The Arrhenius equation indicates the relationship between the reaction temperature (T) and the reaction rate constant (k) in Equation 1, where A represents the preexponential factor, Ea is the apparent activation energy, T and R stand for absolute temperature and universal gas constant, respectively.

$$k = Ae^{\frac{Ea}{RT}}$$
 (Equation 1)

Equation 2 is obtained by taking logarithm of Equation 1 as follows:

$$\ln k = \ln A - \frac{Ea}{RT}$$
(Equation 2)

One straight line is obtained by plotting lnk against 1/T after measuring the reaction rate at different temperatures. As is shown in Equation 2, the slope represents  $E_a$ , and the intercept stands for pre-exponential factor (A). Furthermore, the reaction rate (r) is shown in Equation 3, where [reactants] represents the concentration of reactants. At the very beginning of reaction, the reactant concentration can be approximately constant, and Equation 4 is obtained after taking logarithm of Equation 3.

rate =  $r_0 = k * [reactants]$  (Equation 3)

$$\ln k = \ln r_0 = \ln A - \frac{Ea}{RT}$$
(Equation 4)

The concentrations of reactants and products is roughly the same at low conversions. Consequently, the initial reaction rate is approximately proportional to the reactant conversion  $(X_r)$ .

rate 
$$=r_0 = X_r$$
 (Equation 5)

Therefore, Equation 4 can be expressed as follows in Equation 6. The activation energy and pre-exponential factor can be calculated by plotting  $ln(X_r)$  against 1/RT after measuring the conversions at different temperatures.

$$\ln(X_r) = \ln A - \frac{Ea}{RT}$$
 (Equation 6)

The above procedures to calculate the activation energy are based on some reasonable assumptions. Hence, the kinetics experiments should be designed properly to meet the assumptions. The reaction temperatures and gas hourly space velocity (GHSV) are strictly selected to minimize the influence of side reactions and mass transport limitations. Moreover, the kinetic experiments are performed at low isobutane conversions to guarantee differential conditions.

In this work, non-oxidative DH of isobutane over oxide and sulfide vanadium-based catalysts were performed in the fixed-bed reactor at various temperatures ranging from 490 to 510 °C under atmospheric pressure to calculate the Ea. As indicated above, the reaction temperature was set from 490 to 510 °C to minimize the influence of side reactions. The GHSV was also doubled by halving the mass of loaded catalyst to weaken the effect of mass transport limitations. The conversion of isobutane was controlled lower than 10% under the strictly selected reaction conditions. Additionally, the conversion of isobutane was calculated at the very beginning of DH reaction, to further eliminate the influence of side reactions.



Fig. S1 Fitting image for calculation of Ea over sample 1.5K-S and 1.5K.

As for sample 1.5K and 1.5K-S, the Ea was calculated by plotting  $ln(X_r)$  against 1/RT after measuring the conversions at 490, 500 and 510 °C according to Equation 6. The fitting image is shown in Fig. S1, and the slope of fit line for sample 1.5K and 1.5K-S are -108.3 and -98.5 respectively. Therefore, the Ea for isobutane DH over oxide vanadium-based catalyst is 108.3 kJ/mol, while that decreases to 98.5 kJ/mol over sulfide vanadium-based catalysts. It is demonstrated that sulfidation can decrease the activation energy of vanadium-based catalysts, making it easier for isobutane DH reaction to take place under the same reaction condition.