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Construction of Bifunctional Co/H-ZSM-5 Catalysts for the Hydrodeoxygenation of Stearic Acid to Diesel-range Alkanes

Guangjun Wu,^[a] Nan Zhang,^[a] Weili Dai,^[a] Naijia Guan, ^[a,b] and Landong Li*^[a,b]

Abstract: Bifunctional Co/H-ZSM-5 zeolites were prepared by surface organometallic chemistry grafting route, namely by the stoichiometric reaction between cobaltocene and the Brønsted acid sites in zeolites, and applied to the model reaction of stearic acid catalytic hydrodeoxygenation. Cobalt species existed in the form of isolated Co²⁺ ions at exchange positions after grafting, transformed to CoO species on the surface of zeolite and stabilized inside zeolite channels upon calcination in air, and finally reduced to metallic cobalt species of homogeneous clusters of ca. 1.5 nm by hydrogen. During this process, the Brønsted acid sites of H-ZSM-5 zeolites could be preserved with acid strength slightly reduced. The as-prepared bifunctional catalyst exhibited a ~16 times higher activity in stearic acid hydrodeoxygenation (2.11 g_{SA}g_{cat}-1h-1) than the reference catalyst (0.13 $g_{SA}g_{cat}^{-1}h^{-1}$) prepared by solid-state ion exchange, and a high C_{18}/C_{17} ratio of ~24 was achieved as well. The remarkable hydrodeoxygenation performance of bifunctional Co/H-ZSM-5 could be explained from the effective synergy between the uniformed metallic cobalt clusters and the Brønsted acid sites in H-ZSM-5 zeolite. The simplified reaction network and kinetics of stearic acid hydrodeoxygenation catalyzed by the as-prepared bifunctional Co/H-ZSM-5 zeolites were also investigated.

Introduction

Triglycerides, composed of one mole of glycerol and three moles of fatty acids, are considered as high-energy density liquid molecules of biomass that can be used for the production of liquid fuels.^[1] Transesterification reaction is developed as the firstgeneration technology for triglycerides upgrading to fuels (biodiesel). Typically, transesterification process be realized with acid or base catalysts, which has been commercialized around the world.^[1,2] Despite of the advantages of biodegradability, reduced exhaust emissions, high flash point, and excellent lubricity,^[3] the as-produced biodiesel shows some disadvantages of higher oxygen contents, low oxidative stability, and weak cold flow properties, which severely limit its utilization.^[4]

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Decarboxylation, decarbonylation and hydrodeoxygenation (HDO) are then developed for the upgrading of triglycerides and fatty acid to diesel-range alkanes, namely the second-generation biofuels.^[1,2b,5] Various types of catalysts have been investigated and well summarized recently.^[1,2b,6] Among these catalysts, nonnoble metal catalysts, such as Ni,^[6c,7] Co,^[7f,7g,7h] W,^[8] Mo,^[7g] Fe,^[9] are particularly attractive, due to their sufficient activity, good stability and low price. From the view of atomic economy, HDO process, with less C atom losses, is more desirable for the upgrading of triglycerides and fatty acid in comparison to decarboxylation and decarbonylation processes.[6d] In HDO process, the removal of the hydroxyl group should be the final step, which was proposed to be the rate determining step.^[10] As the hydroxyl group can be easily removed on an acid site via dehydration, acidic supports are favored for HDO process. In this context, bifunctional or multifunctional catalysts on acidic supports are preferred, which have been widely investigated for the upgrading of triglycerides and fatty acids in HDO process.[6d,7,10a] Besides, the properties of support materials could influence the size and distribution of metal particles, which could significantly modulate the catalytic performance of bifunctional or multifunctional catalysts.^[7a,7c] Zeolites, the well-known solid acids with high specific surface area and widely industrial applications, are most promising supports for HDO catalysts, which have been extensively investigated not only for the HDO but also for other biomass upgrading processes.[6d,11]

For bifunctional or multifunctional catalysts containing redox metal centers and acidic zeolite supports, it is most important to promote the synergy between different sites.^[11] The preparation of bifunctional or multifunctional catalysts could significantly influence the synergy between different active sites and, accordingly, show great impacts on their HDO performance. Several approaches, e.g. liquid/solid-state ion-exchange, impregnation, and deposition-precipitation, are commonly employed in the preparation of zeolite supported catalysts. Recently, a simple and reproducible route of surface organometallic chemistry (SOMC) reaction has been developed for the preparation of iron-containing zeolites.^[12] Through SOMC reaction, the iron species are grafted on zeolite surface through the reaction between ferrocene and Brønsted acid sites in zeolites and the specific iron sites could be adjusted at the atomic and molecular level to derive well-defined catalysts for target reactions.[13]

On the basis of above background and inspired by current achievements, we herein report the construction of bifunctional Co/H-ZSM-5 catalysts via SOMC reaction and their applications in stearic acid HDO. The properties of cobalt species and H-ZSM-5 zeolite support are well characterized by multiple techniques and the synergy between them are clearly illustrated by catalytic

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data. Such bifunctional metal/zeolite catalyst system might be extended to other complicated reactions of biomass upgrading.

Results and Discussion

Preparation of Co/zeolite via SOMC grafting

The physicochemical properties of Co/zeolite samples prepared by SOMC grafting and solid-state ion exchange were summarized in Table 1. It was seen that cobalt species could be introduced to various zeolite hosts via SOMC grafting and the Co/Al ratio of ~1 indicates the stoichiometric reaction between cobaltocene and the Brønsted acid sites in zeolites. No significant loss in cobalt species could be observed during the subsequent calcination and reduction processes, in great contrast to the case of Fe/zeolite.^[13b] Moreover, the surface areas and pore volumes, as measured by low temperature N₂ adsorption/desorption, were well preserved during the SOMC grafting, calcination and reduction processes (Table 1), which should be good for the catalytic applications.

Table 1. Physicochemical properties of Co/zeolite samples under study					
Sample	Si/Al ^[a]	Co loading (%)	Co/Al ^[a]	S _{BET} (m ₂ /g)	Pore volume (cm ³ /g)
H-ZSM-5	23.7	/	/	435	0.38
Co/H-ZSM-5-G	23.9	3.93	0.95	422	0.37
Co/H-ZSM-5-GC	24.1	3.82	0.92	437	0.37
Co/H-ZSM-5-GR	24.0	3.80	0.92	439	0.37
Co/H-ZSM-5-I	23.8	4.41	1.05	403	0.36
Co/H-ZSM-5-IC	23.9	4.19	0.99	371	0.36
Co/H-ZSM-5-IR	23.8	4.25	1.00	389	0.35
Co/H-EU-1-GR	23.7	3.73	0.93	366	0.34
Co/H-mordenite-GR	23.5	4.31	1.00	392	0.41
Co/H-beta-GR	24.8	4.45	1.09	526	0.21
Co/H-USY-GR	25.3	4.08	1.04	516	0.52

[a] molar ratio.

The XRD patterns of Co/H-ZSM-5 samples were shown in Figure 1. Clear diffraction lines of H-ZSM-5 were observed for all samples,^[14] and the diffraction lines of cobalt species (cobalt oxides and cobalt metal) could not be distinguished due to their low intensities and/or the overlap by the diffraction lines of H-ZSM-5 zeolite. It could also be observed that the intensities of diffraction lines of H-ZSM-5 zeolite decreased upon the introduction of cobalt species and subsequent calcination. Nevertheless, the framework of ZSM-5 zeolite was well preserved, consistent with the results from N₂ adsorption/desorption analyses.

FTIR spectroscopy was employed for an insight of the reaction between cobaltocene and the Brønsted acid sites of H-ZSM-5, and the results were shown in Figure 2. In the hydroxyl region, three bands, i.e. isolated silanol groups at 3740 cm⁻¹, hydroxyl groups bound to Lewis acid centers at 3700 cm⁻¹ and Brønsted acidic hydroxyl groups at 3605 cm⁻¹,^[15] were observed for parent H-ZSM-5 zeolite. Upon the introduction of cobaltocene to zeolite

via grafting, significant decreases in the intensities of Brønsted acidic hydroxyl groups and hydroxyl groups bound to Lewis acid centers were observed, indicating the interaction between cobaltocene and these hydroxyl groups. Meanwhile, new bands due to cyclopentadienyl groups appeared: stretching vibration of =C-H at 3125 cm⁻¹ and the vibrations of olefinic C=C at 1410 and 1505 cm⁻¹. These results clearly demonstrated the successful grafting of cobaltocene to H-ZSM-5 host, which is also reflected by the color change from white to light purple. With the increasing temperature from 373 to 673 K, distinct decreases in the intensities of IR bands due to cyclopentadienyl groups were observed, indicating the gradual removal of these groups upon thermal treatments.



Figure 1. XRD patterns of zeolite samples employed in this study.



Figure 2. FTIR spectra of Co/H-ZSM-5-G at increasing temperatures.

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The temperature-programmed reaction of Co/H-ZSM-5-G was performed and the results were shown in Figure 3. In flowing He, the decomposition of cobaltocene on H-ZSM-5 started at 423 K and the two mass fragments corresponding to C₅H₆ (m/z=66) and C₅H₅• (m/z=65) were detected as the products. No cobaltcontaining fragments, e.g. Cp₂Co⁺ (m/z=188) and CpCo[•] (m/z=124), could be observed. These results suggested that cobaltocene was stabilized on H-ZSM-5 below 423 K while it decomposed at > 423 K via the loss of one cyclopentadienyl group, in good agreement with in situ FTIR results (Figure 2). In flowing O2, CO2 (m/z=44) was detected as the exclusive product from cobaltocene decomposition and a two-stage CO₂ emission was observed at 553 and 703 K, respectively. It appeared that cobaltocene grafted on H-ZSM-5 was more stable in flowing O2 than that in flowing He. According to the temperatureprogrammed reaction results, the organic species in Co/H-ZSM-5-G could be completely removed through calcination in flowing O2 at 773 K and Co/H-ZSM-5-GC sample could be successfully prepared.



Figure 3. Temperature-programmed reaction profiles of Co/H-ZSM-5-G in flowing He or $\mathsf{O}_2.$

Characterization of Co/H-ZSM-5

The TEM images of selected Co/H-ZSM-5 samples were shown in Figure 4. For Co/H-ZSM-5-G, clear lattice fringes of H-ZSM-5 zeolite were observed and no cobalt species could be distinguished although the presence of cobalt was confirmed by energy dispersive spectroscopy analysis (ca. 4.2 %, not shown here). Upon the removal of organic species through calcination at 773 K (Co/H-ZSM-5-GC), the aggregation of cobalt species did occur and tiny cobalt oxide clusters (vide infra) were observed to disperse on the surface of H-ZSM-5 and/or inside the channels. Subsequent reduction treatment did not result in significant changes in the size of cobalt species and homogeneous clusters (should be metallic cobalt, vide infra) with average size of 1.5 nm were obtained for Co/H-ZSM-5-GR. In contrast, large cobalt clusters with size of 7-20 nm were observed on H-ZSM-5 support for Co/H-ZSM-5-IR. The TEM observations clearly demonstrated the advantage of the grafting route to homogeneous tiny cobalt clusters on H-ZSM-5 support.

The surface states of cobalt species in Co/H-ZSM-5-GC and Co/H-ZSM-5-IC were investigated by means of XPS analysis. As shown in Figure 5, similar binding energy values at 795.1 and 779.9 eV corresponding to Co $2p_{1/2}$ and $2p_{3/2}$ of Co³⁺ and/or Co²⁺ were observed for Co/H-ZSM-5-GC and Co/H-ZSM-5-IC. The

satellite features at ~802 and ~784 eV indicated the presence of Co^{2+} in these samples.^[16] According to the nonlinear least-squares fitting results, Co^{2+} ions were the dominating species on H-ZSM-5 after calcination, similar to previous report on ion-exchanged Co-ZSM-5.^[17]



Cluster Size / nm

Figure 4. TEM images of Co/H-ZSM-5-G, Co/H-ZSM-5-GR, Co/H-ZSM-5-GR and Co/H-ZSM-5-IR; The cobalt cluster size distribution in Co/H-ZSM-5-GR and Co/H-ZSM-5-IR.

Cluster Size / nm



Figure 5. Co 2p XPS of Co/H-ZSM-5-GC and Co/H-ZSM-5-IC.

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The H₂-TPR profiles of Co/H-ZSM-5-GC and Co/H-ZSM-5-IC are shown in Figure 6. Typically, three hydrogen consumption peaks at ~500, ~650 and ~900 K were clearly distinguished for both samples. According to previous H₂-TPR results on Co-ZSM-5 samples,^[18] these hydrogen consumption peaks should be due to the reduction of CoO_x species on the surface of zeolite, CoO_x species stabilized inside zeolite channels and isolated Co2+ ions at exchange positions, respectively. Since Co2+ ions were the dominating species on H-ZSM-5 (Figure 5), the total H/Co ratio of ~2 in the temperature range of 373-1273 K indicated the complete reduction of Co²⁺ to metallic Co. A significant higher proportion of CoO_x species stabilized inside zeolite channels was obtained in Co/H-ZSM-5-GC than that in Co/H-ZSM-5-IC, which should be originated from the different preparation methods. These CoO_x species were efficiently stabilized by the zeolite channels and their aggregation upon reduction treatment could be greatly suppressed, as confirmed by TEM observations (Figure 4). It could be seen from our H₂-TPR results that CoOx species on the surface of zeolite or stabilized inside zeolite channels species could be fully reduced to metallic cobalt at 773 K in flowing H₂/Ar (the typical reduction treatment conditions) while Co2+ ions at exchange positions could not. That is, a large proportion of metallic cobalt and a small proportion of Co2+ ions existed in Co/H-ZSM-5-GR and Co/H-ZSM-5-IR catalysts for the HDO reaction.



Figure 6. H₂-TPR profiles of Co/H-ZSM-5-GC and Co/H-ZSM-5-IC.

The acidic properties of Co/H-ZSM-5 zeolites were evaluated by means of NH₃-TPD and the results were shown in Figure 7. Two ammonia desorption peaks at 493 and 743 K were observed for parent H-ZSM-5, corresponding to the weak and strong acid sites, respectively. It was generally acknowledged that the high temperature ammonia desorption peak was originated from the desorption of ammonia strongly interacting with Brønsted acid sites in H-ZSM-5 zeolite.^[19] With the introduction of cobalt species via SMOC grafting or solid-state ion exchange followed by calcination, the ammonia desorption peak corresponding to strong Brønsted acid sites in H-ZSM-5 disappeared while a small peak centred at 673 K appeared (Figure 7, left-hand chart), which should be due to the desorption of ammonia interacting with Lewis acidic CoOx species (all the Brønsted acid sites occupied by CoOx species, Figure 2). Through reduction treatment, the intensities of ammonia desorption peaks at 673 K increased distinctly (Figure 7, right-hand chart). It was revealed from TPR analysis (Figure 6) that a majority of cobalt species in Co/H-ZSM-5-GC and Co/H-ZSM-5-IC could be reduced to metallic cobalt in flowing H₂/Ar at 773 K, accompanied by the recovery of Brønsted acid sites in H-ZSM-5. Since the interaction between ammonia and metallic cobalt was rather weak, the ammonia desorption peak at 673 K in Co/H-ZSM-5-GR and Co/H-ZSM-5-IR should be mainly originated from the ammonia interacting with Brønsted acid sites in H-ZSM-5 zeolite. Compared with parent H-ZSM-5, the strength of Brønsted acid sites in Co/H-ZSM-5-GR and Co/H-ZSM-5-IR decreased significantly, i.e. ammonia desorption peak shifted from 743 to 673 K, which should be explained from the influence of adjacent metallic cobalt species.[20]



Figure 7. NH₃-TPD profiles of H-ZSM-5, Co/H-ZSM-5-IC, Co/H-ZSM-5-GC, Co/H-ZSM-5-IR and Co/H-ZSM-5-GR.

On the basis of the above-mentioned characterization results, it could be concluded that cobalt species existed in the form of CoO species on the surface of zeolite and stabilized inside zeolite channels and isolated Co²⁺ ions at exchange positions in Co/H-ZSM-5-GC. Through reduction treatment, a majority of these cobalt species could be reduced to metallic cobalt species, which appeared as homogeneous clusters of *ca.* 1.5 nm in Co/H-ZSM-5-GR. The Brønsted acid sites in H-ZSM-5 could be preserved in Co/H-ZSM-5-GR while the acid strength is reduced to some extent. The Co/H-ZSM-5-GR was established as a bifunctional material consisting both metallic cobalt centers and Brønsted acid sites, which should be a promising catalyst for the HDO reaction.

Stearic acid HDO catalyzed by Co/H-ZSM-5

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The catalytic HDO of stearic acid over Co/H-ZSM-5-GR and Co/H-ZSM-5-IR was investigated, and the results were shown in Figure 8. Co/H-ZSM-5-IR exhibited very low activity in the reaction with stearic acid conversion rate of 0.13 g_{SA}g_{cat}⁻¹h⁻¹ at 533 K. 1-(C₁₈H₃₇OH), n-Octadecane $(n-C_{18}H_{38}),$ Octadecanol i-Octadecane (i-C₁₈H₃₈), Octadecene (C₁₈H₃₆) and n-Heptadecane (n-C₁₇H₃₄) were detected as the products. 1-Octadecanol was observed as the dominating product in the early stage of reaction. With the progress of reaction, the percentage of 1-Octadecanol decreased while the percentage of n-Octadecane increased, accompanied by the appearance of Octadecene and i-Octadecane. The ratio of C_{18}/C_{17} in the product is calculated to be ~6 after reaction for 240 min.

Co/H-ZSM-5-GR exhibited a ~16 times higher activity (2.11 $g_{SA}g_{cat}$ ⁻¹h⁻¹) than Co/H-ZSM-5-IR under identical reaction conditions (0.13 $g_{SA}g_{cat}$ ⁻¹h⁻¹). Similar to the case of Co/H-ZSM-5-IR, 1-Octadecanol was observed as the dominating product in the early stage of reaction, which was further converted to alkanes with the progress of reaction. The ratio of C₁₈/C₁₇ in the product was calculated to be ~24 after reaction for 240 min, in great contrast to the value of ~7 obtained with Co/H-ZSM-5-IR. The high stearic acid conversion rate as well as the high C₁₈/C₁₇ ratio in the product made Co/H-ZSM-5-GR a very promising nonprecious metal catalyst for the conversion of stearic acid to diesel-range alkanes.

Figure 8. HDO of stearic acid over Co/H-ZSM-5-GR and Co/H-ZSM-5-IR. Reaction conditions: 1.0 g stearic acid, 100 mL n-Heptane, 0.2 g catalyst, 3 MPa H_2 , temperature = 533 K.

The HDO of stearic acid was known to occur over bifunctional catalysts containing both acid sites and metal functional centers. In this study, both Co/H-ZSM-5-GR and Co/H-ZSM-5-IR appeared to be bifunctional catalysts containing Brønsted acid sites and cobalt centers (see characterization results). However, the cobalt particle size in Co/H-ZSM-5-GR (1.5 nm) was much smaller than that in Co/H-ZSM-5-IR (7-20 nm), which hinted to more accessible cobalt centers and a better synergy between the cobalt centers and the Brønsted acid sites in Co/H-ZSM-5-GR. These features should be responsible for the much higher activity observed for Co/H-ZSM-5-GR in contrast to Co/H-ZSM-5-IR.

Through SOMC grafting route, cobalt catalysts on other zeolite supports, i.e. Co/H-EU-1 (SiO₂/Al₂O₃=24), Co/H-USY (SiO₂/Al₂O₃=25), Co/H-beta (SiO₂/Al₂O₃=25) and Co/H-mordenite (SiO₂/Al₂O₃=25), could be prepared. These catalysts were also

investigated for the HDO of stearic acid, and the results were shown in Figure 9. Co/H-EU-1 and Co/H-mordenite exhibited remarkable activity, similar to the case of Co/H-ZSM-5, while Co/H-USY and Co/H-Beta exhibited distinct lower activity. Obviously, the nature of zeolite supports could significantly influence the catalytic activity of cobalt catalysts, which was probably due to the different strength and distribution of acid sites in different zeolites. In a whole, Co/H-ZSM-5-GR could be optimized among all Co/zeolites investigated and it would be employed as a model catalyst for further kinetic study.

Reaction network and kinetics

The reaction network of stearic acid HDO was simplified in Scheme 1. Stearic acid could undergo the hydrogenation of carbon-oxygen double bond to generate 1-Octadecanol, which could be further dehydrated to Octadecene. The hydrogenation of carbon-carbon double bond in Octadecene led to the formation of n-Octadecane. Alternatively, 1-Octadecanol could undergo dehydrogenation to n-Octadecanal, which could be further converted to n-Heptadecane via decarbonylation. For the conversion of stearic acid to n-Heptadecane, stearic acid could directly undergo decarboxylation or undergo decarbonylation to Heptadecene followed by carbon-carbon double bond hydrogenation. The intermediate product Octadecene could be isomerized to i-Octadecene, followed by hydrogenation to i-Octadecane. The n-Octadecane could also be directly isomerized to i-Octadecane.

For the stearic acid HDO catalyzed by Co/H-ZSM-5-GR, 1-Octadecanol was observed as the dominating product in the early stage of reaction and, therefore, the hydrogenation of carbonoxygen double bond in stearic acid to 1-Octadecanol was proposed as the dominating step. Afterwards, the formation and

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consumption of Octadecene was observed (Figure 9), indicating the dehydration of 1-Octadecanol to Octadecene and the subsequent hydrogenation to n-Otadecane. The relatively low amount of Octadecene observed and its quick conversion revealed that the 1-Octadecanol dehydration and Octadecene hydrogenation were very fast steps. Mass spectroscopy analysis reveals that carbon monoxide was the exclusive carbon containing gas product and, therefore, the direct decarboxylation of stearic acid can be completely excluded. Besides, no Heptadecene was observed in the liquid phase, excluding the possibility of stearic acid decarbonylation-hydrogenation to n-Heptadecane. Thereupon, the only possible pathway of n-Heptadecane formation was the dehydration of 1-Octadecanol followed by decarbonylation, which was in good agreement with the observation of carbon monoxide as gas product. However, no intermediate product n-Octadecanal could be detected in the liquid phase. A possible explanation was that n-Octadecanal existed in the form of adsorbed species on the catalyst surface. which underwent very quick conversion to other products.^[21]

Scheme 1. The reaction network of stearic acid HDO.

Generally, the hydrogenation, dehydrogenation and decarbonylation steps take place on transition metal centers while the dehydration and isomerization steps on Brønsted acid sites.^[22] For Co/H-ZSM-5-GR, the presence of Brønsted acid sites and metallic cobalt centers as well as their effective synergy made it a robust bifunctional catalyst for stearic acid HDO to diesel-range alkanes.

According to the reaction network in Scheme 1, an empirical kinetic model for stearic acid HDO over Co/H-ZSM-5-GR could be established. It should be noted that the internal diffusion of molecules inside zeolite channels could not be assessed, and, in this context, the kinetic data reported here will include the effects of internal diffusion. Besides, considering that the reaction was performed in much excess hydrogen, the effects of gas component on the kinetic model could be ignored.^[23]

Three reaction pathways were considered (Scheme 1, framed by red, green and blue dot-line, respectively), and the conversion rates of major products, i.e. stearic acid (SA), 1-Octadecanol ($C_{18}H_{37}OH$), Octadecane ($C_{18}H_{38}$), Octadecene ($C_{18}H_{36}$) and

Heptadecane ($C_{17}H_{36}$), were investigated according to the following equations:

$$\frac{dC_{SA}}{dt} = -k_1 C_{SA}$$
$$\frac{d(C_{C_{18}H_{38}} + C_{C_{18}H_{36}})}{dt} = k_2 C_{C_{18}H_{37}OH}$$
$$\frac{dC_{C_{17}H_{36}}}{dt} = k_3 C_{C_{18}H_{37}OH}$$
$$\frac{C_{C_{18}H_{37}OH}}{dt} = k_1 C_{SA} - (k_2 + k_3) C_{C_{18}H_{37}OH}$$

Table 2. Hydrodeoxygenation of stearic acid over Co/H-ZSM-5-GR at different temperatures

d

Temperature		Time Stearic acid	Product selectivity (%)				
	(K)	(min) Conversion (%)		C ₁₈ H ₃₇ OH	C ₁₈ H ₃₈	C ₁₈ H ₃₆	$C_{17}H_{36}$
	513	100	37.8	85.9	0.2	13.4	0.3
	523	80	39.2	80.9	3.9	14.2	0.9
	533	60	40.4	43.3	34.7	17.4	4.6
	543	40	45.9	27.6	48.9	18.3	5.1

 Table 3. Rate constants and apparent activation energy values of key pathways in the hydrodeoxygenation of stearic acid over Co/H-ZSM-5-GR

Temperature			Rate constants (s ⁻¹)	
	(K)	K 1	<i>k</i> 2	k3
	513	1.01×10 ⁻⁴	2.65×10 ⁻⁵	6.38×10 ⁻⁷
	523	1.34×10 ⁻⁴	4.67×10 ⁻⁵	2.35×10 ⁻⁶
	533	1.88×10 ⁻⁴	3.35×10 ⁻⁴	2.97×10⁻⁵
	543	3.54×10 ⁻⁴	1.02×10 ⁻³	7.72×10 ⁻⁵
	Ea (kJ/mol)	94	298	392

HDO of stearic acid over Co/H-ZSM-5-GR at 513-543 K was performed and the activity data were summarized in Table 2. With increasing reaction temperature, stearic acid conversion and alkane selectivity increased while 1-Octadecanol selectivity decreased. On the basis of these data, the rate constant values at different temperatures, i.e. k_1 , k_2 and k_3 , could be calculated, as shown in Table 3. Arrhenius plots in Figure 10 revealed that the apparent activation energy value for stearic acid conversion to 1-Octadecanol was 94 kJ/mol, much lower than the conversion of 1-Octadecanol to Octadecane (298 kJ/mol) and Heptadecane (392 kJ/mol). That is, the first hydrogenation of stearic acid to 1-Octadecanol was much easier than the further conversion of 1-Octadecanol to alkanes, in good agreement with experimental observations (Figure 8). Meanwhile, the conversion of 1-Octadecanol to Heptadecane was distinctly difficult than the conversion of 1-Octadecanol to Octadecane, corresponding to the lower selectivity to Heptadecane than Octadecane.

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Figure 10. Arrhenius plots of different reaction pathways in stearic acid conversion catalyzed by Co/H-SZM-5-GR.

Conclusions

Co/H-ZSM-5 zeolites have been successfully prepared through SOMC grafting, followed by calcination in air and reduction in hydrogen. TEM and H₂-TPR results reveal that cobalt species exist in the form of homogeneous metallic clusters of *ca.* 1.5 nm stabilized by zeolite, while the presence of Brønsted acid sites with slightly reduced acid strength compared to parent H-ZSM-5 is confirmed by NH₃-TPD analyses. That is, the as-prepared Co/H-ZSM-5-GR zeolites appear to the bifunctional catalysts containing metallic cobalt clusters and Brønsted acid sites, and their effective synergy can be expected.

Co/H-ZSM-5-GR is very active in the HDO of stearic acid to diesel-range alkanes with a reaction rate of 2.11 g_{SA}g_{cat}⁻¹h⁻¹, being ~16 times higher than that of Co/H-ZSM-5-IR prepared through solid-state ion exchange (reaction rate of 0.13 g_{SA}g_{cat}⁻¹h⁻¹). Meanwhile, a remarkably high C₁₈/C₁₇ ratio of ~24 in diesel-range alkane products is achieved, indicating the neglectable carbon losses during stearic acid conversion. Kinetic analysis results reveal that hydrogenation of stearic acid to 1-Octadecanol (with apparent activation energy of 94 kJ/mol) is much easier than the further conversion of 1-Octadecanol to alkanes, while the lower apparent activation energy value of 1-Octadecanol conversion to Octadecane (298 kJ/mol) than that to Heptadecane (392 kJ/mol) can well explain the high ratio of C₁₈/C₁₇ in the diesel-range alkane products.

Experimental Section

Catalyst Preparation

Alumino-silicate zeolites in their H-form with similar SiO₂/Al₂O₃ ratio of 25, i.e. H-ZSM-5, H-EU-1, H-USY and H-modenite, were provided by Sinopec and employed as supports for cobalt species. Co/zeolite samples were prepared by organometallic grafting method.^[12] During the grafting process, the organometallic cobalt precursor cobaltocene (Cp₂Co) sublimates at

elevated temperature and then reacts with the Brønsted acid sites in zeolites. In a typical experiment, a zeolite sample of 2.5 g was placed in a quartz reaction chamber connected to a vacuum line and treated under vacuum of $5*10^{-2}$ Pa at 573 K for 4 h. After cooling to 323 K, 0.5 g cobaltocene was added into the reaction chamber, which was heated to and kept at 423 K under vacuum for 24 h to insure the complete surface reaction between cobaltocene and the Brønsted acid sites in zeolites. The resulting solid (labelled as Co/zeolite-G) was subjected to calcination in flowing air at 773 K for 6 h and labelled as Co/zeolite-GC. The Co/zeolite-GC sample was further subjected to reduction in flowing 10%H₂/Ar at 773 K for 6 h and then labelled as Co/zeolite-GR.

For reference, Co/H-ZSM-5 sample was also prepared by solid-state ion exchange. In a typical experiment, 2.5 g H-ZSM-5 zeolite was mechanically mixed with 0.5 g cobalt acetate in the glove box and the mixture was placed in a sealed reactor. The reactor was heated to and kept at 573 K for 2 h. The resulting solid was thoroughly washed with deionized water, dried at 353 K overnight (labelled as Co/H-ZSM-5-I), calcined in flowing air at 773 K for 6 h, and labelled as Co/H-ZSM-5-IC. The Co/zeolite-IC sample was further subjected to reduction in flowing 10%H₂/Ar at 773 K for 6 h and then labelled as Co/zeolite-IR.

Characterization techniques

The exact cobalt loadings in Co/zeolite samples were analyzed on an IRIS Advantage inductively coupled plasma atomic emission spectrometer (ICP-AES). The specific surface areas and pore volumes of samples were determined through N2 adsorption/desorption isotherms at 77 K collected on a Quantachrome iQ-MP gas adsorption analyzer. The X-ray diffraction (XRD) patterns of Co/zeolite samples were recorded on a Bruker D8 ADVANCE powder diffractometer using Cu-K α radiation (λ = 0.1542 nm) at a scanning rate of 4°/min in the region of $2\theta = 5-50^\circ$. Transmission electron microscopy (TEM) images of samples were taken on a FEI Tecnai G² F20 electron microscope at an acceleration voltage of 200 kV. A few drops of alcohol suspension containing the sample were placed on a carbon-coated copper grid, followed by evaporation at ambient temperature. Fourier transform infrared (FTIR) spectra of Co/H-ZSM-5-G in flowing He were measured on a Bruker Tensor 27 spectrometer with 128 scans at a resolution of 2 cm⁻¹. A self-supporting pellet made of sample was placed in the reaction chamber and heated to designed temperatures for recording the spectrum. The temperature-programmed reaction of Co/H-ZSM-5-G in flowing He or O2 was performed on quartz tube reactor and the products were on-line analyzed by a Pfeiffer Omnistar GSD 320 mass spectrometer. X-ray photoelectron spectra (XPS) of Co/zeolite samples were recorded on a Kratos Axis Ultra DLD spectrometer with a monochromated AI-Ka X-ray source (hv= 1486.6 eV), hybrid (magnetic/electrostatic) optics and a multi-channel plate and delay line detector. All spectra were recorded by using an aperture slot of 300×700 microns. Accurate binding energies (±0.1 eV) were determined with respect to the position of the adventitious C 1s peak at 284.8 eV. The temperature-programmed desorption of ammonia (NH₃-TPD) experiments were performed on a Quantachrome ChemBET 3000 chemisorption analyzer. A sample of ca. 0.1 g was pretreated in flowing He at 673 K for 1h, cooled to 373 K in He and saturated with 5% NH₃/He. After that, the sample was purged with He for 30 min to eliminate the physisorbed ammonia. NH₃-TPD was then carried out in flowing He in the temperature range of 373-1073 K at a heating rate of 10 K/min. The temperatureprogrammed reduction by hydrogen (H2-TPR) of samples were performed on a chemisorption analyzer (Quantachrome ChemBET 3000) with 10%H₂/Ar at a heating rate of 10 K/min from 373 to 1273 K. Prior to reduction, the sample (100 mg) was calcined in dry air at 673 K for 1 h.

Catalytic reaction and product analysis

The HDO of stearic acid (Adamas, 99%) was performed in a high-pressure stainless autoclave (Xinyuan Chemical Machinery, Series CJK, 300 mL) at a stirring rate of 750 rpm (adequate to exclude the external diffusion limitations). In a typical experiment, 0.2 g catalyst, 1.0 g stearic acid and

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100 mL solvent n-Heptane were well mixed in the autoclave and purged with pure N₂ at room temperature. The autoclave was rapidly heated to desired temperature and H₂ was introduced at 3.0 MPa to initiate the reaction.

After reaction, the liquid organic products were analyzed by gas chromatography (Shimadzu GC-2010) and gas chromatography-mass spectrometry (Shimadzu GCMS-QP2010 SE), both with a RXI-5MS column (30 m, 0.25 mm i.d., stationary phase thickness 0.25 μ m). Eicosane was used as an internal standard for quantification. The following temperature program was employed: Isothermal heating at 323 K for 5 min, heating to 573 K with a rate of 10 K/min, and isothermal heating at 573 K for 10 min. The gas products were qualitatively analyzed with a mass spectrometer (Pfeiffer Omnistar GSD 320).

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Conflict of interest

The authors declare no conflict of interest.

Keywords: bifunctional catalysts • surface organometallic chemistry reaction • Co/H-ZSM-5 • hydrodeoxygenation • stearic acid

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Bifunctional Catalyst: Bifunctional Co/H-ZSM-5 zeolites was prepared by surface organometallic chemistry grafting route. The as-prepared bifunctional catalyst exhibited a ~16 times higher activity (2.11 $g_{SA}g_{cat}$ -¹h⁻¹) in stearic acid hydrodeoxygenation to alkanes than the reference catalyst prepared by solid-state ion exchange and a remarkable selectivity to C₁₈ alkanes with a C₁₈/C₁₇ ratio up to ~24.

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