

Experimental

The commercial Ni-Mo Catalyst was purchased from Sud Chemical India Ltd., New Delhi and Ni-Mo supported on alumina commercial catalyst with a Ni and Mo wt % of 1.8 and 6.5 was used for this reaction. Temperature programmed reduction (TPR) were carried out on the catalyst samples using the Micromeritics 2920 Autochem II Chemisorption Analyser. Prior to the reduction of the sample in TPR, the catalyst was pre-treated by heating under a stream of argon (50 mL/min) at 300 °C for 30 min and then cooled to room temperature. Thereafter, 4.9 % hydrogen in argon was used as a reducing agent at a flow rate of 50 mL/min. Samples were analysed from room temperature to 650 °C using a ramp rate of 5 °C/min. In order to determine the oxygen capacity and oxygen mobility of the catalyst, temperature programmed reoxidation (TPRO) experiments were carried out. For the TPRO experiment, each catalyst was reduced by carrying out using methane (5 % CH₄ in He) with a flow rate of 50 mL/min at 500 °C for 2 h in the absence of oxygen feed in order for the catalyst to consume lattice oxygen. After that the temperature was cooled down to 60 °C, then an appropriate oxidant (10 % O₂ in He, 10 % N₂O in He, 10 % H₂O in He) with a flow rate of 50 mL/min was passed through the catalyst while the temperature was raised to 600 °C at a heating rate of 5 °C/min. The amount of oxidant consumed was measured using a thermal conductivity detector. The physisorption analyses were carried out by degassing the catalysts under N₂ flow for 2 h at 200 °C. The degassed samples were analyzed in a Micromeritics ASAP 2020. Powder X-ray diffraction (XRD) studies were conducted using a PAN analytical X'Pert Pro instrument. Scans from 10 to 90° were carried out using a Cu K α radiation source a wavelength of 1.5406.

Metal dispersion on the surface of the catalyst was measured using O₂-Pulse chemisorption also performed by an AutoChemII 2920 station from Micromeritics in the method illustrated in ¹. The sample (300 mg) were pre-treated under 5% H₂ in Ar a temperature of 500 °C for 2 h. Then, catalyst was cooled down to 80 °C under an He flow of 50 mL/min. O₂-Pulse chemisorption was performed at a temperature of 400 °C. The volume of the injection loop was 0.5 cm³. The carrier gas was Ar in the case of O₂ pulses (10 % O₂ in Ar,) and pulses of O₂ were injected in the catalytic reactor corresponding to 0.5 μ mol of O₂. The O₂ consumption was measured with the same TCD used for TPR equipped with water trap. Pulses injection, sample temperature and TCD signals were controlled and monitored by a computer equipped with the software Micromeritics AutoChemII.

Particle size, morphology and elemental mapping, performed by EDXS analysis, were further investigated using Cs-corrected scanning transmission electron microscope (TEM) (JEOL, JEM-ARM200CF), equipped with JEOL Centurio 100 mm² EDXS system.

The partial oxidation (POX) of methane experiments using the current catalyst were carried out in a reactor described in ¹. Prior to reaction, each catalyst was pre-treated in situ with flowing He (50 mL/min) at 500 °C for 1 h. The reaction was performed at different temperatures from 200 to 400 °C, in steps of 50 °C. The methane to oxidant ratio (O₂ or H₂O or N₂O) was varied from 1 to 2.75. The experiments were conducted at a W/F ratio of 0.3 at a fixed oxidant ratio and temperature. During the methane oxidation reaction, the product stream—comprising methane, methanol, hydrogen, carbon oxides, and nitrogen—was analyzed using an online Perkin Elmer Clarus 500 gas chromatograph equipped with a thermal conductivity detector (TCD) and a quadrupole mass spectrometer (MS). The signals from the TCD and MS were calibrated with varying mole fractions of methane, hydrogen, methanol, carbon oxides, and nitrogen to accurately determine the mole composition of the gases in the product stream. No other gaseous products were detected during the reaction. Blank experiments were done under the same catalytic conditions and carbon balances ranged between 98 and 100% and all data points were obtained in duplicate with an error of ±1%.

The methane conversion (ϕ) was calculated using the following equation:

$$CH_4 \text{ Conversion } (\phi_{CH_4} \text{ mol } \%) = \frac{([CH_4]_{in} - [CH_4]_{out})}{[CH_4]_{in}} \times 100$$

$$N_2O \text{ Conversion } (\phi_{CH_4} \text{ mol } \%) = \frac{[N_2]_{out}}{[N_2O]_{in}} \times 100$$

$$MeOH \text{ Selectivity } (S_{MeOH} \text{ mol } \%) = \frac{[MeOH]_{out}}{\text{total moles of carbon products}} \times 100$$

The amount of coke present on the surface of the used catalyst was determined by using CHNS analysis.

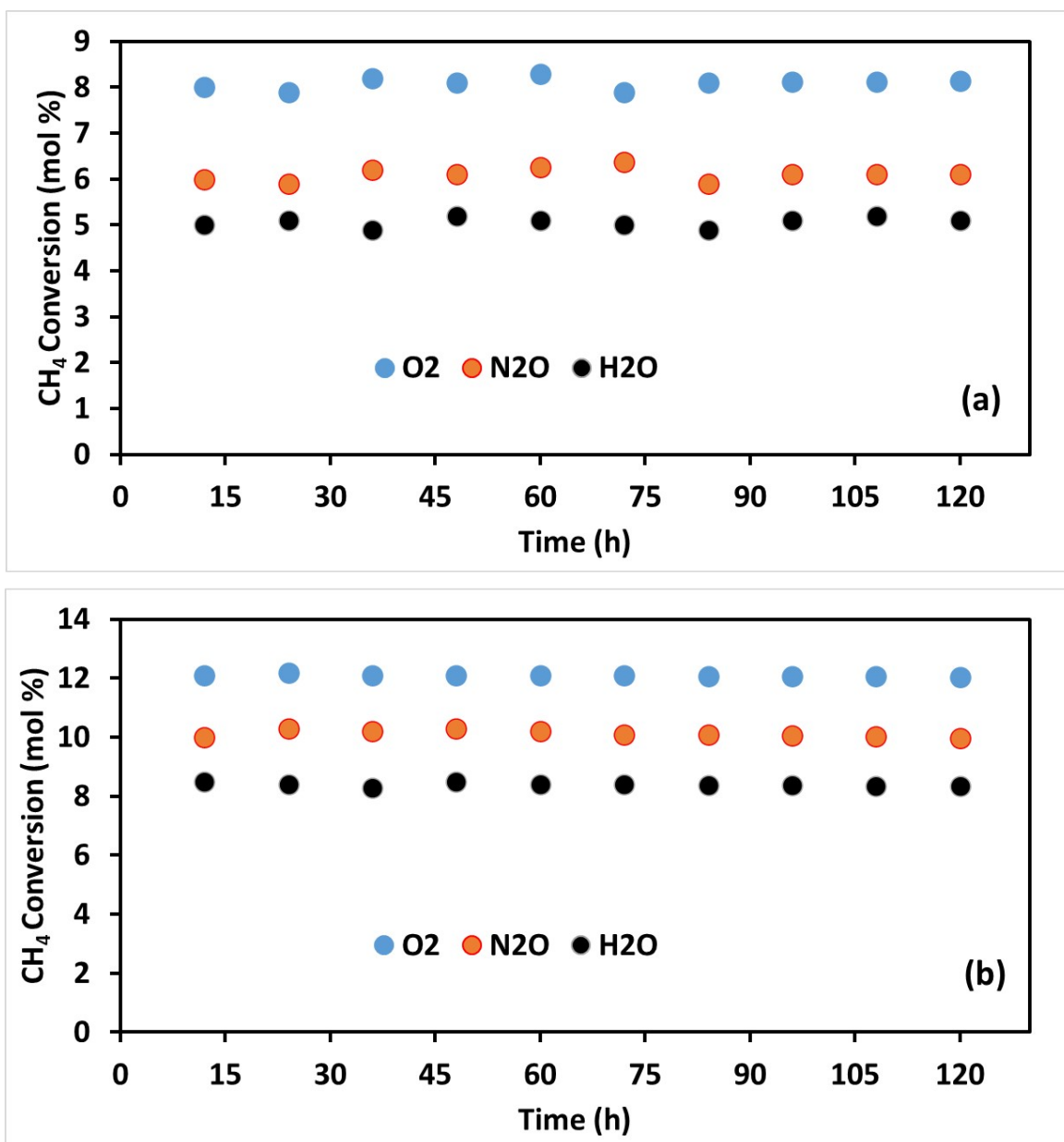


Figure S1: CH₄ Conversion as a function of time at (a) 250 °C and (b) 350 °C (oxidant to molar ratio of 2 and GHSV = 12680 h⁻¹)

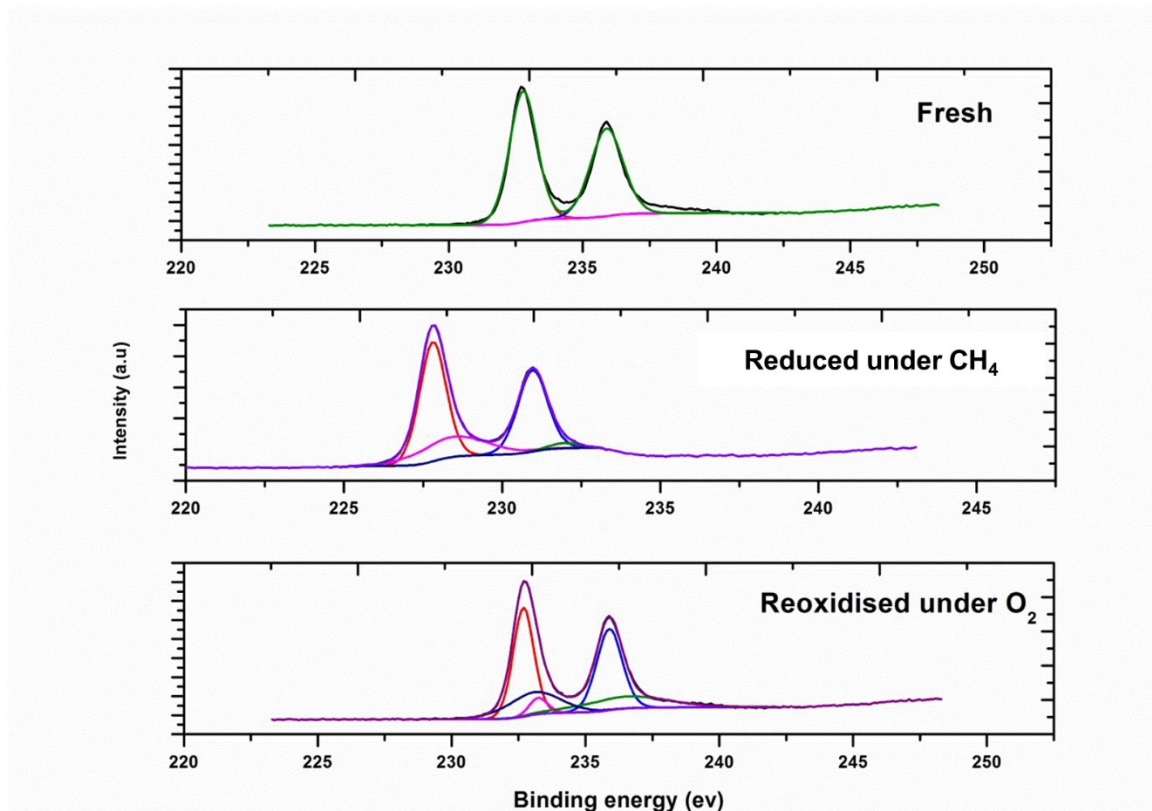


Figure S2: XPS high-energy resolution spectra Mo 3d spectra of fresh, reduced and re-oxidised Ni-Mo/Al₂O₃ catalyst.

References:

1. V. D. B. C. Dasireddy, M. Hus and B. Likozar, *Catal. Sci. Tech.*, 2017, DOI: 10.1039/C7CY01033H.