Electronic Supplementary Information

Investigation the effects of phosphorus on the selective hydrodeoxygenation of anisole over Fe/SiO_2 catalyst

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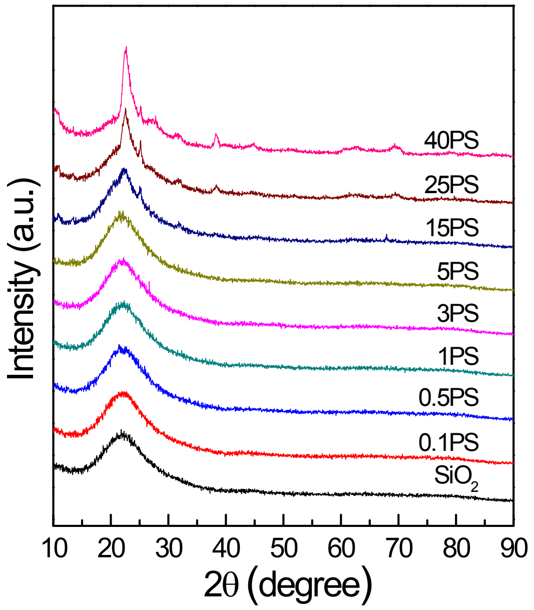

Fig. S1 XRD patterns of catalysts.

The 15PS, 25PS and 40PS samples were prepared by an impregnation method. Briefly, the support, SiO_2, was impregnated with an aqueous solution of $(NH_4)_2HPO_4$ with different nominal loading of P (15, 25, 40 wt.%). Then it was left at room temperature for 12 h and further dried at 120 ^oC for 12 h. Finally, the samples were calcined at 400 ^oC for 4 h in stagnant air. The obtained sample was denoted as nP/SiO_2, where n=15, 25, 40.

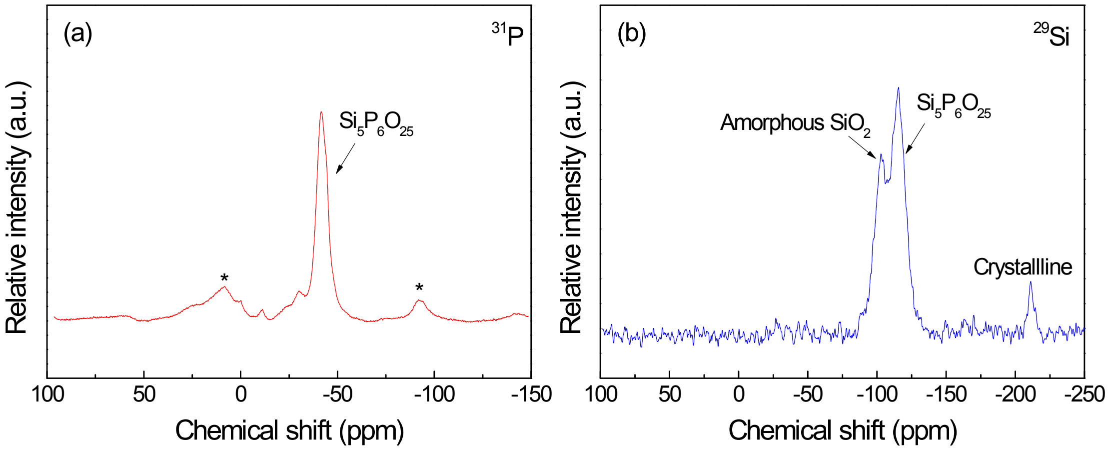

Fig. S2 ^{31}P (a) and ^{29}Si (b) MAS NMR spectra of 25PS sample. * marks spinning sidebands.

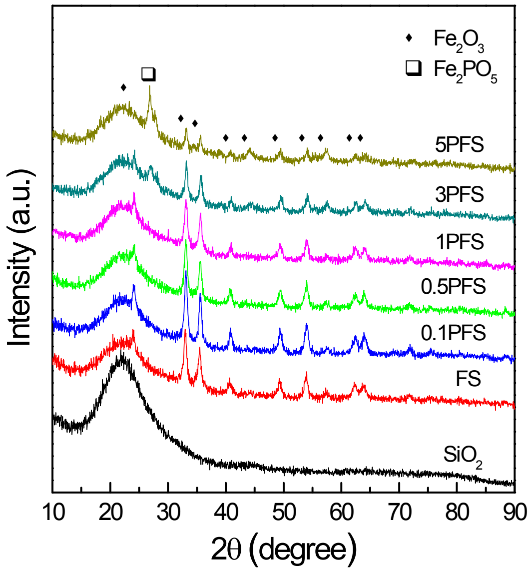

Fig. S3 XRD patterns of as-prepared catalysts.

For the as-prepared catalysts (Fig. S3), peaks characteristic of hematite (α-Fe_2O_3) at 33.2°, 35.6°, 54.1°, 49.5°, 24.1°, 62.4° and 64.0° are detected (JCPDS 33-0664). The intensities of the peak decrease with increasing contents of P on SiO_2. The α-Fe_2O_3 crystallite size of the FS, 0.1PFS, 0.5PFS, 1PFS, 3PFS and 5PFS catalysts is calculated from the Scherrer equation based on the most intensive peak of 33.2° are 16.0, 16.3, 16.2, 16.2, 18.4 and 20.0 nm, respectively. This indicates that the crystallite size of α-Fe_2O_3 has slightly increase at higher contents of P in the catalysts (3 and 5 wt. %). Moreover, new peaks appear at 26.9° and a shoulder peak at 27.7° become obvious with the contents of P reaches up to 3 wt. %, which can be attributed to iron phosphate (Fe_2PO_5, JCPDS 36-0084).

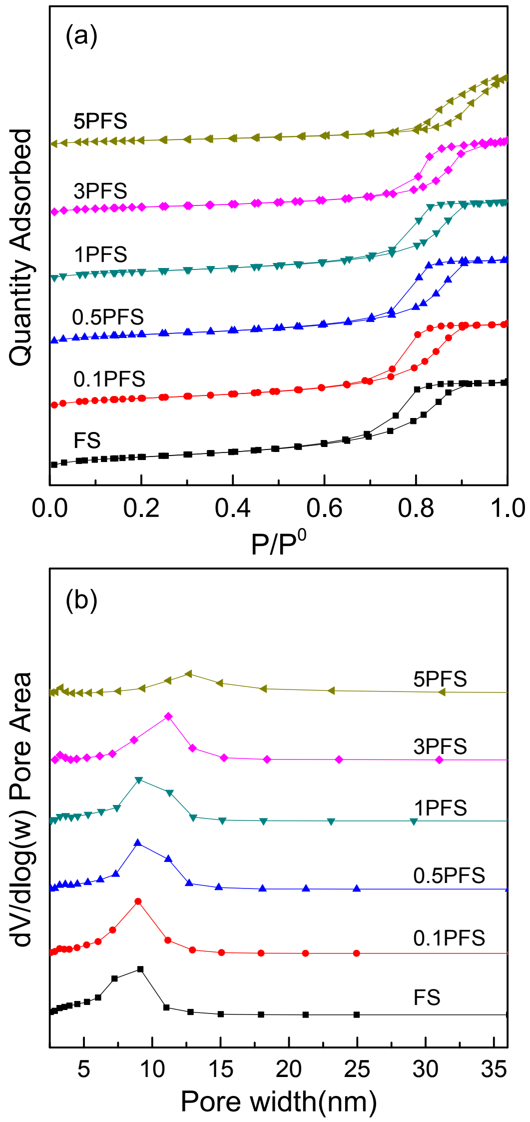

Fig. S4 N_2 adsorption isotherms (a) and BJH pore size distribution (b) of samples.

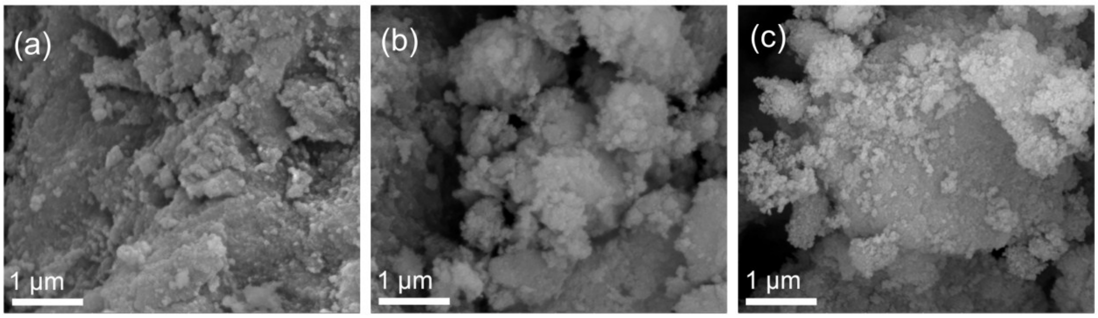

Fig. S5 SEM images of calcined FS (a), 0.5PFS (b) and 5PFS (c) catalysts.

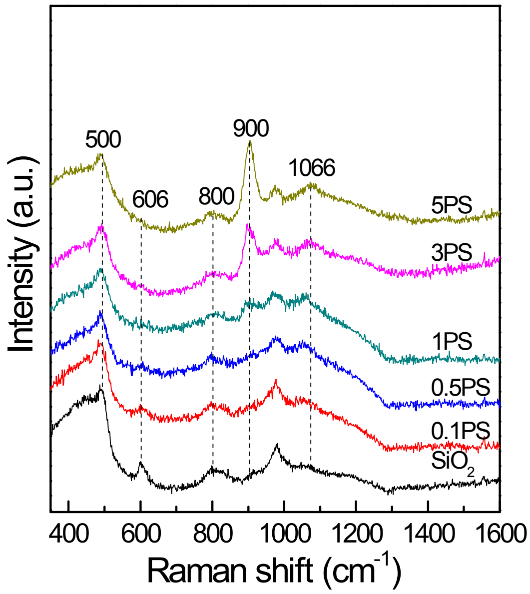

Fig. S6 Raman spectra of SiO_2 and PS catalysts using a UV laser source of 325 nm.

The whole Raman spectral in the range of 400-1300 cm^{-1} is composed of three regions, i.e., 400-650 cm^{-1}, 700-850 cm^{-1} and 850-1300 cm^{-1}. In the range of 400-650 cm^{-1}, two bands are observed for SiO_2 sample, namely, a strong band centered at 500 cm^{-1} and a weak band at 606 cm^{-1}. The band at 500 cm^{-1} is usually called the D1 band and is formed by breathing motions of oxygen atoms (i.e. movements of oxygen perpendicular to the Si-O-Si plane) in regular. The band locates near 606 cm^{-1}, is usually called the D2 band and is ascribed to the breathing motion of oxygen atoms in planar three-membered rings. In the intermediate frequency region (700-850 cm^{-1}), the band at 800 cm^{-1} is attributed to Si-O stretching involving oxygen motions in the Si-O-Si plane or to the motion of the Si atom in its oxygen cage. In the high frequency region (850-1300 cm^{-1}.), a band at 978 cm^{-1} is observed, which is assigned to the stretching vibrations of SiO_4 tetrahedron. In addition, a weak band at 1066 cm^{-1} is also observed, which can be assigned to vibrations involving bridging oxygen atoms in structural units. The band at 900 cm^{-1} ascribed to the P-O increases with increasing the contents of P. It is prominent that the band at 500 cm^{-1} decreases after the addition of P on the SiO_2. Specially, the absent of the band at 606 cm^{-2} when the contents of P increases up to 1 wt.%, suggesting that the interaction between P and oxygen that perpendicular to the Si-O-Si or in planar three-membered rings.

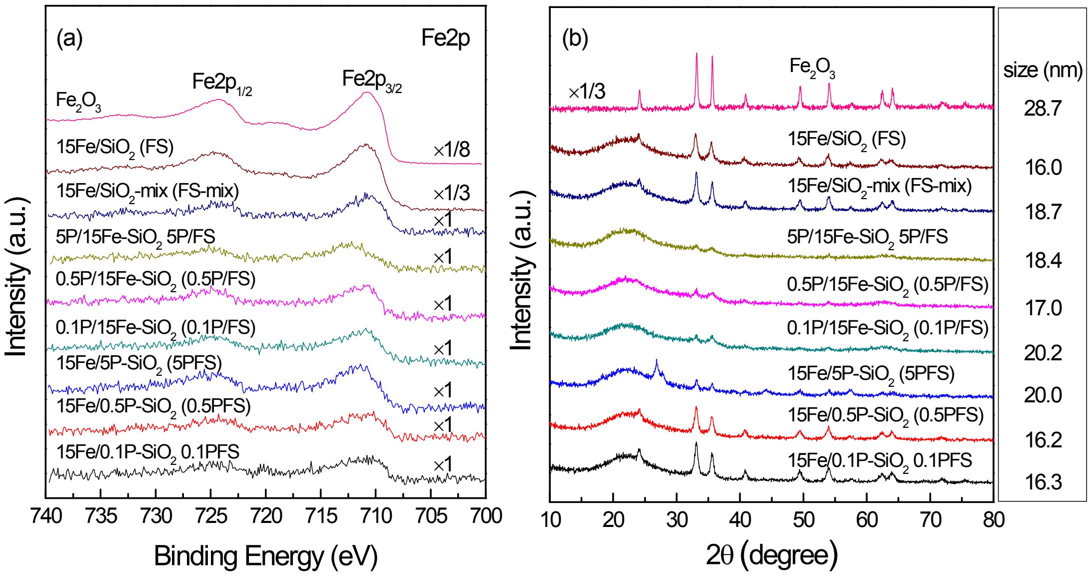

Fig. S7 XPS patterns of Fe2p photoemission spectra (a) and XRD patterns and crystallite size of Fe_2O_3 (b) of the as-prepared catalysts.

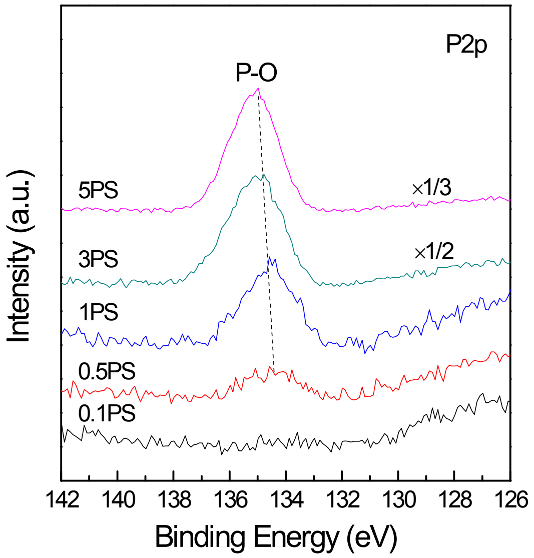

Fig. S8 XPS patterns of P2p photoemission spectra of PS samples.

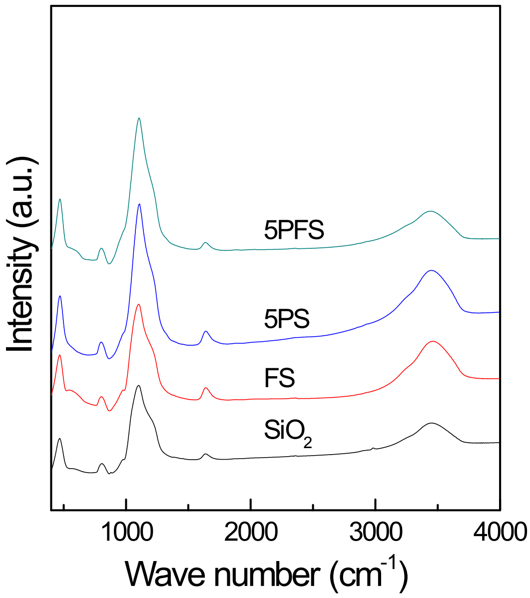

Fig. S9 FT-IR spectra of the different samples.

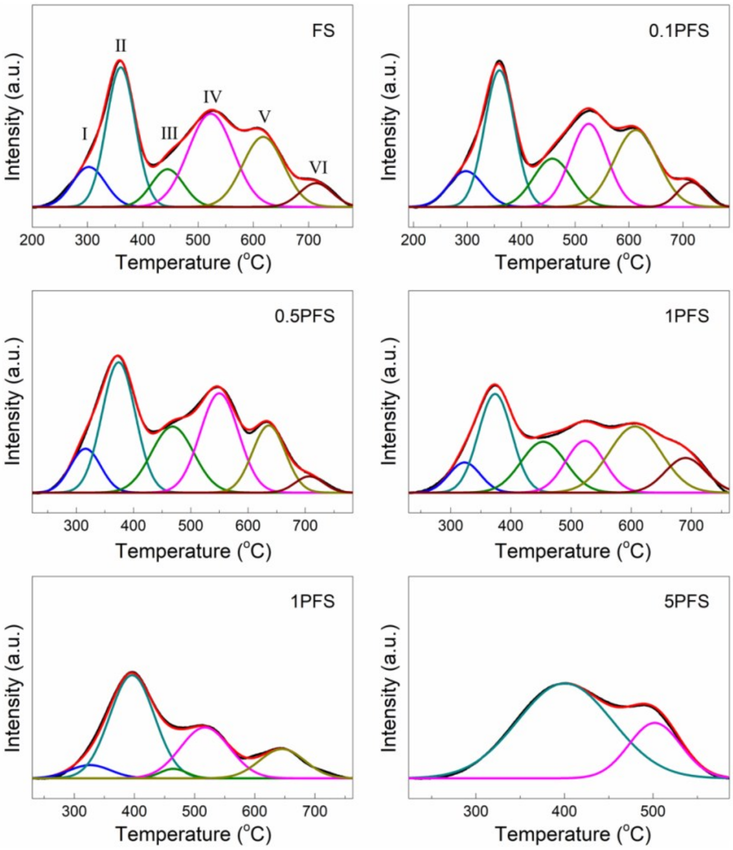

Fig. S10 H_2-TPR profiles of catalysts.

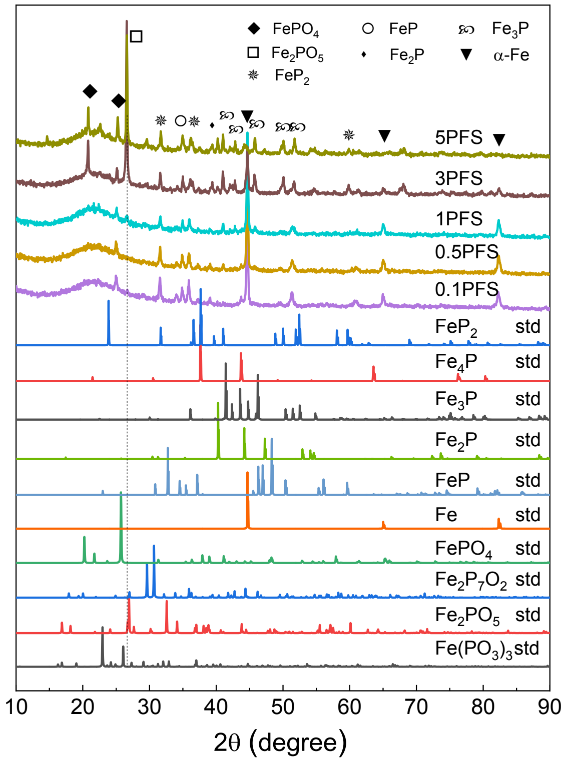

Fig. S11 XRD patterns of products after H_2-TPR process.

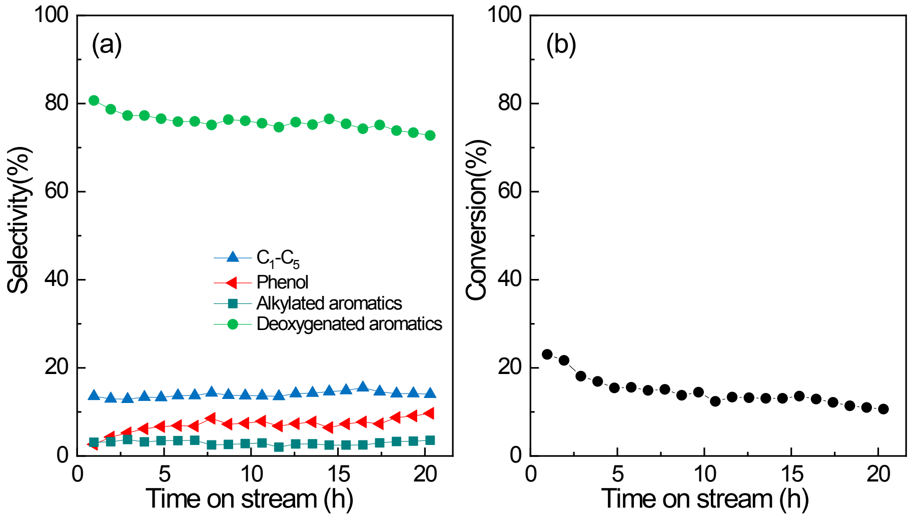

Fig. S12 Catalytic process of 0.5PFS catalyst. (a) Selectivity of C_1-C_5, Phenol, alkylated aromatics (2-methylanisole, *o*-cresol and 2,6-dimethylphenol) and deoxygenated aromatics (benzene and toluene); (b) Stability test of 0.5PFS catalyst for the anisole hydrodeoxygenation. Reaction conditions: 0.1 MPa, 400 ^{o}C, H_2/anisole = 50 and WHSV = 1.0 h^{-1}.

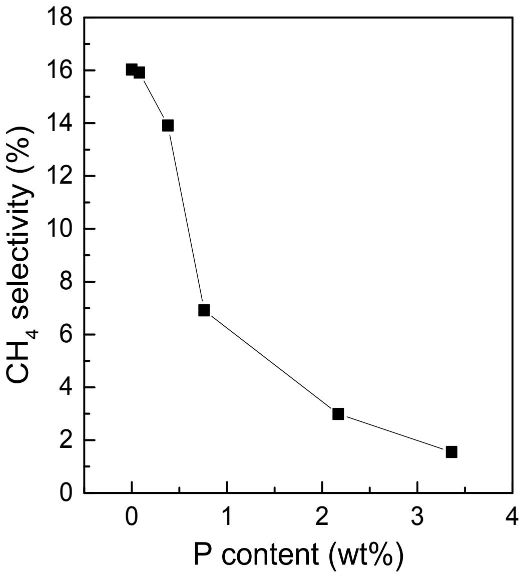

Fig. S13 Correlation between CH_4 selectivity and P contents in the catalysts.

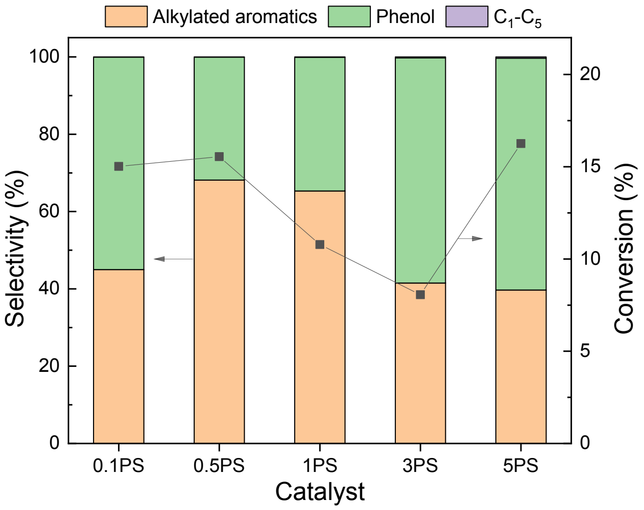

Fig. S14 Catalytic process of 0.1PS, 0.5PS, 1PS, 3PS and 5PS catalysts. Alkylated aromatics: 2-methylanisole, *o*-cresol and 2,6-dimethylphenol. Reaction conditions: 0.1 MPa, 400 ^{o}C, H_2/anisole = 50 and WHSV = 1.0 h^{-1}.

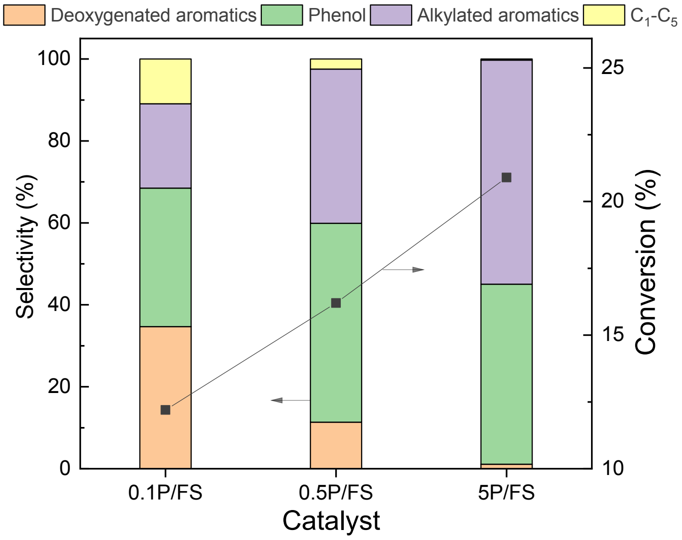

Fig. S15 Catalytic process of 0.1P/FS, 0.5P/FS and 5P/FS catalysts. Deoxygenated aromatics: benzene and toluene. Alkylated aromatics: 2-methylanisole, *o*-cresol and 2,6-dimethylphenol. Reaction conditions: 0.1 MPa, 400 °C, H_2/anisole = 50 and WHSV = 1.0 h^{-1}.

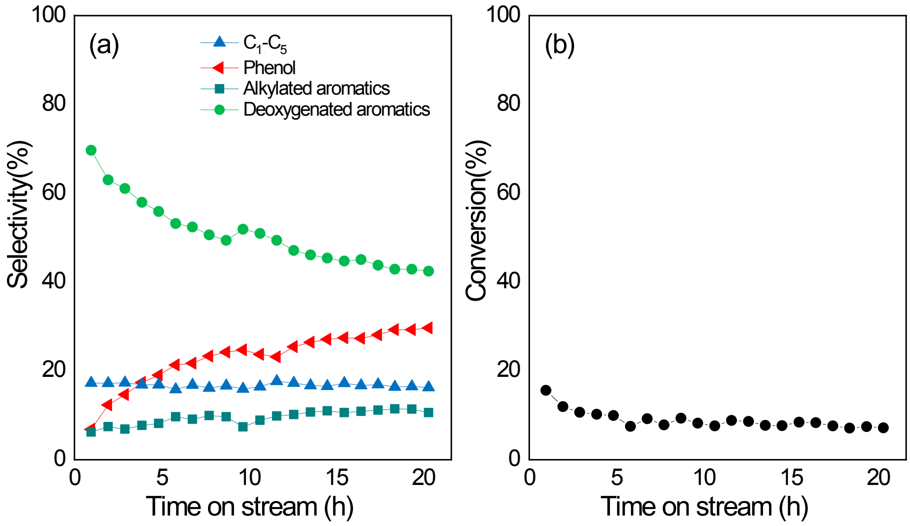

Fig. S16 Catalytic process of FS catalyst: (a) products selectivity (Alkylated aromatics: 2-methylanisole, *o*-cresol and 2,6-dimethylphenol. Deoxygenated aromatics: benzene and toluene.); (b) anisole conversion. Reaction conditions: 0.1 MPa, 400 ^{o}C, H_2/anisole = 50 and WHSV = 1.0 h^{-1}.

Table S1 Quantitative results of H_2 consumption for the catalysts in H_2-TPR.

Catalyst	Peak	Peak center (°C)	H_2 consumption (mol H_2/mol Fe)	Total (mol H_2/mol Fe)
FS	I	302	0.06	
	П	360	0.19	
	III	445	0.06	
	Ⅳ	522	0.20	
	Ⅴ	619	0.14	
	Ⅵ	713	0.03	0.68
0.1PFS	I	297	0.06	
	П	359	0.20	
	III	457	0.09	
	Ⅳ	525	0.15	
	Ⅴ	614	0.16	
	Ⅵ	716	0.02	0.68
0.5PFS	I	316	0.06	
	П	374	0.20	
	III	467	0.09	
	Ⅳ	550	0.15	
	Ⅴ	636	0.16	
	Ⅵ	708	0.03	0.68
1PFS	I	322	0.04	
	П	373	0.14	
	III	453	0.14	
	Ⅳ	523	0.09	
	Ⅴ	605	0.09	
	Ⅵ	689	0.04	0.56
3PFS	I	321	0.02	
	П	396	0.20	
	III	464	0.01	
	Ⅳ	518	0.11	
	Ⅴ	645	0.06	0.40
5PFS	I	400	0.27	
	П	501	0.08	0.35