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Deactivation of HDT Catalysts by Formation of Silica Gels from Silicone Oil. Characterization of Spent Catalysts from HDT of Coker Naphtha Using ^{29}Si and ^{13}C CP/MAS NMR

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Catalysts used for hydrotreating of coker naphtha are found to deactivate very quickly because of deposition of Si-containing species on their surface. These species originate from the silicone oil (polydimethylsiloxane) added to the coker unit in order to suppress foaming during the coking process. Six samples of a spent catalyst from a HDT reactor have been analyzed by ^{29}Si MAS, ^{29}Si CP/MAS, and ^{13}C CP/MAS NMR spectroscopy. From these studies it is concluded that the silicone oil in the naphtha feed is transformed (oxidized) to modified silica gels, i.e., silica with a partly methylated surface, under the operating conditions of the catalyst. Physi- or chemisorption of the silica gels on the catalyst explains the fast irreversible loss of activity during HDT of coker naphtha.

INTRODUCTION

Hydrotreating (HDT) catalysts, such as Co–Mo/Al_2O_3 and Ni–Mo/Al_2O_3, are important catalysts and are widely used in the oil industry to remove sulphur and nitrogen from crude oil by catalytic hydrodesulphurization (HDS) and hydrodenitrogenation (HDN), respectively. Recent attempts to improve these catalysts by modification of their surfaces have lead to the development of additives with favourable effects on the catalytic activity. In particular, phosphorus loading (*1–3*) in the form of phosphates has been shown to improve the HDN activity markedly, and the industrial use of Ni–Mo–P/Al_2O_3 catalysts in HDT is now common.

Delayed coking processes produce coke, gas oil, and naphtha through thermal cracking of heavy residues, for example of vacuum residues (*4*). Typical operating conditions during this thermal process are 500°C and 3–4 bar. Because of gas formation, silicone oil (polydimethylsiloxane (PDMS)) is usually added to the coker drums to suppress foaming of the feedstock (*5*). The present work has been promoted by the observation that Ni–Mo/Al_2O_3 catalysts during HDT of coker naphtha are found to undergo deposition of relatively large quantities of Si (5–8 wt%) as evidenced by X-ray fluorescence (XRF) analysis of spent catalysts. Deposition of the Si species deactivates the catalyst and significantly shortens its lifetime. The origin of the Si deposits must be traced back to the silicone oil added to the heavy residue in the coker since the fresh Ni–Mo/Al_2O_3 catalyst contains virtually no silicon. However, the concentration of PDMS in the coker naphtha is very low since its Si content is $\leq$100 ppm.

In this study we have investigated the nature of the Si present on the deactivated catalyst. A series of aged HDT catalysts from an industrial plant for hydrotreating of naphtha has been investigated by solid-state ^{29}Si and ^{13}C cross-polarization/magic-angle-spinning (CP/MAS) NMR spectroscopy. This has resulted in a detailed characteriza-

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TABLE 1

Results from XRF Analysis of the Six Samples of Spent HDT Catalysts

Sample	C[a] (%)	Si (%)	S (%)	Mo (%)	Ni (%)	Fe (ppm)	V (ppm)
1	2.8	5.6	5.5	7.5	2.0	405	395
2	3.7	7.7	5.4	6.8	2.1	278	365
3	3.0	7.4	5.9	7.4	2.1	376	365
4	3.6	7.8	5.4	6.9	2.0	502	340
5	3.0	4.6	6.0	7.5	2.1	446	405
6	3.0	7.3	5.9	7.5	2.1	328	370

[a] Determined by combustion analysis.

tion of the Si species deposited on the catalyst. We point out that especially ^{13}C CP/MAS NMR has previously been applied to study the deactivation (e.g., coke formation (*6*)) of other catalysts such as zeolites (*7*).

EXPERIMENTAL

Materials. The series of spent Ni–Mo/Al_2O_3 HDT catalysts from coker naphtha was obtained from an industrial unit operating at 320–360°C and 50 bar. Catalyst samples were picked at different heights from a HDT reactor with a height of 10 m which has been in operation for 10 months. The samples are labelled **1** (0 m), **2** (2 m), **3** (4 m), **4** (6 m), **5** (8 m), and **6** (10 m), where the numbers in parentheses indicate the approximate distance from the feed of the coker naphtha to the particular catalyst sample. The fresh catalyst was a commercial Ni–Mo/Al_2O_3 catalyst (Haldor Topsøe TK 551) which contains 2.7 wt% Ni and 9.9 wt% Mo and has a surface area of 180 m^2/g.

NMR spectroscopy. ^{29}Si and ^{13}C MAS and CP/MAS NMR experiments were performed on a Varian XL-300 (7.1 T) spectrometer at 59.59 and 75.43 MHz, respectively. ^{29}Si CP/MAS NMR spectra were also obtained on a Varian UNITY 400 (9.4 T) spectrometer at 79.46 MHz. Homebuilt CP/MAS probes (*8*) and 7-mm-o.d. PSZ (partially stabilized zirconia) rotors with a sample volume of 225 μl were employed on both spectrometers. The rf-field strengths used for the ^{29}Si-$\{^1H\}$ and ^{13}C-$\{^1H\}$ CP Hartmann–Hahn match were $\omega_{1Si}/2\pi = \omega_{1H}/2\pi = 32$ kHz and $\omega_{1C}/2\pi = \omega_{1H}/2\pi = 40$ kHz, respectively. During acquisition of the ^{29}Si and ^{13}C FIDs the ^1H decoupling rf-field strengths were increased to $\omega_{1H}^{dec}/2\pi = 40$ and 62 kHz, respectively. Ordinary MAS spectra were recorded using a spinning frequency (ν_r) in the range $\nu_r = 7.0$–7.2 kHz. For the ^{29}Si CP/MAS experiments a somewhat lower spinning speed was employed ($\nu_r = 4.5$–5.0 kHz) in order to avoid significant averaging of the heteronuclear ^{29}Si–^1H dipole couplings required for the CP experiments. ^{29}Si and ^{13}C NMR spectra of the neat viscous silicone oil were recorded on the 7.1 T spectrometer using the 7 mm MAS probe and employing $\nu_r \approx 500$ Hz to reduce linebroadening caused by the viscosity of the oil. A flip angle of 30° and a repetition delay of 8 s was employed for all ^{29}Si MAS NMR experiments. Because of the low Si wt% for all samples no attempts were made to determine T_1 of the different Si species. However, an experiment of arrayed recycle delays indicated that all Si species are fully relaxed within a repetition delay of 4 s, and all ^{29}Si MAS NMR experiments can therefore be considered quantitatively reliable. The reported ^{29}Si and ^{13}C chemical shifts are in ppm and relative to an external sample of neat TMS.

For the Si species (*vide infra,* see Fig. 3) we have adopted the M, D, T, Q nomenclature used by Engelhardt *et al.* (*9*) in their studies of organosilicones and extended (*10*) for the description of the different structural surface species for modified silica gels.

RESULTS AND DISCUSSION

The results of a quantitative analysis of the elements C, Si, S, Mo, Ni, Fe, and V, as determined by combustion and XRF analysis are given in Table 1 for all six samples. It is noted that the weight percentages of S, Mo, Ni, and V are relatively constant for the different samples whereas larger variations are observed for C, Si, and Fe. The somewhat lower mean-values for the Mo and Ni wt% of the spent catalysts (Mo = 7.3 and Ni = 2.1 wt%) as compared to the fresh catalyst (Mo = 9.9 and Ni = 2.7 wt%) are most likely caused by the additional weight increase of C and Si during HDT (by formation of coke and silica gels, *vide infra*). The rapid irreversible loss of catalytic activity observed during HDT of coker naphtha must be associated with the change in catalyst surface structure induced by Si, since coke formation at a level of 3–4% in the absence of silicone oil does not result in a similar rapid deactivation of the catalyst.

The proton-decoupled ^{29}Si NMR spectrum of the viscous PDMS oil (Fig. 1a) shows a strong resonance at $\delta = -22.4$ ppm and a much weaker peak at $\delta = 6.9$ ppm. In accordance with earlier studies of organosilicones (*9*, *11*, *12*) the $\delta = -22.4$ ppm and $\delta = 6.9$ ppm resonances are assigned to the chain internal and chain terminal silicon atoms (Fig. 3), respectively. The proton-decoupled ^{13}C NMR spectrum of PDMS (Fig. 1e) shows a resonance at $\delta = 1.4$ ppm in agreement with earlier observations (*9*). Furthermore, low-intensity resonances arising from spinning sidebands and from the doublet due to the ^{29}Si satellites ($|^{1}J_{C-Si}| \approx$ 74 Hz) are also observed (*13*).

To characterize the nature of the Si material deposited on the spent naphtha HDT catalysts, ^{29}Si MAS and CP/MAS as well as ^{13}C CP/MAS NMR spectra have been investigated for all six samples. Due to the similarity of the spectra for the different samples only spectra of the samples **1**, **4**, and **6**, corresponding to catalysts picked from the top, centre, and bottom layer, respectively, of a HDT reactor (see experimental section) are discussed and presented here.

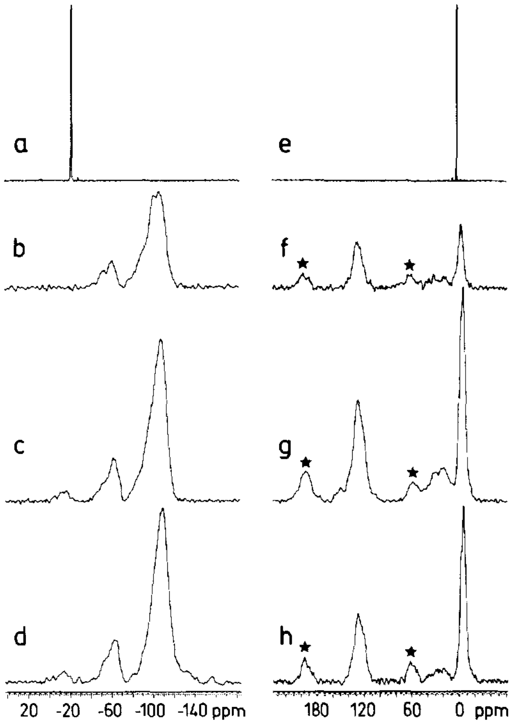


FIG. 1. Proton-decoupled ^{29}Si MAS and ^{13}C CP/MAS NMR spectra of samples **1**, **4**, and **6**, and ordinary liquid-state ^{29}Si and ^{13}C NMR spectra of neat silicone oil (polydimethylsiloxane, PDMS). (a) Proton-decoupled ^{29}Si NMR spectrum of PDMS (656 scans, 8-s repetition delay, $\nu_r \approx 500$ Hz). (b–d) ^{29}Si MAS NMR spectra of samples **1**(b), **4**(c), and **6**(d) obtained using identical spectrometer conditions (8000 scans, 8-s repetition delay, $\nu_r = 7.2$ kHz) and plotted using the same vertical expansion. (e) Proton-decoupled ^{13}C NMR spectrum of PDMS (521 scans, 4-s repetition delay, $\nu_r \approx 500$ Hz). (f–h) ^{13}C CP/MAS NMR spectra of samples **1** (f), **4** (g), and **6** (h) obtained using identical spectrometer conditions (16000 scans, 2-ms contact time, 4-s repetition delay, $\nu_r = 5.0$ kHz) and plotted using the same vertical expansion. Spinning sidebands from aromatic coke resonances are marked with asterisks.

The ^{29}Si MAS NMR spectra of samples **1**, **4**, and **6** (Figs. 1b–1d) generally all show the appearance of resonances in the three regions $\delta = -85$ to -120 ppm, $\delta = -50$ to -70 ppm, and $\delta = -15$ to -20 ppm; the ^{29}Si chemical shifts are summarized and assigned in Table 2. The presence of silicone oil in the samples can be ruled out from these spectra, since even a minor portion of this material would result in a narrow and easily detectable resonance at $\delta \approx -22.4$ ppm. Close inspection of the spectral region from $\delta = -85$ to -120 ppm, for example, for sample **1** (Fig. 1b) or sample **4** (Figs. 1c and 2a), clearly reveals the presence of three overlapping signals positioned approximately at $\delta = -108$, -100, and -90 ppm. These signals are assigned to those of a silica gel (modified, *vide infra*) with the resonance

TABLE 2

^{29}Si Chemical Shifts[a] for samples **1, 4,** and **6**

Sample	Q_2	Q_3	Q_4	T_2, T_3	T_4	D_4
1[b]	−89.8	−101.2	−106.6	−54.2	−61.8	—[e]
4[b]	−88.9	—[d]	−107.6	−55.6	−63.7	−12 to −20
4[c]	−90.0	−99.6	−107.9	−53.8	−64.1	−18.0
6[b]	−89.5	−100.7	−109.5	−54.4	−63.0	−14 to −20
6[c]	−89.6	−99.3	−108.0	−53.8	−63.9	−18.1

[a] Relative to an external sample of neat TMS.
[b] Determined by ^{29}Si MAS NMR.
[c] Determined by ^{29}Si CP/MAS NMR.
[d] Resonance not clearly resolved.
[e] No signal detected.

at $\delta = -108$ ppm representing siloxane groups (bulk SiO_2 or Q_4 sites), while the resonances at $\delta = -100$ and -90 ppm are assigned to silanol (Q_3) and geminal silanol (Q_2) groups, respectively, at surface sites of the silica gel (*14*). This assignment of the three resonances is confirmed by the positive response of all three signals to cross-polarization (*14*), as shown in the ^{29}Si CP/MAS NMR spectra of Figs. 2b and 2c. These spectra show the characteristic features as observed in earlier ^{29}Si CP/MAS NMR studies of silica gels (*14–18*) and is discussed further later in this section. In the region $\delta = -50$ to -70 ppm the ^{29}Si MAS NMR spectra (Figs. 1b–1d) show two partly resolved resonances at $\delta \approx -54$ ppm (shoulder) and $\delta \approx -64$ ppm. Resonances in this region are typically observed in ^{29}Si (CP) MAS spectra of modified (monoalkylsilylated) silica gels (*15–18*), materials used in reversed phase high-performance liquid chromatography (HPLC). For these materials it is known that the frequently encountered structural elements shown in Scheme 1 for the surface monoalkyl species give ^{29}Si resonances at $\delta \approx -56$ ppm, $\delta \approx -59$ ppm, and $\delta \approx -64$ to -70 ppm (*15–18*) tentatively assigned to T_2, T_3, and T_4, respectively (*15–17*). Therefore, the resonances observed for the samples **1, 4,** and **6** (Figs. 1b–1d) are assigned to structural elements of the type T_2 and/or T_3 ($\delta \approx -54$ ppm) and T_4 ($\delta \approx -64$ ppm) depicted in Fig. 3. Finally, the low-intensity resonance observed at $\delta \approx -18$ ppm in the ^{29}Si MAS spectra of samples **4** and **6** is assigned to surface Si-atoms bonded to *two* methyl groups, i.e., corresponding to the structural element D_4 in Fig. 3. The assignment is in accordance with the observation of ^{29}Si resonances in the region $\delta \approx -14$ to -22 ppm for dialkylsilylated structures (D_4) of modi-

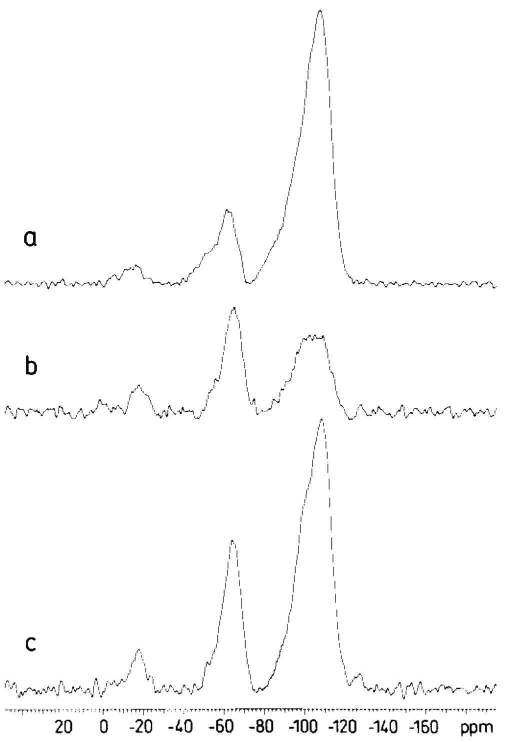
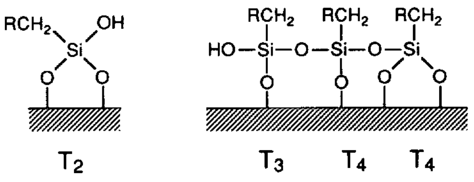


FIG. 2. ^{29}Si MAS (a) and CP/MAS (b,c) NMR spectra of sample **4**. The ^{29}Si CP/MAS spectra were obtained using contact times of 1.0 ms (b) and 2.5 ms (c), respectively, and otherwise identical conditions. The differences in relative signal intensities for the two CP spectra reflect variations in CP dynamics for the various Si species.



SCHEME 1

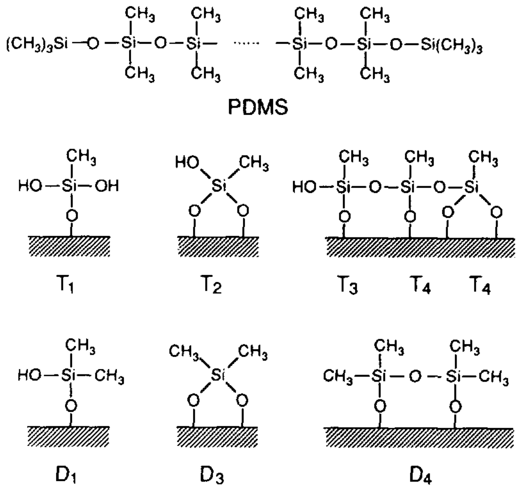


FIG. 3. Structure of PDMS and surface species of modified silica gels relevant for this study.

fied silica gels used in reversed phase HPLC (*15–18*).

Further evidence for the proposed structure of the silica particles formed from the silicone oil is obtained from ^{29}Si CP/MAS NMR experiments. Since the CP efficiency strongly depends on the internuclear distances between the ^{29}Si nuclei and their surrounding protons, enhancements of the resonances for the $=Si(CH_3)_2$ ($\delta \approx -18$ ppm) and $\equiv SiCH_3$ sites ($\delta \approx -64$ and $\delta \approx -54$ ppm) are expected similarly to the ^{29}Si CP/MAS detection scheme used for alkylsilylated silica gels (*15–18*). As an illustration, Fig. 2 compares ^{29}Si CP/MAS NMR spectra for sample **4**, employing CP contact times of 1.0 ms (Fig. 2b) and 2.5 ms (Fig. 2c), with a standard fully relaxed ^{29}Si MAS spectrum (Fig. 2a). A significant enhancement of the $=Si(CH_3)_2$ ($\delta \approx -18$ ppm) and the $\equiv SiCH_3$ resonance at $\delta \approx -64$ ppm is observed using a contact time of 1.0 ms. Increasing the contact time to 2.5 ms leads to an additional intensity enhancement for these resonances. Furthermore, it is noted that for a contact time of 1.0 ms the resonances in the region $\delta = -80$ to -120 ppm for Si atoms not bonded to carbon atoms are dominated by the contributions from $=Si(OH)_2$ ($\delta \approx -90$ ppm) and $\equiv Si(OH)$ ($\delta \approx -100$ ppm) surface sites. However, intensity enhancements of the resonances for the bulk silica sites ($\delta \approx -108$ ppm) with longer distances to the nearest protons require longer contact times (e.g., 2.5 ms) for efficient magnetization transfer as illustrated in Fig. 2c and observed in earlier studies (*14*). Because of the difference in CP dynamics for the different Si species, ^{29}Si CP/MAS NMR experiments render no quantitative information, although the qualitative interpretation of the spectra is generally straightforward. In our experience even the qualitative aspects of ^{29}Si CP/MAS NMR spectra of modified silica gels can be misleading in some cases. The reason is that in addition to the contact time dependence, absolute as well as relative signal intensities for the ^{29}Si CP/MAS NMR spectra of samples **1** to **6** and of different samples of modified silica gels are quite sensitive to the employed spinning frequency. This spin rate dependence is especially pronounced for $\nu_r > 5000$ Hz, and originates from modulations of the Hartmann–Hahn (HH) match condition (*19*) induced by MAS (*20–23*). Therefore, to ensure a valid qualitative interpretation of the ^{29}Si CP/MAS NMR spectra we recommend employing low spinning frequencies for these samples.

An independent proof of the presence of $\equiv SiCH_3$ or $=Si(CH_3)_2$ species on the silica gel formed in the naphtha HDT catalysts was obtained from ^{13}C CP/MAS NMR spectra of samples **1**, **4** and **6** (Figs. 1f, 1g, and 1h). The three spectra all show a ^{13}C resonance from methyl groups directly bonded to Si at a slightly negative chemical shift value from TMS. In fact, close inspection reveals that this resonance is composed of two signals positioned at $\delta \approx -2.7$ and -6.7 ppm. The observation of two resonances is caused by a small chemical shift difference either between the resonances for the $\equiv SiCH_3$ and $=Si(CH_3)_2$ sites and/or between different structural elements for each such species (Fig. 3). The ^{13}C CP/MAS NMR spectra also reveal the formation of coke on the catalysts during hydrotreating. Coke is responsible for the observation of a broad signal at $\delta \approx 127$ ppm for aromatic carbons and for the two aliphatic carbon resonances at $\delta \approx 31$ and 19 ppm. It is noted that the total signal intensity of the ^{13}C CP/MAS spectrum for sample **1** (Fig. 1f) is markedly reduced in comparison with the intensity of the signals observed for samples **4** and **6** (Figs. 1g and 1h). Although this intensity reduction may be explained partly by the somewhat reduced C and Si content of sample **1** (Table 1) as compared to the other samples, it is believed that the presence of paramagnetic metal centres (e.g., Fe and V, 400 ppm each) may have a profound influence on the CP efficiency especially for sample **1** with its reduced coke and silica gel content.

In addition to the structural information provided by the ^{29}Si MAS, ^{29}Si CP/MAS, and ^{13}C CP/MAS NMR spectra, discussed above for the silica gels generated from silicone oil during HDT of coker naphtha, the ^{29}Si MAS spectra shown in Fig. 1 exhibit some interesting features which should be commented on. Although the ^{29}Si MAS spectra of samples **4** and **6** (Figs. 1c and 1d) are quite similar they differ, however, somewhat from the spectrum of sample **1** (Fig. 1b). First, we note that the total ^{29}Si signal intensity for sample **1** is lower than for samples **4** and **6**. This is readily explained by the lower Si content of sample **1** (Table 1). In fact, the total integrated intensities of the ^{29}Si MAS spectra agree with the Si (wt%) values determined by XRF analysis. More importantly, sample **1** shows the presence of a considerably larger quantity of SiOH and $Si(OH)_2$ surface species (represented by the resonances at $\delta = -100$ and -90 ppm) relative to the bulk silica species (resonance at $\delta = -108$ ppm) when compared to samples **4** and **6**. The same is also true when the spectrum of **1** is compared with ^{29}Si MAS spectra (i.e., without CP) of commercial silica gels. The larger number of surface sites relative to the bulk silica for sample **1** indicate that this sample represents an earlier stage in the formation of the silica gel compared to samples **4** and **6**. Furthermore, for sample **1** we also note that the signal at $\delta = -54$ ppm appears as a separate resonance, whereas in the spectra of samples **4** and **6** it only shows up as a low-intensity shoulder overlapping with the $\equiv SiCH_3$ signal at -64 ppm. Thus, larger quantities of T_2 and/or T_3 units relative to T_4 are observed for sample **1**. Since T_2 and T_3 units represent surface species that are only partly condensed (bidendates) (*15–17*), this observation is in agreement with the proposed earlier stage of the formation of silica gel for sample **1**.

The generation of modified silica gel from PDMS must involve a high degree of oxidation of the carbon–silicon bonds. At present it is unknown whether the active sulfided metals of the catalyst take part in the conversion, or if active sites of the alumina carrier are involved. The reaction products, however, seem to be deposited on the catalyst up to an amount of approximately 5–8 wt% Si.

CONCLUSIONS

Hydrotreating catalysts in services for coker feeds have relative short lifetimes because of the accumulation of silicon species on the catalyst. The combined use of ^{29}Si MAS, ^{29}Si CP/MAS, and ^{13}C CP/MAS NMR have lead to a detailed and unambiguous characterization of the Si deposits on aged naphtha HDT catalysts. Silicone oil from the naphtha feed is converted to modified silica gel on the HDT catalyst. The modified silica gel consists mainly of bulk SiO_2 carrying the surface species SiOH, $Si(OH)_2$, $\equiv SiCH_3$, $=SiOHCH_3$, and $=Si(CH_3)_2$.

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