Supplementary Information (SI) for New Journal of Chemistry.

Supporting Information

1. Materials

The synthesis of V_2AlC was carried out through a series of methodical steps. Initially, powders were combined in an equimolar ratio, consisting of vanadium powder (particle size 10-20 μm, 99.0 wt% purity, sourced from Shanghai Pantian Powder Material Co., Ltd., Shanghai, China), aluminium powder (particle size 10-20 μm, 99.0 wt% purity, obtained from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), vanadium carbide powder (particle size 10 μm, 99.0 wt% purity, also from Shanghai Pantian Powder Material Co., Ltd.), sodium chloride powder (particle size 1 μm, 99.7 wt% purity, supplied by Aladdin Industrial Co., Ltd., Shanghai, China), and potassium chloride powder (particle size 1 μm, 99.7 wt% purity, from Aladdin Industrial Co., Ltd.). The mixed powders were then ground for 10 minutes. Subsequently, the mixture was placed into an alumina crucible and heated in a furnace at 1100 °C for 7 hours, with a heating rate of 5 °C /min under an argon atmosphere. After heating, the product was washed with 1 M hydrochloric acid (36.0–38.0 wt%, Sinopharm Chemical Reagent Co., Ltd.), filtered using filter paper, and dried in a vacuum at 40 °C. This procedure successfully yielded the MAX phase V_2AlC. Additionally, MgO doping into the MAX phase V_2AlC was achieved by mixing the two powders with a mortar and pestle.

2. Characterizations

The characterization of the catalysts was carried out using several advanced techniques to ensure comprehensive analysis. Powder X-ray diffraction data were acquired through a Bruker AXS D8 Advance Powder X-ray Diffraction system, utilizing Cu Kα radiation. Data collection was executed with a step size of 0.02°(2θ) and a collection duration of 1 second per step. Microstructural and chemical composition analyses were performed using a QUANTA 250 FEG scanning electron microscope (SEM) equipped with an Energy-Dispersive Spectrometer (EDS). The compositional values were calibrated employing the extended Puchou/Pichoir (XPP) method. The surface composition and valency state of V_2AlC were investigated using X-ray Photoelectron Spectroscopy (XPS) with a Thermo Scientific Escalab 250Xi instrument, which utilized Al Kα radiation. Binding energy (BE) peaks for all elements were calibrated against the C 1s peak at 284.8 eV. Finally, molecular functional groups present in the samples were identified using a LabRamHR Evolution spectrometer from Jobin-Yvon Horiba Scientific. H_2-TPR was measured using Micromeritics AutoChem II 2920 equipped with a thermal conductivity detector (TCD). Prior to the experiments, the samples were treated in argon(50 ml/min) in the TPR mode up to 50°C, followed by dwelling at 50°C for 5 minutes. The H_2-TPRmeasurement were carried out from room temperature to 750°C using a mixture of 10 % H_2/Ar in a heating rate of 10°C/min.

Catalytic tests

Catalytic oxidative dehydrogenation reactions were performed in a fixed-bed tubular reactor with an 8 mm inner diameter under standard atmospheric pressure. A 0.5 g sample of MAX phase V_2AlC was mixed with 1 g of α-alumina particles, homogenized, and packed into a quartz tube reactor, with quartz cotton positioned above the catalyst. The feed gases air, propane at 99.9% purity, and nitrogen at 99.999% purity were regulated via three independent mass flow controllers (ALICAT), ensuring flow rates of 2.0 ml/min for propane, 2.5 ml/min for air, and 25.5 ml/min for nitrogen. This setup achieved an O_2/C_3H_8 molar ratio of 0.25, unless specified otherwise. Reactions were conducted at temperatures ranging from 450 °C to 650 °C and a gas hourly space velocity (GHSV) of 3600 h^{-1}. To localize the maximum temperature, a stainless-steel tube with a 2 mm outer diameter, closed at one end and equipped with a movable thermocouple, was positioned at the centre of the catalyst bed. The reaction commenced with heating the catalyst to 450 °C under a nitrogen (N_2) atmosphere, followed by the introduction of propane and air. During standard reaction conditions, the temperature was incrementally raised to 650 °C, with a one-hour hold at each increment. Reaction products, namely methane, ethane, ethylene, propylene, and C_4 hydrocarbons, were detected using a Flame Ionization Detector (FID), while nitrogen, carbon monoxide, oxygen, and carbon dioxide were measured using a Thermal Conductivity Detector (TCD). The conversion of propane, denoted as $X(C_3H_8)$, and the selectivity of propylene, denoted as $S(C_3H_6)$, were calculated according to prescribed formulas.

$$X\,(C_3H_8) = \frac{N_{C_3H_8\,in} - N_{C_3H_8\,out}}{N_{C_3H_8\,in}}$$

$$S\,(C_3H_6) = \frac{N_{C_3H_6\,out}}{N_{C_3H_8\,in} - N_{C_3H_8\,out}}$$

In this calculation formula, N_{C3H8} in and N_{C3H8} out denote the molar flow rates of propane entering and exiting the reactor, respectively. Moreover, N_{C3H6} out represents the molar flow rate of propylene at the reactor's outlet.

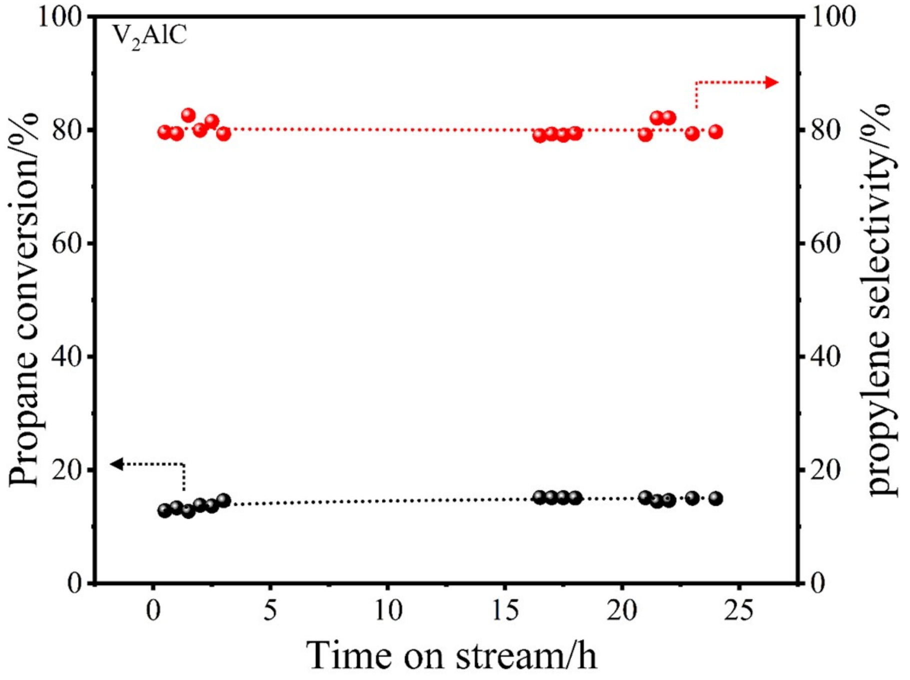
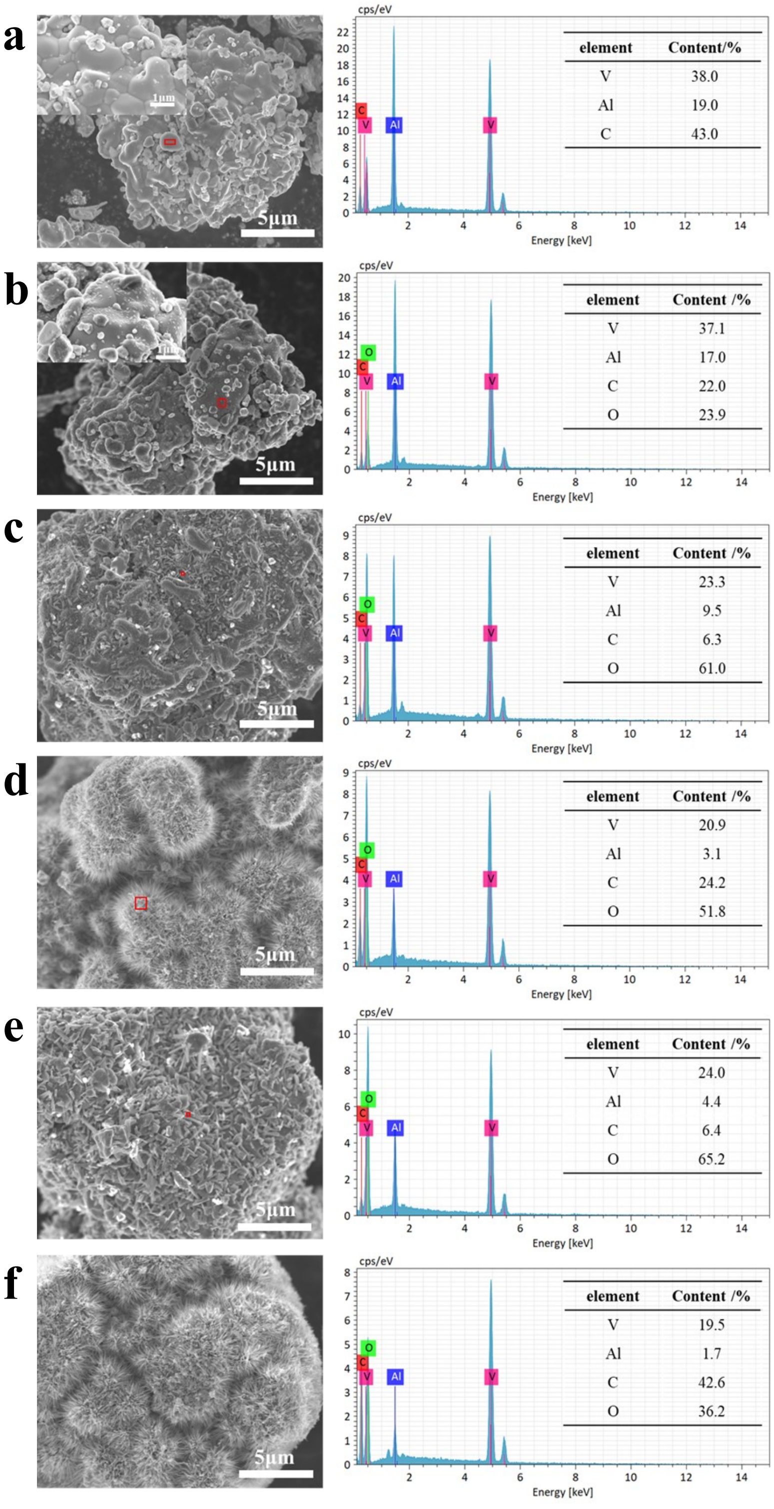


Fig. S1 V_2AlC duration test at 550 °C for 24 hours



element	Content/%
V	38.0
Al	19.0
C	43.0

element	Content /%
V	37.1
Al	17.0
C	22.0
O	23.9

element	Content /%
V	23.3
Al	9.5
C	6.3
O	61.0

element	Content /%
V	20.9
Al	3.1
C	24.2
O	51.8

element	Content /%
V	24.0
Al	4.4
C	6.4
O	65.2

element	Content /%
V	19.5
Al	1.7
C	42.6
O	36.2

Fig. S2 EDS of (a, b) fresh and used V_2AlC, (c, d) fresh and used V_2AlC after 3h preheating, and (e, f) fresh and used V_2AlC after 12h preheating, respectively. All samples used in one reaction cycle.

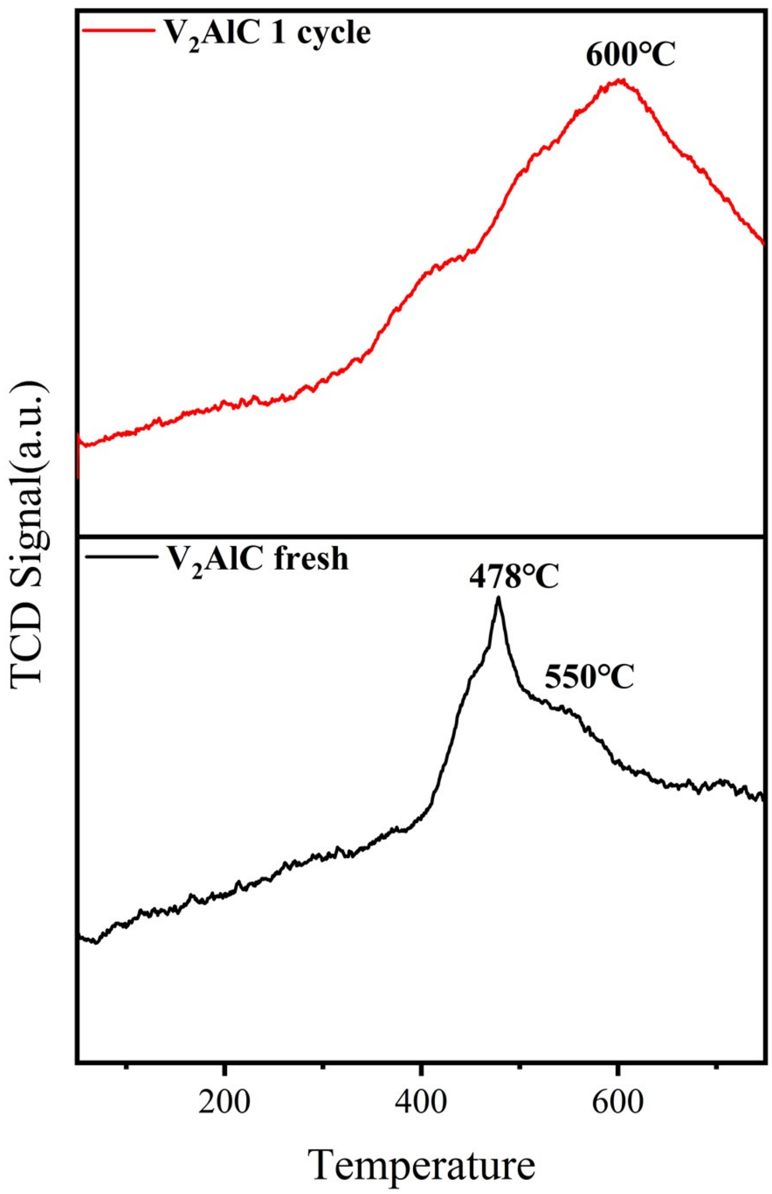


Fig. S3 H_2-TPR profiles of fresh V_2AlC and V_2AlC used in one reaction cycle

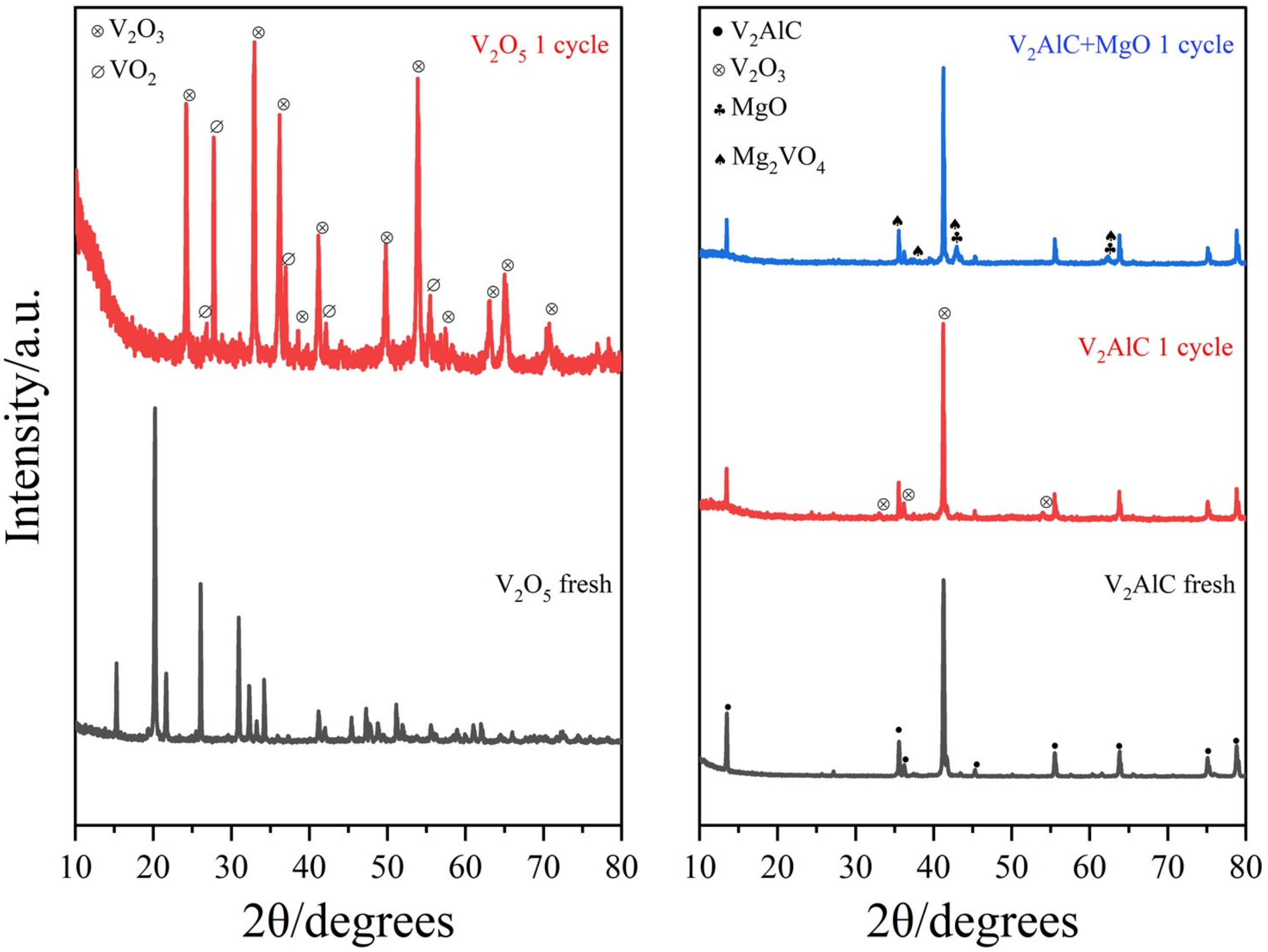


Fig. S4 XRD patterns of various sample including V_2O_5, both fresh and used in one cycle of reaction, V_2AlC, fresh and used in one cycle of reaction, and MgO doped one used in one cycle of reaction.

Table S1 The composition of various V_2AlC including fresh, used sample in one cycle of reaction, MgO doped sample used in one cycle of reaction, pre-heated V_2AlC for 3 hours and12 hours, used in one cycle of reaction.

Catalyst sample	V_2AlC %	VO_X%	Al_2O_3%
fresh V_2AlC	98.5%	0.0%	1.5%
V_2AlC, as used	90.07%	8.16%	1.77%
V_2AlC MgO doping, as used	96.7%	0.0%	3.3%
V_2AlC 3hr pretreated, as used	39.4%	54.2%	6.4%
V_2AlC 12hr pretreated, as use	27.5%	66.4%	6.1%
V_2AlC, as used (24h duration test)	90.89%	4.00%	5.11%
V_2AlC, as used (72h duration test)	81.15%	16.41%	2.44%

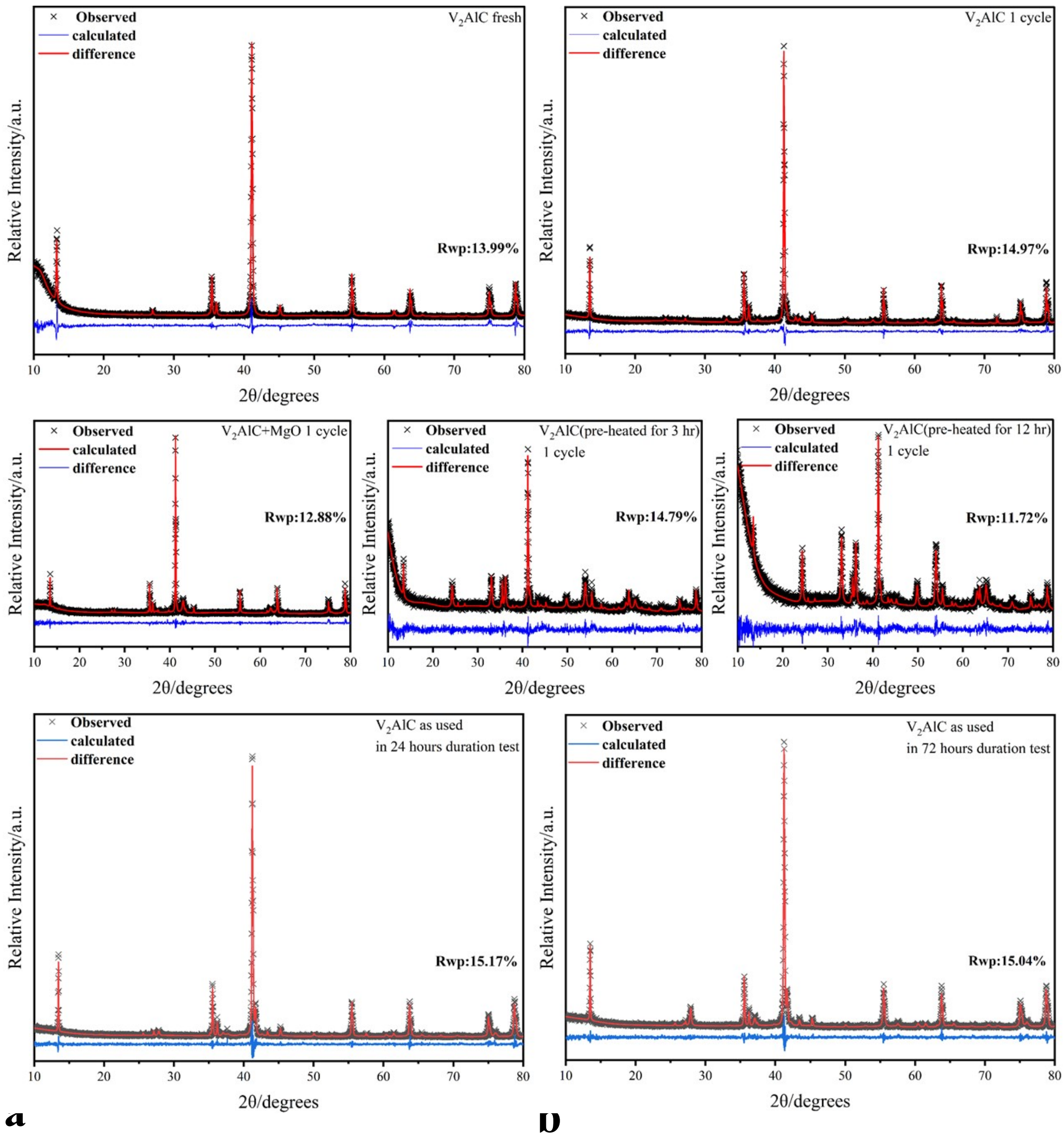


Fig. S5 XRD patterns of various V_2AlC including a) fresh, b) used sample in one cycle of reaction, c) MgO doped sample used in one cycle of reaction, d), e) pre-heated V_2AlC for 3 hours and12 hours, used in one cycle of reaction, f), g) used in duration test for 24 and 72 hours.

c **d** **e**

f **g**

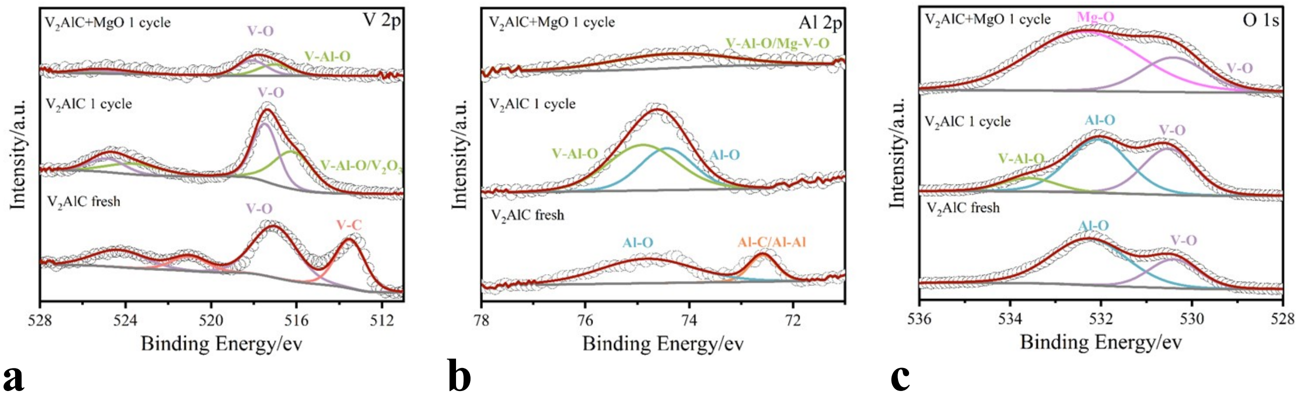


Fig. S6 XPS spectra of (a) V2p, (b) Al2p, (c) O 1s of samples including fresh V_2AlC, used V_2AlC in one cycle of reaction, and MgO doped V_2AlC used in one cycle of reaction.