Supporting Information

# Catalytic conversion of isophorone to jet-fuel range aromatic hydrocarbons over a MoO$_x$/SiO$_2$ catalyst

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# 1. Experimental

## 1.1 Preparation of catalysts

$MO_x/SiO_2$ (M = Mo, V, W, Fe, Cu) catalysts were prepared by the incipient wetness impregnation of $SiO_2$ (Qingdao Ocean Chemical Ltd., BET surface area 509 $m^2$ $g^{-1}$) with the aqueous solutions of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, $NH_4VO_3$, $(NH_4)_6H_2W_{12}O_{40} \cdot xH_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ respectively. The products were kept at room temperature for 12 h, dried at 393 K for 4 h, then calcined at 773 K for 4 h. To facilitate the comparsion, the weight percentages of the metal oxides in the catalysts were controlled as 10 wt%. The $MoO_x$ catalyst was prepared by the calcination of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ at 773 K for 4 h. The $MoO_x$ + $SiO_2$ catalyst was obtained by the physically mixing the $MoO_x$ as obtained and the $SiO_2$ support. The Mo and Si contents in the $MoO_x$ + $SiO_2$ catalyst were controlled the same as the ones in the 15 wt% $MoO_x/SiO_2$ catalyst.

MgO was purchased from Kermel Reagent Company. MgAl-hydrotalcite (MgAl-HT, Mg/Al atomic ratio = 2) was prepared according to literature.[1] A solution of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ in 200 mL deionized water was pumped into a mixture of NaOH and $Na_2CO_3$. The addition process was conducted at 343 K water bath under vigorous mechanical agitation. Then the gel was aged at this temperature for 16 h. The solid as obtained was filtered, washed until filtrate pH became 7 and dried overnight at 353 K. The dried precursor was calcined at 723 K for 8 h. Acidic carbon (AC) was prepared by pre-treating the active carbon (supplied by the NORIT Company) by 33 wt% nitric acid solution (at a mass ratio

of 1:5) at 353 K for 24 h. H-ZSM-5 ($SiO_2/Al_2O_3$ = 25) and H-β ($SiO_2/Al_2O_3$ = 25) zeolites were provided by Nankai University.

## 2. Activity test

The catalytic conversion of isophorone was carried out in a 316L stainless steel tubular flow reactor. For each reaction, 2.0 g catalyst (40-80 mesh in size) was used. The isophorone was pumped into the reactor at 0.04 mL min$^{-1}$ from the top of the reactor, along with hydrogen at a flow rate of 80 mL min$^{-1}$. Before reaching the catalysts, the isophorone was vaporized at reaction temperature over quartz sand. After passing through the reactor and cooling down to room temperature, the products became two phases in a gas-liquid separator. The gaseous products flowed through a back pressure regulator to maintain the system pressure at set pressure and analyzed online by an Agilent 7890B GC. The liquid products were drained from the gas-liquid separator after 5 h and analyzed by an Agilent 7890A GC.

Method for the calculation of conversion of isophorone and the carbon yields of different products:

Conversion of isophorone (%) = (1 - mole of isophorone detected in the liquid product/mole of isophorone fed into the reactor) × 100%

Carbon yield of specific product (%) = Sum of carbon in the specific product detected from the liquid phase product/Carbon fed into the reactor × 100%

Carbon balance (%) = Sum of the carbon identified in the products/Carbon in the converted isophorone × 100%

Carbon selectivity for specific gas phase product (%) = Carbon in specific gas phase

product/Sum of the carbon in the identified gas phase products × 100%

## 3. Characterization

### 3.1 H$_2$-temperature programmed reduction (H$_2$-TPR)

H$_2$-TPR test of the 10 wt% MoO$_x$/SiO$_2$ catalyst was carried out with the Micromeritics AutoChem II 2920 Automated Catalyst Characterization System using 10% H$_2$ in Ar stream. Before the test, the catalyst was pretreated in Ar flow at 773 K for 1 h. After the switching of gas from Ar to 10% H$_2$ in Ar and the stabilization of the base line, the 10 wt% MoO$_x$/SiO$_2$ catalyst was heated from 323 K to 1073 K at the rate of 10 K min$^{-1}$. The consumption of hydrogen during this period was measured by a TCD detector. From Figure S6, a wide peak (from 673 K to 1073 K) can be observed in the H$_2$-TPR profile of 10 wt% MoO$_x$/SiO$_2$ catalyst. This peak can be attributed to the reduction of MoO$_x$ species. According to this result, we can see that the MoO$_x$ species was partially reduced under the investigated conditions (723 K).

### 3.2 X-ray diffraction (XRD)

XRD patterns of the MoO$_x$/SiO$_2$ catalysts were recorded with a PW3040/60X' Pert PRO (PANalytical) diffractometer using a Cu K$_\alpha$ radiation source ($\lambda$ = 0.15432 nm) operated at 40 kV and 40 mA. From the results illustrated in Figure S7a, we can only see the peaks of SiO$_2$ support and MoO$_3$ in the XRD patterns of the unreduced MoO$_x$/SiO$_2$ catalysts. No peak of new phase (such as silicomolybdic acid) was observed. It is also noticed that the relative intensity of some peaks change after loading MoO$_3$ on SiO$_2$ support. This result is consistent with what has been reported in some literature[2] and can be explained by the support effect. With the increasing of

Mo content, the peak of $MoO_3$ in the XRD patterns of unreduced $MoO_x/SiO_2$ catalysts becomes more evident.

To figure out the active Mo species which is active for the catalytic conversion of isophorone to jet fuel range aromatic hydrocarbons, we also compared the XRD patterns of the unreduced, reduced and spent 10 wt% $MoO_x/SiO_2$ catalysts. From the results illustrated in Figure S7b, the Mo species exists as $MoO_3$ phase in the unreduced 10 wt% $MoO_x/SiO_2$ catalyst. In contrast, the Mo species in the reduced or spent 10 wt% $MoO_x/SiO_2$ catalysts exists as $MoO_2$ phase.

## 3.3 X-ray proton spectrum (XPS)

X-ray photoelectron spectroscopy (XPS) experiments were conducted with an ESCALAB 250Xi spectrometer using Al Kα (hυ = 1486.6 eV) as the X-ray source with pass energy of 20 eV, and base pressure of analysis chamber less than $1 \times 10^{-8}$ Pa. Before the XPS experiments, the unreduced and spent 10 wt% $MoO_x/SiO_2$ catalysts were pressed into thin discs. For the reduced 10 wt% $MoO_x/SiO_2$ catalyst, the sample was firstly reduced by hydrogen at 723 K for 1 h, then pressed into disc. From the Mo 3d XPS spectra shown in Figure S8, the valence state of Mo species on the surface of unreduced 10 wt% $MoO_x/SiO_2$ catalyst is about +6, while the valence state of Mo species on the surface of reduced (or spent) 10 wt% $MoO_x/SiO_2$ catalyst is between +4 and +5. This result further proves that the Mo species on the $MoO_x/SiO_2$ catalyst is partially reduced under the investigated condition.

## 3.4 NH$_3$-temperature programmed desorption (NH$_3$-TPD)

The NH$_3$-TPD experiments were conducted on a Micromeritics AutoChem II

2920 Automated Catalyst Characterization System. Before each test, 0.1 g sample was placed in a quartz reactor, pretreated at 723 K for 1 h in a hydrogen flow and cooled down to 373 K. After the saturated adsorption $NH_3$ by impulse injection, the sample was heated at 373 K in helium for 10 min to remove the physically adsorbed $NH_3$. Subsequently, the $NH_3$-TPD experiment was conducted in helium flow from 373 K to 1173 K at a heating rate of 10 K min$^{-1}$. The desorbed $NH_3$ were detected by a mass spectrometry (MS) OminiStar equipped with the software quadstar 32-bit. The amounts of acid sites on the catalysts (see Table S6) were calculated according to the $NH_3$-TPD results.

**3.5 Thermogravimetric- Mass spectrometer (TG- MS)**

The TG analysis of the spent $MoO_x/SiO_2$ catalyst was carried out by the TA Instrument SDT Q 600 connected with an InProgress Instruments GAM 200 mass spectrometer (MS). 20 mg catalyst was used in the test. The experiment was conducted in flowing air (100 mL min$^{-1}$) from 303 K to 1073 K at a heating rate of 10 K min$^{-1}$. From the TG profile of the spent 15 wt% $MoO/SiO_2$ catalyst (see Fig. S9a), one mass loss from 573 K to 873 K was observed. According to the MS result (see Fig. S9b), the mass loss can be attributed to the combustion of coke generated during the reaction (because only $CO_2$ was identified as the combustion product).

**Table S1.** The properties of $C_8$-$C_9$ aromatic hydrocarbons as obtained from the transformation of isophorone.

| Compound | Boiling point (K) | Freezing point (K) | Density (g mL$^{-1}$) |
|---|---|---|---|
| *m*-xylene | 412.3 | 225.6 | 0.87 |
| 1,2,4-trimethylbenzene | 441.9 | 229.2 | 0.88 |
| 1,2,3-trimethylbenzene | 449.0 | 248.0 | 0.89 |
| Mesitylene | 437.7 | 228.2 | 0.86 |

**Table S2.** The conversion of isophorone and the carbon yields of different products from the transformation of isophorone over different catalysts. Reaction conditions: 2.0 g catalyst, hydrogen flow rate: 80 mL min$^{-1}$, isophorone flow rate: 0.04 mL min$^{-1}$.

| | Catalyst | Hydrogen pressure (MPa) | Temperature (K) | Conversion of isophorone (%) | Carbon yield (%) | | | | | | | Carbon balance (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | 3,3,5-Tri-methlcyclo-hexanone | C$_9$ cycloalkenes | Phenols | Toluene | C$_8$-C$_9$ aromatic hydrocarbons | C$_{10}$-C$_{11}$ aromatic hydrocarbons | Gas phase products[a] | |
| 1 | 10 wt% MoO$_x$/SiO$_2$ | 0.1 | 723 | 98.3 | 0 | 12.9 | 0 | 0 | 76.3 | 1.9 | 4.0 | 96.7 |
| 2 | 10 wt% VO$_x$/SiO$_2$ | 0.1 | 723 | 94.5 | 1.5 | 13.3 | 8.0 | 0 | 42.9 | 1.4 | 7.3 | 78.7 |
| 3 | 10 wt% WO$_x$/SiO$_2$ | 0.1 | 723 | 84.8 | 5.0 | 9.2 | 9.8 | 0 | 27.0 | 0.6 | 5.8 | 64.3 |
| 4 | 10 wt% FeO$_x$/SiO$_2$ | 0.1 | 723 | 63.8 | 12.1 | 9.2 | 12.6 | 0 | 18.4 | 0 | 4.1 | 88.7 |
| 5 | 10 wt% CuO$_x$/SiO$_2$ | 0.1 | 723 | 49.7 | 11.6 | 5.3 | 8.6 | 0 | 15.6 | 0 | 0.6 | 83.9 |
| 6 | 10 wt% MoO$_x$/SiO$_2$[b] | - | 723 | 34.2 | 8.56 | 2.97 | 10.2 | 0 | 4.88 | 0 | 2.6 | 85.2 |
| 7 | 10 wt% MoO$_x$/SiO$_2$[c] | - | 723 | 37.3 | 8.5 | 4.4 | 9.6 | 0 | 11.4 | 0.5 | 2.5 | 98.9 |
| 8 | 10 wt% MoO$_x$/SiO$_2$ | 0.5 | 723 | 98.2 | 0 | 8.2 | 0 | 0 | 76.9 | 2.3 | 4.6 | 93.7 |
| 9 | 10 wt% MoO$_x$/SiO$_2$ | 1.0 | 723 | 98.3 | 0 | 13.1 | 0 | 0 | 77.3 | 2.1 | 3.3 | 98.1 |
| 10 | 10 wt% MoO$_x$/SiO$_2$ | 0.1 | 623 | 51.8 | 16.2 | 9.8 | 0.8 | 0 | 14.1 | 2.7 | 1.1 | 86.3 |
| 11 | 10 wt% MoO$_x$/SiO$_2$ | 0.1 | 673 | 98.8 | 0 | 24.3 | 0 | 0 | 58.2 | 2.6 | 3.6 | 90.2 |
| 12 | 10 wt% MoO$_x$/SiO$_2$ | 0.1 | 773 | 97.6 | 0 | 6.0 | 0 | 0 | 78.4 | 2.7 | 7.4 | 96.8 |
| 13 | 1 wt% MoO$_x$/SiO$_2$ | 0.1 | 723 | 75.2 | 9.0 | 10.2 | 9.9 | 0 | 32.1 | 0 | 3.0 | 93.0 |
| 14 | 5 wt% MoO$_x$/SiO$_2$ | 0.1 | 723 | 98.6 | 0 | 11.0 | 1.1 | 0 | 70.8 | 5.1 | 4.4 | 94.5 |
| 15 | 15 wt% MoO$_x$/SiO$_2$ | 0.1 | 723 | 98.2 | 0 | 8.4 | 0 | 0 | 81.0 | 2 | 1.7 | 94.8 |
| 16 | 20 wt% MoO$_x$/SiO$_2$ | 0.1 | 723 | 98.6 | 0 | 9.0 | 0 | 0 | 79.1 | 1.4 | 1.2 | 92.0 |
| 17 | MoO$_x$[d] | 0.1 | 723 | 99.8 | 0 | 59.6 | 0 | 0 | 32.9 | 0.6 | 2.8 | 96.1 |
| 18 | SiO$_2$ | 0.1 | 723 | 33.1 | 10.3 | 3.0 | 8.6 | 0 | 5.8 | 0 | 2.2 | 90.3 |
| 19 | MoO$_x$ + SiO$_2$[e] | 0.1 | 723 | 97.5 | 1.4 | 36.6 | 4.6 | 0 | 48.3 | 0.7 | 3.8 | 97.8 |

[a] The carbon selectivities of different gas phase products were given in Table S3. [b] The experiment was carried out in nitrogen flow over the 10 wt% MoO$_x$/SiO$_2$ catalyst without the pretreatment with hydrogen flow. [c] The experiment was carried out over the reduced 10 wt% MoO$_x$/SiO$_2$ catalyst. [d] MoO$_x$ was prepared by the thermal decomposition of ammonium molybdate at 773 K. [e] The MoO$_x$ + SiO$_2$ denotes the physical mixture of MoO$_x$ and SiO$_2$ which has the same chemical composition as the 15 wt% MoO$_x$/SiO$_2$ catalyst.

**Table S3.** The carbon yields and selectivities of different products from the transformation of isophorone over different catalysts. Reaction conditions: 2.0 g catalyst, hydrogen flow rate: 80 mL min$^{-1}$, isophorone flow rate: 0.04 mL min$^{-1}$.

| | Catalyst | Hydrogen pressure (MPa) | Temperature (K) | Carbon yield of gas phase products (%) | Carbon selectivity (%) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Carbon oxides[a] | Methane | C$_2$ hydrocarbons | C$_3$ hydrocarbons | C$_4$ hydrocarbons | C$_5$ hydrocarbons | C$_6$ hydrocarbons |
| 1 | 10 wt% MoO$_x$/SiO$_2$ | 0.1 | 723 | 4.0 | 15.8 | 28.0 | 5.1 | 8.6 | 21.6 | 10.5 | 10.4 |
| 2 | 10 wt% VO$_x$/SiO$_2$ | 0.1 | 723 | 7.3 | 21.9 | 47.1 | 1.7 | 4.5 | 7.8 | 4.8 | 12.1 |
| 3 | 10 wt% WO$_x$/SiO$_2$ | 0.1 | 723 | 5.8 | 16.3 | 19.4 | 2.3 | 7.5 | 28.2 | 9.5 | 16.8 |
| 4 | 10 wt% FeO$_x$/SiO$_2$ | 0.1 | 723 | 4.1 | 20.3 | 37.3 | 1.1 | 2.8 | 20.6 | 3.3 | 14.6 |
| 5 | 10 wt% CuO$_x$/SiO$_2$ | 0.1 | 723 | 0.6 | 74.3 | 12.2 | 0.8 | 0.8 | 11.9 | 0 | 0 |
| 6 | 10 wt% MoO$_x$/SiO$_2$[b] | - | 723 | 2.6 | 38.4 | 33.5 | 6.2 | 2.1 | 17.6 | 2.1 | 0 |
| 7 | 10 wt% MoO$_x$/SiO$_2$[c] | - | 723 | 2.5 | 24.6 | 49.6 | 2.3 | 2.6 | 19.1 | 1.8 | 0 |
| 8 | 10 wt% MoO$_x$/SiO$_2$ | 0.5 | 723 | 4.6 | 11.2 | 16.8 | 3.4 | 14.6 | 31.7 | 14.5 | 7.8 |
| 9 | 10 wt% MoO$_x$/SiO$_2$ | 1.0 | 723 | 3.3 | 13.8 | 13.7 | 3.4 | 16.0 | 31.8 | 13.9 | 7.3 |
| 10 | 10 wt% MoO$_x$/SiO$_2$ | 0.1 | 623 | 1.1 | 13.6 | 3.4 | 1.3 | 2.7 | 20.8 | 6.0 | 52.3 |
| 11 | 10 wt% MoO$_x$/SiO$_2$ | 0.1 | 673 | 3.6 | 11.1 | 8.5 | 1.6 | 6.0 | 16.7 | 13.5 | 42.7 |
| 12 | 10 wt% MoO$_x$/SiO$_2$ | 0.1 | 773 | 7.4 | 18.3 | 38.0 | 3.4 | 6.8 | 17.7 | 5.8 | 10.0 |
| 13 | 1 wt% MoO$_x$/SiO$_2$ | 0.1 | 723 | 3.0 | 16.8 | 23.3 | 2.6 | 5.5 | 35.4 | 6.5 | 9.9 |
| 14 | 5 wt% MoO$_x$/SiO$_2$ | 0.1 | 723 | 4.4 | 18.2 | 19.4 | 2.6 | 8.1 | 26.1 | 10.6 | 15.1 |
| 15 | 15 wt% MoO$_x$/SiO$_2$ | 0.1 | 723 | 1.7 | 14.9 | 24.0 | 4.6 | 7.7 | 20.9 | 10.1 | 17.8 |
| 16 | 20 wt% MoO$_x$/SiO$_2$ | 0.1 | 723 | 1.2 | 50.6 | 26.5 | 1.7 | 4.0 | 17.2 | 0 | 0 |
| 17 | MoO$_x$[d] | 0.1 | 723 | 2.8 | 30.2 | 62.1 | 1.0 | 1.6 | 5.1 | 0 | 0 |
| 18 | SiO$_2$ | 0.1 | 723 | 2.2 | 34.0 | 36.5 | 1.3 | 2.1 | 17.9 | 3.4 | 4.8 |
| 19 | MoO$_x$ + SiO$_2$[e] | 0.1 | 723 | 3.8 | 20.8 | 24.8 | 2.4 | 5.0 | 17.4 | 8.8 | 20.9 |

[a] Carbon oxides including CO and CO$_2$. [b] The experiment was carried out in nitrogen flow over the 10 wt% MoO$_x$/SiO$_2$ catalyst without the pretreatment with hydrogen flow. [c] The experiment was carried out over the reduced 10 wt% MoO$_x$/SiO$_2$ catalyst. [d] MoO$_x$ was prepared by the thermal decomposition of ammonium molybdate at 773 K. [e] The MoO$_x$ + SiO$_2$ denotes the physical mixture of MoO$_x$ and SiO$_2$ which has the same chemical composition as the 15 wt% MoO$_x$/SiO$_2$ catalyst.

**Table S4.** The conversion of isophorone and the carbon yields of different products from the transformation of isophorone over different catalysts. Reaction conditions: 2.0 g catalyst, hydrogen pressure: 0.1 MPa, reaction temperature: 723 K, hydrogen flow rate: 80 mL min$^{-1}$, isophorone flow rate: 0.04 mL min$^{-1}$.

| Catalyst[a] | Conversion of isophorone (%) | Carbon yield (%) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 3,3,5-Trimethyl-cyclohexanone | C$_9$ cyclo-alkenes | Phenols | Toluene | $m$-xylene | 1,2,4-TMB[b] | 1,2,3-TMB[c] | Mesitylene | C$_{10}$ and C$_{11}$ aromatic hydrocarbons | Jet fuel range C$_7$-C$_{11}$ aromatic hydrocarbons | Gas products[d] |
| 1  MoO$_x$ + MgO | 92.1 | 9.6 | 60.0 | 3.7 | 0 | 5.4 | 2.6 | 1.8 | 0.6 | 0 | 10.4 | 2.0 |
| 2  MoO$_x$ + MgAl-HT[e] | 84.4 | 10.4 | 33.7 | 23.2 | 0 | 6.7 | 0.9 | 0.5 | 0.6 | 0 | 8.7 | 8.2 |
| 3  MoO$_x$ + AC[f] | 99.3 | 0.7 | 34.6 | 0 | 0 | 32.3 | 12.2 | 7.0 | 2.0 | 0 | 53.5 | 10.5 |
| 4  MoO$_x$ + SiO$_2$ | 97.5 | 1.4 | 36.6 | 4.6 | 0 | 5.0 | 24.6 | 13.5 | 5.3 | 0.7 | 49.0 | 3.8 |
| 5  MoO$_x$ + H-β | 95.1 | 1.3 | 11.7 | 0 | 1.7 | 4.1 | 21.6 | 11.1 | 7.2 | 15.6 | 61.3 | 10.7 |
| 6  MoO$_x$ + H-ZSM-5 | 98.1 | 2.2 | 2.4 | 0 | 7.5 | 8.8 | 11.3 | 11.5 | 4.0 | 12.6 | 55.7 | 20.9 |

[a] The catalysts were prepared by the physical mixing the MoO$_x$ and various supports at the mass ratio of 3:17. To facilitate the comparison, the molar ratios of SiO$_2$:Al$_2$O$_3$ in H-β and H-ZSM-5 are 25:1. [b] 1,2,4-TMB: 1,2,4-trimethylbenzene. [c] 1,2,3-TMB: 1,2,3-trimethylbenzene. [d] The carbon selectivity of different gas phase products were given in Table S4. [e] MgAl-HT: MgAl-hydrotalcite. [f] AC: acidic active carbon which was prepared by treating the active carbon with nitric acid.

**Table S5.** The carbon yields and selectivities of different products from the transformation of isophorone over different catalysts. Reaction conditions: 2.0 g catalyst, hydrogen pressure: 0.1 MPa, reaction temperature: 723 K, hydrogen flow rate: 80 mL min$^{-1}$, isophorone flow rate: 0.04 mL min$^{-1}$.

| | Catalyst[a] | Carbon yield of gas phase products (%) | Carbon selectivity (%) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Carbon oxides[b] | Methane | $C_2$ hydrocarbons | $C_3$ hydrocarbons | $C_4$ hydrocarbons | $C_5$ hydrocarbons | $C_6$ hydrocarbons |
| 1 | $MoO_x$ + MgO | 2.0 | 24.7 | 54.4 | 1.6 | 2.7 | 7.3 | 1.8 | 7.4 |
| 2 | $MoO_x$ + MgAl-HT[c] | 8.2 | 18.2 | 42.2 | 1.5 | 2.2 | 9.3 | 3.3 | 23.2 |
| 3 | $MoO_x$ + AC[d] | 10.5 | 20.5 | 42.9 | 1.7 | 1.2 | 2.0 | 3.0 | 28.6 |
| 4 | $MoO_x$ + $SiO_2$ | 3.8 | 20.8 | 24.8 | 2.4 | 5.0 | 17.4 | 8.8 | 20.9 |
| 5 | $MoO_x$ + H-β | 10.7 | 12.6 | 6.4 | 3.8 | 17.5 | 30.2 | 12.6 | 16.9 |
| 6 | $MoO_x$ + H-ZSM-5 | 20.9 | 4.6 | 2.0 | 11.6 | 40.0 | 23.1 | 6.8 | 11.9 |

[a] The catalysts were prepared by the physical mixing the $MoO_x$ and various supports at the mass ratio of 3:17. To facilitate the comparison, the molar ratios of $SiO_2$:$Al_2O_3$ in H-β and H-ZSM-5 are 25:1. [b] Carbon oxides including CO and $CO_2$. [c] MgAl-HT: MgAl-hydrotalcite. [d] AC: acidic active carbon which was prepared by treating the active carbon with nitric acid.

**Table S6.** The amount of acid sites on the surfaces of different catalysts (measured by $NH_3$-TPD experiments).

| Catalyst | Amount of acid sites ($\mu$mol g$^{-1}$) |
| --- | --- |
| 10 wt% VO$_x$/SiO$_2$ | 371.3 |
| 10 wt% WO$_x$/SiO$_2$ | 370.3 |
| 10 wt% FeO$_x$/SiO$_2$ | 119.0 |
| 10 wt% CuO$_x$/SiO$_2$ | 175.4 |
| SiO$_2$ | 63.4 |
| 1 wt% MoO$_x$/SiO$_2$ | 89.1 |
| 5 wt% MoO$_x$/SiO$_2$ | 128.4 |
| 10 wt% MoO$_x$/SiO$_2$ | 181.7 |
| 15 wt% MoO$_x$/SiO$_2$ | 191.3 |
| 20 wt% MoO$_x$/SiO$_2$ | 139.7 |
| MoO$_x$ | 32.8 |
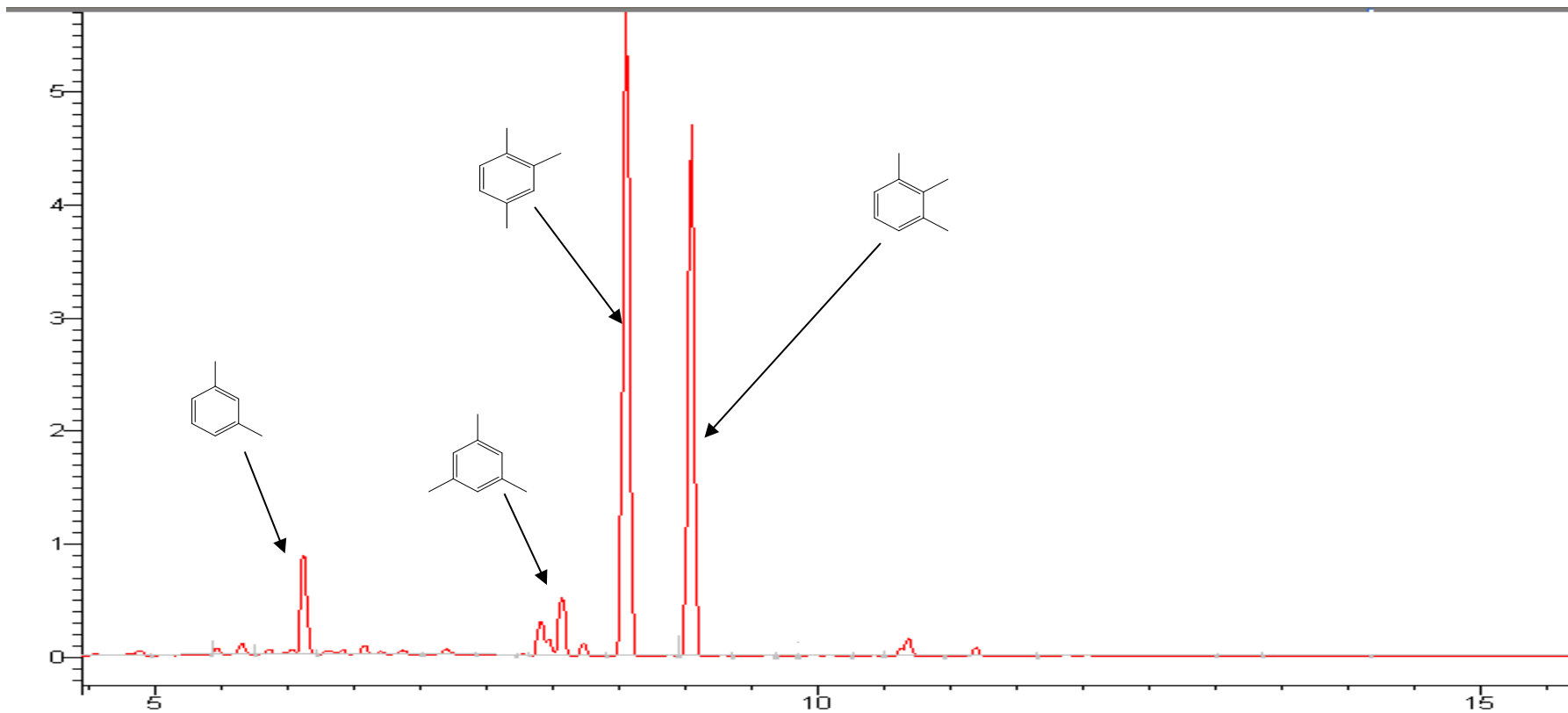
**Figure S1.** GC-MS spectrum of the liquid sample from the conversion of isophorone over the 10 wt% $MoO_x/SiO_2$ catalyst. Reaction conditions: 2.0 g catalyst, hydrogen flow rate: 80 mL $min^{-1}$, isophorone flow rate: 0.04 mL $min^{-1}$.
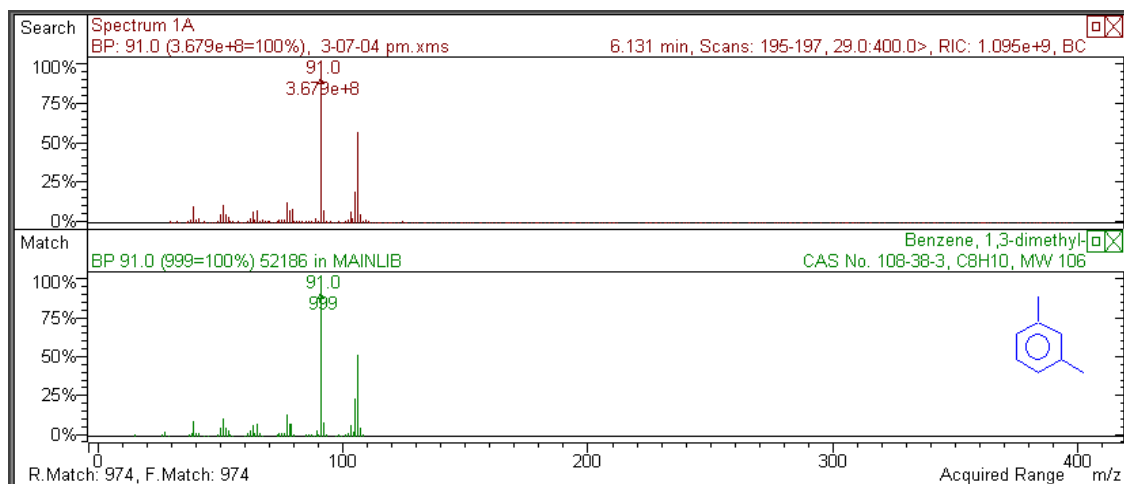
**Figure S2.** Mass spectrograms of the *m*-xylene from the conversion of isophorone over the 10 wt% $MoO_x/SiO_2$ catalyst.
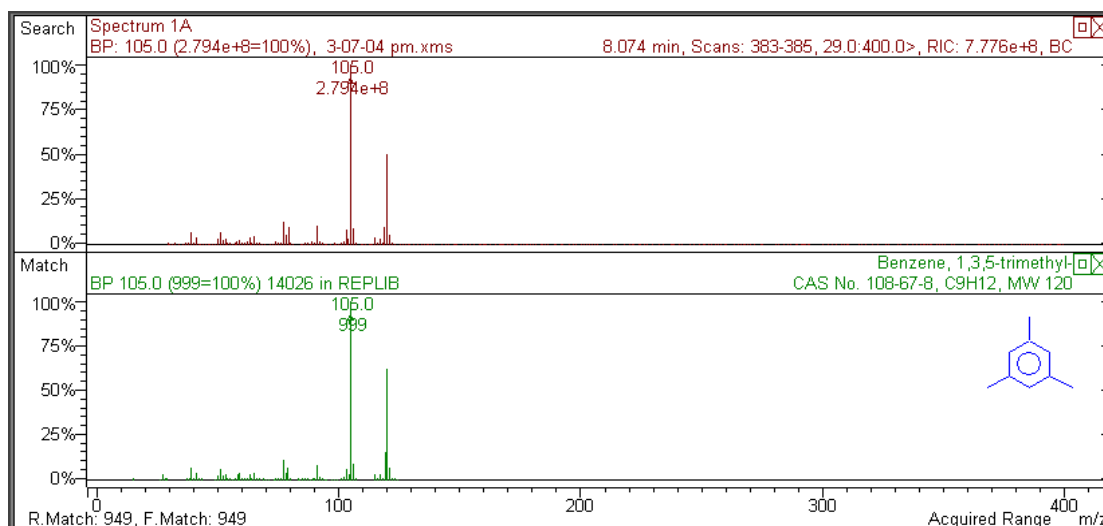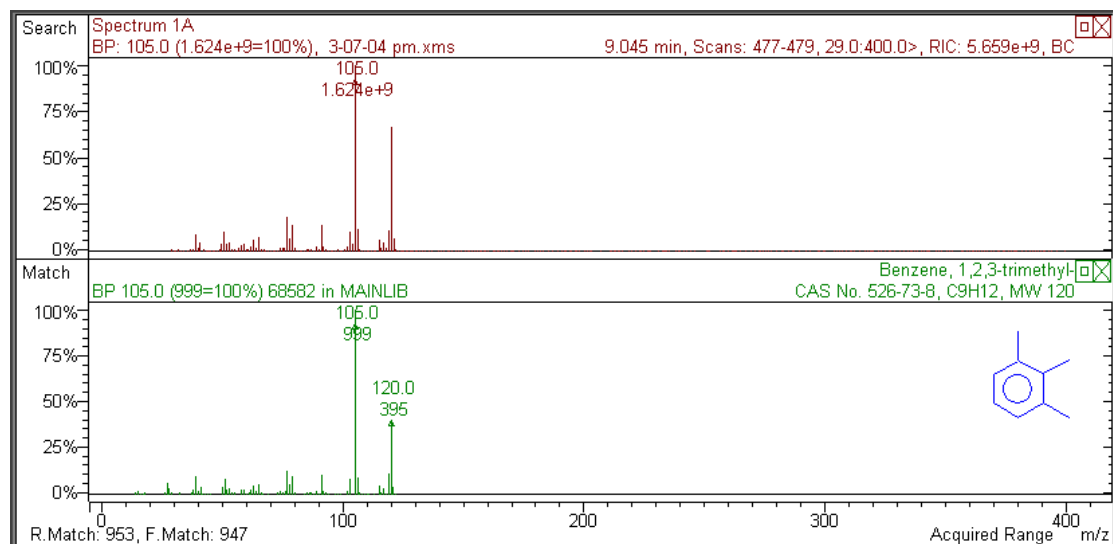
**Figure S3.** Mass spectrograms of the mesitylene from the conversion of isophorone over the 10 wt% MoO$_x$/SiO$_2$ catalyst.
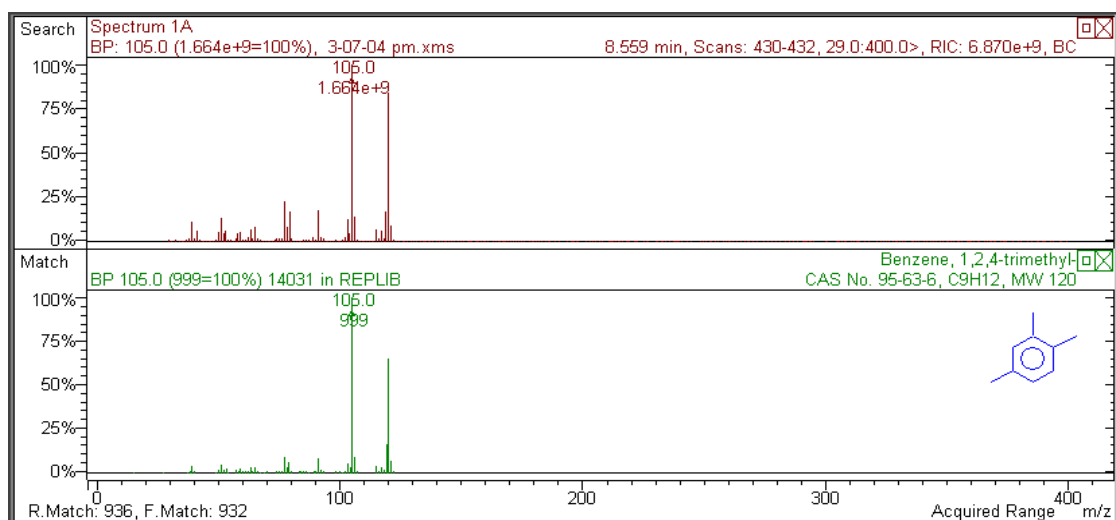
**Figure S4.** Mass spectrograms of the 1,2,4-trimethylbenzene from the conversion of isophorone over the 10 wt% MoO$_x$/SiO$_2$ catalyst.

**Figure S5.** Mass spectrograms of the 1,2,3-trimethylbenzene from the conversion of isophorone over the 10 wt% $MoO_x/SiO_2$ catalyst.
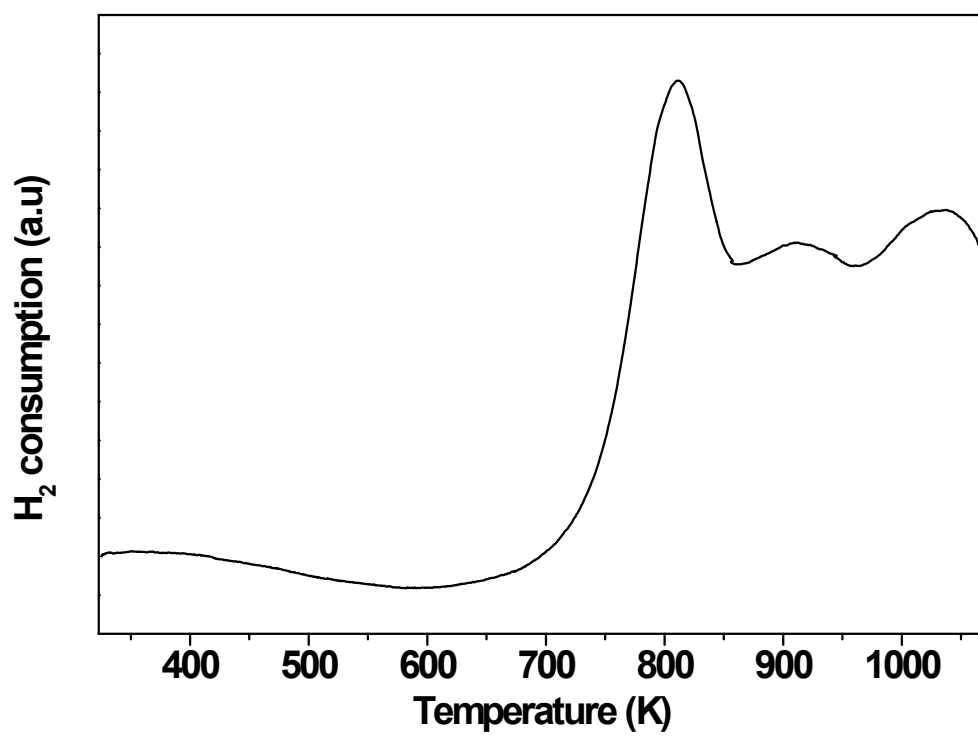
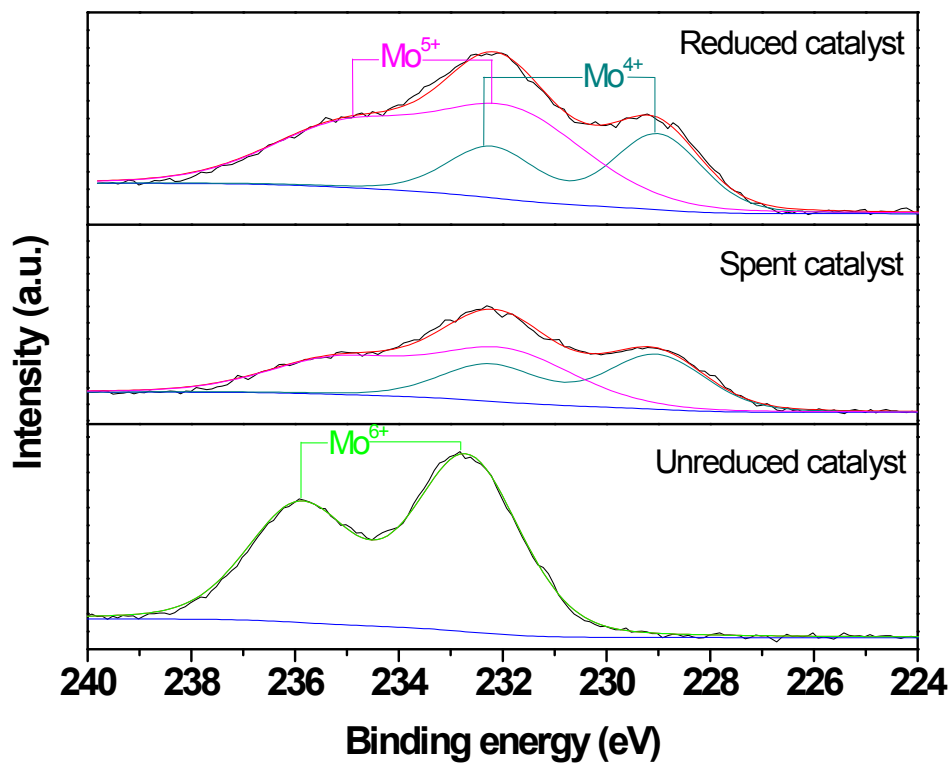**Figure S6.** $H_2$-TPR profile of the 10 wt% $MoO_x/SiO_2$ catalyst.
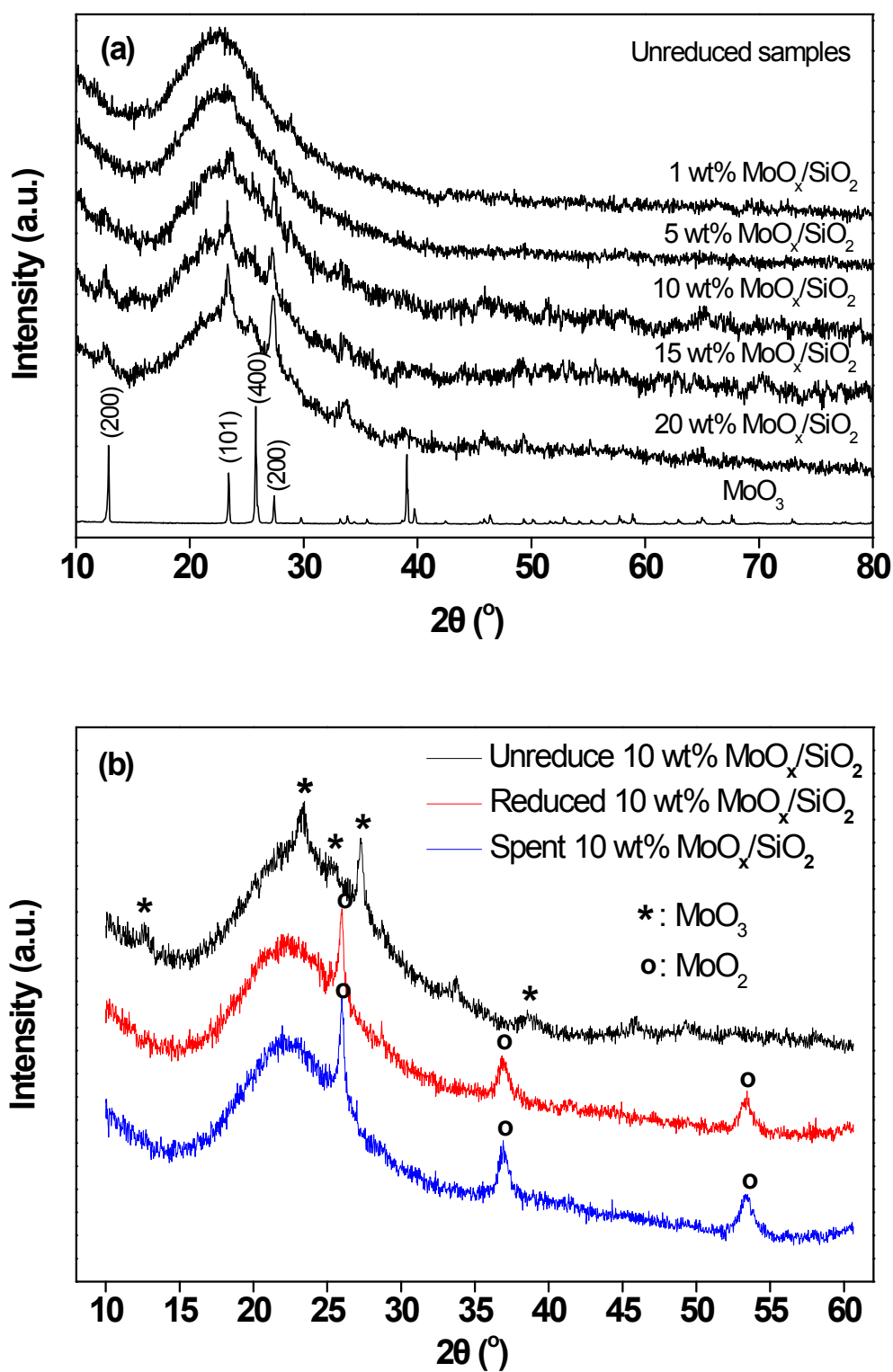
**Figure S7.** XRD patterns of the MoO$_x$/SiO$_2$ catalysts.

**Figure S8.** Mo 3d XPS spectra of the unreduced, reduced and spent 10 wt% $MoO_x/SiO_2$ catalysts.
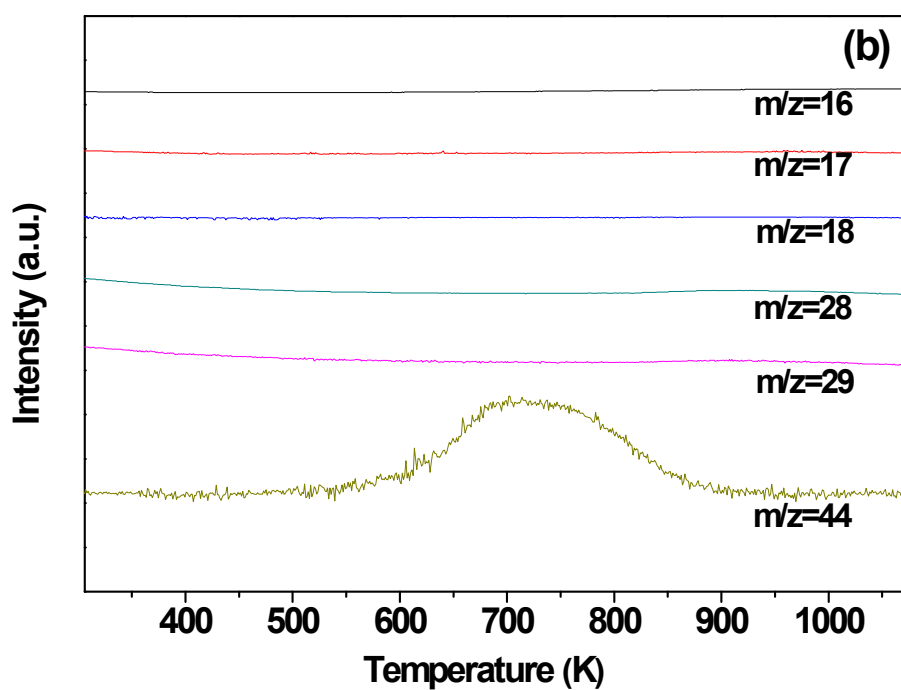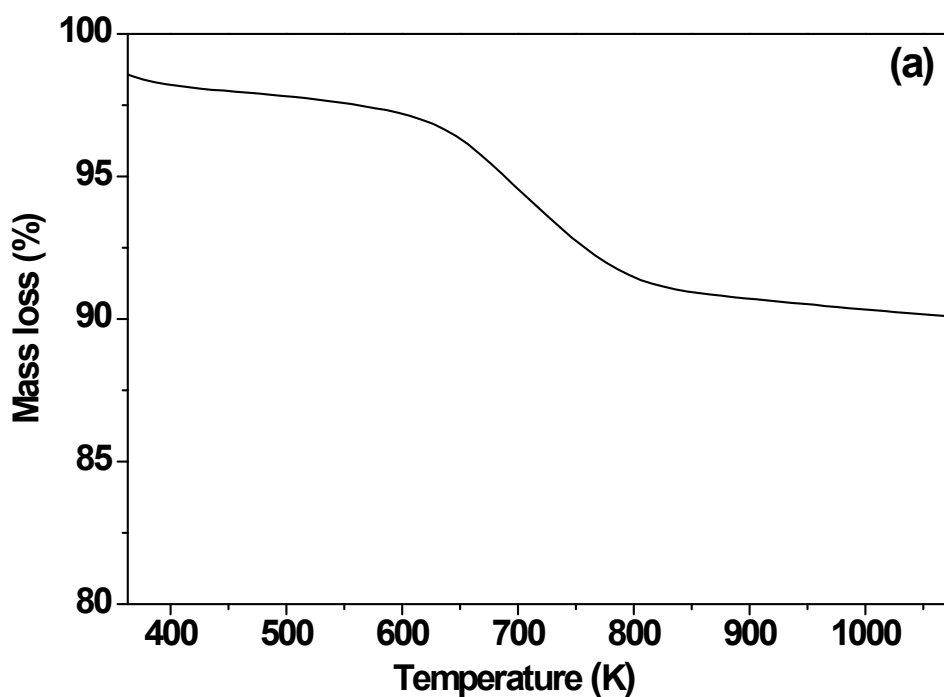
**Figure S9.** TG (a) and synchronous MS (b) profiles of the spent 15 wt% $MoO_x/SiO_2$ catalyst.

## References

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