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ARTICLE TYPE

Alkylation of benzene with carbon monoxide over Zn/H-ZSM-5 zeolite studied by in situ solid-state NMR spectroscopy

Xiumei Wang, Jun Xu*, Guodong Qi, Chao Wang, Qiang Wang, Feng Deng*

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We show by using in situ solid-state NMR spectroscopy that CO can act as an alkylating reagent and react with benzene to produce toluene over Zn/H-ZSM-5 zeolite. In the alkylation reaction, CO provides the methyl group of toluene via a methoxy intermediate.

Catalytic conversion of CO is a subject of extensive interests due to its importance in the industrial process. As an abundant C1 building block, CO in the presence of H₂ is well utilized for industrial manufacture of methanol over zinc-copper-based oxide catalyst¹ as well as hydrocarbons mainly consisting of alkenes and alkanes through the Fischer-Tropsch process². Among of various transformations, alcohols and alkenes can be potentially employed in acid-catalyzed alkylation of aromatics to produce alkylaromatics that are important petrochemical commodities³. Thus, direct use of CO as an alkylating reagent would be of considerable interest for both synthesis of alkylbenzenes and efficient utilization of CO. However this desired route is not quite straightforward. Carbonylation of benzene with CO can readily occur over solid acid catalysts via the Friedel-Crafts type formylation reaction, forming benzaldehyde or benzoic acid instead of alkylbenzenes⁴. Nevertheless, it has been reported that certain transition-metal carbonyls M(CO)_n (M=W, Rh, Ru, Cr, Co) with AlCl₃ can catalyse alkylation of benzene with CO in the presence of H₂ to give rise to alkylbenzenes⁵. It was revealed that CO inserting into the initially formed benzene complex followed by reduction resulted in the alkylated products. On the contrary, other researchers claimed that although the alkylbenzenes were produced, CO was unnecessary for the alkylation of benzene⁶. It was proposed that the cleavage and transformation of benzene by AlCl₃ was responsible for the formation of alkylbenzenes. Thus, alkylation of aromatic with CO still remains controversial. In this work, we report the direct alkylation of benzene with CO over a Zn modified HZSM-5 catalyst (Zn/H-ZSM-5) by in situ solid-state NMR spectroscopy. We show that CO can be converted into surface methoxy species which act as intermediate interacting with benzene to produce toluene. CO provides the methyl group of toluene, while benzene alone does not give rise to the alkylated products.

The Zn/H-ZSM-5 catalyst was prepared by reaction of metallic Zn vapour with HZSM-5 zeolite in according to our previous report⁷ (see Supporting information for details). In-situ ¹³C NMR spectroscopy was employed to monitor the alkylation reaction

(Fig. 1). After co-feeding ¹³C-labeled ¹³CO and unlabelled C₆H₆ over Zn/H-ZSM-5 zeolite at 298 K (Fig. 1a), besides the adsorbed benzene molecule (132 ppm), the oxidation of CO produced carbonate species (163 ppm), which was usually observed after adsorption of CO or CO₂ onto zeolites or metal oxides⁸. In addition, the formation of CO₂ was observed in the

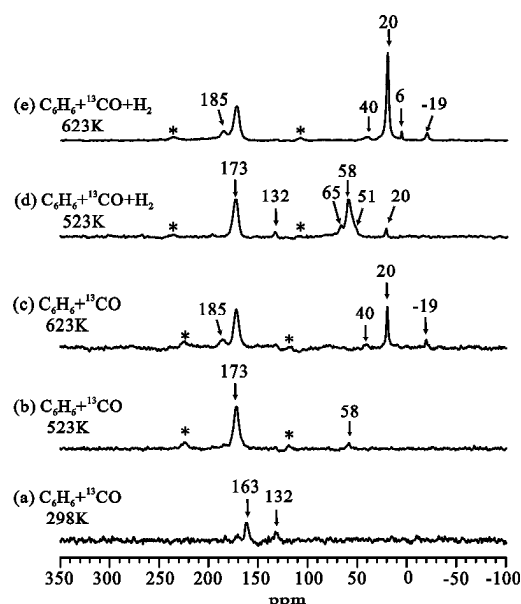


Fig. 1 ¹³C CP/MAS NMR spectra of products formed from co-adsorption of carbon monoxide and benzene on Zn/H-ZSM-5 catalyst heated for one hour at different temperatures. a) ¹³CO and C₆H₆ at 298 K. b) ¹³CO and C₆H₆ at 523 K. c) ¹³CO and C₆H₆ at 623 K. d) ¹³CO, C₆H₆ and H₂ at 523 K. e) ¹³CO, C₆H₆ and H₂ at 623 K. Asterisks denote spinning sidebands.

corresponding ¹³C MAS NMR spectrum due to the oxidation of CO (Fig. S1). Further heating the sample at 523 K for one hour (Fig. 1b) led to the formation of surface formates (173 ppm)⁸⁻⁹. This is due to the hydrogenation of carbonate species by the surface protons (Brönsted acid sites) of the zeolite support. In addition, a weak signal appeared at 58 ppm, which can be assigned to surface methoxy species^{7, 10}. In the catalytic conversion of methane or methanol, methoxy species are normally formed as an important intermediate by initial activation of the reactants. Here, the methoxy species might be produced from consecutive hydrogenation of the formate species⁸. The stepwise oxidation and hydrogenation of CO to form methoxy

species shows similarity to the reaction of methanol synthesis via CO over zinc-copper-based oxide catalysts, where methoxy species was formed as an intermediate prior to the formation of methanol¹¹. A new strong signal at 20 ppm appeared when the temperature was elevated to 623 K (Fig. 1c), which falls in the chemical shift range of terminal methyl group of hydrocarbons or oxygenated hydrocarbons^{8, 12}. Indeed, our GC-MS analysis shows that toluene dominates the product extract at the reaction temperature of 623 K (Fig. S2). Thus the 20 ppm signal can be assigned to the methyl group attached to the phenyl ring¹³. The consumption of methoxy species along with the formation of toluene suggests the intermediate role of the methoxy species in the alkylation process. Analogously, the intermediate role of methoxy species was also found in the course of alkylation of benzene with methane^{12b, 14}.

Besides the dominant alkylation reaction, the high reactivity of methoxy species also led to some side reactions at higher temperatures. Zinc methyl species (-19 ppm)^{7-9, 15} is formed by dissociation of methane resulting from methanation of CO via methoxy intermediate. Carbonylation of CO with methoxy species brings about acetic acid (carbonyl carbon at 185 ppm)⁸. Additionally, further transformation of toluene occurs, reflected by the formation of diphenylmethane (-CH₂- group, 40 ppm) due to the interaction of toluene with benzene over the Brønsted acid sites of zeolites^{9a, 16}.

Now, we have determined the intermediate role of methoxy species in the alkylation of benzene with CO. It is expected that the alkylation would be promoted by optimizing the conversion of CO into methoxy species before the alkylation reaction. Since the conversion of CO into methoxy species depends on the initial hydrogenation, adding a trace of H₂ as co-reactant may promote the hydrogenation process. It can be seen from Fig. 1d that the addition of hydrogen notably increases the formation of methoxy species (58 ppm) at 523 K. Moreover, two signals appear at 51 ppm and 65 ppm, corresponding to methanol and dimethyl ether (DME) respectively. The conversion of methoxy species into methanol and DME is due to a typical chemical equilibrium in the process of methanol conversion over acidic zeolites¹⁰. Due to the presence of hydrogen, water molecule is probably formed by the reverse water-gas shift reaction that prevails in the process of methanol synthesis from CO/CO₂/H₂¹⁷. Methanol and DME are thus generated by the reaction of methoxy species with the in-situ formed water molecule. The promoting effect of H₂ on the alkylation reaction is evidenced by the observation of the methyl group signal of toluene (20 ppm), which in contrast, is invisible at the same temperature (523 K) without adding H₂ (Fig. 1b). Further increasing the reaction temperature to 623 K considerably facilitates the formation of toluene, and leads to a partial decomposition of methoxy species into ethane (6 ppm, see Fig. 1e)¹⁸. The disappearance of methanol and DME along with the reaction demonstrates that they can act as the alkylation agent as well and react with benzene to produce toluene via the methoxy intermediate.

In order to gain insight into the role of benzene in the alkylation reaction, ¹³C labelled benzene was used, and thus the evolution of the carbon atoms of phenyl ring could be traced (Fig. 2a-c). No reaction took place until 623 K, and only partial oxidation of benzene occurred, evidenced by the appearance of phenol (-OH

bound ¹³C atom signal at 153 ppm)¹⁹ (Fig. 2b). It was reported that phenol was usually produced by reaction of benzene over metal (Fe, Ga, Cu) modified H-ZSM-5 zeolites²⁰. As known from the above results (Fig. 1), the alkylation reaction has occurred under this condition. The absence of ¹³C NMR signal at 20 ppm indicates that the methyl groups of toluene could be originated from the unlabelled CO rather than the ¹³C labelled benzene. Similar result was found for the reaction in the presence of H₂ as

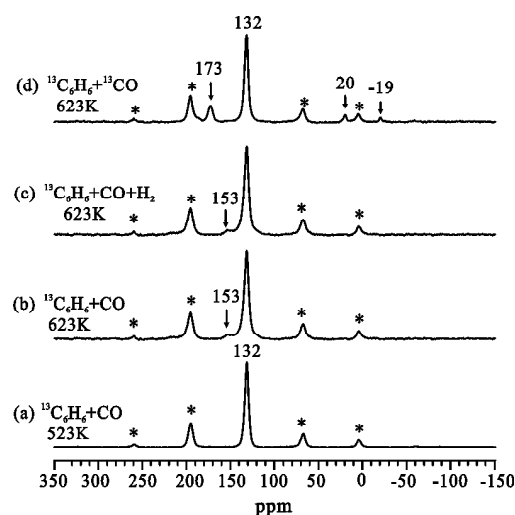
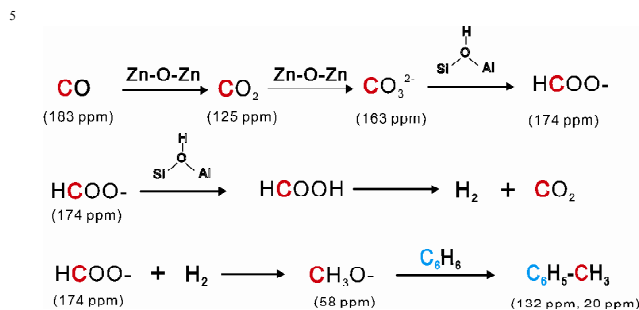


Fig. 2 ¹³C CP/MAS NMR spectra of products formed from co-adsorption of carbon monoxide and benzene on Zn/H-ZSM-5 catalyst heated for one hour at different temperatures. a) ¹³C₆H₆ and CO at 523 K, b) ¹³C₆H₆ and CO at 623 K, c) ¹³C₆H₆, CO and H₂ at 623 K, d) ¹³C₆H₆ and ¹³CO at 623 K. Asterisks denote spinning sidebands.

co-reactant (Fig. 2c), indicating that the reducing atmosphere has no observable effect on the conversion of benzene to alkylbenzene. In contrast, when ¹³CO was used (Fig. 2d), the ¹³C NMR signal of methyl group (20 ppm) appeared, confirming that the origin of the methyl group of toluene is from ¹³CO, in agreement with the result of co-feeding ¹³CO and unlabelled benzene (Fig. 1c). Moreover, feeding ¹³CO alone did not produce alkylbenzenes under the identical reaction condition (Fig. S3). These results lead to the conclusion that methyl group of toluene is exclusively produced by CO while benzene affords the phenyl ring. Mass spectra analysis of the toluene obtained from reactions with alternative ¹³C labeled reactant shows detailed information on the carbon atoms distribution and provides solid confirmation of the above results (Fig. S4).

Based on the ¹³C NMR experimental results, we propose a reaction pathway (Scheme 1) for the alkylation of benzene with CO over Zn/H-ZSM-5 to form toluene. CO is first oxidized into CO₂ on the Zn-O-Zn cluster which was previously identified on Zn/H-ZSM-5⁷, and then CO₂ is transformed into carbonate species. The carbonate species is further converted into formate species through hydrogenation by proton transfer from the Brønsted acid site of H-ZSM-5 support. The subsequent hydrogenation of formate species gives rise to methoxy species^{11, 21}. In the absence of additional H₂, the decomposition of formate species via transient formic acid may bring about the required H₂ and CO₂, which also prevails on the other Zn modified zeolite and ZnO complex catalyst²¹⁻²². The formation of methanol from methoxy intermediate is facilitated by water molecule which is

generated via reaction of added H₂ with CO₂ (reverse water gas shift reaction). Upon the formation of methoxy intermediates, toluene is produced by reaction of methoxy group with benzene molecule.



Scheme 1 Proposed reaction pathway for the formation of toluene from alkylation of benzene with CO over Zn/H-ZSM-5 catalyst.

10 The redox properties of our Zn/H-ZSM-5 catalyst are characterized by the simultaneous presence of Zn-O-Zn cluster and Brønsted acidic protons⁷⁻⁸. CO might be initially oxidized by the Zn-O-Zn cluster, and the acidic protons contribute to the following hydrogenation, which could be notably promoted by

15 co-feeding H₂. Since the simplest carbenium ion has not been identified on acidic zeolites up to now, the methoxy species has been widely considered as ‘stabilized carbenium ion’ and active intermediate in various zeolite-catalysed reactions¹⁸. As an electrophilic reagent, the methoxy species can readily interact

20 with phenyl ring to provide the methyl group of toluene.

The Brønsted acidity (H⁺) on the Zn/H-ZSM-5 catalyst plays a critical role in the alkylation reaction, particularly in the initial conversion of CO, which functions differently compared with the previously reported solid acid catalysts²³. SO₄²⁻/ZrO₂^{23b}, for instance, having much stronger Brønsted acidity, is capable of protonating benzene followed by the formation of acylium intermediate, preferably leading to carbonylation of benzene. For comparison, the lower acidity of Zn/H-ZSM-5 makes it difficult to directly protonate CO or benzene and thus makes the

30 carbonylation of benzene unfavourable. It is the bifunctionality of the Zn/H-ZSM-5 catalyst that provides a viable way to activate CO and promote the alkylation reaction.

In summary, we have reported the activation of CO and its alkylation reaction with benzene over the Zn/H-ZSM-5 catalyst.

35 The redox property of Zn/H-ZSM-5 leads to conversion of CO into methoxy species via a consecutive oxidation and hydrogenation process. The alkylation reaction occurs due to the electrophilic substitution of aromatic by the methoxy species. Our experimental results also demonstrate that the alkylation reaction

40 necessitates both benzene and CO, in which CO provides the methyl groups while benzene affords phenyl ring of the substituted product. It is widely recognized that CO molecule is the simplest carbonylating/acylating reactant for generation of products containing CO group in a variety of catalytic reactions.

45 The alkylating role of CO presented herein implies that different pathways could be developed to selectively convert CO into desired functional group of final product by pre-activation of CO into specific intermediates over acidic zeolites. We hope this will be helpful for the rational design of multifunctional catalysts for

50 efficient activation and transformation of CO into industrially

important chemicals.

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State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Center for Magnetic Resonance, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, P. R. China; E-mail: xujun@wipm.ac.cn; dengf@wipm.ac.cn

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Alkylation of benzene with CO produces toluene over Zn/H-ZSM-5 zeolite, in which CO provides the methyl group of toluene via a methoxy intermediate.

