Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Roles of Niobium on the Dehydrogenation of Propane to Propylene over Pt/Nb-modified Al_2O_3 Catalyst

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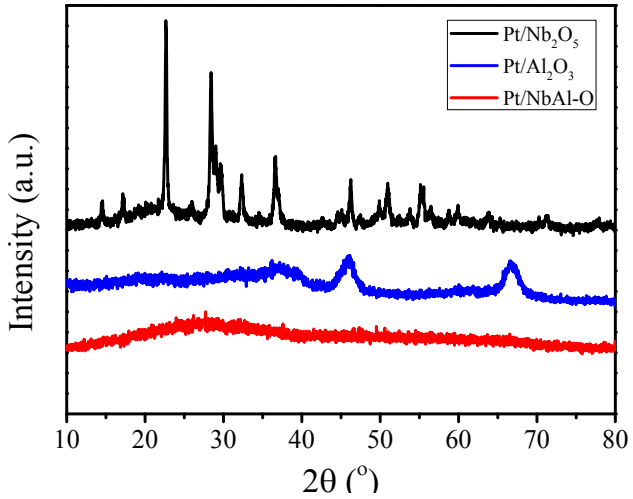

Figure S1. XRD patterns of fresh Pt/Nb_2O_5, Pt/NbAl-O and Pt/Al_2O_3.

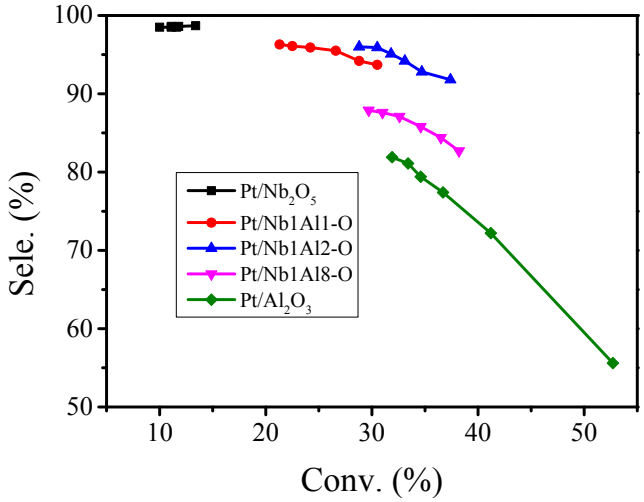

Figure S2. The curve of selectivity vs. conversion rate over different catalysts.

The figure of Selectivity vs. conversion over various catalysts was shown in Figure S2. Although there are differences in the conversion of these catalysts, but the selectivity over

Pt/Nb1Al2-O is always the highest at the same conversion, which means that Pt/Nb1Al2-O has the best performance among these catalysts.

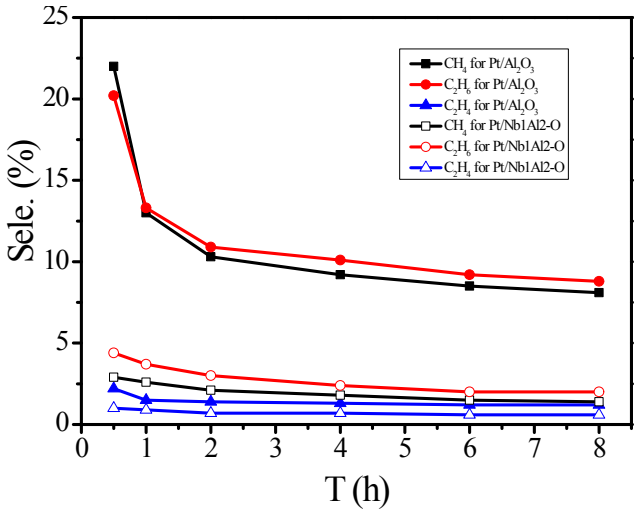

Figure S3. The selectivity of by-products (CH_4, C_2H_6 and C_2H_4) over Pt/Al_2O_3 and Pt/Nb1Al2-O.

Table S1. The deactivation rate parameter of each sample.

	Pt/Nb_2O_5	Pt/Nb1Al1-O	Pt/Nb1Al2-O	Pt/Nb1Al8-O	Pt/Al_2O_3
κ_d	0.0442	0.0644	0.0520	0.0507	0.1155

Notes: The reaction time is 8 h. The calculation formula is

$$\kappa_d = \frac{\ln\left[\left(1 - Conv_{end}\right)/Conv_{end}\right] - \ln\left[\left(1 - Conv_{start}\right)/Conv_{start}\right]}{t}$$

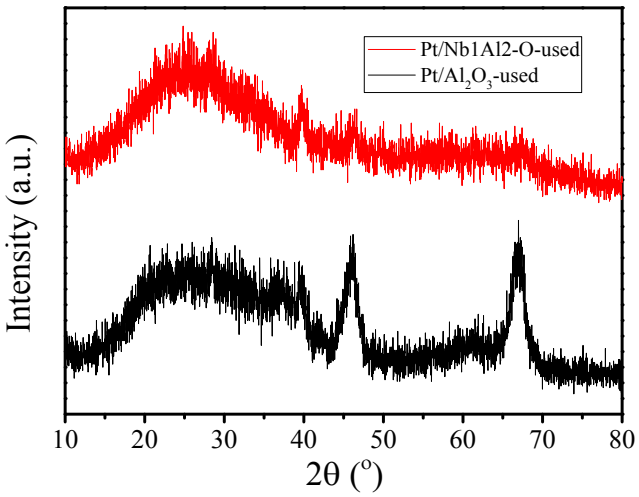

Figure S4. XRD patterns of the used catalysts (Pt/Al_2O_3 and Pt/Nb1Al2-O).

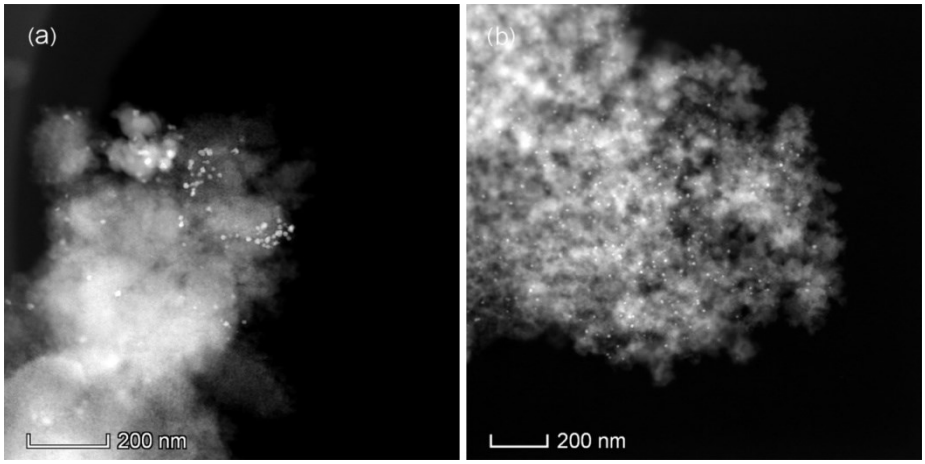

Figure S5. HAADF-STEM images of (a) Pt/Al_2O_3-used, (b) Pt/Nb1Al2-O-used.

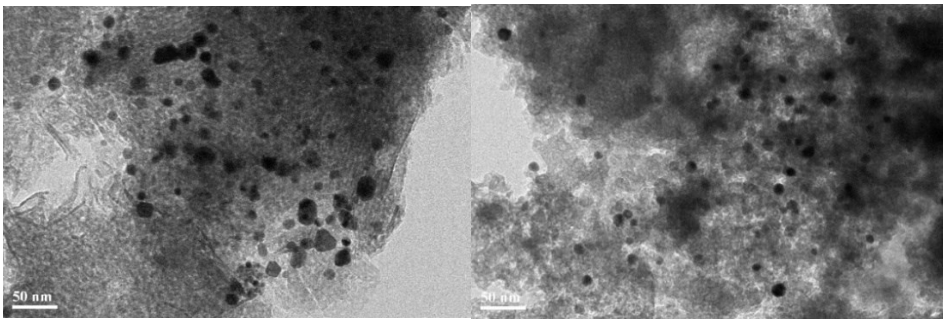

Figure S6. TEM images of Pt/Al_2O_3-used 3 cycles (left) and Pt/Nb1Al2-O-used 3 cycles (right).

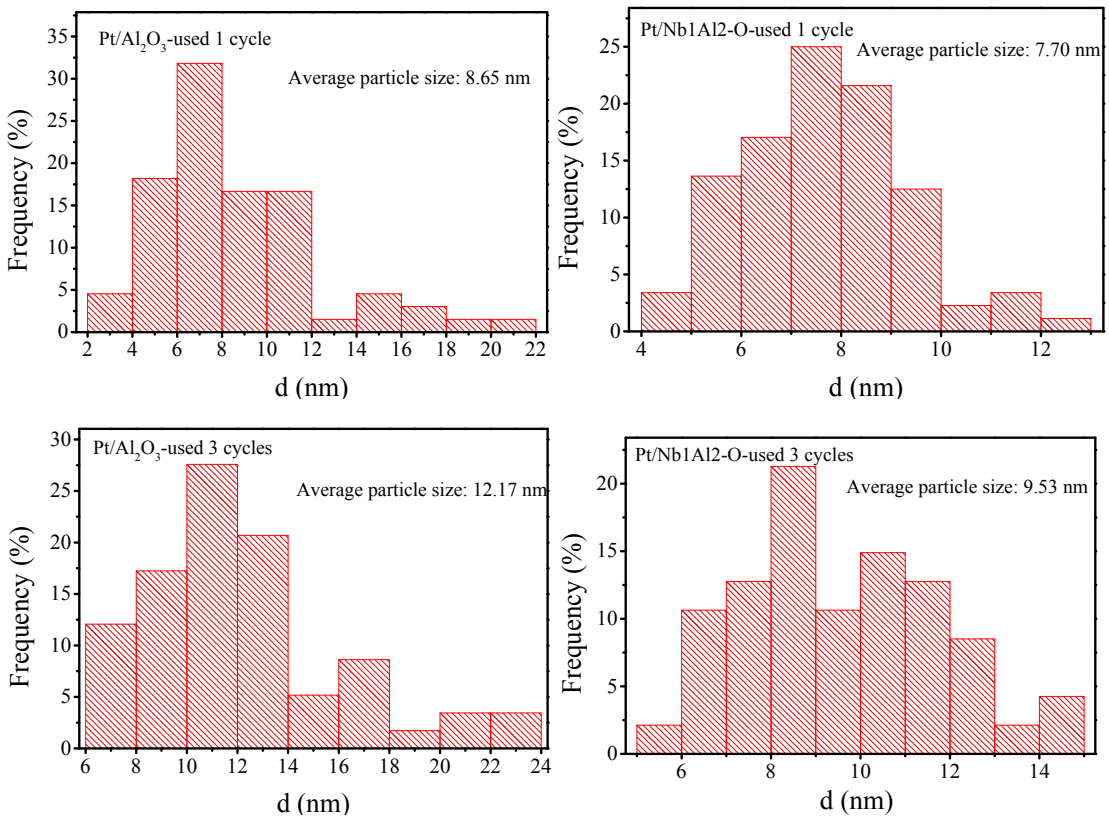

Figure S7. The distribution of Platinum particle size over different used catalysts.

Table S2. The amount of each acid site in Pt/Al2O3 and Pt/Nb1Al2-O.

	NH_3 uptaken (μmol·g^{-1})		
	Weak acid	Medium acid	Strong acid
Pt/Al_2O_3	166.4	95.9	264.6
Pt/Nb1Al2-O	163.0	207.9	238.9

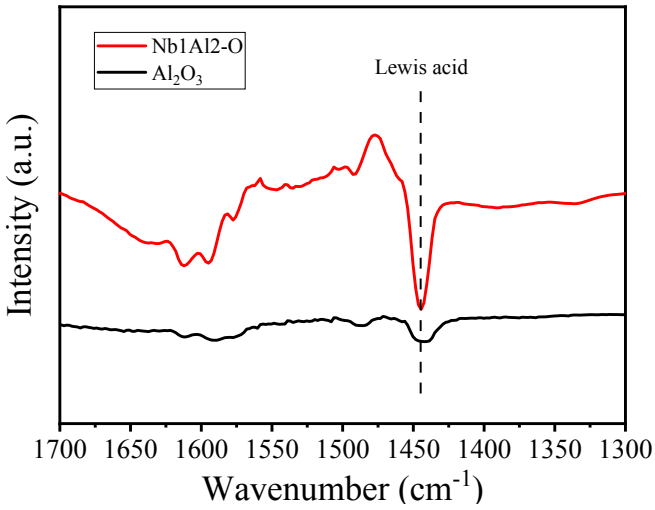

Figure S8. Py-FTIR spectra under vacuum of various catalysts.

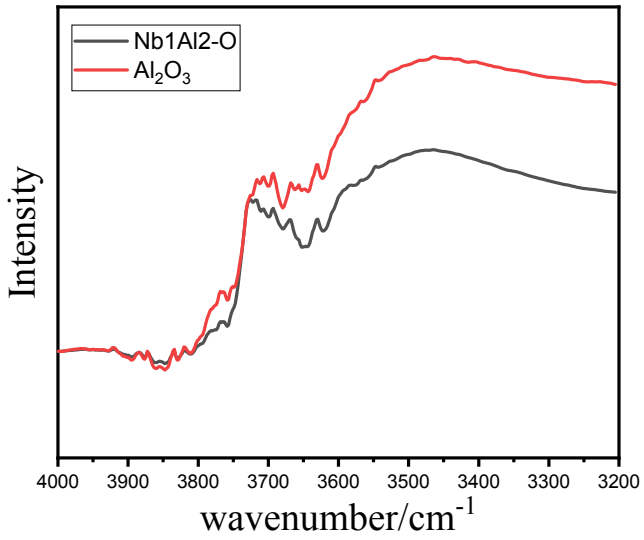

Figure S9. The DRIFTS spectra of both catalysts in 500 ℃.

We carried out the Py-FTIR to identify the Lewis and Brønsted acidity under vacuum, the spectra is present in Figure S8. It can be seen that Nb1Al2-O catalyst has markedly higher Lewis acid amount than Al_2O_3, which results in the excellent reaction performance over Pt/Nb1Al2-O. However, the Brønsted acid, located in 1540 cm^{-1}, can hardly be found in all kinds of samples. This inconsistency with NH_3-TPD may come from the larger molecular size of pyridine than ammonium, which cannot reach –OH groups in the pores of samples.

Therefore, additional diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to compare the numbers of –OH groups on each sample, as it is known that Brønsted acid is always related to -OH groups and it was demonstrated that the peak between 3700 cm^{-1}

and 3680 cm^{-1} is ascribed to surface hydroxyl groups. Before measurement, all samples were pretreated at 500 ℃ and the DRIFT is shown in Figure S9. It can be seen clearly that the amount of hydroxyl groups on Al_2O_3 is larger than that on Nb1Al2-O, which may be come from the transformation of Al-OH species to Al-O-Nb after introducing Nb into Al_2O_3 and lead to the decrease of Brønsted acid sites in the Nb1Al2-O.

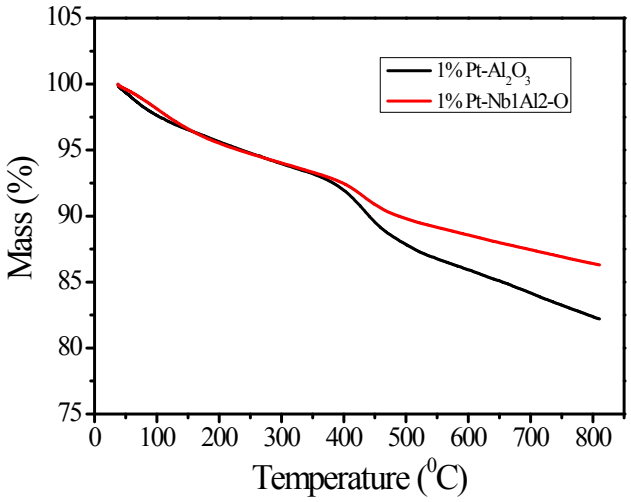

Figure S10. TG curve of the used Pt/Al_2O_3 and Pt/Nb1Al2-O catalysts.

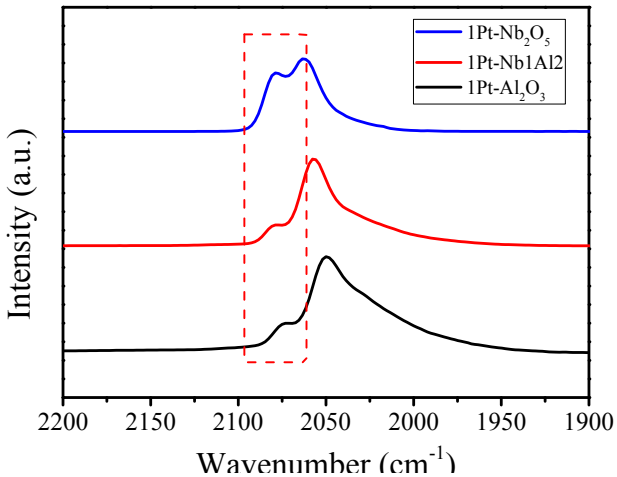

Figure S11. CO-DRIFTs of the Pt/Al2O3, Pt/Nb1Al2-O and Pt/Nb2O5.

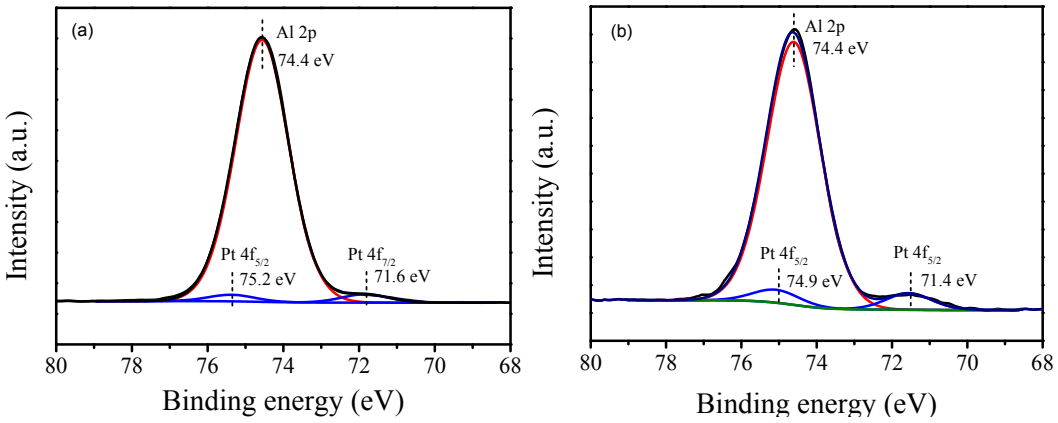

Figure S12. Pt 4f and Al 2p XPS spectra of (a) Pt/Al_2O_3 and (b) Pt/Nb1Al2-O.

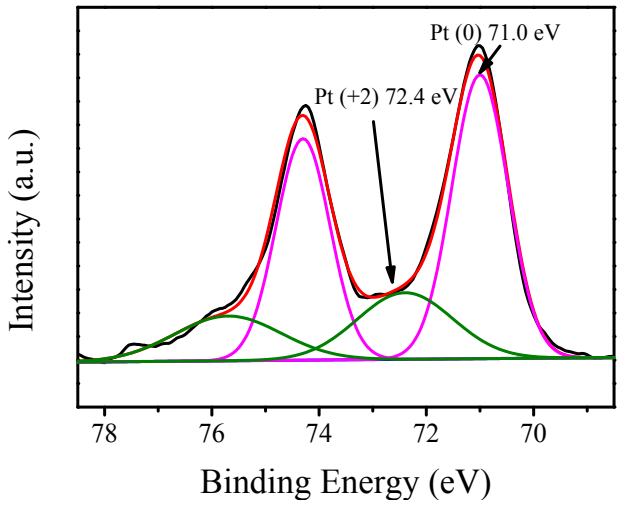

Figure S13. Pt 4f XPS spectra of Pt/Nb_2O_5.

The spectra of Pt 4f and Al 2p over Pt/Al_2O_3 and Pt/Nb1Al2-O catalysts were present in Figure S12. With carefully deconvolution from the overlapped peaks of Al 2p and Pt 4f, it can be seen that the binding energy of Pt is close to that of metallic Pt in both samples. The binding energy of Pt $4f_{7/2}$ in Pt/Al_2O_3 is 71.6 eV, a little bit higher than that of Pt/Nb1Al2-O (71.4 eV), indicating there is less electron on Pt over Pt/Al_2O_3 catalyst. XPS spectra of Pt 4f for Pt/Nb_2O_5 catalyst was given in Figure S12, and an obvious lower binding energy (71.0 eV) was observed, which means there may be an electron transfer from NbO_x to Pt. Compared with Pt/Al_2O_3, more electrons around Pt over Pt/Nb1Al2-O can decrease the adsorption of propylene and

reduce coke formation.

The XPS spectrum of Pt 4f over Pt/Nb_2O_5 was given in Figure S12. Consistent with our expectations, the binding energy of Pt 4f 7/2 is 71.0 eV, which is the lowest over these three catalysts (Pt/Nb_2O_5, Pt/Nb1Al2-O and Pt/Al_2O_3). However, there are still peaks of Pt (+2) over Pt/Nb_2O_5 catalyst, which may be due to the slight oxidation process.

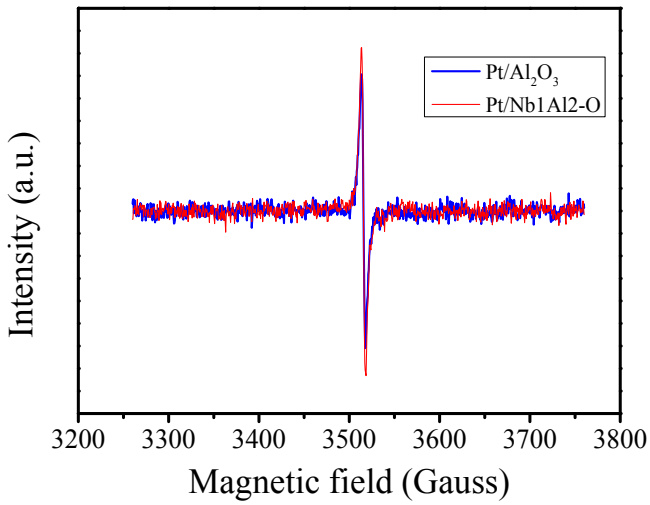

Figure S14. Low temperature EPR spectra of Pt/Al_2O_3 and Pt/Nb1Al2-O catalysts.