New method for the preparation of nonuniform distributed Co/SiO$_2$ catalysts†

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Received (in Cambridge, UK) 5th August 2008, Accepted 12th September 2008
First published as an Advance Article on the web 25th September 2008
DOI: 10.1039/b813641f

Egg-shell, egg-yolk and egg-white types of Co/SiO$_2$ catalysts were prepared by utilizing entrapped air to inhibit the entrance of impregnation or leaching solution into the cores of catalyst pellets during the preparation procedure; the entrapped air played the important role because the capillary pressure was reduced to a suitable range by adjusting the concentration of ethanol in the impregnation or leaching solution for a hydrophobized silica surface.

For a supported catalyst with identical chemical composition and overall loading, its performance depends critically on the distribution of its active ingredient on the support.[1–5] Egg-shell catalysts can enhance the selectivity to the intermediates for two consecutive first-order, irreversible reactions or diffusion limited reactions. Egg-yolk catalysts are excellent for the so-called negative order reactions since the diffusion limitation increases the reaction rates. Egg-white catalysts are good candidates for the reactions where the catalysts centers are diffusionally restricted and the external surfaces are subjected to poisoning or abrasion. The distribution type is crucially relied on the preparation method, which should be chosen according to the adsorption strength of the precursor of the active ingredient on the support.[1] Strong adsorption tends to yield nonuniform distribution, which results in facile generation of egg-shell catalysts. Egg-white and egg-yolk catalysts can be prepared when suitable types and amount of co-adsorbents are added into the impregnation solution.[1,6] In contrast, weak adsorption readily leads to a uniform distribution, because the enormous capillary pressure causes the liquid to distribute evenly throughout the support pellets in a short time.[2,3] To obtain nonuniform distribution in case of weak adsorption, some methods have been developed, which include (1) spraying the impregnation solution onto a hot support,[7] (2) impregnating the catalysts with high viscosity liquid,[8] such as melt salts or aqueous solution containing hydroxyethylcellulose and controlling the contact time of the liquid with support, (3) using porous hollow silica as support,[9] or (4) partially covering the pores of support with other agents,[10] *e.g.* *n*-undecane, to inhibit the entrance of impregnation or leaching solution during the preparation process. However, only egg-shell catalysts would be obtained by utilizing methods (1), (2) and (3). For method (4), although egg-shell, egg-yolk and egg-white types of Co/SiO$_2$ catalysts can be obtained, the boundary of the section that the active ingredient is located is not sharp.

To the best of our knowledge, few studies focus on the reduction of the capillary pressure during the impregnation process. In this study, we prepared Co/SiO$_2$ catalysts of different types: egg-yolk, egg-white and egg-shell with various shell thicknesses by reducing the capillary pressure. The key of our method is to achieve a suitable contact angle between the support surface and the impregnation solution. Two steps are involved in our approach: hydrophobizing the surface of silica gel and choosing a suitable ethanol concentration in the impregnation solution. Prior to hydrophobization, the silica (silica gel pellets, 2.2–3.0 mm, >99.5% SiO$_2$, Johnson Matthey) was treated by several steps to obtain a rich hydroxyl surface (see ESI†). This hydroxylated silica is denoted as S1. Hydorphobization was carried out by silanizing the silica gel with trimethylchlorosilane (TMCS), by the addition of 10 g of S1 to a mixture of 200 ml toluene and 5 g TMCS (Acros, 98%), and subsequently refluxing for 16 h with continuous stirring. The material (denoted as MS) was filtered off and washed eight times with ethanol and five times with cyclohexane followed by drying at 393 K for 8 h in air. It was shown in the IR spectrum that the trimethylsilyl (TMS) groups (–Si(CH$_3$)$_3$) were grafted on the surface of S1 during the procedure of silanization (ESI†). The amount of TMS groups was determined by elemental analysis (of carbon) in the samples (Table 1).

Table 1 Carbon contents and surface coverage ratios of samples containing TMS groups

Sample	MS	Reduced U	Reduced ES-3
Carbon content (wt%)	1.012	0.631	0.653
A_{TMS}/A_S[a]	0.750	0.468	0.484

[a] The surface coverage ratios of sample by TMS groups (–Si(CH$_3$)$_3$); the details of calculation procedure can be found in the ESI.†

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† Electronic supplementary information (ESI) available: Experimental details of silanization of silica and Fischer–Tropsch synthesis reaction, the calculation procedure for the surface coverage ratios of samples by trimethylsilyl groups, and IR spectra and physical adsorption results of S1 and MS. See DOI: 10.1039/b813641f

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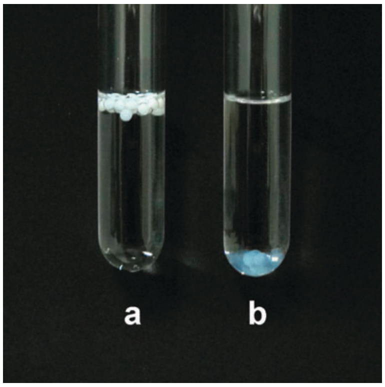

Fig. 1 Optical photographs of MS in different solvents: (a) water, (b) ethanol.

After the treatment, the material has a hydrophobic surface with a contact angle between MS surface and water $>90^\circ$. However, it is necessary that the surface of support can be wetted by the impregnation solution during the impregnation process. So some reagent, which can wet the MS surface, and is dissolvable in the impregnation solution, should be added into the solution to carry out the impregnation step. In our method, ethanol, by which the surface of MS could be wetted, as shown in Fig. 1, was added to the impregnation solution. The optimal concentration of ethanol was determined by putting a few of support pellets (MS) into ethanol–aqueous solutions with a series of concentrations and maintaining for a period, typically 15 min, then recording the penetration depths of the solution into the pellets. As shown in Fig. 2, there were "air bags" in the centers of the support pellets and the higher the ethanol concentration is, the smaller was the "air bag" volume. The addition of ethanol to water leads the surface tension of the liquid decreasing, which accounts for the reduction of the contact angles of the ethanol–aqueous solution on the surface of MS.[11] In theory, there is a critical ethanol concentration at which the solution is able to start wetting the MS surface. In this situation, the contact angle is just 90°, and the capillary pressure is zero according to the Young–Laplace equation.[12] Additionally, the pressure that originates from the gravity of liquid can be neglected because the solution usually just immerses into the support for the impregnation method. Consequently, the impregnation solution can not automatically enter into the pores of the support. Once the ethanol concentration is higher than the critical value, the liquid starts penetration into the pores, which leads to air inside the pores being entrapped and compressed. The liquid penetration must stop when the pressure of the entrapped air balances the capillary pressure. Thus, an "air bag" forms. It is logical that the higher the ethanol concentration in the solution is, the larger is the capillary pressure, which results in a smaller volume of the "air bag" in the center of the support pellet. In most of impregnation processes, the role of the entrapped air was negligible because of the enormous capillary pressure.[2] However, in our case, the capillary pressure can be controlled in a suitable range so that the entrapped air can exist stably in the pellets and resist the entrance of the impregnation solution.

Based on the "air bag" resisting method described above, egg-shell type catalysts with various shell thicknesses were prepared as follows: 10 g of MS pellets were impregnated in a solution composed of 7.41 g cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$, Sinopharm, $>99.0\%$) and 20 mL ethanol–aqueous solution, in which the ethanol concentration was 30, 45 or 60 vol.%, respectively. After thorough mixing, the impregnated pellets were treated in a rotary evaporator at 313 K in vacuum (50 mbar) for 2 h, then dried at 393 K in air for 8 h in oven. After cooling to room temperature, the dried materials were heated to 623 K (5 K $\min^{-1}$) in a flow of Ar (1000 h^{-1}) and maintained under these conditions for 8 h. The egg-shell catalysts were denoted as ES-1, ES-2 and ES-3, respectively. The Co/SiO_2 catalyst has noticeable activity in the Fisher–Tropsch (FT) synthesis,[13] in which transport plays an important role.[14] Egg-shell catalysts can be used to avoid or at least reduce the transport restriction in FT synthesis.[15] The performances of ES-1, ES-2 and ES-3 were tested in FT synthesis conditions and details of the catalysts evaluations can be found in the ESI.† For comparing the reduction extent of transport restriction, the uniformly distributed Co/SiO_2 catalyst (denoted as U) was prepared by impregnating 10 g MS in a solution of 7.41 g cobalt nitrate and 20 mL absolute ethanol and adopting the same drying and calcination processes. The results of egg-shell catalysts and uniform catalyst for the FT synthesis are summarized in Table 2. The egg-shell catalysts are more active and selective for C_5^+ synthesis than the uniform catalyst, in addition, the CO conversion and selectivity of C_5^+ increase with the reduction of the shell thicknesses of egg-shell catalysts. The results can be interpreted in that the egg-shell structure effectively shortens the diffusion distance of reactants, which leads to the reduction of

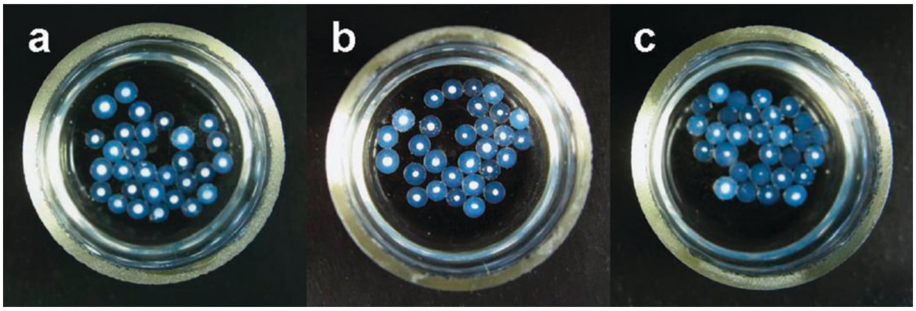

Fig. 2 Optical photographs of "air bags" (MS pellets soaked in ethanol–aqueous solution with different ethanol concentrations, contact time of 15 min): (a) 30, (b) 45, (c) 60 vol.%.

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Table 2 FT synthesis data on ES-1, ES-2, ES-3 and U[a]

Catalyst	ES-1	ES-2	ES-3	U
Conv. CO (%)	16.95	13.47	12.24	11.25
Selectivity (C%)[b]				
CH_4	9.55	11.74	12.87	14.37
C_2–C_4	5.40	5.53	5.89	7.82
C_5^+	85.05	82.73	81.24	77.81

[a] *Reaction conditions*: 493 K, 2.0 MPa, $H_2/CO = 2$ and GHSV = 2000 h^{-1} (see ESI† for further details). [b] Selectivity based on carbon efficiency.

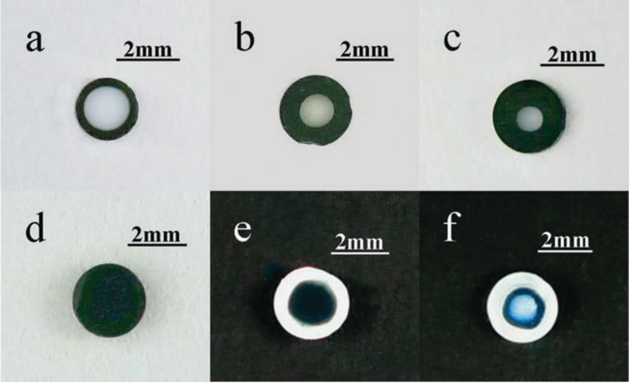

Fig. 3 Optical micrographs of cross sections of Co/SiO_2 catalysts: egg-shell (ES-1), (b) egg-shell (ES-2), (c) egg-shell (ES-3), (d) uniform (U), (e) egg-yolk (f) egg-white.

transport restriction, and this is more notable when the shell is thinner.

Addition to the egg-shell catalysts, egg-yolk and egg-white catalysts were also prepared by utilizing the "air bag" resistance. Similar as the method used by Zhuang *et al.*,[10] egg-yolk and egg-white catalysts were prepared by leaching the shell of reduced U and ES-3, respectively. The reduction of U and ES-3 were completed by heating them in a flow of H_2 (1000 h^{-1}) from room temperature to 623 K (5 K min^{-1}) and maintaining at 623 K for 8 h. The elemental analysis results, shown in Table 1, indicates that the methyl groups on the support surface for both uniform and egg-shell catalysts were partially removed during calcination and reduction. The reduced catalysts were still hydrophobic, though the degree of hydrophobicity decreased, and so ethanol was still essential for the leaching process. It is plausible that the ethanol concentration used for the leaching process should be lower than that for the impregnation process. The most suitable ethanol concentration in the leaching solution was determined by the same way as that used for the impregnation solution. The leaching process was carried out by contacting the reduced catalysts with 100 mL solvent composed of 5 ml 16 mol L^{-1} nitric acid, 15 ml ethanol and 80 ml deionised water for 5 min, then filtering and repeating the whole process five times. The leached catalyst pellets were rinsed five times, each time with 50 mL of deionised water. Finally, the catalyst pellets were dried at 393 K for 12 h in air. All samples were split with a razor and polished to view cross-sectional areas of them, as shown in Fig. 3.

In conclusion, we have reported a new method to prepare nonuniform distributed Co/SiO_2 catalysts. In this method, the entrance of the solution (either the impregnation solution or the leaching solution) was inhibited by the entrapped air, acting as an "air bag", which is able to play this important role due to remarkable reduction of capillary pressure by hydrophobizing the silica surface and choosing a suitable ethanol concentration in the solution. This method has great potential for the large scale preparation of nonuniform distributed Co/SiO_2 catalysts, by which the sharp shell boundary is achieved and the shell thickness is easily adjusted. Moreover, this method is more suitable for the preparation of egg-shell catalysts because not all metals (*e.g.* Rh) can be leached to prepare egg-yolk or egg-white catalysts and the loadings are difficult to be defined for egg-yolk and egg-white catalysts before preparation, which is easy for egg-shell catalyst.

This work was financially supported by the Science and Technology Ministry of China (2005CB221402).

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