DALTON
FULL PAPER

Simulation of ethylene insertion in an aluminium catalyst

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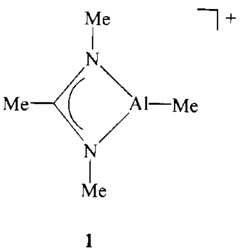
Ethylene insertion into $[AlMe\{MeC(NMe)_2\}]^+$ has been studied using quantum mechanical simulations. Both plane-wave Car–Parrinello and localised basis set DFT calculations predict an insertion barrier of approximately 25 kcal mol^{-1}, in close agreement with estimates derived from experimental data. The calculated barrier for insertion into a methyl bridged dinuclear aluminium species is over 10 kcal mol^{-1} higher, suggesting that the monomeric species is the active catalyst.

Simple aluminium compounds, AlR_3, are known to be active in olefin oligomerisation, but their use in catalytic polymerisation has proved more problematic, due to rapid chain termination. The inactivity of these main group complexes is in marked contrast to the numerous catalytic pathways involving complexes of metals of the transition and lanthanide series. However, recent work by Coles and Jordan[1] has shown that simple cationic aluminium complexes $[AlMe\{RC(NR')_2\}]^+$ (see **1** where $R = R' = Me$) can catalyse ethylene polymerisation with activities of several thousand gram polyethylene (PE) mol^{-1} h^{-1} (atm $C_2H_4)^{-1}$, yielding PE with molecular masses up to 10^5 Daltons. Since this initial report, a range of aluminium-based compounds has been synthesized and tested for ethylene polymerisation activity, but the nature of the active species remains unknown. Given the propensity of the electron deficient aluminium centres to form bridged dinuclear species, it is possible that the observed catalytic activity is not due to the mononuclear complex, $[AlMe\{RC(NR')_2\}]^+$, but instead a methyl-bridged dinuclear adduct such as $[\{[AlMeRC(NR')_2]\}_2(\mu\text{-}Me)]^+$ (**2**, $R = R' = Me$). Spectroscopic investigations[2] into the equilibrium distribution of species in solution are currently underway in this laboratory, but in the context of the current paper it is sufficient to note that if several species are present the overall polymerisation rate will be determined by their relative concentrations, as well as the catalytic activity of each one.



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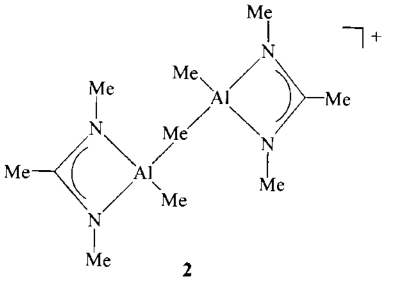

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In recent years quantum mechanical simulations have greatly enhanced our understanding of the mechanisms of catalytic cycles. Static calculations have been used in a number of cases to construct potential energy profiles, from which the energy barrier for the reaction can be abstracted (see, *e.g.*, Margl *et al.*[3] and refs. therein). More recently, first principles molecular dynamics[4] simulations using plane-wave based methods such as the Car–Parrinello (CP) technique have been reported for catalytic cycles.[5–7] The computational cost of the plane-wave calculations is less size-dependent than the corresponding calculations using localised basis sets, and so the former are more suited to the study of larger systems such as the dinuclear species noted above. There are, however, relatively few papers in the literature providing a direct comparison of the two methodologies, and so here we employ both techniques to study the insertion of ethylene into the mononuclear species $[AlMe\{MeC(NMe)_2\}]^+$ **1**. Having established that the CP code gives similar results to static DFT for the monomeric system, we then apply the plane-wave technique to compare ethylene insertion into the monomer **1** with the corresponding process in the model dinuclear species **2**.

Computational details

Density functional calculations were performed using the Amsterdam Density Functional code ADF, version 2.3.0.[8–10] Carbon, nitrogen and hydrogen atoms were described by a double zeta + polarisation basis set, while a triple zeta + polarisation basis was used for aluminium. The local density approximation was employed throughout, along with the correlation functional of Vosko, Wilk and Nusair[11] and gradient corrections to exchange (Becke)[12] and correlation (Perdew)[13]. The first principles molecular dynamics calculations are based on the original Car–Parrinello code.[4] The Perdew–Zunger parametrisation[14] of the exchange-correlation function was used, along with non-local corrections according to Perdew and Becke[12,13]. Soft Vanderbilt[15] pseudo-potentials were employed, except for Al. The cell size chosen ensured empty space left between images in neighbouring cells in order to minimise unwanted interaction between images. The common geometry optimisation step by steepest descent or conjugate gradient techniques was replaced by a short series of low temperature dynamics simulations, at $T = 50$, 20 and finally 10 K. In the CP simulations a 15 Rydberg cut-off energy was found to be sufficient by comparing to the entire set of equivalent data obtained for a 25 Rydberg cut-off.

Results and discussion

Potential energy curves for ethylene insertion into the mononuclear aluminium complex **1**, obtained using both DFT and CP calculations, are shown in Fig. 1. All parameters are freely optimised, with the exception of the distance between the methyl carbon attached to Al (C3) and one carbon of the ethylene molecule (C2), which is used to define the reaction coordinate. The energy profiles derived from the two methodologies are very similar, both predicting a barrier to insertion of around 25 kcal mol^{-1}. For the aluminium catalyst with $R = {}^tBu$ and

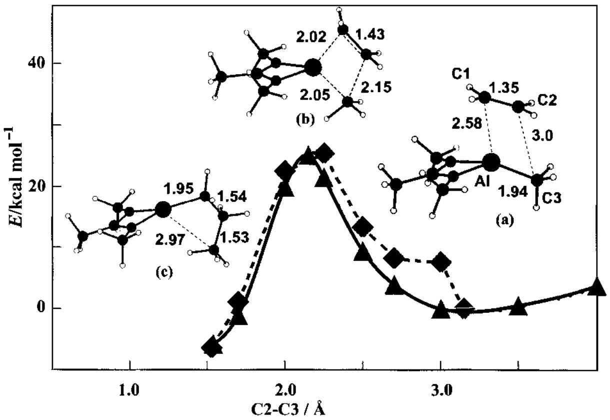

Fig. 1 Energy profile for the insertion of ethylene into the Al–CH_3 group of mononuclear complex $\{MeC(NMe)_2\}AlMe^+$ (results from ADF calculations are shown as triangles, those from the CP method as diamonds). The reaction coordinate is defined by the C2–C3 distance. ADF Calculated structures of the van der Waals complex (C2–C3 3.0 Å), the transition state (C2–C3 2.15 Å) and the product (C2–C3 1.53 Å) are also shown.

R′ = ^{i}Pr, the highest experimentally determined activities[1] at 60 and 85 °C are 2480 and 3050 g PE mol^{-1} h^{-1} (atm C_2H_4)$^{-1}$ respectively (details are given in the Supplementary Material to ref. 1). Assuming that the pressure applied is 1 atm, these values correspond to reaction rates of approximately one ethylene insertion every 30 s. From the Arrhenius rate equation, $k = A{\cdot}\exp(-E_{act}/RT)$, and assuming $A = 10^{13}$ s^{-1}, the estimated activation energy lies in the range 22–24 kcal mol, in excellent agreement with our predicted values. The structures of three key points along the curve are shown in the figure, corresponding to (a) the van der Waals complex between catalyst and ethylene, (b) the transition state,† (c) the final product (the structures shown are generated from the static DFT calculations, but those from the CP code are very similar). The van der Waals complex between the catalyst and ethylene complex (C2–C3 3.0 Å) lies in a shallow minimum in the potential energy curve, with Al–C1 and Al–C2 separations of 2.58 and 2.42 Å respectively. In the transition state (C2–C3 2.15 Å) the aluminium centre is approximately symmetric with respect to the terminal carbon atoms (Al–C1 2.02, Al–C3 2.05 Å), and the methyl group is forced below the plane of the amidinate ring, causing a distinct pyramidalisation at the aluminium centre. In the product (C2–C3 1.53 Å) the Al–C3 bond is completely cleaved (2.97 Å), and the co-ordination about the aluminium centre reverts to approximately trigonal planar, with the metal-bonded carbon of the newly formed propyl group lying in the amidinate plane.

Preliminary studies, using the CP methodology, suggest that the energetics of insertion into one of the non-bridging methyl groups of the dinuclear aluminium complex **2** are rather different from those discussed above. The overall reaction is thermochemically neutral, and shows a substantially larger barrier (40 kcal mol^{-1}) to insertion. We are currently investigating the electronic origin of these differences, but initial results suggest that it is the mononuclear complex which is the active species in the polymerisation.

Conclusion

Plane-wave based Car–Parrinello techniques, along with static density functional methods using localised basis sets, have been used to calculate the barrier to insertion of ethylene into a model aluminium catalyst, $[AlMe\{MeC(NMe)_2\}]^+$. The two techniques predict almost identical values of approximately 25 kcal mol^{-1}, in excellent agreement with the estimate of 22–24 kcal mol^{-1} extracted from experimental polymer yields. Initial calculations indicate that the barrier to insertion in a dinuclear methyl-bridged species is much higher, suggesting that the mononuclear species is the active catalyst.

Acknowledgements

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† Here taken as the maximum along the reaction coordinate, which was located to within 0.02 Å.