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Supporting Information

Si-modified Mn-Ce oxide catalyst for selective catalytic reduction of NO_x with NH_3 at low temperature

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1.1 Catalytic activity test

The NH_3-SCR performance of the catalysts was evaluated in a fixed-bed quartz reactor. The catalyst samples (40-60 mesh) were put into a quartz tube with an inner diameter of 6 mm, which was placed in a tube furnace, and the temperature was controlled at 50 to 300 °C. The simulated flue gas was composed of 500 ppm NO, 500 ppm NH_3, 50 ppm SO_2 (when used), 5% O_2 and N_2 balance. The total flow rate was 500 mL·min^{-1}, and the corresponding gas hourly space velocity (GHSV) was 5×10^4 h^{-1}. The effluent gases, including NH_3, NO, N_2O and NO_2, were analyzed by a Nicolet IS50 FTIR gas analyzer. Activity data were collected when the catalytic reaction actually reached steady-state conditions at each temperature.

1.2 Catalyst Characterization

The specific surface area and pore characteristics of the samples were measured by N_2 adsorption/desorption analysis on a physisorption analyzer (MicrotracBEL). The samples need to be degassed at 300 °C for 1 h before N_2 physisorption at 77 K.

X-ray diffraction (XRD) patterns of the samples were recorded on a diffractometer (Bruker D8 Advance, Germany) with CuKα radiation (= 0.154056 nm) in a 2θ of 10°–80° at 0.02 °s^{-1}.

The temperature programmed desorption of NH_3 (NH_3-TPD) was carried out on an FTIR spectrometer (Nicolet IS50). The catalyst sample (50 mg) was first pretreated in air at 300 °C for 0.5 h, and then cooled down to 50 °C under N_2 conditions. Afterwards, the catalyst sample was exposed to 500 ppm NH_3/N_2 until saturation, followed by N_2 purging for 0.5 h. Finally, the catalyst sample was heated from 50 °C to 650 °C in a N_2 flow (100 mL·min^{-}

^{1}) at a constant heating rate (10 °C·min^{-1}). The concentration of NH_3 was detected using Nicolet IS50 FTIR spectroscopy.

The H_2 temperature programmed reduction (H_2-TPR) experiments were performed on an Autochem 2920 (Micromeritics) analyzer. The samples (50 mg) were pretreated at 300 °C in a quartz reactor in a flow of Ar (50 mL·min^{-1}) for 1 h and cooled down to room temperature. Then, from room temperature to 800 °C, H_2-TPR was performed in a 10 vol.% H_2/Ar gas flow of 50 mL·min^{-1} at a heating rate of 10 ^{o}C·min^{-1}.

The surface element compositions and chemical states of each catalyst sample were evaluated by an X-ray photoelectron spectroscopy (XPS) analyzer (Axis Ultra, Kratos Analytical Inc.) using Al Kα X-ray radiation (1486.6 eV). All of the binding energies were calibrated using the C 1s peak (binding energy = 284.8 eV) as a standard.

The adsorption behavior of the reactants and their surface reactions were studied by *in situ* diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS), which was carried out on a Brooker VERTEX 80/80V Fourier transform infrared spectrometer (Brück, Germany) equipped with liquid nitrogen-cooled MCT detection. The powder sample was pretreated in 20 % O_2/N_2 at 450 °C for 0.5 h prior to adsorption experiments. The following conditions were controlled as follows: 500 ppm NH_3, or 500 ppm NO + 5% O_2, N_2 balance, and the total flow rate was kept at 300 mL·min^{-1}. For the experiments on NH_3 or NO_x adsorption, the sample was saturated with NH_3/N_2 or NO_x/N_2 for 40 min, and then purged with N_2 for 30 min. All spectra were recorded by accumulating 100 scans with a resolution of 4 cm^{-1}.

1.3 Kinetics experiment

In order to obtain a further understanding of the effect of Si doping and sulfation after-treatment on the NH_3-SCR reaction, the kinetics experiments were studied on Mn_4Ce_6, $Mn_4Ce_5Si_1$ and $Mn_4Ce_5Si_1$-1S% catalysts. The samples with particles of 40-60 mesh and a total gas flow rate of 500 mL·min^{-1} were selected to rule out internal and external transfer diffusion. The NO_x conversion was controlled below 20%. The NO_x reduction rates (mol·g·s^{-1}) and activation energy (E_a) were calculated based on the following equations:

$$-r = \frac{F}{w}\ln(1-x)$$

$$k = \frac{r}{[NO]_0} = A e^{-Ea/RT}$$

where F is the NO_x flow rate, $[NO_x]_0$ is the NO_x concentration at the inlet, W is the mass of catalyst, E_a is the apparent activation energy, T is the Kelvin temperature, R is the gas constant (8.314 J/(mol·K)), and A represents the pre-factor.

2 Results

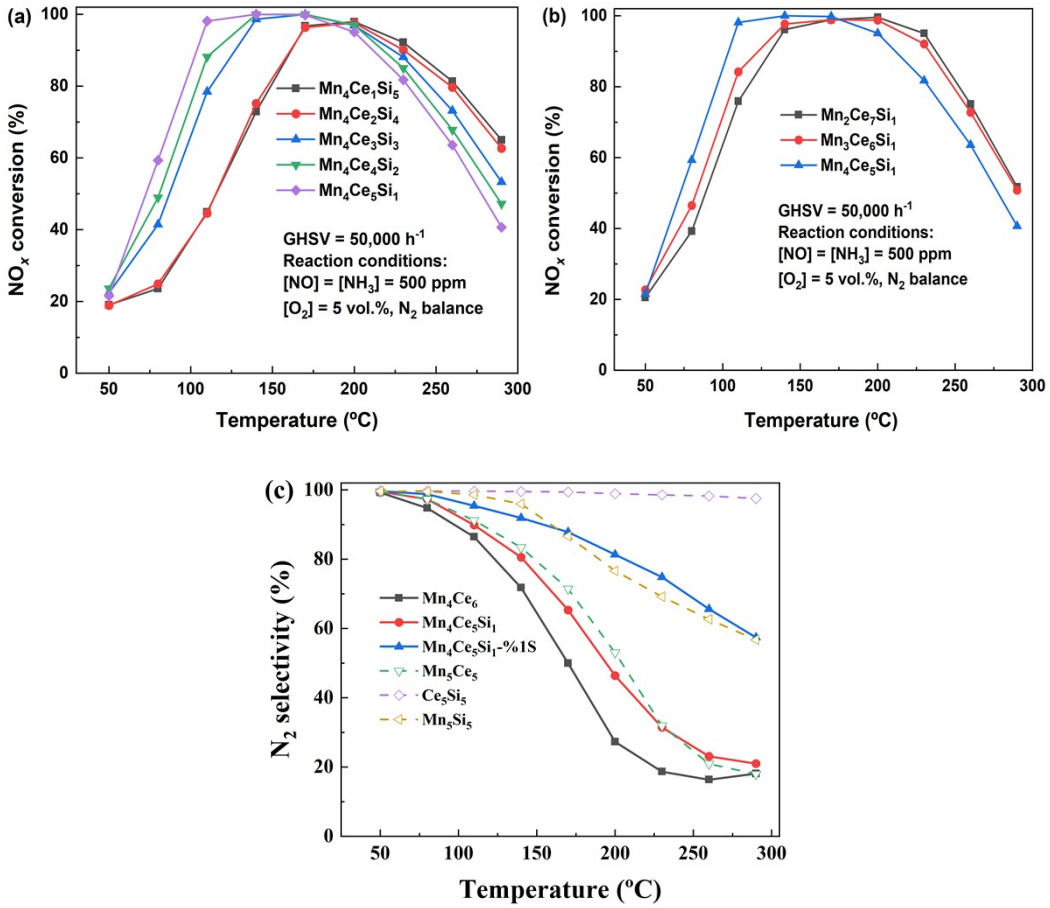

Fig. S1 NO_x conversion and N_2 selectivity versus temperature over different catalysts: different Ce/Si molar ratios (a), different Mn/Ce molar ratios (b), and N_2 selectivity (c).

A series of Si-modified Mn-Ce oxide catalysts were prepared to study the effect of the Si element on the NH_3-SCR activity of Mn-Ce oxide catalysts, as shown in Fig. S1. When the content of Mn was constant, the increase of Si/Ce ratio resulted in a decrease in NO_x conversion at low temperature. However, the catalyst activity (>200 °C) was in the order following: $Mn_4Ce_1Si_5$ > $Mn_4Ce_2Si_4$ > $Mn_4Ce_3Si_3$ > $Mn_4Ce_4Si_2$ > $Mn_4Ce_5Si_1$. The $Mn_aCe_bSi_c$ with different Mn/Ce ratios was also investigated, and the $Mn_4Ce_5Si_1$ catalyst showed the widest temperature window and highest NO_x conversion (> 90%) at 100-260 °C.

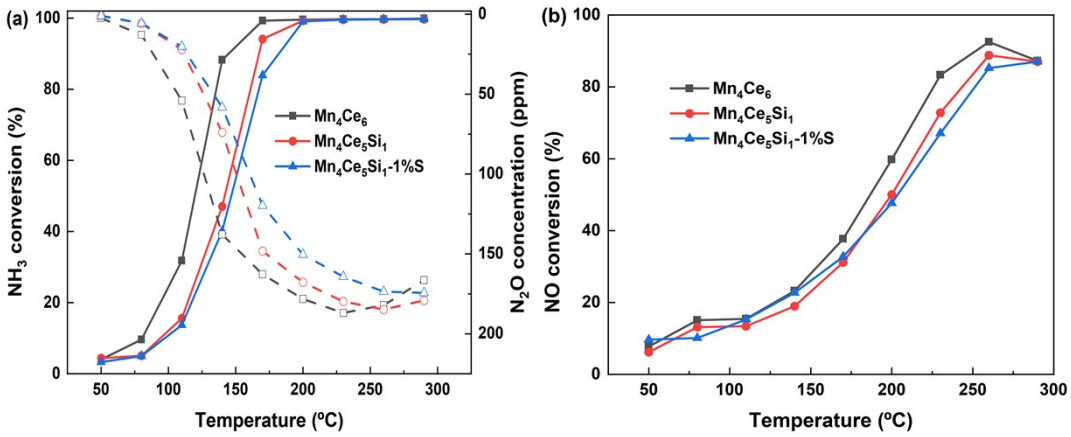

Fig. S2 (a) NH_3 conversion and (b) NO conversion in separate NH_3 and NO oxidation reactions over Mn_4Ce_6, $Mn_4Ce_5Si_1$ and $Mn_4Ce_5Si_1$-1%S.

As shown in Fig. S2, the Mn_4Ce_6 catalyst showed the best NH_3 oxidation activity and NO oxidation activity. The introduction of Si resulted in the decrease of activation of NH_3 and NO, which is the reason of the enhanced N_2 selectivity and decreased catalytic activity at low temperature.

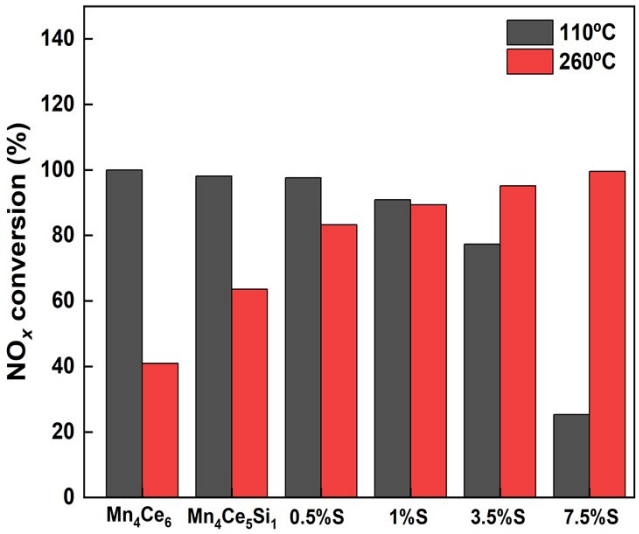

Fig. S3 NO_x conversion of catalysts with different H_2SO_4 loadings at 260 and 110 °C.

$Mn_4Ce_5Si_1$ was sulfation after-treated with varying concentrations of sulfuric acid solution, and the NO_x conversions at 110 °C and 260 °C of catalysts are shown in Fig. S3. With the increase in sulfuric acid concentration, the NO_x conversion at 110 °C decreased and the NO_x conversion at 260 °C increased over $Mn_4Ce_5Si_1$-*x*%S catalysts. When the loading amount of sulfuric acid was 1%, the $Mn_4Ce_5Si_1$-1%S catalyst showed a high NO_x conversion above 90% in the range of 110-260 °C.

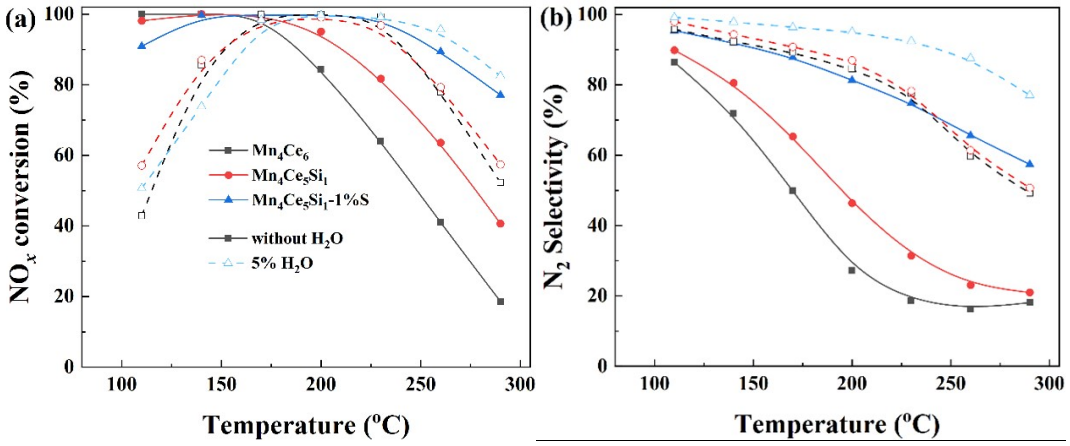

Fig. S4 Effect of H_2O on the performance of catalyst.

As shown in Fig. S4, when 5% H_2O was added to the reaction gas, the NO_x conversion of all the catalysts decreased below 170°C due to the competitive adsorption of H_2O, while that increased above 170°C, which may be attributed to the inhibition of the unselective oxidation of NH_3 at high temperature. The N_2 selectivity of all the catalysts was enhanced significantly at the present of H_2O (Fig. S4b). In comparison, the H_2O tolerance of Mn-Ce oxide catalysts was improved after Si modification and sulfation after-treatment.

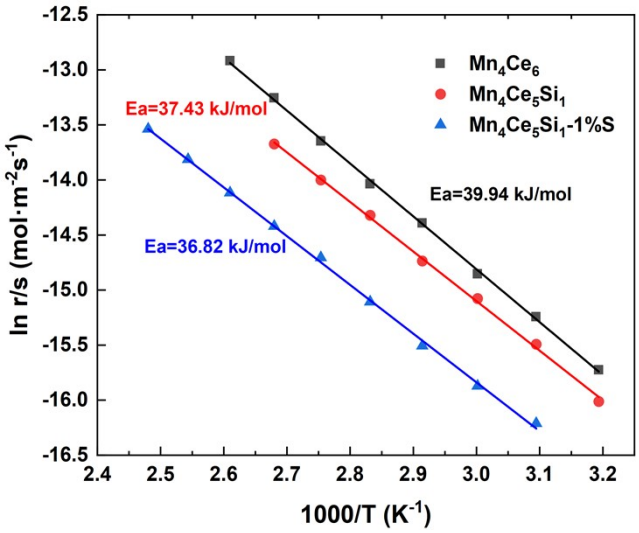

Fig. S5 NO_x reduction rates as a function of reaction temperature over Mn_4Ce_6, $Mn_4Ce_5Si_1$ and $Mn_4Ce_5Si_1$-1%S catalysts.

To further understand the effect of Si and sulfation after-treatment on the reaction kinetics of NO_x reduction over Mn-Ce oxide catalysts, Arrhenius plots of the NH_3-SCR reaction are shown in Fig. S4. It can be seen that Mn_4Ce_6, $Mn_4Ce_5Si_1$ and $Mn_4Ce_5Si_1$-1%S have similar Ea (~37 kJ/mol), indicating of identical catalytic centers and rate-limiting steps.

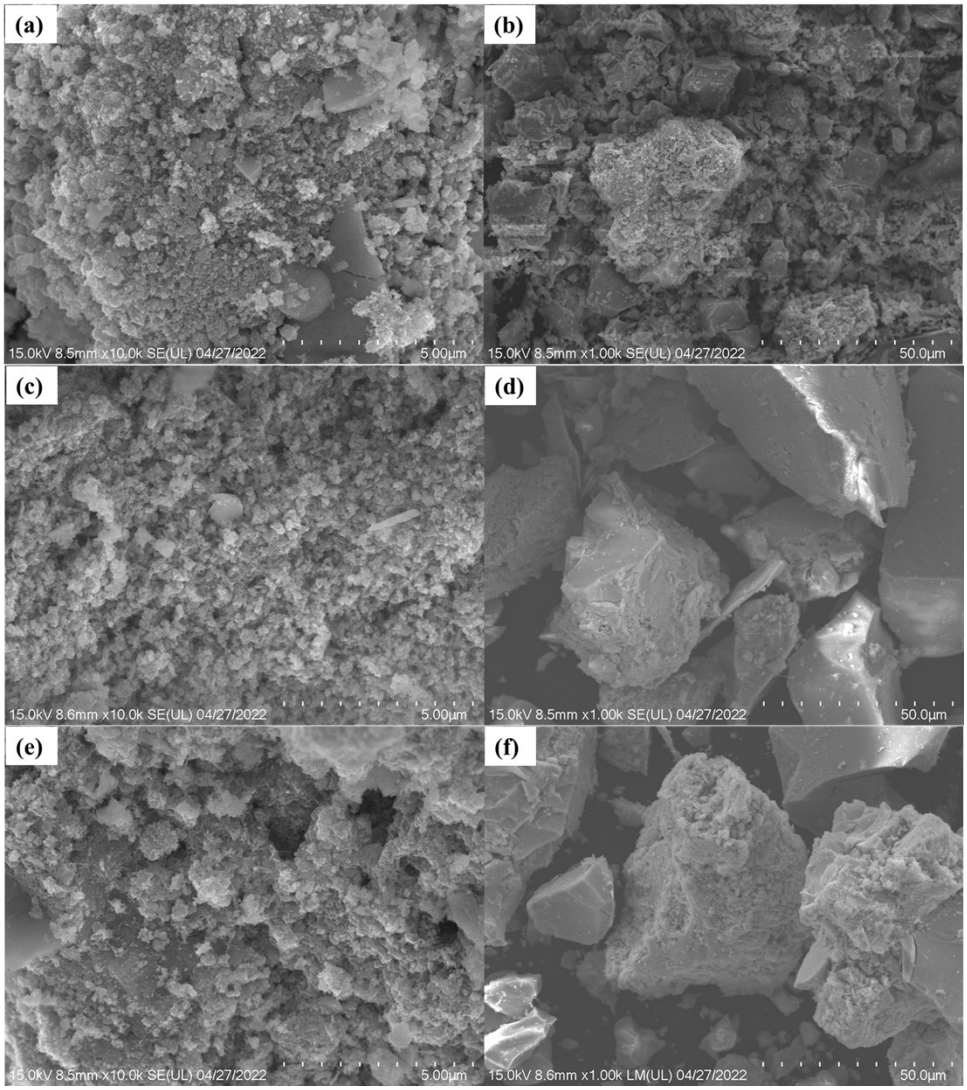

Fig. S6 SEM images of (a and b) Mn_4Ce_6, (c and d) $Mn_4Ce_5Si_1$, and (e and f) $Mn_4Ce_5Si_1$-1%S catalysts.

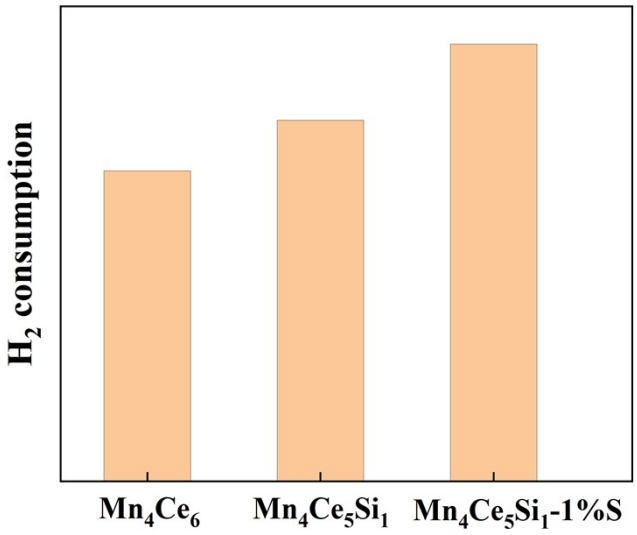

Fig. S7 H_2 consumption of Mn_4Ce_6, $Mn_4Ce_5Si_1$, and $Mn_4Ce_5Si_1$-1%S catalysts.

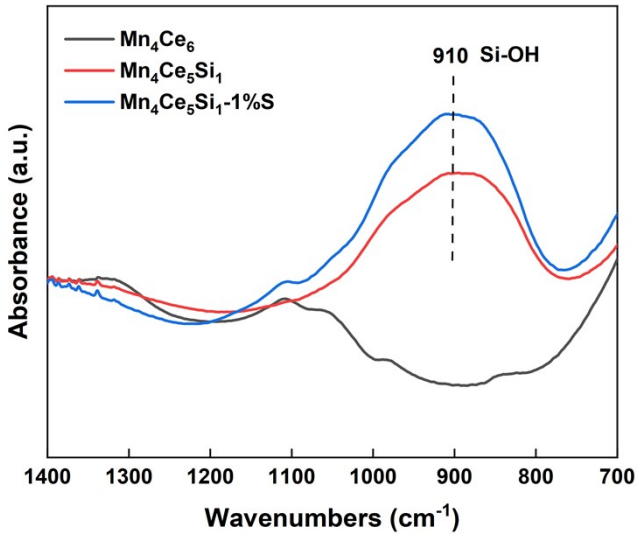

Fig. S8 FT-IR spectra of Mn_4Ce_6, $Mn_4Ce_5Si_1$, and $Mn_4Ce_5Si_1$-1%S catalysts.

A distinct band attributed to the Si-OH bond (ca. 910 cm^{-1}) was detected on $Mn_4Ce_5Si_1$ and $Mn_4Ce_5Si_1$-1%S, suggesting the abundant surface hydroxyl groups formed on the catalyst surface after the introduction of Si and sulfation after-treatment.[1]

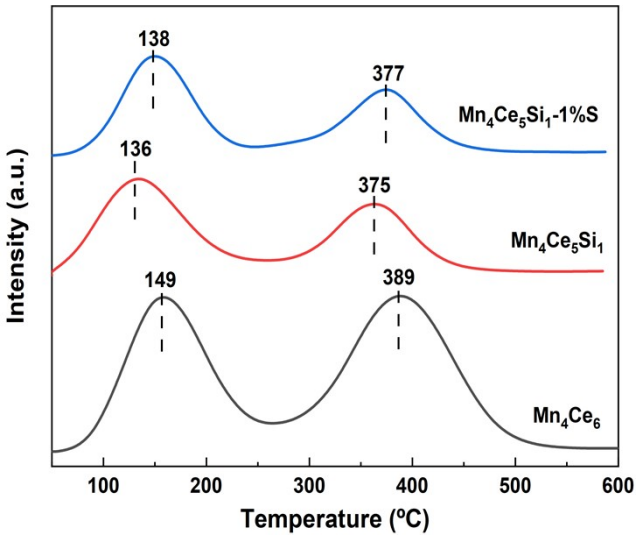

Fig. S9 NO-TPD profiles of Mn_4Ce_6, $Mn_4Ce_5Si_1$ and $Mn_4Ce_5Si_1$-1%S.

The NO-TPD profiles (Fig. S9) showed two distinct desorption peaks at 136-149 °C and 375-389 °C, which were attributed to physical-absorbed NO_x or the decomposition of monodentate nitrate species and the decomposition of bidentate nitrates or bridged nitrate species, respectively.[1]

References

1. W. Tan, A. Liu, S. Xie, Y. Yan, T. Shaw, Y. Pu, K. Guo, L. Li, S. Yu, F. Gao, F. Liu and L. Dong, *Environ. Sci. Technol.*, 2021, **55**, 4017-4026.