Reaction kinetics and mechanism of CH_4-SCR on Ru-In/H-SSZ-13

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Issues of mass transport effects

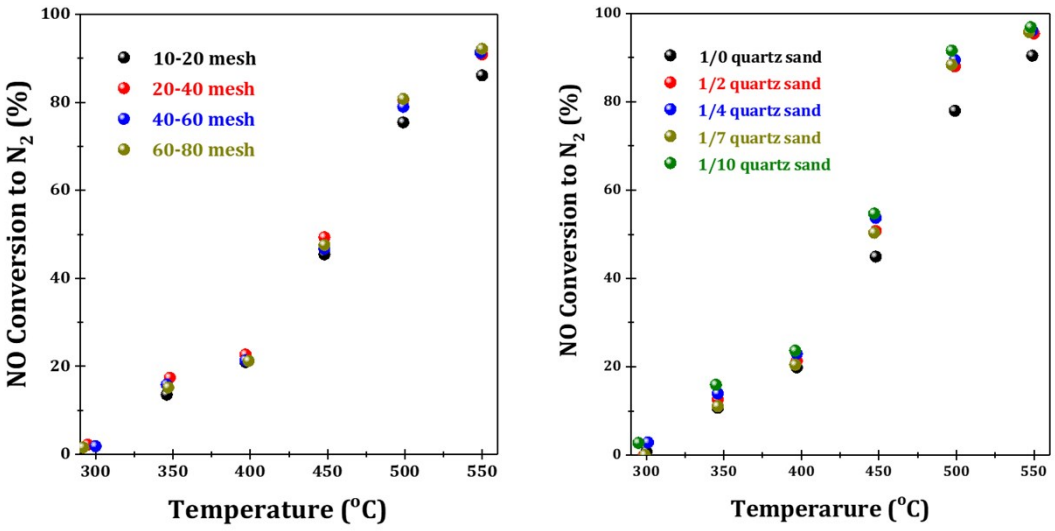

Figure S1 CH_4-SCR activity on Ru-In/H-SSZ-13 with different particle sizes (left-chart) and with different catalyst/quartz ratios while the particle sizes are kept at 20-40 mesh (right-chart). Reaction conditions: 2500 ppm NO, 4000 ppm CH_4, 4% O_2, He balance; GHSV=75,000 h^{-1}

In order to ensure that the steady-state activity tests were taken in kinetics regions free of internal diffusion and external mass transfer resistances, two types of experiments were done [1-4]:

(i) The activities of Ru-In/H-SSZ-13 for NO conversion to N_2 were measured at different temperatures by changing the particle size while the ratio between catalyst and quartz sand is kept at 1:5. The intracrystallite mass transport limitations were also assessed by applying the following inequality [5]:

$$\frac{R_v \cdot (r_p)^2}{C_s \cdot D_e} < 1$$

Where R_v is the observed reaction rate per unit volume of catalyst, r_p is the crystallite radius, C_s is the product concentration at the crystallite surface, and D_e is the effective diffusivity of product. For CH_4-SCR, the reaction rate per volume ($R_v = \frac{n \cdot w\% \cdot sel\%}{t \cdot m}$) and the product concentration at the external crystallite surface ($C_s = \frac{n \cdot w\% \cdot sel\%}{v}$) at 250 ^oC and 300 ^oC were calculated to be 0.149 mol m^{-3} s^{-1}, 0.0089 mol m^{-3}, and 0.372 mol m^{-3} s^{-1}, 0.022 mol m^{-3}, respectively, under the employed reaction conditions. The crystallite radius (r_p) was estimated to <400 nm according to the SEM observation. The effective diffusivity of methane on CHA zeolite (D_e) was calculated to be 7 * 10^{-12} m^2 s^{-1} at 300 K [6]. The higher temperature, the lower D_e value. Therefore, according to all these values, the $\frac{R_v \cdot (r_p)^2}{C_s \cdot D_e}$ value in CH_4-SCR was calculated to be <0.39, which satisfied the inequality and the intracrystallite mass transport limitations appeared to be neglectable in the kinetic studies.

(ii) The activities of Ru-In/H-SSZ-13 for NO conversion to N_2 were measured at different temperatures by changing the ratio between catalyst and quartz sand while the amounts of catalyst is fixed.

According to these results (**Figure S1**), catalyst samples with particle size of 20-40 mesh and catalyst to quartz sand (1:5) were used for kinetic studies.

Steady-state reaction of CH_4-SCR

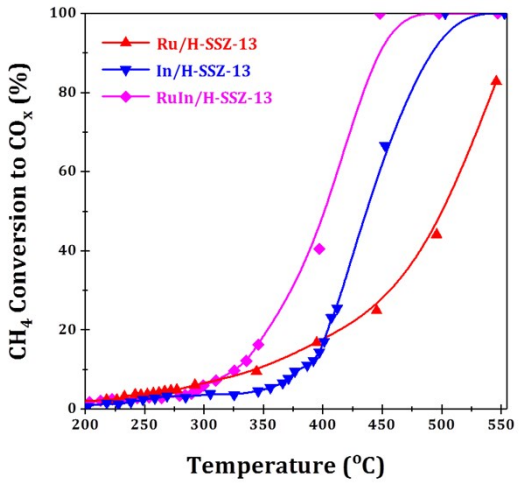

Figure S2 Steady-state reaction of CH_4-SCR over Ru/H-SSZ-13, In/H-SSZ-13 and Ru-In/H-SSZ-13 catalysts. Reaction conditions: 2500 ppm NO, 1250 ppm CH_4, 4% O_2, He balance; GHSV=60,000 h^{-1}

Decomposition of NO at low temperatures

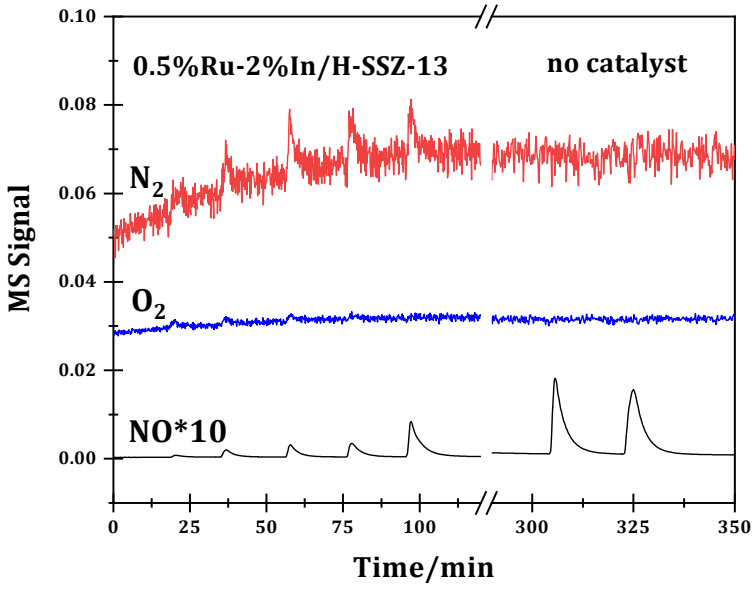

Figure S3 Pulse-response experiments of NO feeding to 0.5%Ru-2%In/H-SSZ-13 at 250 °C. Reaction conditions: 0.12g catalyst; 5, 10, 15 and 25 ml/min × 10 s, and 33 ml/min × 20 s of NO; 50 ml/min of He balance; or 0g catalyst; 10 and 15 ml/min × 10 s of NO; 50 ml/min of He balance.

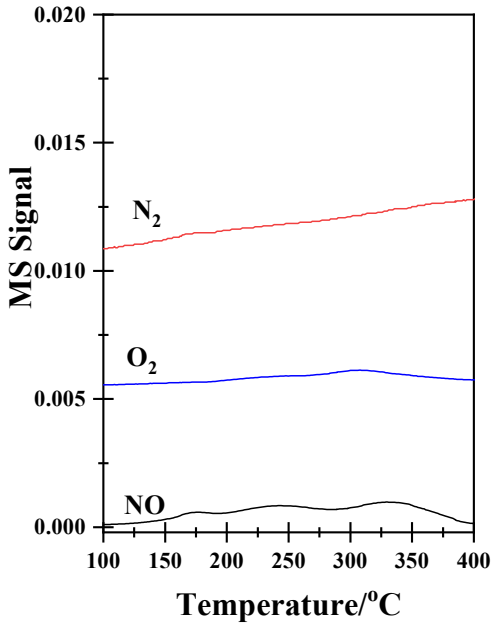

Figure S4 NO-TPD profiles on 0.5%Ru-2%In/H-SSZ-13 catalyst.

Referances

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