Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information

Direct conversion of isopropanol to C_{6+} branched compounds as high-octane gasoline blendstock

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Experimental

Catalyst Synthesis

α-MoC was prepared through a two-step nitridation-carbonization process. Firstly, MoO_3 was obtained by calcinating $(NH_4)_2Mo_7O_{24}\cdot 4H_2O$ (>99.0%, Sinopharm Chemical) under air at 500 ℃ for 4 h. Then the nitridation of MoO_3 was carried out under 160 mL/min NH_3 flow at 700 ℃ for 2 h, with a ramping rate of 2 ℃/min. After cooling to room temperature, the NH_3 flow was switched to 20% CH_4/H_2 and the subsequent carbonization to α-MoC was conducted using the same program. For the synthesis of β-Mo_2C, MoO_3 was heated under 160 mL/min 20% CH_4/H_2 to 300 ℃ (5 ℃/min) and then to 700 ℃ (1 ℃/min) for 2 h. All catalysts were passivated under 25 mL/min 0.5% O_2/Ar for 12 h at room temperature before exposure to air. The α-MoC was labelled as MoC for simplicity.

For the synthesis of MoC supported metal catalyst, the passivated MoC was firstly activated in 40 mL/min 15% CH_4/H_2 at 590 ℃ for 2 h, then it was transferred (without exposing to air) to 10 mL aqueous solution with calculated amount of metal precursor. After stirring at room temperature for 2 h, the sample was dried using rotary evaporator at 45 ℃ and kept in glove box before reaction. The metal precursors used in this work are $Ni(NO_3)_2\cdot 6H_2O$ (Aladdin, 98%), $PdCl_2$ (Alfa, 99.999%), $Cu(NO_3)_2\cdot 6H_2O$ (Aladdin, 99%),

$HAuCl_4 \cdot 4H_2O$ (Macklin, 49 wt.% Au), $IrCl_3$ (Aladdin, 99.9%), $H_2PtCl_6 \cdot 6H_2O$ (Macklin, Pt⩾37.5 wt.%), $RuCl_3 \cdot 3H_2O$ (Macklin, 98%), $RhCl_3 \cdot 3H_2O$ (Aladdin, Rh⩾39.5 wt.%).

Catalytic reactions

The isopropanol condensation reaction was carried out in a 100 mL stainless steel autoclave. The catalyst was activated at 590 ℃ under 15% CH_4/H_2 for 2 h, and then transferred into the cyclohexane solution of isopropanol at room temperature. After purging with 5% Ar/N_2, the pressure of the reactor was raised to 1 MPa with 5% Ar/N_2 (Ar as internal standard for gas product analysis) and then the system was heated to the reaction temperature, with a stirring speed of 500 rpm. After reaction, the gas products were analyzed by the gas chromatograph of Agilent 7820A with a thermal conductivity detector (TCD, connected by the column of Porapark Q and 5 Å molecular sieves). The liquid products were analyzed using the gas chromatograph (Agilent 7820A) with a FID and an INNOWWAX column. n-Heptane was introduced as the internal standard for liquid products analysis.

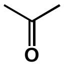
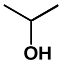
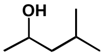
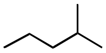
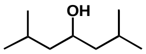
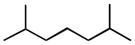
Catalyst Characterization

The metal loadings of MoC supported metal catalysts were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES). X-ray diffraction (XRD) was conducted using the Rigaku D/MAX-PC 2500 powder X-ray diffractometer (40 kV, 100 mA), with a radiation source of Cu Kα. The scan ranges from 20 ° to 80 °, with a speed of 8 °/min.

Ammonia-temperature programmed desorption (NH_3-TPD) was performed on a fix-bed reactor with a mass spectrometer detector (MS, AMETEK). Before the adsorption, 50 mg catalyst was activated at 590 ℃ under 15% CH_4/H_2 for 2 h and then cooled to room temperature. Subsequently, 10% NH_3/He was introduced to the system and kept for 30 min, with a flow rate of 20 mL/min. After that, the catalyst was purged with Ar (30 mL/min) for 30 min. After the baseline was steady, the temperature of catalyst bed was raised to 700 ℃ with a ramping rate of 10 ℃/min, and the signal of NH_3 (m/z = 17) was recorded.

Isopropanol-TPD experiments were also carried out on the apparatus above. After the activation of catalyst under 15% CH_4/H_2 and cooling to 50 ℃, the gas was switched to 30 mL/min Ar to purge out residual CH_4/H_2. Then isopropanol was introduced to the system by bubbling of Ar and kept for 2 h. After that, the catalyst was purged again by Ar for 30 min, followed by the TPD process to 400 ℃ (2 ℃/min). The signals of isopropanol (m/z=45), propylene (m/z=42), acetone (m/z=58) and H_2 (m/z=2) were recorded by MS during TPD.

Table S1 Estimated lower heating value and research octane number of typical components of the products.

components						
lower heating value[a] (MJ/kg)	28.6	30.5	35.8	44.7	38.1	44.2
research octane number[b] (RON)	--	--	102	54	93	30

[a] Estimated using Aspen Plus (V11.0)

[b] Predicted by Andrew D. Sutton et al.[1]

We estimate the energy density of typical components of the products using Aspen Plus. The energy density here is defined as lower heating value. As shown in Table S1, the lower heating value of oxygenated chemical is enhanced with increasing the carbon chain length. And if the oxygen is moved, this value will be higher. For the octane number, some of the values are predicted by Sutton et al.[1], and presented here in Table S1. We can see that the RONs of oxygenated C_{6+} compounds are high. Although C_{6+} alkanes have relatively lower RONs, it is still acceptable when used as blend in gasoline because branched alkanes have higher RONs than linear ones when they have a same carbon number. Based on these results, the products in this work can be used as gasoline blendstock, which meet the requirements of both high energy density and octane number.

Table S2 Ni concentration of typical Ni/MoC samples measured by ICP-AES.

Catalyst	Ni loading measured by ICP-AES (%)
MoC	0.00
1.2Ni/MoC	1.03
2.4Ni/MoC	2.04

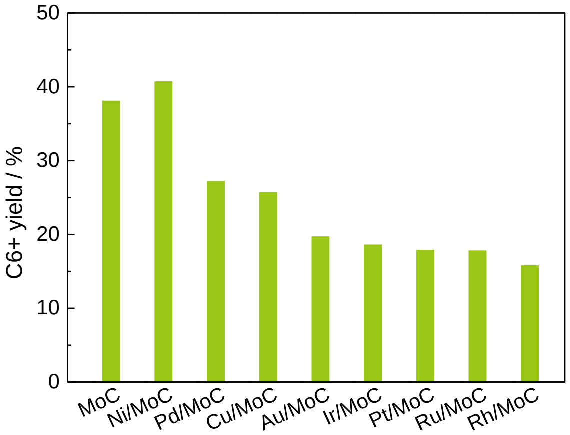


Fig. S1 C_{6+} yield over various MoC supported metal catalysts. The loading amount of Ni is 0.3 wt.%, and the metal loadings on other catalysts are the same with that on Ni/MoC by mole amount, with the weight loading of 0.5% (Pd), 0.3% (Cu), 1.0% (Au), 1.0% (Ir), 1.0% (Pt), 0.5% (Ru), 0.5% (Rh), respectively. Reaction conditions: isopropanol 5 g, cyclohexane 35 g, catalyst 50 mg, N_2 1 MPa, 250 ℃, 500 rpm, 6 h

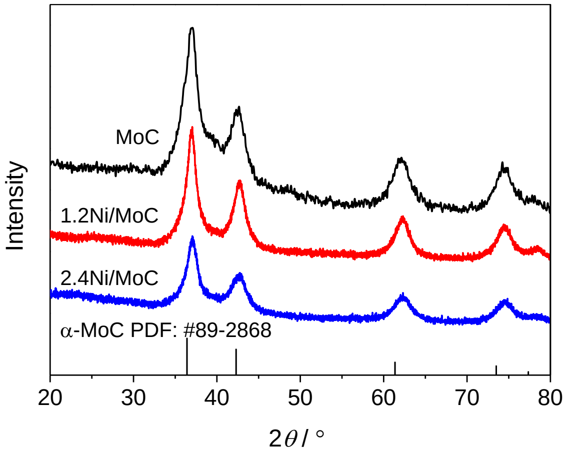


Fig. S2 XRD patterns of Ni/MoC catalysts.

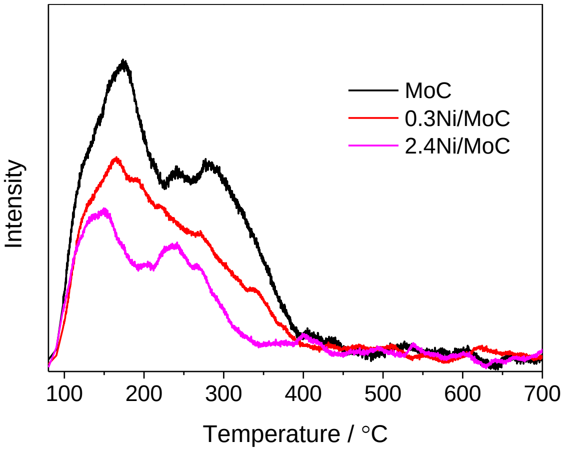


Fig. S3 NH_3-TPD curves of Ni/MoC catalysts.

NH_3-TPD results above show that the NH_3 desorption intensity is decreased with the increase of Ni amount. Moreover, MoC shows two peak center of NH_3 desorption at 173 ℃ and 281 ℃, while they move to lower temperature at 149 ℃ and 237 ℃ on 2.4Ni/MoC. The results indicate that the acid amount and acid strength decrease with the addition of Ni, consistent with results from benzaldehyde-acetone condensation reaction (Fig. 4) and isopropanol-TPD characterization (Fig. 5).

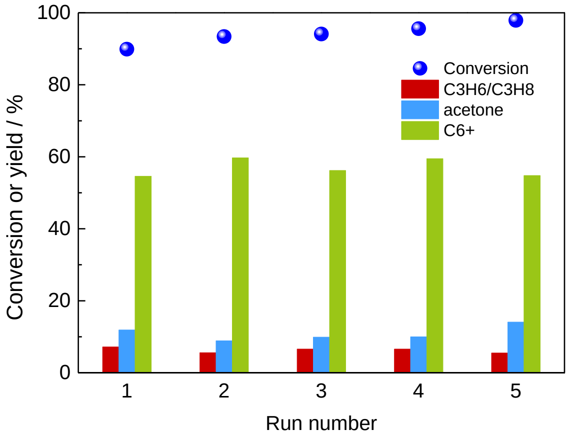


Fig. S4 Reusability test of 1.2Ni/MoC catalyst. Reaction conditions: isopropanol 2 g, cyclohexane 38 g, catalyst 100 mg, N_2 1 MPa, 250 ℃, 500 rpm, 3 h.

References

[1] C. M. Moore, R. W. Jenkins, M. T. Janicke, W. L. Kubic, E. Polikarpov, T. A. Semelsberger and A. D. Sutton, *ChemSusChem*, 2016, **9**, 3382-3386.