Formation of 3-buten-1-ol over metal encapsulated ZSM-5 from formaldehyde and propene: A Density Functional Theory study

Selvaraj TAMILMANI[1,a,b], Rajalingam RENGANATHAN[a], Balasubramanian VISWANATHAN[b]

[a] School of Chemistry, Bharathidasan University, Tiruchirappalli -24, India.
[b] National Centre for Catalysis Research, Indian Institute of Technology -Madras, Chennai-36, India.

Abstract: Carbonyl-ene reaction, which involves C-C bond formation, is an essential organic reaction. The possibility of the C-C bond formation between HCHO and propene catalyzed with Ni2+, Pd2+, and Pt2+ exchanged on ZSM-5 zeolite (metal-ZSM-5) has studied by density functional theory. Pt-ZSM-5 exhibits a better activity than other metal-ZSM-5 reported due to high charge transfer between platinum and formaldehyde.

1. Introduction

The carbonyl-ene reaction is one of the crucial reactions in the chemical process, which involves the carbon-carbon bond formation. It is an enantioselective reaction which occurs between a carbonyl compound and allylic hydrogen which is present in the alkene [1-3]. Lewis acids used as catalyst for these reactions and it requires strong electrophilic carbonyl compounds. The product, 3-buten-1-ol is used to produce polypropylene from propylene copolymerization. This reaction also involves in tetrahydrofuran synthesis, but it has two disadvantages, (i) low boiling point of formaldehyde (-19.5°C) makes it complicate to handle and (ii) rapid polymerization into trioxane and paraformaldehyde solid which makes its life time is relatively short. To preserve formaldehyde in monomer form, it has to be deploymerized by Lewis acid. However formaldehyde requires more attention in its handling as it is corrosive and causes toxic waste problems, making environmentally frosty [4-23]. To overcome this problem discovering an appropriate storage material for maintaining formaldehyde in monomer form is important. Considering these issues, the proposal of new storage materials is an urgent need.

Materials like zeolites and Metal Organic Frameworks (MOF) which are widely used for gas storage applications can be suitable candidate for formaldehyde storage. Many researchers theoretically demonstrated the utilization of MOF-11, alkaline-exchanged and metal-exchanged faujasite zeolite as a formaldehyde storage material [25-28]. Here, we theoretically demonstrate formaldehyde-propene carbonyl-ene reaction on M-ZSM-5 zeolite (M = Ni, Pd, and Pt) using density functional theory with the B3LYP functional. This work investigates the opportunity of using group 10 metal-exchanged zeolites as catalysts for the above reaction.
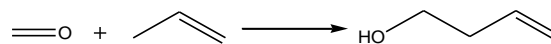
Scheme 1 Carbonyl-ene reaction scheme between HCHO and propene.

2. Computational Method

All the density functional calculations were done using G09 program with B3LYP hybrid functional with exchange and correlation functional using LANL2DZ basis set [29-32]. Formaldehyde-propene reaction over M/ZSM-5 zeolite were

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[1] Corresponding authors
E-mail: stamilmani89@gmail.com

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studied using MAl2Si6O9H14 cluster model, which represent two contiguous five-membered rings from the straight channel of ZSM-5 zeolite wall. Aluminum atoms were positioned in T12 and T6 lattice location for the modeling of a conventional ion exchange site. The distance among two aluminum ions was equal to 4.76 Å for the cluster model. The Si-O bonds are saturated by using hydrogen atoms. The XRD data of ZSM-5 zeolite is taken for calculations [33]. Transition states are confirmed by one imaginary frequency [34, 34]. The charge distributions and population analyses done by Natural Bond Orbital analysis (NBO) [36, 37].

3. Results and Discussion

Quantum chemical calculations for extrapolating the reaction mechanism are shown in scheme 1. The electronic behavior of the reactive site is influenced by a small fraction of the zeolite framework. The geometries and reaction path of the encapsulated formaldehyde on metal-ZSM-5 for carbonyl-ene reaction were investigated. The reaction is assumed to proceed on a concerted mechanism in which both reactants are involved in the rate limiting step.

3.1 Geometry and adsorption of the formaldehyde

The optimized geometry of Ni-ZSM-5, Pd-ZSM-5, and Pt-ZSM-5 are illustrated in figure 1.

The metals are located in the five membered ring plane. The adsorption energies are found to be -18.2, -18.8, and -38.3 kcal/mol for Ni-, Pd-, and Pt-ZSM-5, respectively. The geometrical parameters of the all the states are tabulated in table 1. The value at column 1 and 2 describes the metal exchanged zeolite and formaldehyde interaction. The metal ions move a little bit away from the five membered plane when HCHO adsorbs on the zeolite. This is due to the interaction of the metal with formaldehyde oxygen. The reaction begins with formaldehyde encapsulated on the metal-ZSM-5 catalysts, to preserve formaldehyde. The C-O bond length in the formaldehyde is slightly larger than isolated formaldehyde C-O value due to the metal and the lone pair electron of carbonyl oxygen interaction. The C-O bond distance is increases by 0.041, 0.046 and 0.050 Å for Ni-, Pd-, and Pt-ZSM-5, respectively. The metal cations and the zeolite binding energies were found to be -110.4, -46.9, and -55.4 kcal/mol for Ni-, Pd-, and Pt- ZSM-5 respectively. From the binding energy, the metal and the zeolite framework charge transfer amount was revealed by the charge reduction of metals. The charge reduction follows the following order, Ni^{2+} > Pt^{2+} > Pd^{2+}. The HOMO-LUMO energy gap for M-ZSM-5 also found to be in the same order of Ni^{2+} > Pt^{2+} > Pd^{2+} shown in supporting information figure S2. All optimized geometries are given in the Supporting Information, figure S1.

Table 1. Geometrical parameters of reactants, transition state, and product of the carbonyl-ene reaction between formaldehyde encapsulated in ZSM-5 and propene

	Isolated molecule (Å)	Formaldehyde Adsorption (Å)			Co-adsorption complex (Å)			Transition state (Å)			Product (Å)		
		Ni-ZSM-5	Pd-ZSM-5	Pt-ZSM-5	Ni-ZSM-5	Pd-ZSM-5	Pt-ZSM-5	Ni-ZSM-5	Pd-ZSM-5	Pt-ZSM-5	Ni-ZSM-5	Pd-ZSM-5	Pt-ZSM-5
C-C1								1.593	1.790	1.551	1.542	1.539	1.541
C1-C2	1.333				1.355	1.352	1.358	1.476	1.421	1.484	1.517	1.516	1.519
C2-C3	1.501				1.509	1.512	1.509	1.427	1.468	1.418	1.352	1.349	1.352
C3-H3	1.094				1.098	1.099	1.095	1.173	1.126	1.229	2.632	3.044	2.526
H3-O					4.082	5.539	5.077	2.578	2.064	1.546	0.985	0.983	0.989
C-O	1.207	1.248	1.253	1.257	1.252	1.255	1.269	1.419	1.369	1.479	1.489	1.484	1.498
M-O		2.223	2.094	2.027	2.168	2.088	2.038	1.832	2.042	2.005	2.139	2.109	2.053

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Ni-ZSM-5
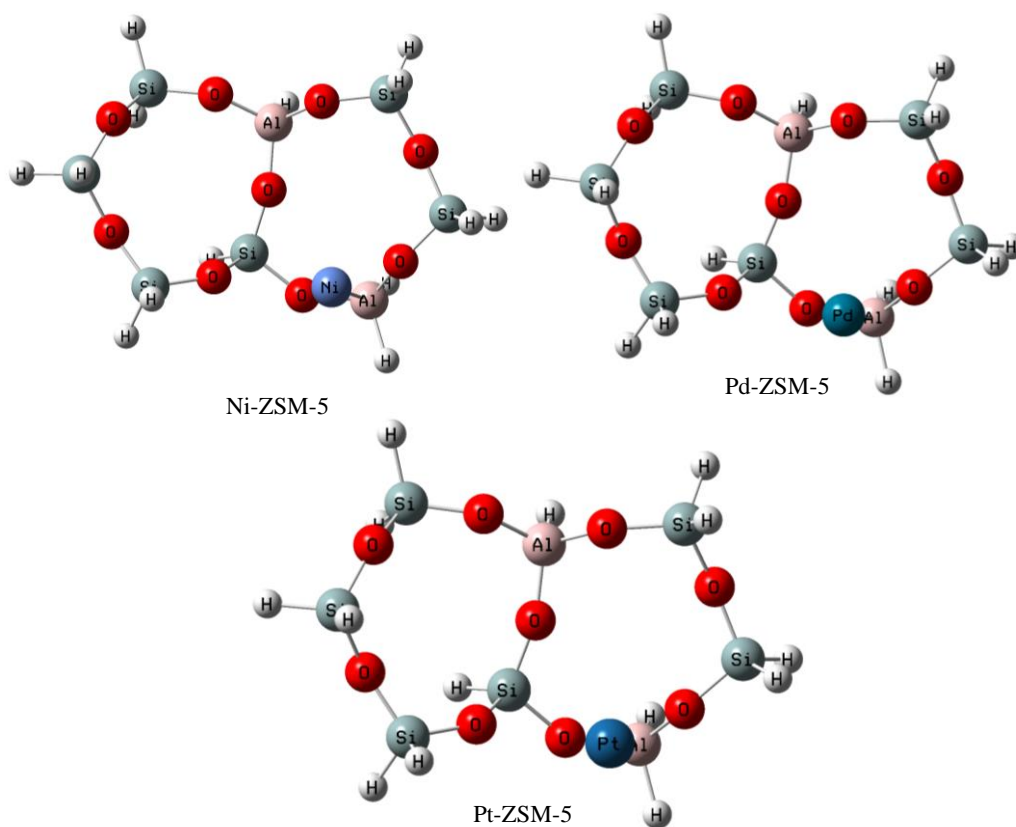
Pd-ZSM-5

Pt-ZSM-5

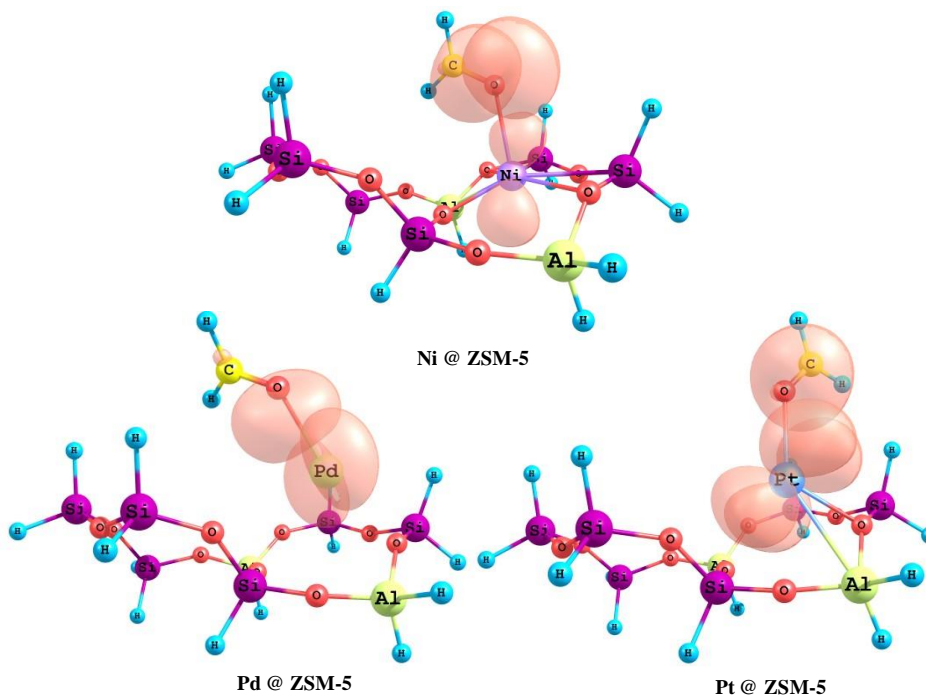**Fig.1.** Optimized geometry of Ni-ZSM-5, Pd-ZSM-5, and Pt-ZSM-5

Ni @ ZSM-5

Pd @ ZSM-5

Pt @ ZSM-5

Fig.2. Pictorial representation of the M-O bonding character from the NBO calculations using B3LYP/LANLDZ method.

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3.1.1 NBO Analysis

Figure 2 shows the NBO calculations which reveal the high ionic bonding property of Pt-formaldehyde interaction. The interaction is the outcomes of hybridization of 3.82% of 6s orbital corresponding to Pt atom and 96.17% of 2p orbital corresponding to oxygen atom with absence of metal to formaldehyde electron back-donation. While formaldehyde was encapsulated, the total occupancies of Ni and Pd atoms were nearly unchanged, whereas Pt atom received more electrons at 6s orbital after encapsulation of formaldehyde. These observations optimizes to the relativistic effect of a bulky metal atom like Pt which transforms formaldehyde molecule to become as an active electrophile in Pt-ZSM-5. As a result, the carbonyl carbon of the HCHO attached in the Pt-ZSM-5 system favors the nucleophilic attack of propene.

The carbonyl (CO) stretch vibrational frequencies of HCHO and its complexes with different Ni-, Pd-, and Pt-ZSM-5 zeolites were predicted. The CO vibrational frequencies of metal(II)/ZSM-5complexes were predicted to be 1677, 1637, and 1616 cm^{-1} for Ni-, Pd-, and Pt-ZSM-5 zeolites, respectively. For all the complexes, the carbonyl (CO) stretch vibration is red shifted by 25-86 cm^{-1} in respect to CO vibrational frequency observed at 1702 cm^{-1} in formaldehyde (Table 2). The frequency shifts to lower wave number. From these evidences it is clear that the reaction between HCHO and propylene is physical adsorption. They just form co-adsorption complex without any bond formation.

Table 2 Vibrational frequencies (cm^{-1}) and frequency shift ($\Delta\upsilon_{CO}$) of the carbonyl bond of the encapsulated formaldehyde on M- ZSM-5

System	Calculated (cm^{-1})	$\Delta\upsilon_{CO}$ (cm^{-1})
HCHO	1702	-
HCHO @ Ni-ZSM-5	1677	25
HCHO @ Pd-ZSM-5	1637	45
HCHO @ Pt-ZSM-5	1616	86

Adsorption energies when metal cations namely Ni^{2+}, Pd^{2+}, and Pt^{2+} bind to the formaldehyde molecule are -128.9, -65.6, and -93.7 kcal/mol

respectively. At these energies, the corresponding bond length between oxygen atom of formaldehyde and the metal atom are in order of Ni-O < Pt-O < Pd-O (1.96, 2.03, and 2.06 Å). Charge transfer occurs when metals' are adsorbed on the zeolite framework and the amount of charge transfer between metal exchanged zeolite and formaldehyde is exhibited for the Pt-ZSM-5 which reports the highest adsorption energy. After the formaldehyde encapsulation, the reaction is followed by the co-adsorption of propene to the encapsulated complex and then by a concerted transition state.

3.2 Carbonyl-ene reaction between HCHO over Metal–ZSM-5 and propene

Co-adsorption step has two parts; first, the adsorbed HCHO interacts with diffusing propene via a π electron forming the co-adsorption complex with energy lower than formaldehyde adsorption. This co-adsorption complex makes some changes in the geometry. Secondly, it converts into product and M-ZSM-5 via transition state. Propene and the encapsulated formaldehyde forms a concerted transition structure in which new C-C1 and O-H bonds are formed simultaneously with breaking of C3-H bond. The C-O bond of formaldehyde is extended from 1.24 Å to about 1.25 Å for the Ni and Pd systems whereas the Pt system is slightly longer, 1.29Å. This is compatible with the lowest activation energy of 14.8 kcal/mol, for the reaction in Pt-ZSM-5, compared to 19.3 and 16.5 kcal/mol observed in Ni- and Pd-ZSM-5, respectively. The obtained results associate well with the same reaction studied using Cu(I), Ag(I) and Au(I)-FAU catalysts reported by the researcher [28].

We also examined the atomic charges of the molecules in the reaction by means of Natural Population Analysis (NPA) method and partial charges are documented in Table 3. Table ST1 represents the electronic configurations of all the systems (Supporting Information). It can be seen, metal on the ZSM-5 zeolite bears positive charge, which is compensated by the surrounding oxygen atoms. The calculated charges were found to be +0.729, +0.587, and + 0.669 e for the Ni, Pd, and Pt atoms respectively. When HCHO adsorbs on the metal, it is slightly changing because the formaldehyde carbonyl group dispersed the metal partial positive charge. Simultaneously, the

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interaction between metal and formaldehyde makes the carbonyl electron cloud deviates from carbon atom. Thus makes formaldehyde oxygen atom more negative and carbon atom more positive. The concentration of negative charge on oxygen can stabilize the adsorption of formaldehyde. At the TS structure, the O atom becomes more -ve than the charge over carbon. The increased negative charge on oxygen enhances the interaction between 3

butenol and ZSM-5. This shows the compensation between the zeolite oxygen atoms and the metal charges. The charge of the formaldehyde carbon was found to be +0.310, +0.293 and +0.323 e in the Ni, Pd and Pt-ZSM-5 system. This indicates that Pt-ZSM-5 causes the formaldehyde molecule to become an active electrophile. So that the carbon of the HCHO adsorbed on Pt-ZSM-5 system favours the nucleophilic attack of another molecule.

Table 3 Partial Electronic Charges of the Metal Atom and the Probe Molecules

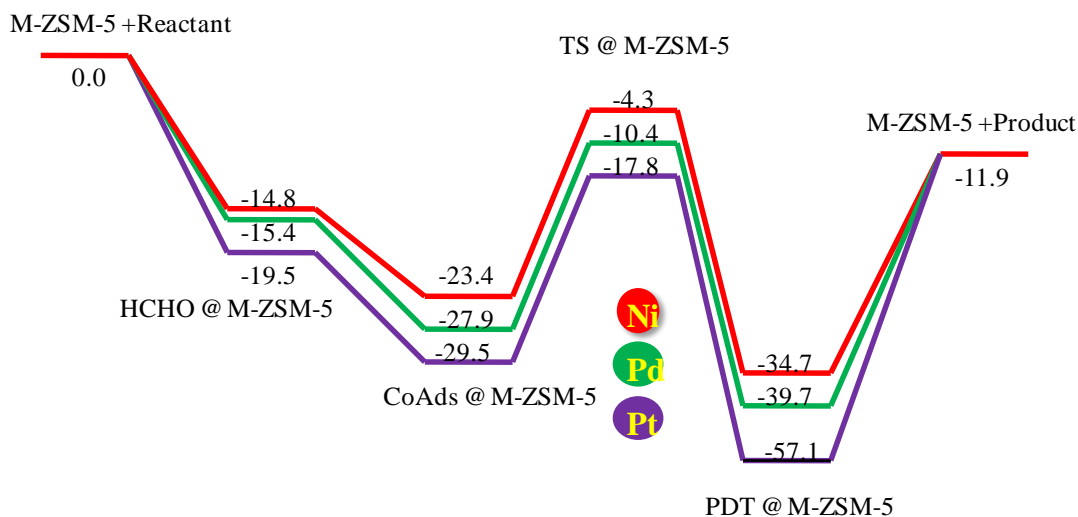| Step		NPA - charges/e		
		Ni-ZSM-5	**Pd-ZSM-5**	**Pt-ZSM-5**
Catalysts	metal	0.729	0.587	0.669
Ads	C	0.310	0.293	0.323
	O	-0.562	-0.567	-0.538
	HCHO	0.095	0.103	0.169
	metal	0.695	0.683	0.762
CoAds	C	0.311	0.302	0.289
	O	-0.592	-0.568	-0.566
	CoAds	0.078	0.118	0.141
	metal	0.703	0.687	0.756
TS	C	-0.046	0.023	-0.075
	O	-0.703	-0.687	-0.751
	TS	0.291	0.214	0.374
	metal	0.699	0.723	0.807

Fig. 3. The energetic reaction profile calculated by the B3LYP/LANLDZ level of theory (all energies in kcal/mol).

The energetic reaction profile is shown in the figure 3. In co-adsorption step, the co-adsorption energy for the propene bound to be encapsulated formaldehyde is increases by ~10 kcal/mol

compared to the formaldehyde adsorption energies in all the cases. For carbonyl ene reaction, it is initiated by co-adsorption of propene and the adsorbed HCHO at the active site of the ZSM-5

zeolite. The co-adsorption energy is lower than the formaldehyde adsorption. From figure 3 it can be seen that the required higher energy barrier to generate 3 butenol from the co-adsorption complex due to electrostatic field generated by the metal and the zeolite oxygen atoms. In step 3, the adsorbed 3 butenol product would endothermically desorbs from the zeolite active acid site, which requires 11.9 kcal/mol. The complete reaction is exothermic.

4. Conclusion

To conclude, we have demonstrated the carbonyl-ene reaction over Ni-, Pd-, and Pt - exchanged ZSM-5 zeolites. The Pt^{2+} ion shows a high performance in the formaldehyde encapsulation process and exhibits better catalytic activity. By analyzing the electronic configuration, Pt 6s orbital plays a vital role in this high activity. It accepts an electron and induces a significant charge in the probe molecules. This inductive effect is enhanced by the zeolite framework. Although the activity of the Ni- and Pd-ZSM-5 was not as high as that of the Pt-ZSM-5, the zeolite structures are suitable for use as a catalyst for Carbonyl-ene reaction. From the obtained results, Pt-exchanged ZSM-5 zeolite might be a better candidate for carbonylene reactions.

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