Supplementary Material

Promotive Effect of Ce Addition on Catalytic Oxidation of Vinyl Chloride over ZSM-5 Zeolite Supported Ru Catalysts

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1. Synthesis of HZSM-5 Zeolite

0.123 g of $NaAlO_2$ (AR, Aladdin) was dissolved in 5 mL deionized water, followed by the addition of 12.18 g of tetrapropylammonium hydroxide (TPAOH) aqueous solution (40 wt.%, Adamas) and 15.6 g of tetraethyl orthosilicate (TEOS, AR, Adamas). The mixture was stirred at room temperature for 4 h. Subsequently, the resultant gel was transferred to a Teflon-lined autoclave and subjected to a two-step crystallization process consisting of hydrothermal treatments at 120 °C for 2 h and 170 °C for 24 h. Afterwards, the mixture was centrifuged, washed with deionized water, dried in an oven, and finally calcined at 550 °C for 8 h to obtain the Na-type ZSM-5 zeolite. After consecutive three times of ion exchange treatment in 1 M ammonium acetate solution at 80 °C for 2 h, the collected solid was calcined in a muffle furnace at 550 °C for 8 h to obtain the HZSM-5 zeolite.

2. Characterization and Experimental Details

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV diffractometer with Cu Kα (λ = 0.154184 nm) radiation at 40 kV and 40 mA. Field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) were collected on the JSM-7800F and JEOL JEM-2100 Plus microscope, respectively. Nitrogen adsorption-desorption isotherms were first degassed at 200 ^oC for 10 h, and then tested by Quantachrome Autosorb-IQ3 sorptometer. Nitrogen adsorption-desorption isotherms were performed on a Quantachrome Autosorb-iQ3 sorptometer. Prior to the measurement, each catalyst was pretreated at 180 °C for 3 h under degassing conditions. Chemisorption experiments including temperature-programmed reduction of hydrogen (H_2-TPR) and temperature-programmed desorption of ammonia (NH_3-TPD) were conducted on a Quantachrome Chembet Pulsar analyzer with a thermal conductivity detector (TCD). The H_2-TPR profiles were collected in the range of 50-800 ^oC under 5% H_2/Ar flow after a pretreatment at 300 ^oC for 1 h under helium atmosphere. For NH_3-TPD, the catalyst was pretreated at 100 ^oC for 1 h under 10% NH_3/He until the adsorption saturation of ammonia. Afterwards, the helium flow was purged into the reactor to remove those physically adsorbed ammonia until the baseline stabilization of TCD signal. Ammonia desorption was conducted in the range of 100-800 ^oC at a ramp rate of 10 ^oC min^{-1} under a helium atmosphere. X-ray photoelectron spectroscopy (XPS) spectra were conducted on PHI 5000 Versa Probe III spectrometer with a monochromatized Al Kα X-ray source (1486.6 eV). The binding energy (BE) was determined by utilizing C 1s of adventitious carbon (284.6 eV) as a reference. For the deconvolution of Ru 3d/C 1s spectra, a Shirley-type background was applied over the entire Ru 3d/C 1s binding energy window (278–292 eV). The Ru $3d_{5/2}$–Ru $3d_{3/2}$ spin-orbit splitting energy was fixed at 5.0 eV, and the peak-area ratio of Ru $3d_{5/2}$ to Ru $3d_{3/2}$ was constrained to the theoretical value of 3:2. Adventitious carbon C-C (284.6 eV) and C=O (288.6 eV) peaks were fitted as separate contributions within the same energy range, with their FWHM allowed to vary independently from Ru 3d peaks.

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTs) was performed on a Nicolet iS50 spectrometer (Thermo Fisher SCIENTIFIC) with a mercury-cadmium-telluride (MCT) detector, and the DRIFTs cell with ZnSe windows is connected with a gas flow system. For VC adsorption analysis at 50 °C, the catalyst was pretreated at 50 °C in Ar atmosphere for 30 min. After the background spectra were recorded at the temperature, 1vol.% C_2H_3Cl/Ar with a flow rate of 20 mL min^{-1} was fed into the catalyst surface for adsorption, and in situ DRIFTs data of the catalyst was taken at different times. For VC temperature-programmed oxidation under an inert atmosphere, the catalyst was pretreated at 300 °C in Ar atmosphere for 30 min. After the background spectra were recorded at the temperature, Then, 1 vol.% C_2H_3Cl/Ar with a flow rate of 20 mL min^{-1} was fed into the catalyst surface, and the in situ DRIFTs data was recorded from 50 to 350 °C by temperature-programmed operation. For VC temperature-programmed oxidation under an oxygen-containing atmosphere, the catalyst was pretreated at 300 °C in Ar atmosphere for 30 min. After the background spectra were recorded at the temperature, Then, 1vol.% C_2H_3Cl/Ar (20 mL min^{-1}) and O_2 (5 mL min^{-1}) was fed into the catalyst surface, and the in situ DRIFTs data was recorded from 50 to 350 °C by temperature-programmed operation.

3. Reaction Kinetics Measurement

The reaction rate, $r_{C_2H_3Cl}$ (mol g_{Ru}^{-1} s^{-1}), is calculated with $X_{C_2H_3Cl}$ as shown in the following equation.

$$r_{C_2H_3Cl} = \frac{N_{C_2H_3Cl} \times X_{C_2H_3Cl}}{g_{Ru}}$$

where $N_{C_2H_3Cl}$ is the VC gas flow rate (mol/s) and g_{Ru} is the weight of Ru (g) in the catalyst.

When the VC conversion is below 15%, a dependence of the reaction rate ($r_{C_2H_3Cl}$) on the products of CO_2 and H_2O may be ignored; hence, the empirical kinetic expression of the reaction rate equation of VC oxidation can be described as follows.

$$r_{C_2H_3Cl} = A \exp\left(-\frac{E_a}{RT}\right) P_{C_2H_3Cl}^{\alpha} P_{O_2}^{\beta}$$

Taking the logarithm of the above equation yields the following equation

$$\ln r = \ln A + \alpha \ln P_{C_2H_3Cl} + \beta \ln P_{O_2} - E_a / (RT)$$

The components of the reactant feed gas are hardly changed during the kinetics testing with a low VC conversion below 15%. Therefore, $\ln A$, $\alpha \ln P_{C_2H_3Cl}$, and $\beta \ln P_{O_2}$ can be supposed to be approximately constant, and the equation can be simplified to $\ln r = -E_a / (RT) + C$. The activation energy (E_a) can be obtained from the slope of the resulting linear plot of $\ln r$ versus $1/T$.