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Core/Shell Catalysts

A Core/Shell Catalyst Produces a Spatially Confined Effect and Shape Selectivity in a Consecutive Reaction

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In general, an active catalyst for a consecutive reaction (A$\rightarrow$B$\rightarrow$C) usually has two types of active sites, one of which accelerates the reaction of A to B and the other the reaction of B to C. Taking the synthesis of isoparaffins from syngas ($CO + H_2$) as an example, the most efficient catalysts usually contain both Fischer–Tropsch synthesis (FTS) sites and acidic sites.[1] The FTS sites convert the syngas into linear hydrocarbons, which then migrate to the acidic sites where they undergo further hydrocracking and isomerization to form branched hydrocarbons.

Improving the dispersion of these two kinds of active sites whilst ensuring they are still close to each other is the most efficient approach to enhancing catalytic performance.[2] However, a crucial factor that affects the product selectivity of this consecutive reaction is the ease of migration of the first reaction products to the active sites of the second reaction. The different active sites in conventional bifunctional catalysts are randomly distributed on their surface, which provides an unrestricted, open reaction environment where the coupled reactions occur independently and randomly even though the distance between the two active sites is very short. This means that the products desorbed from the first reaction sites can leave the catalyst without reacting further at the other active sites.

To enhance the ease of migration of the reactants to the active sites and improve the selectivity of this consecutive reaction we have designed a novel bifunctional catalyst with a core/shell structure where the core and shell components independently catalyze the different reactions. The shell consists of a membrane layer containing a pore path. The reactants must first pass through the shell membrane to reach the inner core catalyst, where they react to form the intermediate products. To leave the catalyst all the intermediates must enter the membrane channels, where they have a very good chance of being converted into the final products at the active sites in the membrane. This core/shell bifunctional catalyst is expected to show high selectivity in a consecutive reaction as it improves the collision possibility between intermediates and active sites significantly. Furthermore, a shape selectivity for the reactants and/or products may also be expected since molecules of different sizes have a different diffusion efficiency in the membrane channels.

Although it was developed over 80 years ago, the FTS is still an important technology for the production of clean transportation fuels and chemicals.[3] In general, the products of a FTS are almost always normal aliphatic hydrocarbons which follow the Anderson–Schultz–Flory (ASF) distribution and are suitable only as synthetic diesel fuel. They must be further hydrocracked and isomerized into branched, light hydrocarbons in a separate reaction to be used as synthetic gasoline. The combination of a conventional FTS catalyst and a zeolite is an effective method for producing isoparaffins in one step since zeolites, owing to their acidic sites, are hydrocracking/isomerization catalysts.[4] Several groups have tried to synthesize isoparaffins by utilizing an FTS catalyst consisting of a metal supported on a zeolite.[5,6] However, these catalysts suffer from very low CO conversion and an extremely low reduction degree owing to a strong interaction between the metal and the zeolite.

Previous studies from our group[7] have shown that physically mixing a zeolite and a cobalt catalyst can increase the yield of branched hydrocarbons in the FTS reaction. Herein, we report the synthesis of an H-beta zeolite membrane coated Co/Al_2O_3 core/shell catalyst and its performance in the direct synthesis of isoparaffins from syngas. This core/shell catalyst promotes the formation of isoparaffins and improves the product distribution.

The H-beta membrane is coated directly onto the surface of a Co/Al_2O_3 pellet by a hydrothermal synthesis method. The reactants used were selected carefully to avoid deactivation of the catalysts obtained. For example, the frequently used templates containing Cl^- or Br^- ions as well as the conventional ion-exchange method for obtaining H-type zeolite from Na-type zeolite via NH_3-type zeolite could not be used because even small amounts of Cl^-, Br^-, or Na^+ ions will deactivate the FTS catalyst completely. The reaction mixture, after hydrothermal synthesis, contained coated Co/Al_2O_3 pellets and some solid particles, which were filtered, washed, and calcined in the same way as the coated Co/Al_2O_3 pellet. The X-ray diffraction (XRD) patterns of these solids, zeolite-coated Co/Al_2O_3, and pure Co/Al_2O_3 are shown in Figure 1, where it can clearly be seen that these solids are H-beta zeolite that has crystallized from solution. Diffraction peaks assigned to H-beta zeolite are also observed for the coated Co/Al_2O_3 pellets along with those for Co species and Al_2O_3, thereby indicating that the zeolite has successfully been coated onto the surface of the FTS catalyst.

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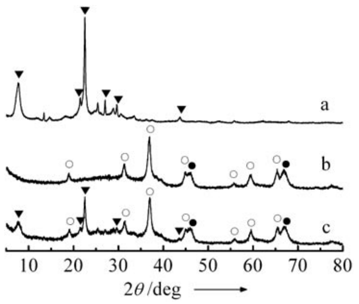

Figure 1. XRD patterns of a) H-beta zeolite, b) Co/Al_2O_3, and c) zeolite-coated Co/Al_2O_3. ○ Co_3O_4, ● Al_2O_3, ▼ H-beta zeolite.

The surface elemental distributions of the Co/Al_2O_3 pellet before and after the zeolite coating are shown in Figure 2. The analytical results confirm the integrity of the zeolite membrane on the Co/Al_2O_3 pellet. Thus, $Co_{K\alpha}$ and $Co_{L\alpha}$ peaks are clearly detected on the Co/Al_2O_3 surface before the zeolite coating is applied but there is no Co signal visible after this step, which suggests that there are no pinholes or cracks in the zeolite membrane. The SiO_2/Al_2O_3 molar ratio of the membrane surface, as determined by energy dispersive spectroscopy (EDS) analysis, is 47, which is almost the same as that of the precursor solution.

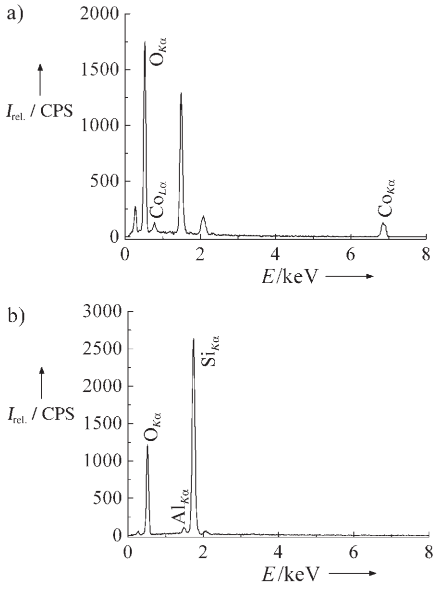

Figure 2. The surface EDS analysis results: a) Co/Al_2O_3 pellet; atomic ratio: Al 91.24%, Co 8.76%; b) after the hydrothermal synthesis; atomic ratio: Al 4.08%, Si 95.92%.

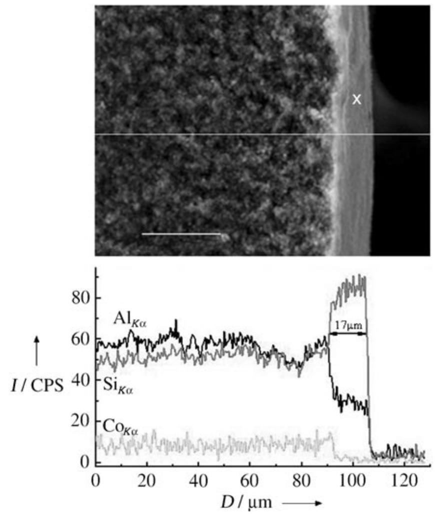

Figure 3. Top: Cross-sectional SEM image of the coated Co/Al_2O_3 pellet (scale bar 30μm). Below: EDS line analysis along the long white line in the top image. EDS analysis of the point "X" is given in Figure 4.

Figure 3 shows the SEM images and the elemental distribution of a coated Co/Al_2O_3 pellet. A compact H-beta zeolite shell can be observed crystallized on the surface of the Co/Al_2O_3 pellet. The thickness of this shell is about 17 μm. The abrupt changes of the Al and Si signal intensities at the interface between the Co/Al_2O_3 pellet and the zeolite layer indicate a change from Al_2O_3 to H-beta zeolite. The Si signal inside the FTS catalyst is caused by diffusion of the zeolite precursor solution into the pores of Co/Al_2O_3.

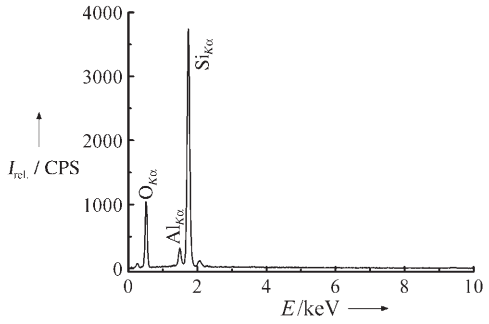

Figure 4. The EDS point analysis at point "X" inside the zeolite membrane (see Figure 3); atomic ratio: Al 8.17%, Si 91.83%.

The EDS analysis at point "X" in Figure 3, which is located in the middle of the membrane, is shown in Figure 4. The SiO_2/Al_2O_3 molar ratio at this point is about 23, which is only half the value for the membrane outer surface. As also illustrated in Figure 3, the EDS signal for Si increases from the inner to the outer surface of the H-beta membrane while that of Al decreases. The distribution gradient of the SiO_2/Al_2O_3 ration inside the zeolite shell has been suggested to be related to the basicity of the solution used to synthesize the zeolite.[8] In this case, the high pH value of the synthesis solution means that the surface Al of the core pellet dissolves to a small extent and the resulting Al species diffuse away from the interface and establish a concentration profile. These Al species are incorporated into the zeolite during the synthesis and the concentration gradient in solution leads to a composition gradient inside the zeolite framework. The distribution gradient of the SiO_2/Al_2O_3 ratio reflects the fact that the zeolite membrane is crystallized directly onto the surface of the pellet.

The experimental results confirm that a compact H-beta zeolite membrane without cracks can be directly synthesized on the surface of a Co/Al_2O_3 pellet by a hydrothermal method. It should be noted, however, that the Co/Al_2O_3 pellets need to be heated under reflux in TEAOH and soaked in ethanol before mixing with the hydrothermal-synthesis precursor solution as no H-beta zeolite can be coated onto the FTS catalyst without this pretreatment. This process activates the surface Al–OH groups of the pellet with which the Al–OH and Si–OH groups in the zeolite can easily react to form Al–O–Al and Al–O–Si bonds between the substrate and the membrane. The surface Al–OH groups of the Co/Al_2O_3 pellet therefore anchor the zeolite membrane to the pellet.

The zeolite-coated Co/Al_2O_3 catalyst was used for the direct synthesis of isoparaffins from syngas to investigate the effect of the core/shell structure. Pure Co/Al_2O_3 and a physical mixture of H-beta zeolite and Co/Al_2O_3 were also tested under the same conditions for comparison. Table 1 shows the catalytic performance of these catalysts and the product distributions are presented in Figure 5.

Table 1: Comparison of the catalytic performance of conventional Co/Al_2O_3, a physical mixture of Co/Al_2O_3 and beta-zeolite, and the zeolite-coated Co/Al_2O_3 catalyst.[a]

Catalyst	Zeolite [%]	Conv. [%] CO	Select. [%] CH_4	CO_2	C_{iso}/C_n[b]	$C^{=}/C_n$[c]
Co/Al_2O_3	–	84.04	21.89	4.77	0.19	0.17
Co/Al_2O_3-β mix[d]	20.0	80.79	16.64	3.86	1.44	0.52
β-zeolite/Co/Al_2O_3	20.7	74.34	13.58	2.65	2.34	0.46

[a] Reaction conditions: 1.0 MPa, 533 K, $W_{cat.} = 0.5$ g (10 wt% Co/Al_2O_3 weight base), flow $(CO+H_2) = 37.3$ mL min^{-1} (STP), $W_{cat.}/F_{(CO+H_2)} = 5$ g h mol^{-1}, $CO/H_2 = 1/2$. [b] C_{iso}/C_n is the ratio of isoparaffins to *n*-paraffins with C_{4+}. [c] $C^{=}/C_n$ is the ratio of olefins to *n*-paraffins with C_{2+}. [d] Physical mixture of Co/Al_2O_3 and H-beta zeolite.

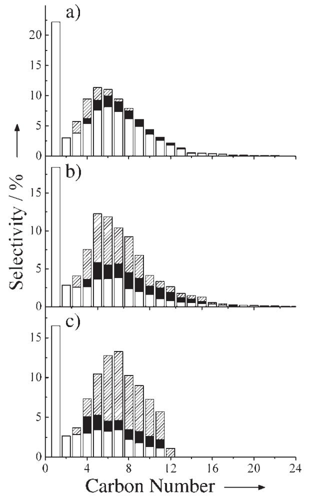

Figure 5. Product distributions for a) conventional Co/Al_2O_3, b) the physical mixture of Co/Al_2O_3 and beta-zeolite, and c) the zeolite-coated Co/Al_2O_3 catalyst. □ = *n*-paraffin, ■ = olefin, hatched = isoparaffin.

It is clear from Figure 5 that the conventional Co/Al_2O_3 FTS catalyst exhibits a wide product distribution in which straight-chain hydrocarbons are the main products. When mixed with H-beta zeolite, the product distribution strays from the ASF law and the selectivity for isoparaffins and olefins increases, although heavy paraffins up to C_{20} are still present. The zeolite-coated catalyst gives a completely different product distribution to the other two samples as the product distribution deviates from the ASF law and the formation of heavy paraffins (C_{12+}) is completely suppressed. Furthermore, the middle isoparaffins are now the main products. This difference is caused by the unique core/shell structure of the zeolite-coated catalyst. For the mixture of Co/Al_2O_3 and zeolite, there is no spatial restriction between the FTS and hydrocracking/isomerization reactions, which means that this is a random process and the two reactions occur independently. Thus, the hydrocarbons desorbed from the FTS site might therefore leave the catalyst directly without undergoing cracking at the zeolite sites. In contrast, the core/shell structure of the zeolite-coated catalyst provides an integrated, confined reaction environment. As illustrated in Figure 6, syngas passes through the zeolite membrane channel to reach the core catalyst, where it forms normal paraffins (by FTS). These hydrocarbons must diffuse through the zeolite membrane to leave the catalyst, and those with a straight-chain structure have a chance of being cracked at the acidic sites of the zeolite. Since the hydrocarbon diffusion rate in the membrane depends on the chain length, the longer the chain length is, the longer the hydrocarbons will stay inside the zeolite, and the higher the chance that they will be cracked, which leads to a high C_{iso}/C_n ratio and a narrow product distribution. It is also important to note that the zeolite-coated Co/Al_2O_3 catalyst shows a highly desirable lower methane selectivity than that of the normal FTS catalyst, this selectivity might be related to the hydrophilicity of the zeolite. It is well known that the hydrophilicity of a zeolite increases as the Si/Al ratio decreases.[9] The SiO_2/Al_2O_3 distribution in the zeolite membrane of the membrane-coated catalyst is not uniform and there is a distribution gradient. The part near the Al_2O_3 substrate has a relatively

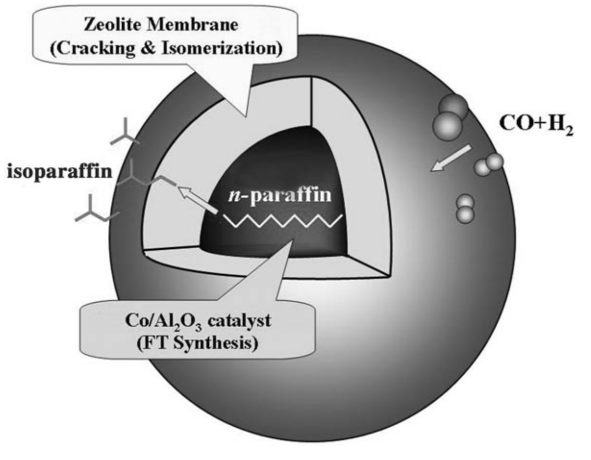

Figure 6. Representation of the core/shell catalyst.

high Al content, which suggests a high hydrophilicity. As a result of the solubility rule (that, like dissolves like) the presence of water can promote the accumulation of CO, which leads to a higher CO/H_2 ratio in the interior of the catalyst and might lower the methane selectivity.[10] Furthermore, some of the isoparaffins and olefins formed in the membrane channels might diffuse in the reverse direction back to the surface of the core catalyst, where they can easily recombine with the adsorbed CH_2 intermediate on Co/Al_2O_3.[11] This process is driven by the concentration gradient and also suppresses methane formation owing to hydrogenation of the CH_2 species.

The CO conversion of the zeolite-coated Co/Al_2O_3 catalyst is slightly lower than with the other catalysts, which can be ascribed to coverage of some of the Co active sites by the zeolite coating. The zeolite membrane might therefore restrict the adsorption of CO and H_2 onto the active Co sites to some extent. The membrane-coated catalyst has a much larger membrane area per unit reactor volume than conventional membrane reactors, which is another reason for the high selectivity for isoparaffins. Furthermore, the simple preparation method of this membrane-coated catalyst has great potential for practical applications.

In summary, a compact, complete H-beta zeolite membrane has been directly coated onto the surface of Co/Al_2O_3 catalyst pellets to form a core/shell structure following an improved hydrothermal synthesis method. The prepared catalyst shows excellent performance for the direct synthesis of isoparaffins based on the FTS reaction. The formation of C_{12+} hydrocarbons is suppressed completely and the middle isoparaffins become the main products. A desirable low methane selectivity is also achieved. This core/shell membrane catalyst provides a tailor-made confined reaction environment that results in spatially confined effects and shape selectivity, which can be extended to various consecutive reactions as the shell and core components are independent catalysts of different reactions.

Experimental Section

The conventional Co/Al_2O_3 FTS catalyst was prepared by incipient wetness impregnation of γ-Al_2O_3 (JRC-ALO-6, JGC Universal Ltd.; specific surface area: 180.0 m^2g; pore volume: 0.93 cm^3g; pellet size: 0.35–0.83 mm) with an aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$. The catalyst precursors were dried in air at 393 K for 12 h after the impregnation and then calcined in air at 673 K for 2 h. The cobalt loading in the samples was 10 wt%.

The H-beta membrane was coated onto the Co/Al_2O_3 pellet surface by a hydrothermal synthesis method. Fumed SiO_2 and $((CH_3)_2CHO)_3Al$ (aluminum isopropoxide) were used as Si and Al sources, respectively, with TEAOH (tetraethylammonium hydroxide) as template. The molar ratio of the reactants in the precursor solution was 48.24 SiO_2:17.40 TEAOH:1.0 Al_2O_3:519.3 H_2O. The Co/Al_2O_3 pellets were heated under reflux in TEAOH at 387 K for 4 h, washed three times with deionized water, and then soaked in absolute ethanol for 24 h before being added to the precursor solution. Crystallization of the zeolite was carried out in a hydrothermal synthesis equipment (DRM-420DA, Hiro Company, Japan) at 428 K and a rotation speed of 2 rpm for three days. The coated catalyst was separated from the solution and washed until its pH value was less than 8. It was then dried at 393 K for 12 h and calcined at 823 K for 8 h. All the chemicals were supplied by Wako Pure Chemicals Ltd, unless indicated otherwise.

X-ray diffraction (XRD) patterns were measured with a Rigaku RINT-2000 diffractometer with $Cu_{K\alpha}$ radiation ($\lambda_a = 0.154$ nm). Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were performed with a JEOL JSM-6360LV scanning electron microscope equipped with a JED-2300 energy dispersive X-ray analysis system. The BET surface area, pore-size distribution, and pore volume were determined by an adsorption method (Quantachrome AUTOSORB-1) with N_2 as the adsorbent.

The FTS reaction was conducted in a continuous-flow-type fixed-bed reactor. A detailed account of the experimental setup and product analysis has been reported elsewhere.[12]

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