

Benchmark Study of Density Functionals for the Insertions of Olefin and Polar Monomers Catalyzed by α -Diimine Palladium Complexes

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Abstract

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Βενζημαρκ Στυδψ οφ Δενσιτψ Φυνςτιοναλς φορ τηε Ινσερτιονς οφ Ολεφιν ανδ Πολαρ Μονομερς αταλψζεδ βψ α -Διιμινε Παλλαδιου δμπλεξες

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Abstract : The performance of a series of density functionals has been tested for the insertions of ethylene, methyl acrylate (MA), and vinyl bromide (VB) catalyzed by α -diimine palladium complexes. Sixty-seven density functionals are screened, and the results are compared with available experimental data. Eleven hybrid functionals (M06, BHandH, mPW1PW91, HSEh1PBE, mPW3PBE, LC- ω PBE, mPW1PBE, PBE0, M06-HF, M06-2X, M05-2X) showed better performance in the insertions of both ethylene and MA, and could be therefore suitable for ethylene-MA copolymerization. Meanwhile, three GGA (PW91PW91, HCTH, HCTH407), two *meta* -GGA (TPSSTPSS, tHCTH), and ten hybrid functionals (M06, BHandH, TPSSh, B971, B98, B1B95, PBE0, M06-2X, tHCTHhyb, M05-2X) perform well in ethylene-VB copolymerization. Besides, nine D3 or D3BJ augmented functionals are found to be suitable for both copolymerization systems. The D2 dispersion correction overestimated insertion energy barriers of these monomers and is unsuitable for such copolymerization. In addition, the double-zeta basis set is found to be sufficient for solvation single-point calculation of these systems.

Keywords: Benchmark of DFT, Diimine palladium, Olefin insertion, Polar monomer, Cross-coupling

INTRODUCTION

Diimine ligated late-transition-metal complexes are capable of catalyzing not only Heck, Suzuki, and Hiyama coupling reactions,¹ but also (co)polymerization of olefins.^{2,3} In this context, the catalytic copolymerization of ethylene and polar monomers is a straightforward and atom-economic method to synthesize functionalized polyolefin materials of industrial importance.³⁻¹⁵ However, there are many challenges in these copolymerization systems, such as low reaction activity and low polar monomer incorporation. It is obvious that further study of such copolymerization mechanisms at molecular and electronic levels is highly required to develop more efficient copolymerization systems. In this instance, the issues of large size of such catalytic systems and computational resources could rule the highly accurate *ab-initio* wavefunction based methods out. Density functional theory (DFT) offered an ideal solution to study the mechanism of such copolymerization systems.¹⁶⁻²² However, many density functionals have no broad application range, and the application of individual functionals to specific systems needs performance test according to either experimental or *ab-initio* results. It is therefore necessary to choose a suitable and accurate DFT method to deal with the system of interest. Given the importance of developing the ethylene/polar monomer copolymerization system, it is worth of performing a benchmark study of DFT functionals for the mechanistic study of such copolymerizations catalyzed by late transition metal complexes.

In 2006, Martin et al.²³ performed a benchmark study on C-C and C-H activations by bare palladium atom, and found that *meta*-GGA functionals have good performances. Recently, Checink et al. conducted thermochemical benchmark set of closed-shell metal organic system including carbene-ligated Pd complex and presented a series of applicable functionals. It is noteworthy that two commonly used functionals, BP86(D3) and B3LYP(D3) had poor performance.²⁴ Schreckenbach et al. carried out a benchmark study on thermodynamics of hydrocarbon isomerization and olefin monomer insertion, but without consideration of metal catalysis. They found that the dispersion augmented BPBE, PBEPBE, and B3LYP functionals showed better performance compared with other functional investigated.²⁵ Maron et al. studied the solvation and dispersion effects on group 3 and 4 metallocene-catalyzed propylene coordination and insertion reactions. It was revealed that dispersion effects generally overestimate the stability of olefin complexes and B3PW91 functional performed well in a comprehensive consideration of computational cost and precision.²⁶ Although significant progress has been achieved in this field, as far as we are aware, the benchmark study of theoretical methods for olefin copolymerization systems catalyzed by late transition metal has not been reported to date. In the present work, a benchmark study on the insertion of three monomers, viz. ethylene, methyl acrylate (MA) and vinyl bromide (VB) into (α -diimine)Pd-Me bond has been conducted, respectively, where there is available experimental data (Table 1).^{4, 27} By screening 67 functional methods, a series of functionals have been found to perform well in the prediction of insertion activation energies of these monomers, and their intersection could be suitable for dealing with such copolymerization systems. It is also found that double-zeta basis sets are sufficient for solvation single-point calculations with SMD or CPCM models.

Table 1. Κινητικα Δατα φορ Μονομερ Ινσερτιον ιντο (α -διιμινε)Πδ-Με Βονδ ιν Διςηλορομετηανε.

COMPUTATIONAL METHODS AND STRATEGIES

All calculations were performed with the Gaussian 16 program.²⁸ Various types of functionals, such as GGA, *meta*-GGA, hybrid, and functionals with semi-empirical dispersion correction (D2²⁹, D3³⁰, and D3BJ³¹) were used for geometry optimizations. In these geometrical optimizations, the LANL2DZ basis set³² together with effective core potential (ECP) was used for Pd and Br atoms and the 6-31G(d) basis set was used for C, H, O and N atoms. In order to verify the optimized stationary points and obtain the thermodynamic data at the actual reaction temperature, vibration frequency analyses were conducted at the same level of theory. Based on each optimized structure, single point calculation was performed with the corresponding DFT functional used for its geometrical optimization. In these single-point calculations, larger basis sets, viz., the SDD and associated effective core potential³³ for Pd and Br atoms and the triple-zeta 6-311G(d,p) basis set for the remaining atoms, are applied, and the solvation effect of dichloromethane generally used in such copolymerization systems was considered by using SMD solvation model.³⁴ The Gibbs free energy in solution, including gas-phase free energy correction, was used for discussion, unless otherwise

specified. The functionals were screened by comparing the experimentally measured activation energy with the corresponding calculated value. For a comparison of the effect of solvation models, CPCM model³⁴ was also considered for some calculations. Three model chemistries used for fitting the parameters of SMD solvation model by Truhlar et al. were selected in the solvation calculations, namely, M05-2X/6-31G(d), M05-2X/6-31+G(d,p), and M05-2X/cc-pVTZ.³⁵ Similarly, in the CPCM solvation calculations, the two model chemistries of PBE0/6-31+G(d) and PBE0/6-31+G(d,p) were utilized, which was previously used for testing the accuracy of CPCM solvation model by Barone et al.³⁴

The calculation strategy is shown in Figure 1. Based on the catalytic active species, the energy barrier for ethylene insertion is calculated and compared with the corresponding experimental value to screen the density functionals. Then, using the functionals with better performance, the insertion energy barrier of the two polar monomers were calculated, respectively. Compared with the corresponding experimental values, the functionals with better performance for the insertions of both ethylene and the polar monomer are considered to be suitable for the calculation of copolymerization system. According to the obtained results, single-point energy was further calculated at the specific theoretical levels together with the SMD and CPCM models, respectively, to evaluate the effect of solvation models. The density functional, which produces less than an energy barrier error of 1.0 kcal/mol compared with corresponding experimental values, is considered to be better for the calculations of such copolymerization systems.

Figure 1 . Flow chart of calculation strategy.

RESULTS AND DISCUSSION

Forty-one density functionals shown in Table 2 has been tested, including eight GGA, three meta-GGA, and thirty hybrid functionals. Among them, additional D2, D3, and D3BJ dispersion corrections were also considered for five (B97D functional employing D2 correction as a default in the program), thirteen, and eight functionals (Table 2), respectively. Therefore, the total 67 methods have been applied.

Table 2. All Tested Density Functionals¹⁾

	functional	D2	D3	D3BJ	Reference
GGA	BP86	[?]	[?]		36,37
	B97D	[?]			38
	PW91PW91	[?]	[?]	[?]	39 40
	PBEPBE				
	HCTH				41,42,43
	HCTH407				41,42,43
	BLYP	[?]	[?]	[?]	36
	BPBE		[?]	[?]	36,40
Meta-GGA	TPSSTPSS	[?]	[?]	[?]	44
	M06L		[?]		45
	tHCTH				46
Hybrid	M06				47
	B3LYP	[?]	[?]	[?]	48,49
	B3P86				50
	B3PW91		[?]	[?]	51
	B1B95				52
	mPW1PW91				53,54
	mPW1LYP				53,55
	mPW1PBE				40,53
	mPW3PBE				40,53
	B98				54
	B971				41
	B972				56

functional	D2	D3	D3BJ	Reference
PBE0		[?]	[?]	57
B1LYP				58
O3LYP				59
M062X		[?]		47
tHCTHhyb				46
HSEh1PBE				60,61
ω B97XD				62
ω B97				63
TPSSh				44,64
X3LYP				65
LC- ω PBE		[?]		66,67
CAM-B3LYP			[?]	68
BMK				69
BHandH				70
M06-HF				71,72
BHandHLYP				70
M05-2X		[?]		73
M05		[?]		74

The mark “[?]” indicates that the functional includes the corresponding dispersion correction, respectively.

Functional screening for copolymerization systems

Firstly, functionals in Table 2 are used to calculate the energy barrier for ethylene insertion into the Pd-Me bond of initial active species (Table 1). The obtained results are compared with the experimental kinetic data (free energy barrier of 17.2 kcal/mol at the temperature of 243.6 K). As shown in Figure 2, B97D functional has the largest positive deviation of 3.8 kcal/mol and M05 has the largest negative deviation of -2.3 kcal/mol. On the other hand, the functionals with semi-empirical dispersion correction (D2, D3, or D3BJ) overestimate the ethylene insertion barrier except for B3PW91-D3, PBE0-D3, and M05-D3 (Figure 3). A similar situation was reported by Maron et al. that dispersion correction could overestimate the energy barrier for propene insertion into early transition metal complexes.²⁶ To get an image about the effect of dispersion correction on the calculated energy barrier, the absolute error of the barrier for ethylene insertion calculated by individual functional without and with available additional dispersion correction to the functional has been compared (Figure S1). It is found that the TPSSTPSS (*meta*-GGA) functional produced an error of 0.9 kcal/mol. In the case of dispersion correction to this functional, viz., TPSSTPSS-D2, TPSSTPSS-D3, and TPSSTPSS-D3BJ, the errors are 3.0, 1.7, and 1.6 kcal/mol, respectively, suggesting an overestimation of insertion energy barrier by the dispersion correction. Although some dispersion correction augmented functionals produced an error of less than 1.0 kcal/mol, such an overestimation caused by dispersion correction was also observed for BPBE, BP86, PBEPBE, BLYP, and B3LYP functionals, compared with corresponding functionals without dispersion correction. There are 38 methods with better performance (energy barrier error of less than 1.0 kcal/mol) for the ethylene insertion. These functionals includes 6 GGA, 2 *meta*-GGA, 20 hybrid types of functionals, PBEPBE (D2), 5 functionals with D3 dispersion correction and 4 functionals with D3BJ dispersion correction (Figures 2 and 3).

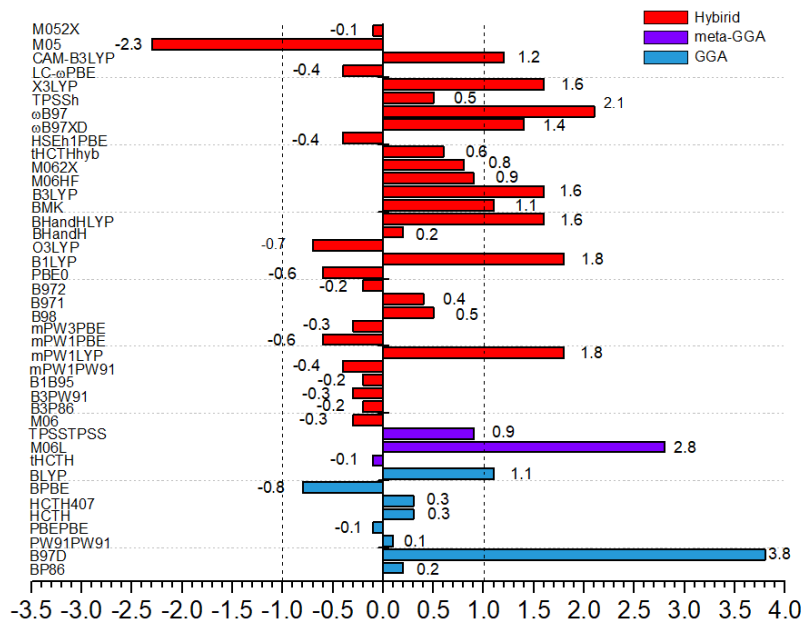


Figure 2. The error bar of calculated energy barriers (ΔG^\ddagger , kcal/mol) for ethylene insertion in comparison with the experimental value (17.2 kcal/mol).⁴ The positive error value means overestimation of energy barrier, and the negative error means underestimation. The same is true for the following figures.

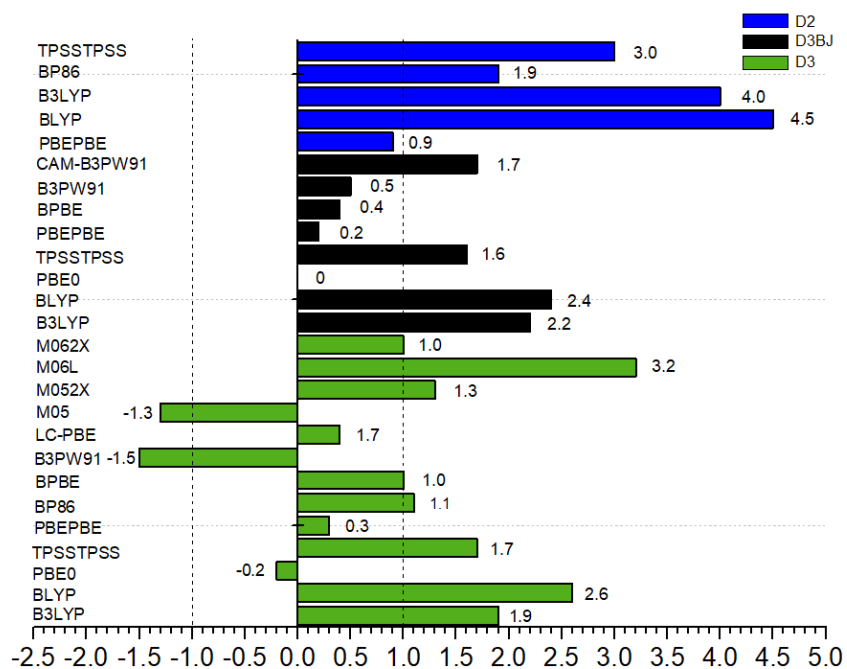


Figure 3. The error bar of calculated energy barriers (ΔG^\ddagger , kcal/mol) for ethylene insertion in comparison with the experimental value (17.2 kcal/mol).⁴ The functionals shown include available semi-empirical dispersion corrections.

By using the 38 methods with better performance for ethylene insertion, the insertion energy barriers of two polar monomers, MA and VB, have been further calculated (Table 1, Figures 4 and 5). The reported kinetic data for MA insertion are $\Delta H^{[?]} = 12.1 \pm 1.4$ kcal/mol and $\Delta S^{[?]} = -14.1 \pm 7.0$ cal/K[?]mol.²⁷ Due to the large range of entropy change (+7.0 cal/K[?]mol), the corresponding Gibbs free energy could vary significantly from the central value and is unsuitable for functional screen. Therefore, the enthalpy value for MA insertion was used instead. The reported kinetic data for VB insertion are $\Delta H^{[?]} = 11.9 \pm 0.1$ kcal/mol, $\Delta S^{[?]} = -16.8 \pm 0.1$ cal/K[?]mol at 236.5 K, and the corresponding $\Delta G^{[?]}$ is estimated to be 15.9 ± 0.1 kcal/mol.

The calculated energy barriers for MA insertion are shown in Figure 4. It is found that 11 hybrid functionals, 5 functionals with D3 correction and 4 functionals with D3BJ correction showed an error of less than 1.0 kcal/mol. That is, these methods behave better for the calculation of α -diimine palladium catalyzed ethylene-MA copolymerization. All the GGA and *meta*-GGA functionals produced an error of more than 1.0 kcal/mol. Among these functionals, B1B95 gives the worst result ($\Delta H^{[?]}$ of 16.8 *vs* 12.1 \pm 1.4 kcal/mol). As a result, GGA and *meta*-GGA functionals produced relatively large errors for ethylene-MA copolymerization, and the inclusion of D3 or D3BJ dispersion correction tend to reduce the energy barrier for MA insertion compared with their original form without such corrections.

Unlike the case of ethylene/MA copolymerization, GGA and *meta*-GGA functionals such as PBEPBE, PW91PW91, HCTH407, HCTH, TPSSTPSS and tHCTH showed good performance in ethylene/VB copolymerization (Figure 5). Moreover, several functionals with D3 and D3BJ correction and 10 hybrid functionals have better performance. Functional TPSSTPSS-D2 gives the worst result with the energy barrier value up to 18.1 kcal/mol (experimental value of 15.9 ± 0.1 kcal/mol). In addition, the functional such as BPBE with D3 or D3BJ dispersion correction generally overestimated energy barrier compared with its original form (without the dispersion correction).

Schreckenbach et al. found that the functionals, viz., BPBE, PBEPBE, and B3LYP, augmented by D3BJ dispersion correction showed good performance in the calculations of hydrocarbon isomerization and metal-free olefin insertion model system.²⁵ For the two copolymerization systems in this study, BPBE(D3BJ) and PBEPBE(D3BJ) also performs well. In a previously reported organocatalytic systems,⁷⁵ the M06-2X functional with implicit dispersion correction tended to give high accuracy. This is also found in the current work. However, the commonly used B3LYP functional showed relatively poor performance for ethylene insertion regardless of the inclusion of dispersion correction (with errors of 1.6 kcal/mol for B3LYP, 2.2 kcal/mol for B3LYP-D3BJ, and 4.0 kcal/mol for B3LYP-D2). The hybrid functionals M06-2X and PBE0 have also good performance without dispersion correction. Besides, D2 dispersion correction significantly overestimated the insertion energy barriers of these monomers (Figures 3-5). Therefore, D2 dispersion correction could be unsuitable for such polymerization systems.

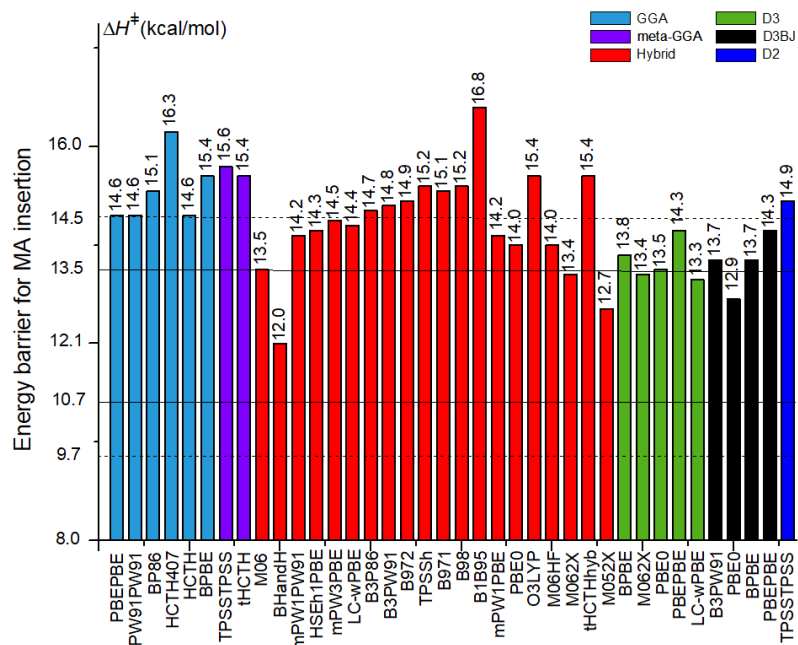


Figure 4. The energy barriers (ΔH^\ddagger , kcal/mol) for MA insertion calculated by various functionals.

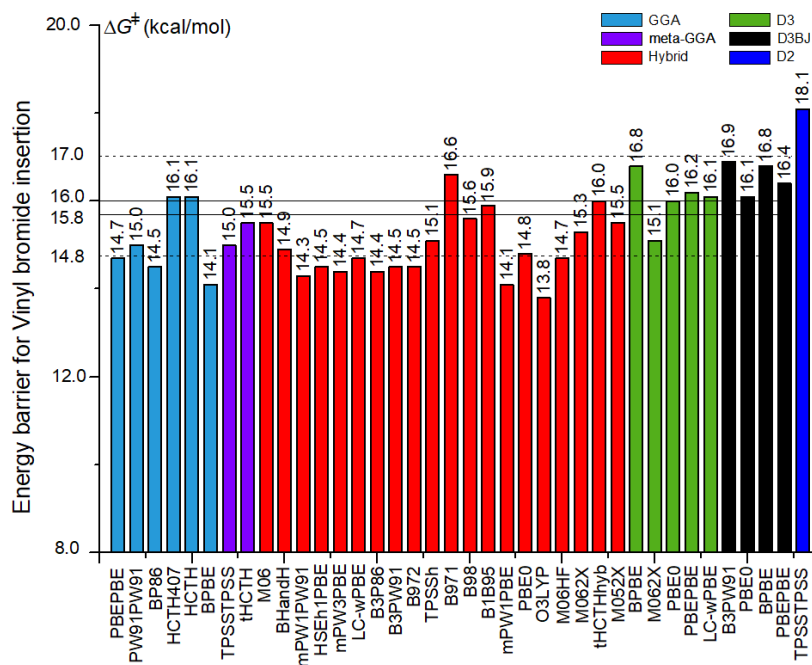


Figure 5. The energy barriers (ΔG^\ddagger , kcal/mol) for the VB insertion calculated by various functionals.

Effects of solvation model and associated methods

On the basis of screened density functionals discussed above, the effect of solvation models together with specific theoretical levels have been further investigated. Solvation single-point calculations were performed

with consideration of two common solvation models (SMD and CPCM) at the theoretical level originally used for fitting the parameters or recommended for the corresponding solvation model.^{34,35}

SMD model

All tested functionals having good performance (error of < 1.0 kcal/mol) for ethylene insertion are collected in Table 3. As shown in this table, at the level of M05-2X(SMD)/6-31G(d)[?]SDD, all functionals except HCTH407, HCTH, and BPBE(D3BJ) performs well for ethylene insertion using the SMD model. It is noted that double-zeta basis set is sufficient to obtain accurate result and there is (usually) no need to use the triple-zeta basis 6-311G(d,p) shown above. For copolymerization of ethylene and MA, all the selected functionals give relatively accurate insertion energy barriers. In addition, the M06 functional shows good performance, which may be due to the fact that this functional takes into account the weak interactions. This is also reflected in both the functional with implicit weak interactions and that with the correction of long-range interactions. For copolymerization of ethylene and VB, the functional BPBE(D3) shows good performance. All tested hybrid functionals gave good results except M06, TPSSh, and M06-HF. The GGA and *meta*-GGA functional underestimate the barrier and have relatively poor performance (error of > 1.3 kcal/mol). It is also found that the error derived from PBEPBE functional is still relatively large after adding D3 and D3BJ dispersion correction (error of > 1.5 kcal/mol). For the functionals with dispersion correction, viz. PBE0(D3), LC- ω PBE(D3), B3PW91(D3BJ), and PBE0(D3BJ), perform well. Therefore, the M05-2X functional together with double-zeta basis set 6-31G(d) (SDD for metal atom) can be used for the solvation single-point calculation on the geometries optimized by most functionals tested for such copolymerization systems. To further confirm this, larger basis sets (6-31+G(d,p) and cc-pVTZ) were also considered for the non-metal atoms, respectively. The results are almost the same as that from M05-2X/6-31G(d) level. (Figure S2-S7 in SI).

CPCM model

To test the performance of CPCM solvation model in such copolymerization systems, single-point solvation calculations have been performed at the level of PBE0/6-31+G(d), which was shown to be suitable for CPCM model.³⁴ As shown in Table 3, in the case of ethylene insertion, all the tested functionals underestimated the reaction energy barrier, among which the hybrid M06-HF performs the worst with an error of 2.3 kcal/mol. For MA insertion, all the functionals shown in Table 3 perform well. In the case of VB insertion, like the case of SMD model, GGA and *meta*-GGA functionals underestimated the reaction energy barrier with errors of larger than 1.0 kcal/mol. The hybrid functional LC- ω PBE with D3 dispersion correction overestimated the barrier (17.9 *vs* 15.9 \pm 0.1 kcal/mol). This can be ascribed to that the functional LC- ω PBE itself considered the long-range interaction, and further D3 dispersion correction may lead to overcorrection. The hybrid functional BHandH also overestimated the energy barrier (17.3 kcal/mol). When larger basis set 6-31+G(d,p) was used for the non-metal atoms, similar results was obtained (Table S1). Therefore, with the CPCM solvent model, the lower theoretical level of 6-31+G(d) for single-point calculation is sufficient to obtain accurate energy barriers in such copolymerization system. It is noteworthy that, although some functionals produced errors of > 1.0 kcal/mol, the errors are not so large (< 3 kcal/mol), suggesting a wide range of functionals suitable for dealing with such (α -diimine)Pd-catalyzed copolymerizations.

Table 3. The Calculated Energy Barriers (kcal/mol) in Solution for the Monomer Insertion by Using the SMD and CPCM Solvation Models¹⁾

DFT Method	DFT Method	M05-2X/6-31G(d) ²⁾ , SMD	M05-2X/6-31G(d) ²⁾ , SMD	M05-2X/6-31G(d) ²⁾ , SMD	PBE0/6-31+G(d) ²⁾ , CPCM	PBE0/6-31+G(d) ²⁾ , CPCM	PBE0/6-31+G(d) ²⁾ , CPCM
		Et ³⁾ $\Delta G^{[?]}$	MA $\Delta H^{[?]}$	VB $\Delta G^{[?]}$	Et $\Delta G^{[?]}$	MA $\Delta H^{[?]}$	VB $\Delta G^{[?]}$
GGA	PW91PW91	16.6	-	14.0	16.4	-	14.5

DFT Method	DFT Method	M05-2X/6-31G(d) ²⁾ , SMD	M05-2X/6-31G(d) ²⁾ , SMD	M05-2X/6-31G(d) ²⁾ , SMD	PBE0/6-31+G(d) ²⁾ , CPCM	PBE0/6-31+G(d) ²⁾ , CPCM	PBE0/6-31+G(d) ²⁾ , CPCM
<i>meta</i> -GGA	HCTH407	16.1	-	-	16.0	-	-
	HCTH	16.1	-	-	16.0	-	-
	tHCTH	16.3	-	14.3	16.2	-	14.5
Hybrid	TPSSTPSS	16.4	-	13.9	16.4	-	14.4
	M06	17.5 17.8	13.6 13.6	14.4 15.5	16.4 16.7	13.6 14.1	14.8 17.3
DFT-D3	BHandH						
	mPW1PW91	17.2	13.3	-	16.5	13.1	-
	HSEh1PBE	17.0	13.4	-	16.3	13.6	-
	mPW3PBE	17.0	13.3	-	16.5	13.6	-
	LC- ω PBE	17.6	14.2	-	16.5	14.1	-
	TPSSH	16.6	-	14.0	16.4	-	14.3
	B971	17.0	-	16.1	16.4	-	15.8
	B98	17.1	-	15.4	16.5	-	15.1
	B1B95	17.2	-	16.1	16.6	-	16.1
	mPW1PBE	17.1	13.4	-	16.5	13.6	-
	PBE0	17.0	13.0	-	16.4	13.6	-
	M06-HF	17.2	12.7	13.8	14.9	-	-
	M06-2X	17.8	13.5	14.9	16.3	12.4	14.3
	tHCTHhyb	17.1	-	15.6	16.6	-	15.3
	M05-2X	17.9	12.9	16.0	16.5	11.8	15.9
	BPBE	16.2	12.4	14.9	16.1	-	-
	M06-2X	17.9	13.6	14.8	16.6	12.5	14.3
	PBE0	17.0	13.5	15.3	16.1	-	-
	PBEPBE	16.4	13.1	13.8	16.1	-	-
	DFT-D3BJ	LC- ω PBE	17.5	13.6	16.4	16.5	12.6
B3PW91		16.8	13.5	15.4	16.1	-	-
PBE0		17.1	13.0	15.1	16.5	12.7	16.0
Experiment ^{4,27}	BPBE	15.7	-	-	15.7	-	-
	PBEPBE	16.2	12.8	14.2	16.1	-	-
	Experiment ^{4,27}	17.2	12.1±1.4	15.9±0.1	17.2	12.1±1.4	15.9±0.1

¹⁾ The symbol “-” denotes that the corresponding functional produced larger error for corresponding monomer or ethylene insertion and was not considered here for the comparison of the effect of solvation models on copolymerizations.

²⁾ The SDD basis set and associated effective core potential was used for Pd atom, while the corresponding full-electron basis set was used for non-metal atoms.

³⁾ Et: ethylene; MA: methyl acrylate; VB: vinyl bromide.

CONCLUSION

The benchmark of DFT for α -diimine palladium catalyzed insertions of ethylene, methyl acrylate, and vinyl bromide has been studied, during which sixty-seven functional methods have been screened on the basis of experimental kinetic data.

For the ethylene/methyl acrylate copolymerization featuring the insertions of the both monomers, when the single-point calculation is performed at the level of M05-2X(SMD)/6-31G(d)[?]SDD, 11 hybrid functionals (M06, BHandH, mPW1PW91, HSEh1PBE, mPW3PBE, LC- ω PBE, PBE0, M06-HF, M06-2X, mPW1PBE, M05-2X), 5 functionals with D3 dispersion correction (BPBE-D3, M062X-D3, PBE0-D3, PBEPBE-D3, LC- ω PBE-D3), and 3 functionals with D3BJ dispersion correction (B3PW91-D3BJ, PBE0-D3BJ, PBEPBE-D3BJ) used for geometrical optimization could give better results compared with other tested functionals. However, GGA and some *meta*-GGA functionals showed poor performance in the geometry optimization with respect to calculated free energy barrier in solution (SMD model). The hybrid functional B1B95 produced the worst result. When the CPCM model is applied at the level of PBE0(CPCM)/6-31+G(d)[?]SDD, the aforementioned 11 hybrid functionals except M06-HF also showed good performance. At this single-point calculation level, the M06, M062X-D3, LC- ω PBE-D3, and PBE0-D3BJ geometries can also produce accurate free energy barrier in solution.

For the copolymerization ethylene and vinyl bromide, when the single-point calculation is carried out at the level of PBE0(CPCM)/6-31+G(d)[?]SDD, the tested hybrid functionals except BHandH, TPSSh, and M06-2X perform well. However, the GGA and *meta*-GGA functionals have poor performance, like the case of ethylene/MA copolymerization. And, LC- ω PBE-D3 overestimated the energy barrier of vinyl bromide insertion, possibly due to the over-correction of dispersion force. At the level of M05-2X(SMD)/6-31G(d)[?]SDD for single-point calculations, the GGA and *meta*-GGA still have poor performance. The dispersion correction augmented PBEPBE functional underestimated the barrier and showed worst performance among the tested functionals. The hybrid functionals except M06, TPSSh, and M06-HF perform well at this level.

It is noted that the performance of the common B3LYP functional with or without dispersion is not ideal in these systems. Compared with SMD solvation model, CPCM model slightly underestimated the energy barrier of ethylene insertion, but it is still within the acceptable error range.

ASSOCIATED CONTENT

Supporting Information

Additional table and figures showing the effect of dispersion corrections on the error of ethylene insertion energy barrier and monomer insertion energy barriers calculated at various levels together with SMD and CPCM solvation models as well as Cartesian coordinates of optimized stationary points. The Supporting Information is available free of charge on the ACS Publications website.

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Notes The authors declare no competing financial interest.

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Βενσημαρκ Στυδψ οφ Δενσιτψ Φυνςτιοναλς φορ τηε Ινσερτιονς οφ Ετηψλενε ανδ Πολαρ Μονομερς αταλψζεδ βψ α-Διιμινε Παλλαδιυμ ομπλεξες

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