

# **Nature of vanadium species on vanadium silicalite-1 zeolite and their stability in hydroxylation reaction of benzene to phenol**

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We applied a series of control experiment to test the heterogeneity, and the experiment was described as follow:

(i) 0.5 g VS-1 (1.9 wt% vanadium content) catalyst was bathed in 150 mL mixed solution of H<sub>2</sub>O<sub>2</sub> and HOAc (H<sub>2</sub>O<sub>2</sub>: HOAc = 1:10 v/v) at 343 K for 4 hours, the catalyst was separated from the resultant mixture and named C-A, and the solution was named S-A.

(ii) 0.1 g C-A catalyst was used in hydroxylation of benzene reaction with 30 mL HOAc, 3 mL H<sub>2</sub>O<sub>2</sub> and 1 mL benzene at 343 K for 2 hours, 11.7% yield (TOF= 67.0) and 94.5% selectivity to phenol was obtained.

(iii) 1mL benzene and 3mL H<sub>2</sub>O<sub>2</sub> were added into 30 mL S-A at 343 K reacted for 2 hours, 5.9 % yield (TOF=37.5) and 85.0 % selectivity to phenol were obtained.

(iv) 0.3 g C-A samples were treated in 90 mL mixed solution of H<sub>2</sub>O<sub>2</sub> and HOAc (H<sub>2</sub>O<sub>2</sub>: HOAc = 1:10 v/v) at 343 K for 4 hours, the catalyst was separated from the resulted mixture and named C-B, and the solution was named S-B.

(v) 0.1 g C-B catalyst was used in hydroxylation of benzene reaction with 30 mL HOAc, 3 mL H<sub>2</sub>O<sub>2</sub> and 1 mL benzene at 343 K for 2 hours, 11.5% yield (TOF=64.5) and 93.1% selectivity to phenol was obtained.

(vi) 1mL benzene and 3mL H<sub>2</sub>O<sub>2</sub> were added into 30 mL S-B and reacted at 343 K for 2 hours; no phenol was detected in resultant solution.

Based on experiment (i and iii) results, it could be concluded that the vanadium species on the fresh VS-1 leached partly in the hydroxylation system, and the leaching vanadium species also have catalytic performance on the hydroxylation of benzene,

but the lower TOF value (37.5) indicated that the homogenous vanadium species was not as efficient as the heterogenous ones. The results of experiment (i, ii, iv and v) indicated that the stable vanadium species showed a stable and high efficient catalytic performance (TOF=67.0). Furthermore, no phenol was detected in the resultant of experiment vi, indicating no vanadium leaching in the treated process. So, the VS-1 catalyst was a heterogeneous catalyst under the hydroxylation of benzene condition.

Table 1 Assignment and leaching behavior of the V species

V species	Location <sup>a</sup>	TPR peak (K)	XPS BE (eV)	UV-Vis (nm)	Stability in the solution			
					NH <sub>4</sub> Ac	HAc	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub> +HAc
Tetrahedral V <sup>V</sup>	F	840-950	517.5	230-240	Stable	Stable	Stable	Stable
Tetrahedral V <sup>IV</sup>	F	-	516.3	270-280	Stable	Stable	Stable	Stable
Octahedral V <sup>V</sup>	F	750-830	517.5	320-350	Leaching	Stable	Stable	Stable
Highly dispersed V species	EF	800	517.5	450	Leaching	Leaching	Stable	Leaching
Octahedral V <sup>V</sup>	EF	710	517.5	320-350	Leaching	Stable	Leaching	Leaching
Hexahedral/ Octahedral V <sup>IV</sup>	EF	-	516.3	310-320	Leaching	Stable	Leaching	Leaching

<sup>a</sup> F: Framework; EF: Extra-framework