Scheme 1. Reaction mechanism for fatty acid methyl ester reduction using methanol as proton donor and sodium borohydride as hydride donor.

$$CH_3\text{-}(CH_2)_7\text{-}CH=CH\text{-}(CH_2)_7\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}CH_3 \ + \ NaBH_4 \ + \ 3\,CH_3\text{-}O\text{-}H \longrightarrow CH_3\text{-}(CH_2)_7\text{-}CH=CH\text{-}(CH_2)_7\text{-}CH_2\text{-}OH \ + \ NaB(OCH_3)_4 \ + \ 2\,H_2$$

Methyl oleate (MO)   Sodium borohydride   Methanol   Oleyl alcohol (OA)   Sodium tetramethoxyborate
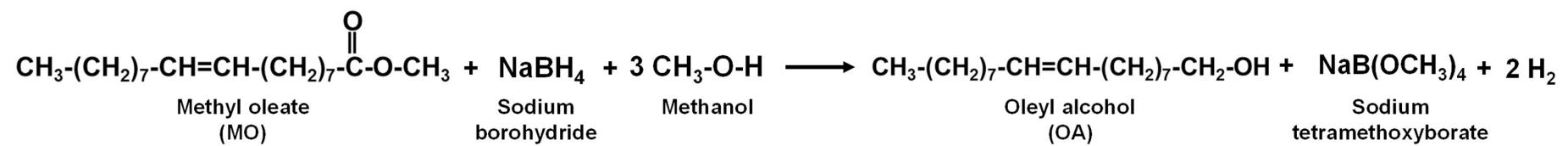
Scheme 2. Stoichiometry of oleyl alcohol (OA) synthesis reaction from methyl oleate, methanol and sodium borohydride.

2 CH_3OH

2 H_2 2 CH_3OH

2 H_2 2 CH_3OH

2 H_2 2 CH_3OH

P2

P4
2 $[B(OCH_3)_4]^-$

2 $[BH_4]^-$ → TS1 → 2 $[BH_3(OCH_3)]^-$ → TS2 → 2 $[BH_2(OCH_3)_2]^-$ → TS3 → 2 $[BH(OCH_3)_3]^-$ → TS4 →

P1

P3

+
2 H_2

CH_3COOCH_3
R4

TS5

TS6

$BH(OCH_3)_2$
+
$(OCH_3)^-$

P5 CH_3-CHO

$[BH_2(OCH_3)_2]^-$

TS7

$BH(OCH_3)_2$

$(OCH_2CH_3)^-$

TS8 H^+

CH_3-CH_2-OH
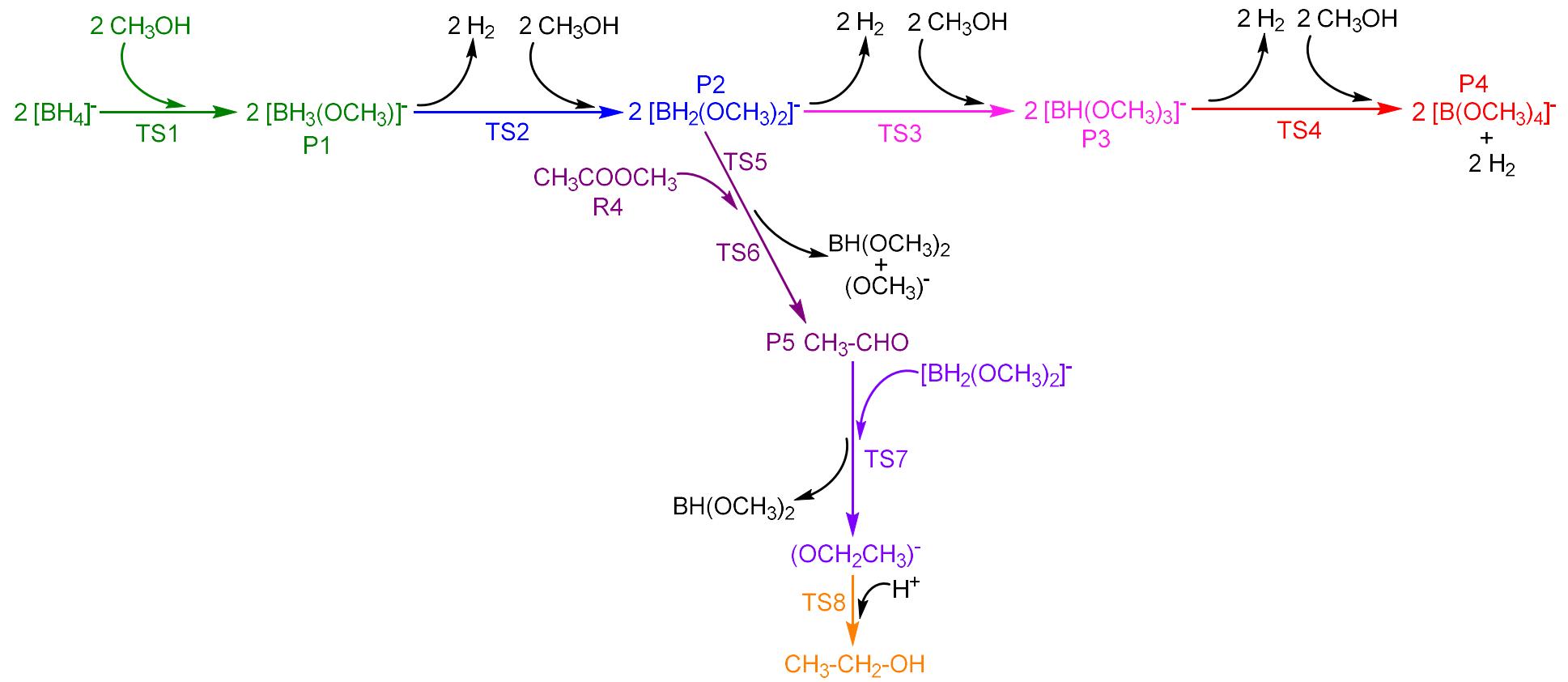
Scheme 3. Possible mechanisms involved in the methyl acetate reduction reaction used for DFT calculations.
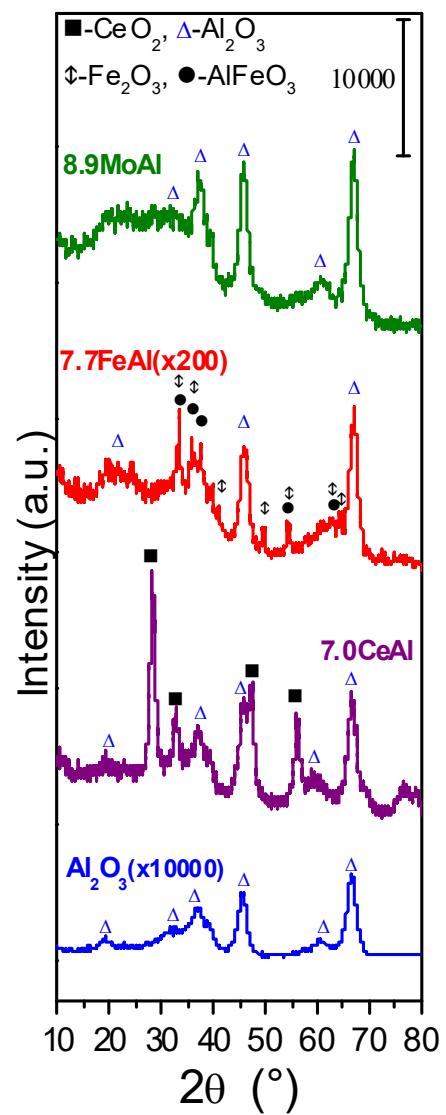
Figure 1. Diffractograms obtained on *x*MAl samples.
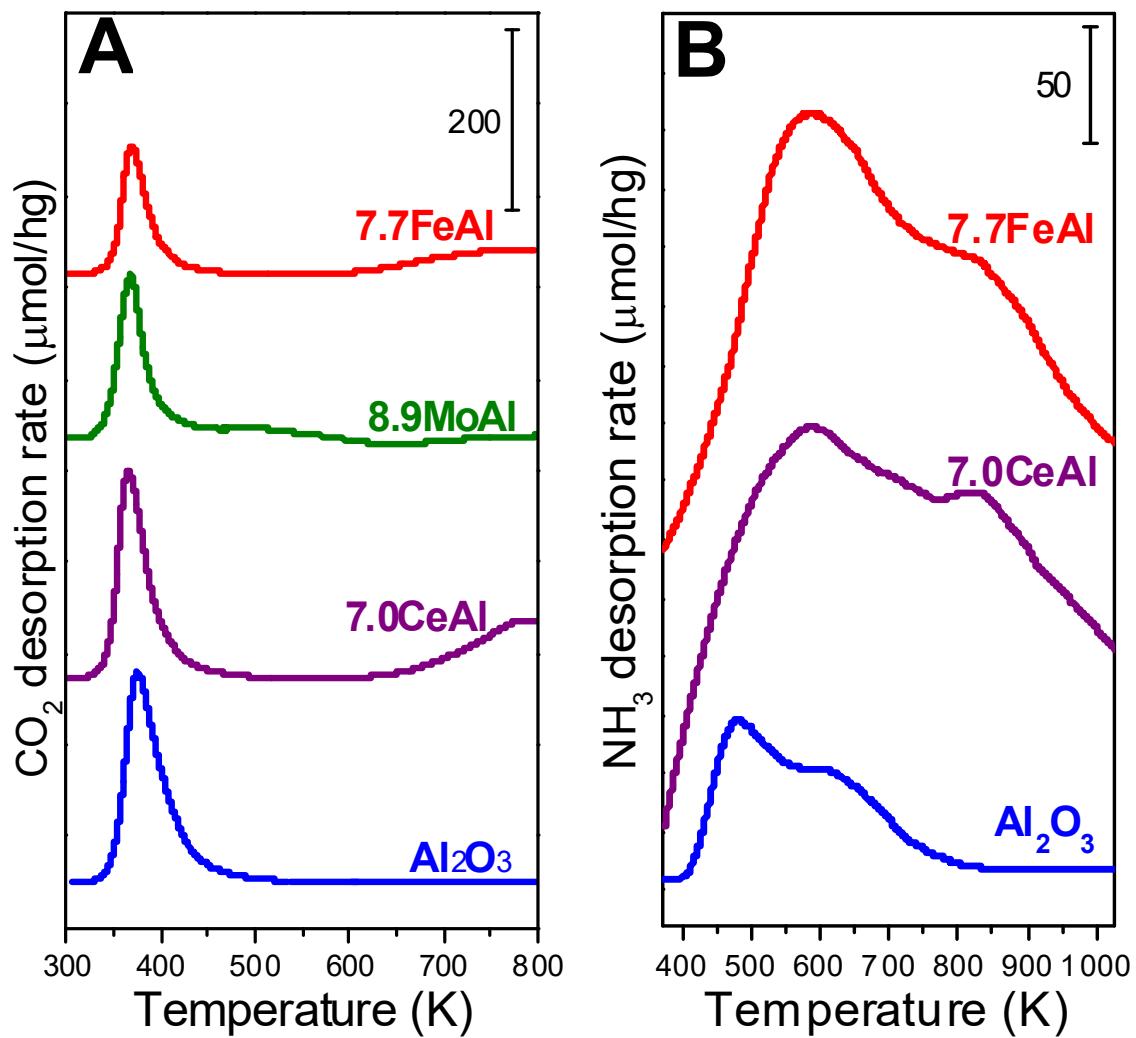
**Figure 2.** CO_2 TPD (A) and NH_3 TPD (B) profiles for xMAl solids.
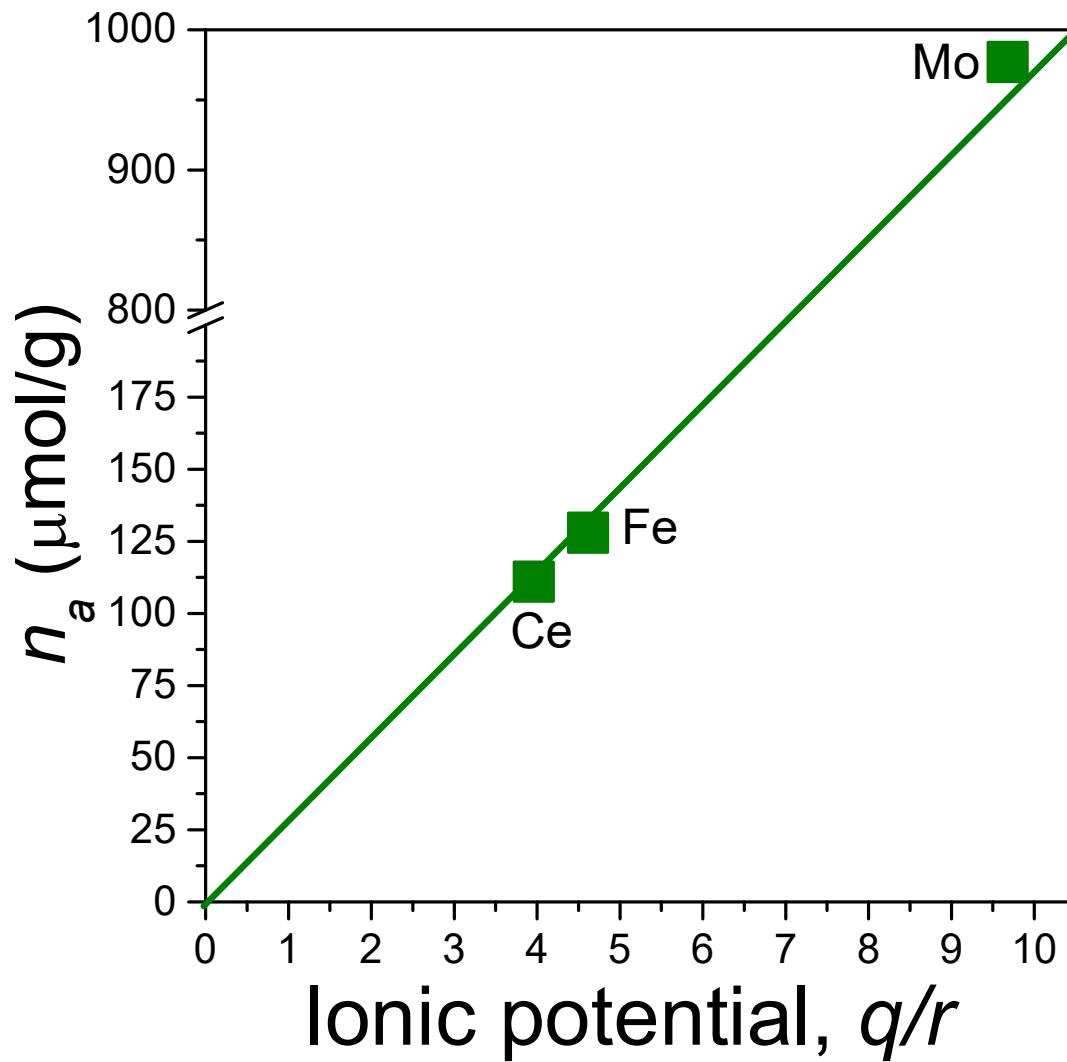
**Figure 3.** Relation between n_a and q/r for xMAl catalysts.
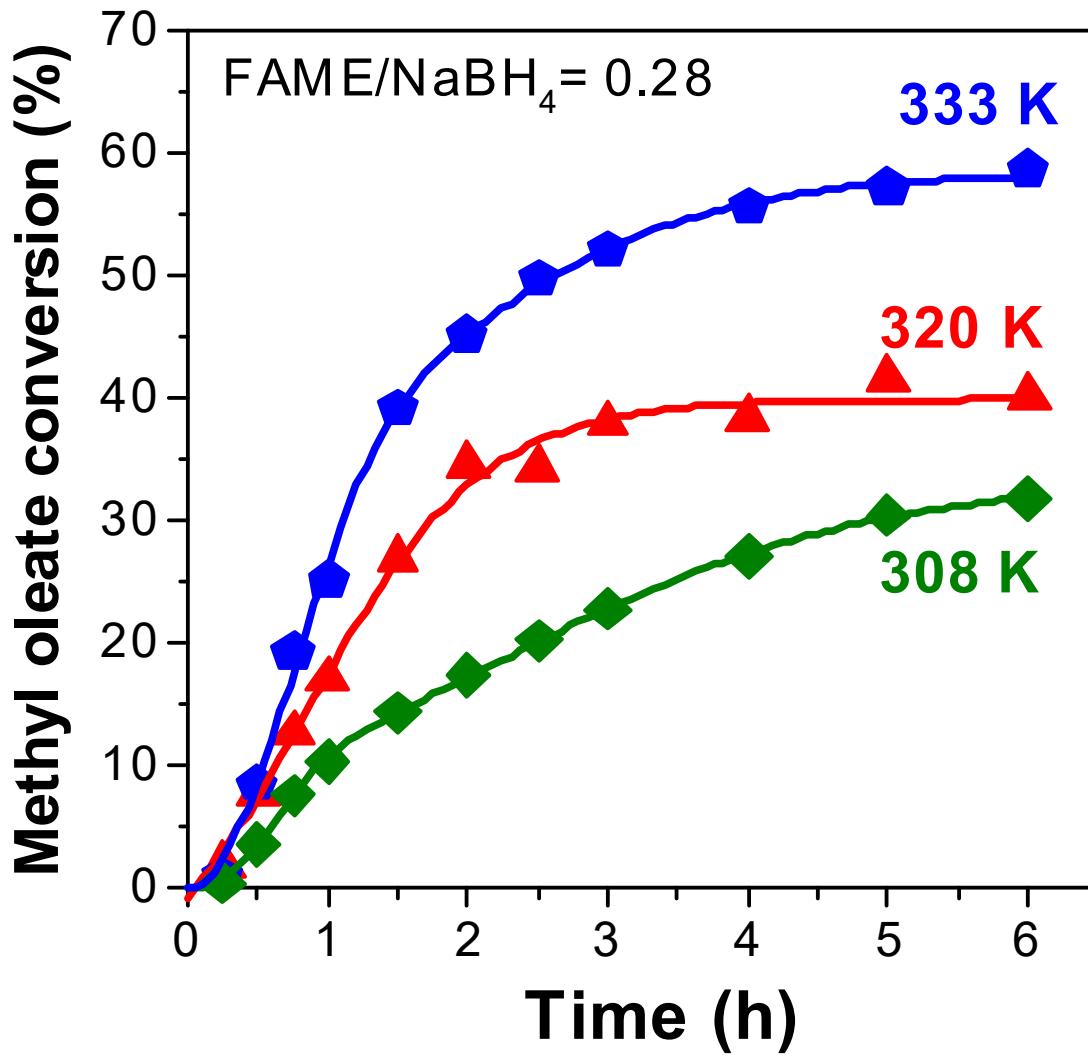
Figure 4. Effect of reaction temperature during methyl oleate conversion to oleyl alcohol (T = 308 K, 320 K, 333 K; FAME/NaBH$_4$ molar ratio = 0.28; methanol/NaBH$_4$ molar ratio = 6.0; NaBH$_4$ as reducing solid).
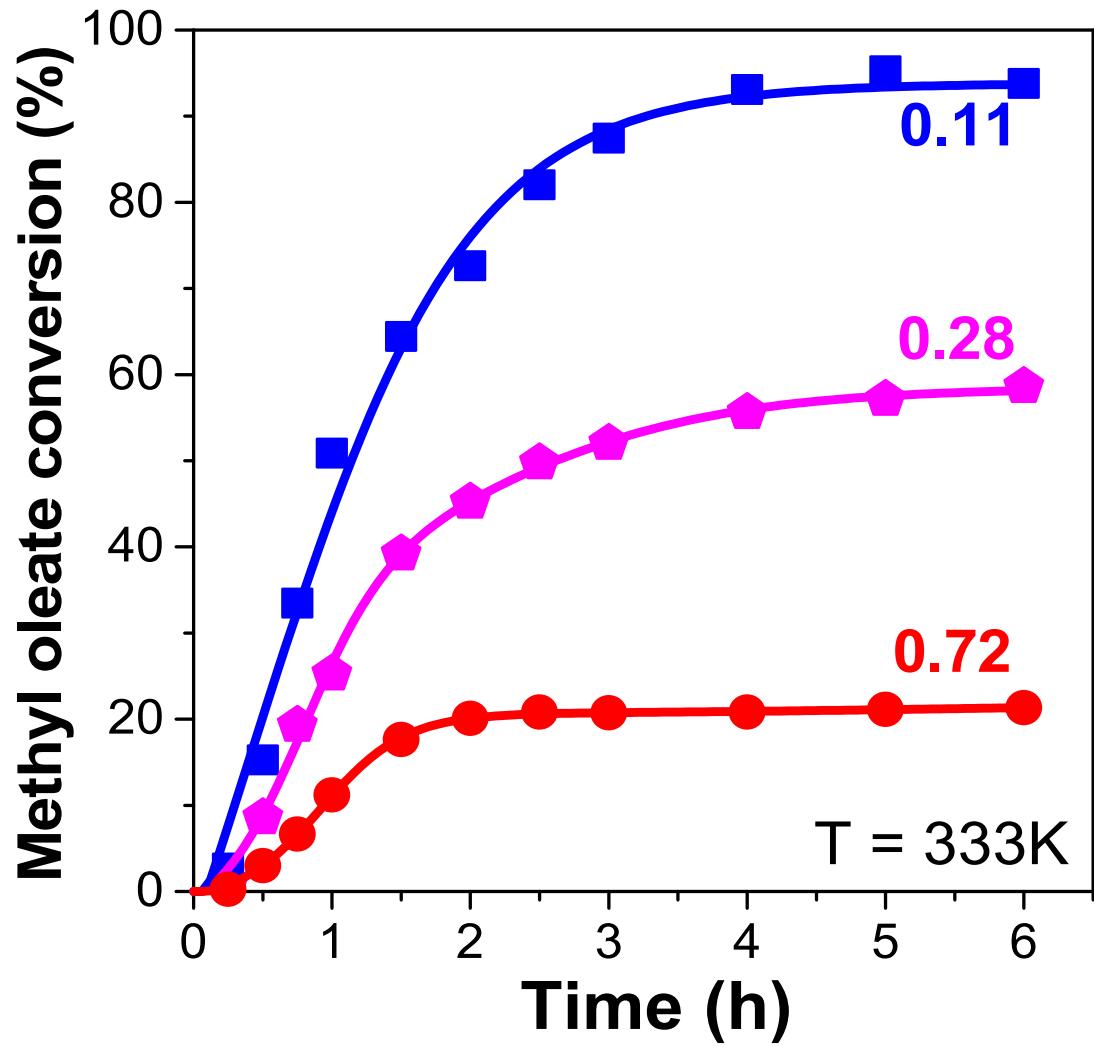
Figure 5. Effect of varying FAME/NaBH$_4$ molar ratio during methyl oleate conversion to oleyl alcohol (T = 333 K; methanol/NaBH$_4$ molar ratio = 6.0; NaBH$_4$ as reducing solid).
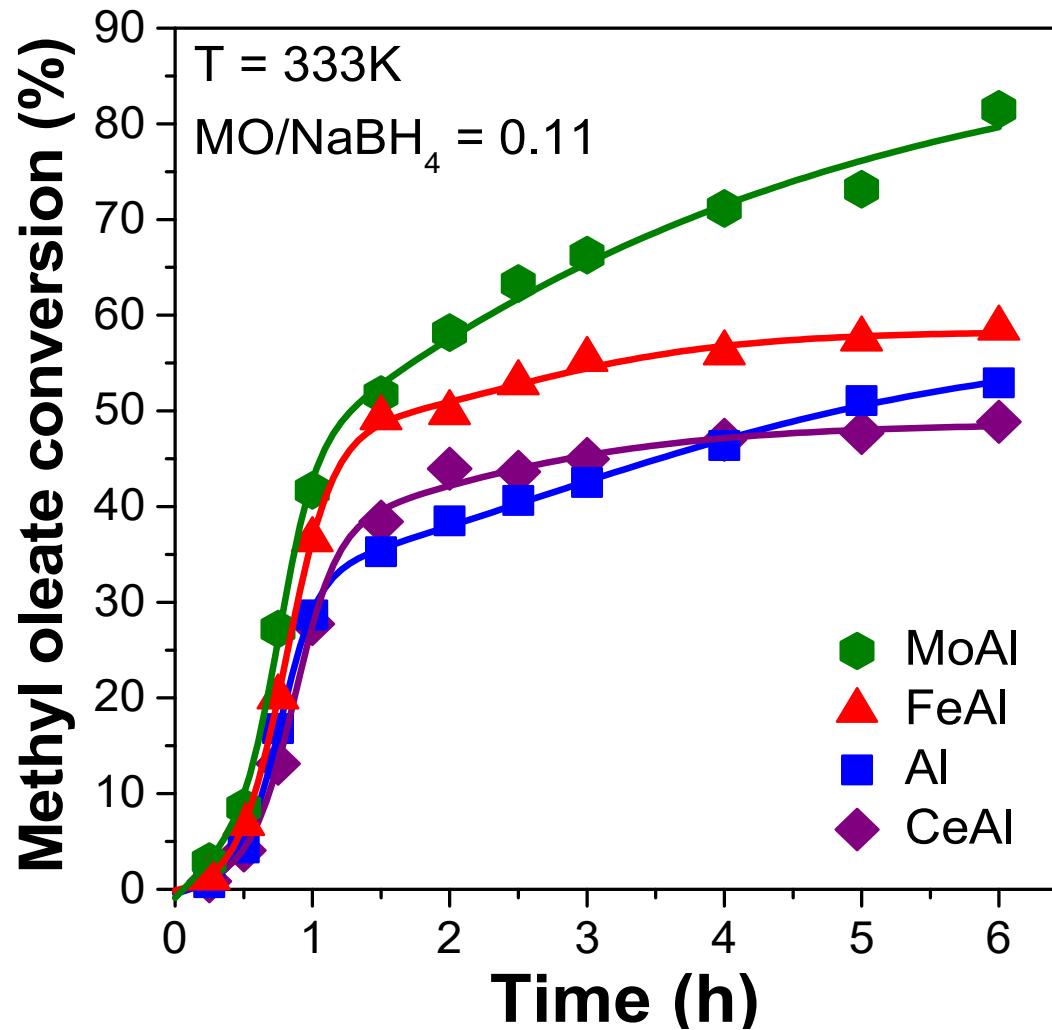
**Figure 6.** MO conversion as a function of reaction time on xMAl catalysts (T = 333 K; $MO/NaBH_4$ molar ratio = 0.11; methanol/$NaBH_4$ molar ratio = 6.0; $NaBH_4$/MAl as reducing solid).
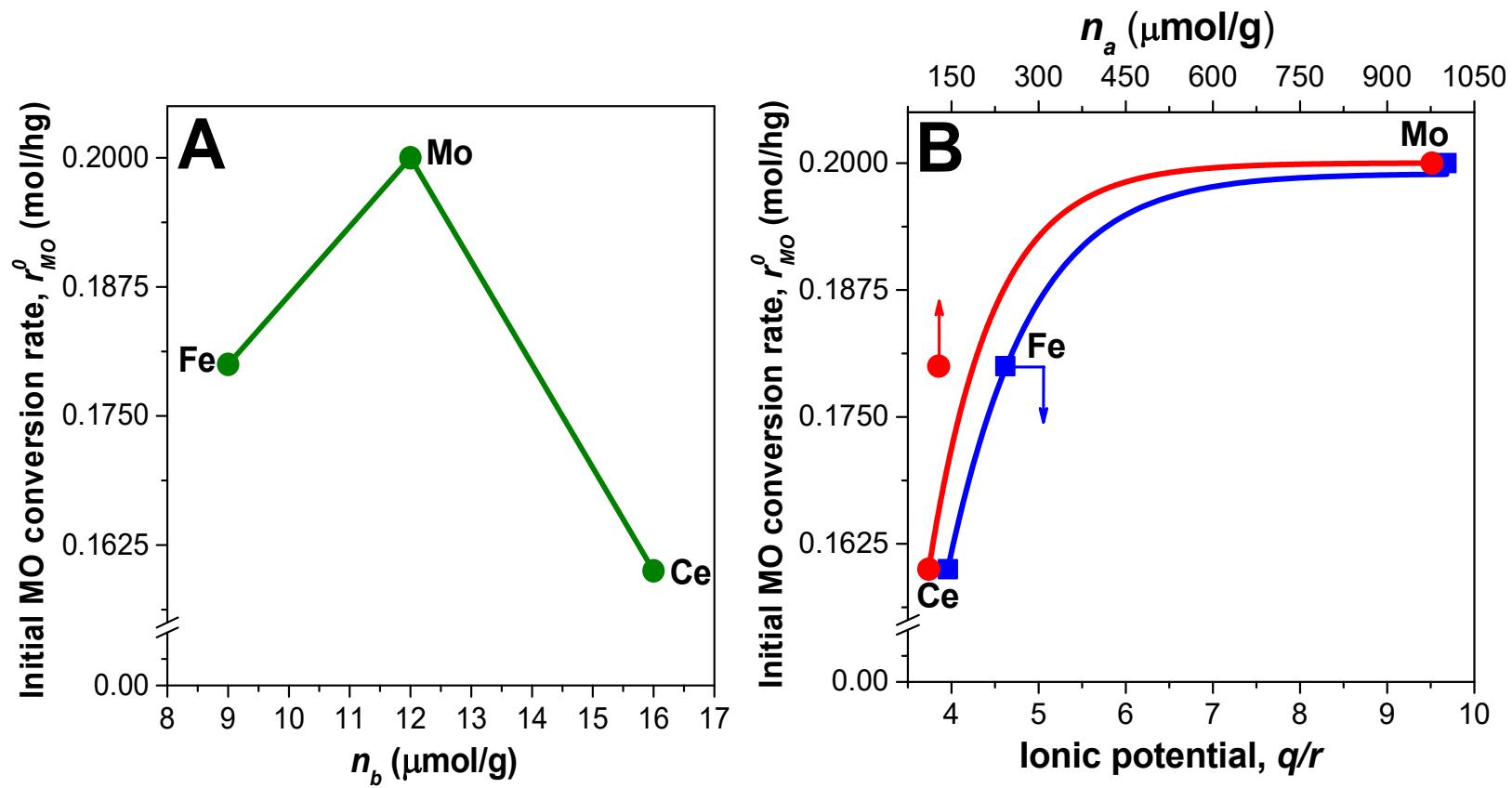
**Figure 7.** Relation between r^0_{MO} and n_b (A) and, r^0_{MO} and q/r and n_a (B) for xMAl catalysts (T = 333 K; MO/NaBH$_4$ molar ratio = 0.11; methanol/NaBH$_4$ molar ratio = 6.0).
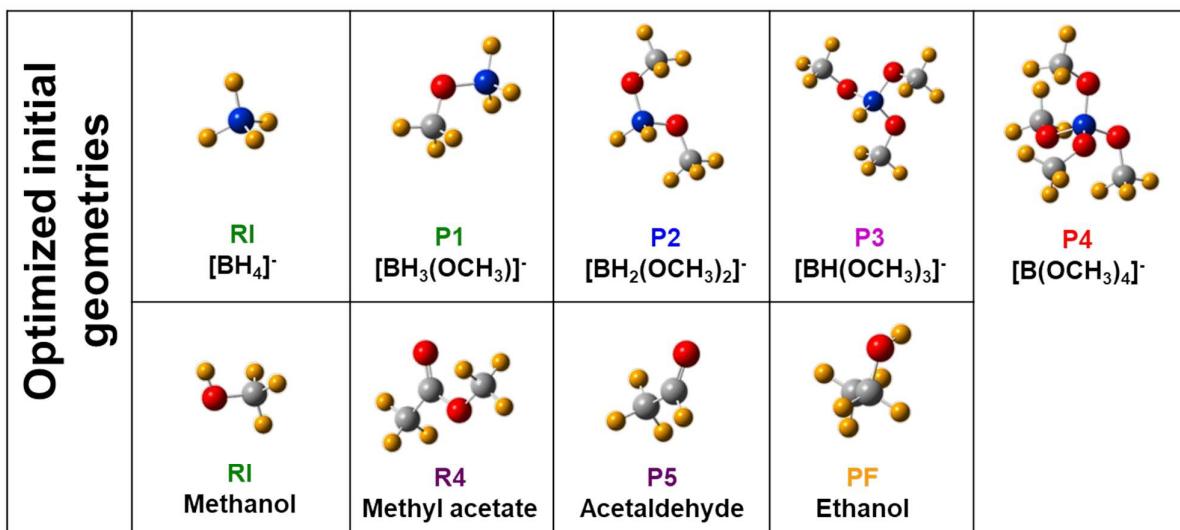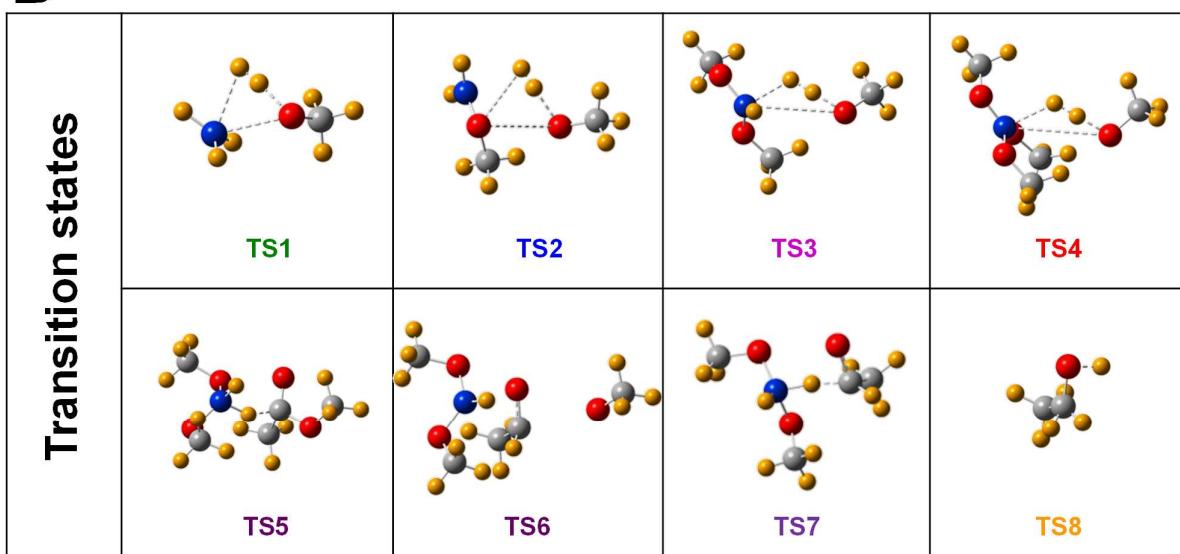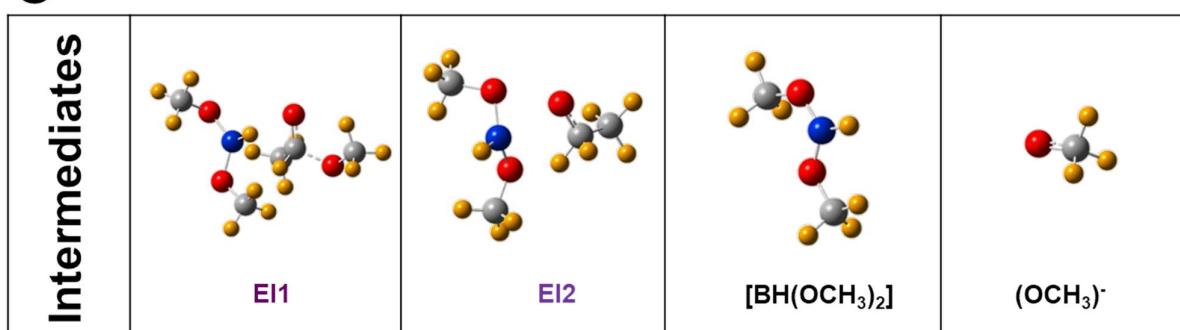
**Figure 8.** Different optimized initial geometries (A), transitions states (A) and intermediates (C) found for methyl acetate reduction reaction obtained from DFT calculations.
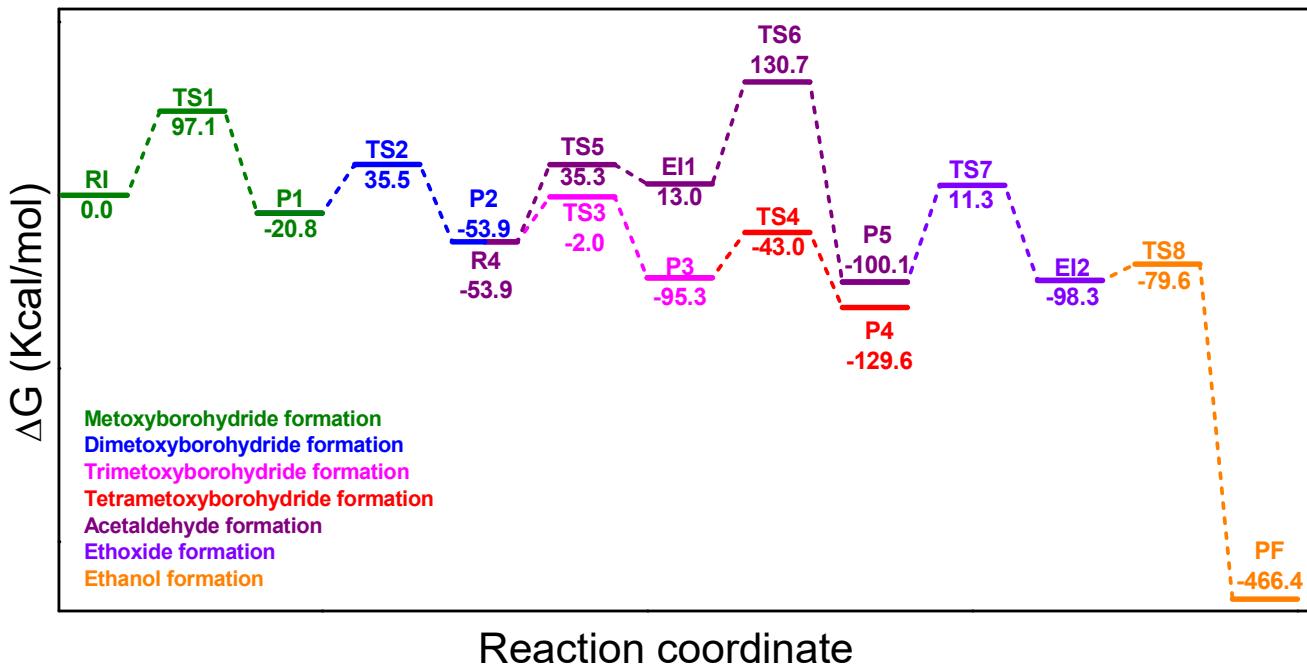
Figure 9. Reaction energy profile for methyl acetate reduction toward ethanol formation obtained from DFT calculations.