

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: X. Wang, R. Wang, X. Gu, J. Jia and Z. Zheng, *Catal. Sci. Technol.*, 2019, DOI: 10.1039/C8CY02579G.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/catalysis

Catalysis Science & Technology

Provensor States States

COMMUNICATION

Light-assisted O-methylation of Phenol with Dimethyl Carbonate over Layered Double Oxide Catalyst

Received 00th January 20xx, Accepted 00th January 20xx

Xiaoyu Wang,^{a,b} Ruiyi Wang,*^a Xianmo Gu,^a Jianfeng Jia^c and Zhanfeng Zheng*^{a,b}

DOI: 10.1039/x0xx00000x

www.rsc.org/

Published on 11 March 2019. Downloaded on 3/21/2019 1:53:29 AM.

Layered double oxide (LDO) exhibit high catalytic activity in Omethylation of phenol under light irradiation, owing to the synergism of the light absorption of phenol molecules to achieve excited states as well as the facilitated adsorption of reactant molecules by acid-base pairs of Mg₃Al-LDO, which can both promote phenol deprotonation.

The O-methylation of phenols is of crucial importance in synthesis products for used as stabilizers for plastics and antioxidants for oils and grease as well as intermediates in the field of dyes, agricultural chemicals, and fragrances.¹ Traditional synthesis methods generally involved the use of toxic alkylating agents (methyl halide, phosgene or dimethyl sulfate), high reaction temperature ²⁻⁵ and generating large quantity of waste. Dimethyl carbonate (DMC) is found to be an efficient methylating agent, the by-product methanol can be recycled for the production of DMC.⁶ The O-methylation of phenol with DMC has been reported over potassium carbonate ^{7,8} and 1-n-butyl-3-methylimidazolium chloride.⁹ To avoid the limitations of homogeneous catalytic process with the difficulty of catalyst recovery and product separation, the development of an environmentally benign heterogeneous catalyst for the O-methylation of phenol continues to attract significant interest.

A variety of catalysts have been investigated for the Omethylation of phenol reaction. Bal and co-workers found that alkali loaded silica catalyst can efficiently drive the selective Oalkylation of phenol at 673 K.¹⁰ Fu et al. reported that X-zeolites can be used for the O-methylation of phenol with DMC at 553K.¹¹ Both of the above reactions need to be completed in the gas phase and high temperature conditions. Recently, Gadge and co-workers demonstrated that magnesium oxide was used as heterogeneous catalyst for the O-methylation of phenol with DMC, in which reduce the reaction temperature to 443 K by using microwave method.¹² Layered double oxides (LDO) originated from thermal decomposition of Layered double hydroxides (LDHs). LDO have the advantages of high surface area and thermal stability, along with the tunable acidity and basicity, which are characterized by the presence of acid-base pairs.¹³⁻¹⁵ These acid-base pairs could facilitate the adsorption of reactants molecules. According to Chizallet et al.,¹⁶ the contact between a protic reactant molecule and an oxide surface can provoke its deprotonation. Jyothi and coworkers demonstrated that LDO catalysts can efficiently drive the O-methylation of phenols at a milder condition is rarely reported.

Herein we describe a light-assisted green process for Omethylation of phenol with dimethyl carbonate to synthesize anisole on LDO catalysts with high conversion and product selectivity. The catalytic performance of various LDO catalysts: Mg₃Al-LDO, Ni₃Al-LDO, and Zn₃Al-LDO in the O-methylation of phenol were evaluated in presence and absence of light (highpressure mercury lamp), respectively. As shown in Fig. 1a, Mg₃Al-LDO exhibits the highest activity with the DMC conversion at 82.5% and selectivity to anisole at 95.6% under high-pressure mercury lamp irradiation at 160 °C for 6 h, which is much higher than Ni₃Al-LDO (Conv.=56.3%, Sel.=88.4%) and Zn₃Al-LDO (Conv.=47.2%, Sel.=69.7%). It is noted that all the catalyst exhibit much higher activity under light irradiation than in the dark. Normally, the difference between the activation energies of the light irradiated system and the system in the dark indicates the contribution of irradiation towards reducing the apparent activation energy.¹⁸ The activation energies of light-driven and thermal-driven reaction were calculated according to the Arrhenius equation shown in Fig. 1b (calculation details shown in the ESI), being 97.55 and 106.58 kJ/mol, respectively. This means that light energy can facilitate the reaction.¹⁸ The catalyst activity remained stable (Fig. S4a) and the structure of Mg₃Al-LDO had no obvious change (Fig. S4b) after reused for five cycles. Thus we choose catalyst Mg₃Al-LDO to investigate the activation of reactants.

^{a.} State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, Shanxi 030001, PR China. Email: wangruiyi@sxicc.ac.cn, zfzheng@sxicc.ac.cn

^{b.} Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, PR China

Chinese Headering of Steinees, Deging Tooley, Fit China or The School of Chemical and Material Science, Shanxi Normal University, Linfen, Shanxi 041004, PR China

⁺ Electronic Supplementary Information (ESI) available: More experimental details, catalyst characterization and reaction test results. See DOI: 10.1039/x0xx00000x



Fig. 1 (a) Catalytic performance: conversion rate under irradiation and dark, selectivities of DMC using varied catalysts under irradiation. (b) Plot of $(1-X_b)^{-1}$ versus reaction time at different temperatures on the Mg₃Al-LDO catalyst: the reaction was conducted in light (solid line) or in the dark (dotted line), and the activation energy scheme (upper left corner). **Reaction conditions:** catalyst, 0.28 g; phenol, 135 mmol; DMC, 67.5 mmol; Ar, 1 atm; light intensity, 66 mW/cm²; reaction temperature, 160 °C; reaction time, 6 h. MgO-Al₂O₃: MgO and Al₂O₃ were mechanically mixed in a mortar according to n(Mg): n(Al)=3:1.

In-situ FT-IR spectra after coadsorption of phenol and DMC on Mg_3AI -LDO was conducted (Fig. 2a and Fig. 2b) to understand the activation process of the reactants (detailed explanation shown in the ESI). The diminished in intensity of O-H stretching vibrations band of phenol at 3662 cm⁻¹ and 3639 cm⁻¹ indicating the hydroxyl of phenol has been deprotonated.¹⁹ Low frequency shift of the C-H stretching vibrations bands of the aromatic ring of phenol at 3064 cm⁻¹ and 3036 cm⁻¹ indicating the phenol H-bonded (of hydroxyl) to base sites of LDO. Low frequency shift of the vibration band of DMC carbonyl oxygen group at 1683 cm⁻¹ indicating the carbonyl oxygen atoms of DMC associated with the acidic sites of LDO.20 The asymmetric variable angle vibration band of anisole methyl group at 1446 cm⁻¹ appeared from nothing and increased in intensity indicating the anisole production. It is revealed that both reactants are adsorbed on the catalyst surface during the O-methylation reaction. Phenol is activated by H-bonding (of hydroxyl) to the basic Journal Name

Page 2 of 5

sites of LDO, while DMC is adsorbed on the acidic sites of LDO, while DMC is adsorbed on the acidic sites of LDO, while DMC is adsorbed on the acidic sites of LDO, while DMC is adsorbed on the acidic sites of LDO, while DMC is adsorbed on the acidic sites of LDO, while DMC is adsorbed on the acidic sites of LDO, while DMC is adsorbed on the acidic sites of LDO, while DMC is adsorbed on the acidic sites of LDO, while DMC is adsorbed on the acidic sites of LDO, while DMC is adsorbed on the acidic sites of LDO, while DMC is adsorbed on the acidic sites of LDO, while DMC is adsorbed on the acidic sites of LDO, while DMC is adsorbed on the acidic sites of LDO, while DMC is adsorbed on the acidic sites of LDO, while DMC is adsorbed on the acidic sites of LDO, while DMC is adsorbed on the acidic sites of LDO, while DMC is adsorbed on the acidic sites of LDO, while DMC is adsorbed on the acidic sites of LDO, while DMC is adsorbed on the acidic sites of the aci

The surface acidic and basic sites were determined by CO₂-TPD and NH₃-TPD technique as shown in Table S2, Fig. 2c and Fig. 2d. For the CO₂-TPD profiles (Fig. 2c), broad CO₂ desorption peak in the range 100-700 °C can be deconvoluted into two peaks with desorption peaks with maximal temperatures at 300 °C and 500 °C, which can be assigned to the medium and strong basic sites, respectively. The weak, medium and strong basic sites are derived from OH⁻, metal-oxygen pair (Mg²⁺-O²⁻, Al³⁺-O²⁻) and lowcoordination oxygen anion (O2-), respectively.²² In the NH₃-TPD profiles (Fig. 2d), a broad peak from NH₃ desorption between 100-800 °C can be deconvoluted into three contributions with a maximal temperature in the region 120-220 °C, 250-450 °C and 450-700 °C, which can be identified as the weak (Mg²⁺), medium and strong acidic site (Al³⁺), respectively.²³ Notably, it is observed that the catalyst Mg₃Al-LDO gives the largest amount of both medium basic site with 1.50 mmol/g and medium and strong acidic site with 0.71 mmol/g and 0.29 mmol/g, respectively (Table S2). It indicates that the medium strength Lewis basic sites (mostly Mg2+-O2-) serve as active center to activate phenol to produce phenoxyl species, while medium and strong acidic site (Al3+) act as active site toward associated to carbonyl oxygen of DMC.



Fig. 2 (a) *In-situ* FT-IR spectra of Mg₃Al-LDO after co-adsorption of phenol and DMC: from 4000 cm⁻¹ to 2000 cm⁻¹ and (b) from 2000 cm⁻¹ to 600 cm⁻¹. (downward arrow: band intensity decreases with the increase of time; upward arrow: band gradually appears with the increase of time); (c) TPD profiles of CO₂-TPD and (d) NH₃-TPD of Mg₃Al-LDO, Ni₃Al-LDO, and Zn₃Al-LDO.

To further prove the role of acidic and basic sites, control experiments with a series of catalysts with different amount of acidic and basic sites (Mg₃Al-LDHs, MgO, Al₂O₃, MgO-Al₂O₃) were conducted (Fig. 1a). The physical properties of catalysts are shown in Table S1. Obviously, the surface area is not the decisive factor on the performance, as the optimal catalyst has a relatively small

Journal Name

specific surface area. Basic sites on the catalysts surface alone cannot simply be the dominate factor enhancing the catalyst performance, since MgO and Mg₃Al-LDHs have basic surface sites but both exhibit low activity under irradiation and in the dark, respectively. Acidic sites on the catalysts alone also cannot be the dominating factor, since Al₂O₃ have acid surface sites but exhibit low activity either. Physically mixed MgO and Al₂O₃ catalyst also exhibit lower activity than layered double oxide, which due to that LDO containing the acid-base pairs. It should be noted that excellent catalytic results have been obtained with catalysts containing acid-base pairs.^{24,25} In this case, a cooperative role of acid-base sites has been found that allow substituting strong bases by very simple catalysts with mild acid-base pairs. The superior behavior of LDO could be due to a combined acid-base catalyzed Omethylation of phenol, the acidic sites of LDO associated to carbonyl oxygen of DMC and the basic sites of LDO associated to hydrogen of phenolic hydroxyl which can activate the hydroxyl group of phenol adsorbed on the surface of catalyst.^{17,21} Besides, MgAl-LDO with varied Mg/Al ratios were synthesized (Mg1Al-LDO, Mg₂Al-LDO, Mg₃Al-LDO) and the catalytic performance also agree with the above results (Fig. 1a). Mg₃Al-LDO, which has the maximum amount of basic sites and acidic sites among the varied Mg/Al ratio of MgAl-LDO, exhibited the best catalytic performance. Catalyst Zn₃Al-LDO with the conversion of 47.2% and Ni₃Al-LDO with the conversion of 56.3% exhibit slightly better performance under high-pressure mercury lamp irradiation than in the dark with the conversion of 35.9% and 45.0%, respectively. Mg₃Al-LDO exhibited the best performance under irradiation could be attributed to the better ability to adsorbed reactant molecule and the fact that irradiation can enhance the catalytic performance. Besides, according to the UV-Vis spectra of Mg₃Al-LDO, Ni₃Al-LDO, and Zn₃Al-LDO shown in Fig. S6a, Mg₃Al-LDO shows no light absorption in the high-pressure mercury lamp output spectrum range. Although Ni₃Al-LDO and Zn₃Al-LDO both exhibit bandgap absorption at ca. 370 nm in the UV-Vis spectra and can generate electron-hole pairs under high-pressure mercury lamp irradiation, but their catalytic activities are much lower than that of Mg₃Al-LDO. When a full-spectrum Xe lamp (350-880 nm) is used, both of Ni₃Al-LDO and Zn₃Al-LDO exhibit activity similar to that under dark condition (Fig. S6b). Moreover, the catalytic activity of O-methylation of phenol over TiO₂-P25 catalyst under high-pressure mercury lamp irradiation was conducted and the activities under irradiation and in the dark are similar (Fig. S6b). Therefore, it can be concluded that photogenerated electrons and holes in LDOs and TiO₂ are not the

& lechnology Accepted Manu

Catalysis Science

key factors to promote the reaction. In addition, the influence of light intensity on the reactivity was conducted (fig0 \$7). If is found that the conversion rate of DMC decreases with the decrease of light intensity, which indicates that the reaction is driven by light in the presence of Mg₃Al-LDO.

To further investigate the role of light in our reaction system, the UV-Vis spectra of DMC and phenol were conducted shown in Fig. 3a. Although DMC display an absorption band in 201 nm ascribed to π - π^* transition,²⁶ the energy of light source used (high-pressure mercury lamp, 240-740nm) was not enough to stimulate it. While phenol display strong absorption in 205 nm and 270 nm ascribed to π - π * transition, indicating that phenol molecules can absorb light to achieve the excited states.²⁶ Using the long-range corrected cam-B3LYP method of density functional theory (DFT) with 6-311++g (d,p) basis set, we have investigated the structure of phenol-DMC aggregate both in the ground state and in the first excited state. The calculation of the excited state was performed with time-dependent DFT method. As shown in Fig. 3b, in the ground state, the phenol interacts with DMC through a hydrogen bond. The calculated O-H hydrogen bond length is 1.825 Å. The C=O bond length of the carbonyl in DMC is 1.212 Å, which obviously longer than the C=O bond length (1.203 Å) in free DMC. The calculated irradiation wavelength for the first excited state is 240 nm. The transition density of this excitation is shown in Fig. 3b, it is mainly a $n-\pi^*$ transition on the phenol. It is obviously that the hydrogen bond between phenol and DMC were enhanced in the excited state. As shown in Fig. 3b, the calculated hydrogen bond length is 1.740 Å in the excited state. The enhanced hydrogen bond further activates the carbonyl of DMC. The C=O bond length slightly elongates to 1.214 Å in the excited state. The above results demonstrate that phenol molecules absorbed light to achieve the first excited states, then hydrogen bond between phenol and DMC were enhanced, resulting in deprotonation occurs more readily in the excited state. This is consistent with the literature report that the lone pair of electrons on the phenolic hydroxyl groups tend to become more conjugated to the aromatic ring system in the excited state, resulting in the hydroxyl group more acidic.27

On the basis of above analysis, a tentative mechanism for the O-methylation of phenol is proposed (Scheme 1). Firstly, phenol and DMC are adsorbed on the surface of LDO, the acidic sites of LDO (AI^{3+}) associated to carbonyl oxygen of DMC and basic sites of LDO ($Mg^{2+}-O^{2-}$) associated to hydrogen of phenolic hydroxyl (I).



Fig. 3 (a) UV-Vis spectra of DMC and phenol. (b) DFT calculation results of ground and excited states of phenol-DMC aggregate.

COMMUNICATION

Secondly, when phenol molecules absorb light to achieve the excited states, the deprotonation of phenolic hydroxyl group occurs more readily because the electrons on the phenolic hydroxyl groups are shifted into the phenol ring in the excited state, making this hydroxyl group more acidic (II). Meanwhile, the basic sites of catalyst can bind the hydrogen atom of the phenol molecule and also facilitate the O-H cleavage on the surface.²² Thirdly, the formation of anisole proceeds presumably via nucleophilic attack at the methyl carbon of DMC by the phenol oxygen (III and IV). Finally, the catalyst surface regenerates for another reaction cycle by desorption of methanol and CO_2 which are decomposed from the residual methyl hydrogen carbonate (V). It noted that the amounts of methanol and CO_2 generated during reaction are in good stoichiometric relation and the carbon balance of the reaction is satisfied within experimental error (Table S3).

Scheme 1 Schematic diagram of the proposed reaction mechanism.

In summary, Mg₃Al-LDO prepared by the facile calcination of hydrotalcite is found to be an efficient catalyst for O-methylation of phenol using dimethyl carbonate as alkylating agent under light irradiation. The excellent catalytic performance can attribute to the synergistic effects of two factors: (1) The phenol molecules can absorb light to achieve the excited states, which promote its deprotonation occurs more readily; (2) The acid-base pairs of Mg₃Al-LDO can facilitate the adsorption of reactants molecules and provoke deprotonation. This simple, cost-effective, and environmentally benign catalytic process exhibits great potential in the alkylation of phenols.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

View Article Online DOI: 10.1039/C8CY02579G

Journal Name

This work was supported by the National Natural Science Foundation of China (Nos. 21773284, 21703276), the Shanxi Science and Technology Department (Nos. 201801D221093, 201601D021032) and the Hundred Talents Programs of the Chinese Academy of Sciences and Shanxi Province.

Notes and references

- 1 E. Fuhrmann and J. Talbiersky, *Org. Process Res. Dev.*, 2005, 9, 206-211.
- 2 S. Oae and R. Kiritani, Bull. Chem. Soc. Jpn., 1966, **39**, 611-614.
- 3 S. C. Lee, S. W. Lee, K. S. Kim, T. Jin. Lee, D. H. Kim and J. C. Kim, *Catal. Today*, 1998, **44**, 253-258.
- 4 M. C. Samolada, E. Grigoriadou, Z. Kiparissides and I. A. Vasalos, J. Catal., 1995, **152**, 52-62.
- 5 P. Tundo and M. Selva, Acc. Chem. Res., 2002, **35**, 706-716.
- 6 D. Delledonne, F. Rivetti and U. Romano, *J. Organomet. Chem.*, 1995, **488**, 15-19.
- 7 S. Ouk, S. Thiebaud, E. Borredon, P. Legarsb and L. Lecomte, *Tetrahedron Lett.*, 2002, **43**, 2661-2663.
- 8 A. Bomben, M. Selva, and P. Tundo, Ind. Eng. Chem. Res., 1999, 38, 2075-2079.
- 9 Z. L. Shen, X. Z. Jiang, W. M. Mo, B. X. Hua and N. Sun, Green Chem., 2005, 7, 97-99.
- R. Bal and S. Sivasanker, Appl. Catal. A: Gen., 2003, 246, 373-382.
- 11 Z. H. Fu and Y. Ono, Catal. Lett., 1993, 21, 43-47.
- 12 S. T. Gadge, A. Mishra, A. L. Gajengi, N. V. Shahi and B. M. Bhanage, *RSC Adv.*, 2014, **4**, 50271-50276.
- 13 D. G. Costa, A. B. Rocha, W. F. Souza, S. S. X. Chiaro, and A. A. Leitao, *J. Phys. Chem. C.*, 2012, **116**, 13679-13687.
- V. R. L. Constantino and T. J. Pinnavaia, *Inorg. Chem.*, 1995, 34, 883-892.
- 15 D. P. Debecker, E. M. Gaigeaux and G. Busca, *Chem. Eur. J.*, 2009, **15**, 3920-3935.
- 16 C. Chizallet, M. L. Bailly, G. Costentin, H. L. Pernot, J. M. Krafft, P. Bazin, J. Saussey, M. Che, *Catal. Today*, 2006, **116**, 196-205.
- 17 T.M. Jyothi, T. Raja, M. B. Talawar, B. S. Rao, *Appl. Catal., A: Gen.*, 2001, **211**, 41-46.
- 18 S. Sarina, E. R. Waclawik and H. Zhu, Green Chem., 2013, 15, 1814-1833.
- 19 T. Ebata, T. Watanabe and N. Mikami, J. Phys. Chem., 1995, 99, 5761-5764.
- 20 J. S. Byrne, P. F. Jackson and K. J. Morgan, *Perkin Trans.*, 1975, 2, 1800-1802.
- 21 T. Beutel, J. Chem. Soc., Faraday Trans. 1998, 94, 985-993
- 22 B. N. Zope, D. D. Hibbitts, M. Neurock, R. J. Davis, Science, 2010, 330, 74-78.
- 23 D. Tichit and F. Fajula, *Stud. Surf. Sci. Catal.*, 1999, **125**, 329-340.
- 24 B. M. Bhat, Orient. J. Chem., 2012, 28, 1751-1760.
- 25 A. H. Padmasri, A. Venugopal, V. D. Kumari, K. S. Rama Rao, P. K. Rao, J. Mol. Catal. A: Chem., 2002, **188**, 255-265.
- 26 DMS Documentation of Molecular Spectroscopy: UV Atlas of organic compounds, *London*, 1960–1971.
- Z7 J. R. Lakowicz, Springer Science+Business Media, New York, 1999.



Page 4 of 5

Published on 11 March 2019. Downloaded on 3/21/2019 1:53:29 AM.

Table of Content:

Light-assisted O-methylation of Phenol with Dimethyl Carbonate over Layered Double Oxide Catalyst

Xiaoyu Wang,^{a,b} Ruiyi Wang,^{*a} Xianmo Gu,^a Jianfeng Jia^c and Zhanfeng Zheng^{*a,b}

^a State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, Shanxi 030001, China

^b Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, PR China

^c The School of Chemical and Material Science, Shanxi Normal University, Linfen, Shanxi 041004, PR China



Phenol molecules can adsorb light to achieve the excited states, which promote its deprotonation occurs more readily.