEM) images were obtained with a JSM840F scanning microscope (JEOL, Tokyo, Japan). Sample powders were deposited onto the dust–free scanning platform and trapped on the surface before analysis. Transmission electron microscopy (TEM) measurements were undertaken using a JEOL JEM-2100UHR microscope at 200 kV (JEOL, Tokyo, Japan).

The surface area was measured in Brunner Emmett Teller (BET) analysis (JW-BK132f surface area analyzer, Beijing JWGB, Beijing, China) for the as-prepared catalysts (both extrudates and ground powders) and the post-reaction samples (extrudates only). The total surface area was calculated from adsorption data at $p/p_0 = 0.003-0.05$.

²⁷Al-, ²⁹Si- and ¹³C-NMR experiments carried out with a VNMRS spectrometer (Varian, Santa Clara, California, USA) at ambient temperature at a resonance frequency of 104.198, 79.438 and 100.562 MHz, respectively. Cross polarization (CP) for ¹³C-NMR and direct excitation (DE) for ²⁷Al- and ²⁹Si- were employed in the experiments. The ²⁷Al-NMR were performed in a 4 mm probe, with an acquisition time of 20.0 ms, a recycle time of 5.0 s, and a sample spinning rate of 12.118 KHz. The 29 Si-NMR spectra were recorded with a 6 mm probe at a sample spinning rate of 6 KHz, and an acquisition time of 20.0 ms, with a recycle delay of 5.0 s. The 13 C CP-NMR experiments used a 6 mm probe, with data acquisition in 30.0 ms, recycle delay of 2.0 s and sample spinning rate at 6 KHz. The conditions are based on relevant previous studies [33].

XRD data was obtained with a PANalytical X'Pert PRO Diffractometer (Oxford University, Oxford, UK) using Cu K α 1 radiation, the scan diffraction angle from 5° to 70° (2 θ) and a scan rate of 0.8°/min in 2 θ .

The NH₃-TPD analysis was performed using a TP–5078 Auto TPD system (Xianquan Co. Ltd., Tianjin, China). Samples (500 mg) were carefully pre-treated in N₂ at 400 °C for 2 h to remove the moisture. The NH₃ adsorption (NH₃:N₂ = 1:3) performed at 120 °C for 30 min, and the system was then cooled down to room temperature for 1 h in pure N₂. The samples were then heated at 8 °C/min from room temperature to 600 °C, the desorbed NH₃ was recorded with a thermal conductivity detector (TCD).

FT-IR data were collected using a Spectrum RX1 FT-IR spectrometer (Perkin-Elmer, Waltham, MA, USA). Ground sample powders were diluted with KBr, then shaped into tablets for the IR measurements.

Raman spectra were recorded on a Perkin-Elmer Raman Station 400F Raman Spectrometer. The samples were supported on a piece of clean glass for scanning.

A SDT Q600 (TA Instruments, New Castle, Delaware, USA) thermogravimetric analyser was used to analyse the coke contents over the used catalysts. The coke amount is measured based on the weight loss during temperature programmed calcination of coked sample in air from 20 to 1120 °C (temp. ramp 10 °C/min). 50 mg of spent sample was used each time.

The catalyst tests employed a fixed bed reactor system, connected with gas chromatography system (online GC, off line GC/MS). 20 g (bulk density: 0.4779 g/mL for extrudates, 0.1550 g/mL for zeolite powders) of each sample were loaded in the middle of the tubular reactor, supported by carborundum (Fisher, 24 grit). Methanol (Sigma, Shanghai, China) was injected by a HPLC pump, and preheated in the preheater at 150 °C to fully vaporize into gas phase. A reduced WHSV of $1.5 h^{-1}$ was applied in the reaction. N₂ was used as carrier gas to bring the vaporized methanol into reactor (300 mL/min; a higher speed is not recommended and may result in inner tubular jam). The catalyst bed temperature was set at 450 °C under 6 bar inner pressure. The gas and liquid products were well separated at the end of the system (cool water condenser used). Gas products were analyzed with a GC-2010SE GC system (Shimadzu, Tokyo, Japan) equipped with a MXT-1HT column (RESTEK, Bellefonte, PA, USA). The data were obtained from a thermal conductivity detector (TCD) for non-hydrocarbons and a flame ionization detector (FID) for hydrocarbons every 30 min after the methanol injection started. Liquid products were collected after the reaction and separated into water and oil phases. Each phase was analyzed with a Shimadzu GCMS-QP2010 Ultra High-end GC-MS system (SHIM-5MS column, FID). The catalyst testing system, and the tubular design are shown in the Figure S12. The methanol conversion was determined by the amount of methanol remaining in the liquid product (both oil and water phases). Upon the current instrumental efficiency, and a requirement on continuous analysis of gas output every 30 min, our research focuses on the TOS yield of major gas products including methane, ethane, ethylene, propane, propylene and a total C₄. The value (mol%) was calculated by comparing the instantaneous gas production with methanol injection rate. The corresponding yield of major liquid aromatics after 5 h reaction, including benzene, toluene, and xylenes (BTX) as well as trimethyl benzene was calculated from methanol consumption of selected products and total methanol injected. The definitions below are based on previous studies and modified for this research [44,45]:

Methanol	convers	ion -	М	ethanol		in	_	Metha	ano1	(out			
Methanoi conversion		1011 -			Met	han	no1	in	L					
Gas product yield =	ield =	pro	oduct in	n T	0S	×	number	of	С	atom	in	mole	cule	
			Meth	nanc	51	inj	iecti	on		TOS				
Liquid product yield	vield	_	amount	of	pro	odu	ct × 1	numb	er	of C	ato	om in	molecule	
	yiciu	_			Tot	al	m€	ethar	101		inje	cted		

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10 .3390/catal11101140/s1, Figure S1. C1-C4 product yields, Al-H-ZSM-5 20, Figure S2. C1-C4 product yields, H-ZSM-5 20, Figure S3. C1-C4 product yields, Al-H-ZSM-5 60, Figure S4. C1-C4 product yields, H-ZSM-5 60, Figure S5. C1-C4 product yields, Al-H-ZSM-5 120, Figure S6. C1-C4 product yields, H-ZSM-5 120, Figure S7. De-convoluted 29Si NMR spectra of H-ZSM-5 20, Al-H-ZSM-5 20, post reaction H-ZSM-5 20 and post reaction Al-H-ZSM-5 20, Figure S8. De-convoluted 29Si NMR spectra of H-ZSM-5 60, Al-H-ZSM-5 60, post reaction H-ZSM-5 60 and post reaction Al-H-ZSM-5 60, Figure S9. De-convoluted 29Si NMR spectra of H-ZSM-5 120, Al-H-ZSM-5 120, post reaction H-ZSM-5 120 and post reaction Al-H-ZSM-5 120, Figure S10. FT-IR spectra (3500–400 cm⁻¹) of post reaction samples, Figure S11. Mini Industrial Screw Extruder for catalyst shaping, Figure S12. Reactor design and product analysis, Table S1 BET surface area of samples.

Author Contributions: B.L.: Conceptualization, Writing—original draft preparation; X.Z.: Investigation, Formal analysis; J.Z.: Validation; D.W.: Investigation; W.M.: Supervision, writing—review and editing. All authors have read and agreed to the published version of the manuscript.

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