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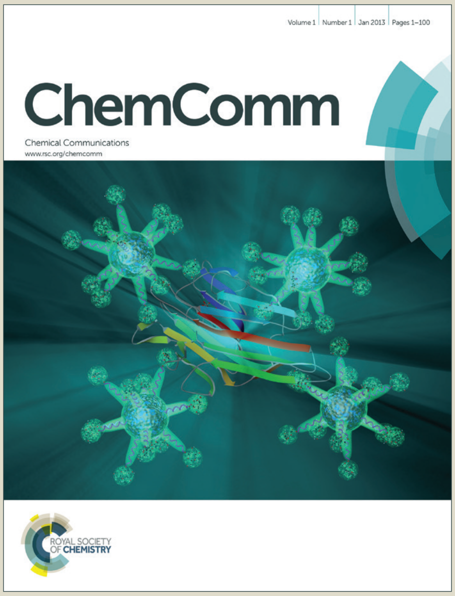

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DOI: 10.1039/C5CC03087K

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Catalytic conversion of isophorone to jet-fuel range aromatic hydrocarbons over a MoO_x/SiO_2 catalyst

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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For the first time, jet fuel range C_8-C_9 aromatic hydrocarbons were synthesized in high carbon yield (~80%) by the catalytic conversion of isophorone over the MoO_x/SiO_2 at atmosphere pressure. The possible reaction pathway was proposed according to the controlled experiments and the intermediates generated during the reaction.

With the increase of social concern about the energy and environmental problems, the catalytic conversion of abundant, renewable and CO_2-neutral biomass to fuels[1] and chemicals[2] becomes a very attractive research topic. Lignocellulose is the main component of agriculture wastes and forest residues. Jet fuel is one of the most demanded liquid transportation fuels. In recent years, the synthesis of jet fuel range hydrocarbons with the lignocellulosic platform chemicals has drawn tremendous attention.[3] So far, most of the reported work about bio-jet fuel was focused on the synthesis of C_8-C_{16} chain alkanes. Compared with the conventional jet fuel (a mixture of chain alkanes, cycloalkanes and aromatic hydrocarbons), these chain alkanes have shortage at their relatively lower densities and volumetric heating values. In real application, they must be blended with conventional jet fuel to meet the specification of aviation fuel.

Aromatic hydrocarbon is a very important component of jet fuel. Compared with chain alkanes, aromatic hydrocarbons have evidently higher densities and volumetric heating values. Moreover, the presence of aromatic hydrocarbons in the jet fuel is also necessary to ensure the shrinkage of aged elastomer seals and prevent the leakage of fuel. For safety reason, there must be 8-25% aromatic hydrocarbons in the current jet fuels. To fulfil the need of real application, it is imperative to develop highly efficient technologies for the production of jet fuel range aromatic hydrocarbons with the lignocellulose derived platform chemicals. Several methodologies, such as catalytic fast pyrolysis of biomass,[4] Diels–Alder reactions of furan compounds,[5] aromatization of γ-valerolactone[6] as well as the hydrodeoxygenation (HDO) of phenolic model compounds (which can be derived from lignin)[7] have been reported.

Isophorone is the trimerization product of acetone[8] which can be produced in industry scale by the Acetone-Butanol-Ethanol (ABE) fermentation of lignocellulose. In this work, it was reported for the first time that isophorone can be selectively converted to jet fuel range C_8-C_9 aromatic hydrocarbons under the promotion of the MoO_x/SiO_2 catalyst. The possible pathway for this reaction was also explored.

The catalytic transformation of isophorone was carried out in hydrogen flow under atmosphere pressure over a series of SiO_2 loaded metal oxide catalysts at 723 K. To facilitate the comparison, the weight percentages of the metal oxides in the investigated catalysts were controlled as 10 wt%. According to the analysis of GC-MS, *m*-xylene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene and mesitylene were identified in the liquid products (see Figure S1-S5 in supporting information). These C_8-C_9 aromatic hydrocarbons have high densities (see Table S1 in supporting information) and can be blended with current bio-jet fuels to increase their volumetric heating values. As another potential application, these C_8-C_9 aromatic hydrocarbons have high octane numbers. Therefore, they can also be used as additive to improve the combustion property of gasoline. Compared with the literature work which was concentrated either on the aromatization of isophorone to phenols[9] or on the conversion of phenol to aromatic hydrocarbons,[7, 10] the method developed in this work is simpler. Among the investigated catalysts, the MoO_x/SiO_2 exhibited the best performance (see Table 1). Over it, high carbon yield (76.3%) of C_8-C_9 aromatic hydrocarbons can be achieved under atmosphere pressure at 723 K (Table 1, entry 1). The carbon yields of C_8-C_9 aromatic hydrocarbons over different catalysts decrease in the order of MoO_x/SiO_2 > VO_x/SiO_2 > WO_x/SiO_2 > FeO_x/SiO_2 > CuO/SiO_2 (Table 1, entry 1-5). Moreover, it is also noticed that the carbon yields of various C_8-C_9 aromatic hydrocarbon products decrease in the order of 1,2,4-trimethylbenzene > 1,2,3-trimethylbenzene > mesitylene, *m*-xylene.

To figure out the role of hydrogen during the reaction, we investigated the catalytic performance of MoO_x/SiO_2 under nitrogen atmosphere. It was found that the unreduced MoO_x/SiO_2 catalyst is inactive for the conversion of isophorone to aromatic hydrocarbons (Table 1, entry 6). After being pre-treated with hydrogen flow at 723 K for 1 h, the activity of MoO_x/SiO_2 catalyst was improved. However, the carbon yield of C_8-C_9 aromatic hydrocarbons over the reduced MoO_x/SiO_2 catalyst was still lower than the one which was observed under hydrogen atmosphere (Table 1, entry 7). From these results, we can see that the presence of hydrogen is essential for the generation of active MoO_x species and the conversion of isophorone to aromatic hydrocarbons. From the H_2-TPR profile of the

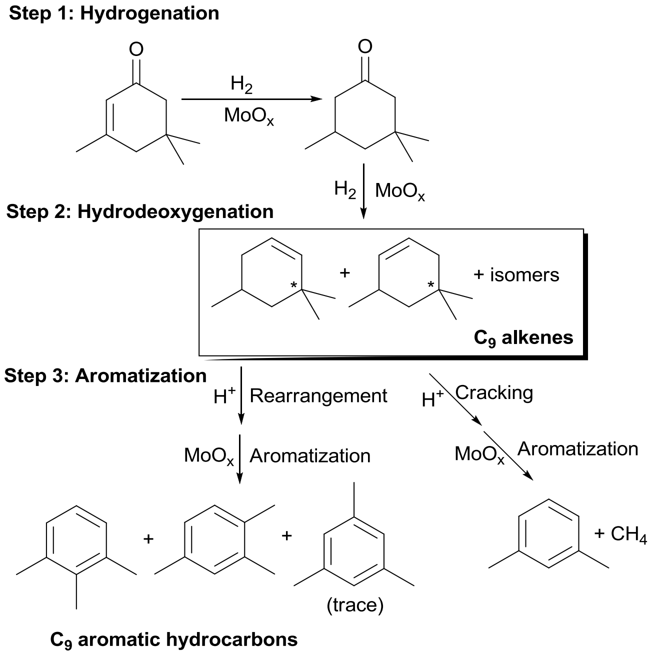
Table 1. The conversion of isophorone and the carbon yields of different products from the transformation of isophorone over different catalysts. Reaction conditions: 2.0 g catalyst, hydrogen flow rate: 80 mL min^{-1}, isophorone flow rate: 0.04 mL min^{-1}.

	Catalyst	Hydrogen pressure (MPa)	Temperature (K)	Conversion of isophorone (%)	Carbon yield (%)[a]						
					3,3,5-Trimethlcyclohexanone	C_9 cycloalkenes	*m*-xylene	1,2,4-TMB	1,2,3-TMB	Mesitylene	C_8-C_9 aromatic hydrocarbons
1	10 wt% MoO_x/SiO_2	0.1	723	98.3	0	12.9	5.8	38.7	26.1	5.7	76.3
2	10 wt% VO_x/SiO_2	0.1	723	94.5	1.5	13.3	7.1	18.9	13.4	3.5	42.9
3	10 wt% WO_x/SiO_2	0.1	723	84.8	5.0	9.2	0.9	12.7	9.6	3.8	27.0
4	10 wt% FeO_x/SiO_2	0.1	723	63.8	12.1	9.2	1.2	7.9	6.4	2.9	18.4
5	10 wt% CuO_x/SiO_2	0.1	723	49.7	11.6	5.3	0	6.4	6.0	3.2	15.6
6	10 wt% MoO_x/SiO_2[b]	-	723	34.2	8.56	2.97	0.44	1.67	1.52	1.25	4.88
7	10 wt% MoO_x/SiO_2[c]	-	723	37.3	8.5	4.4	1.1	4.5	4.2	1.7	11.4
8	10 wt% MoO_x/SiO_2	0.5	723	98.2	0	8.2	3.5	41.8	21.7	10.0	76.9
9	10 wt% MoO_x/SiO_2	1.0	723	98.3	0	13.1	5.9	39.2	26.5	5.7	77.3
10	10 wt% MoO_x/SiO_2	0.1	623	51.8	16.2	9.8	0.5	6.6	6.5	0.5	14.1
11	10 wt% MoO_x/SiO_2	0.1	673	98.8	0	24.3	2.2	29.6	23.7	2.6	58.2
12	10 wt% MoO_x/SiO_2	0.1	773	97.6	0	6.0	11.0	37.6	22.4	7.4	78.4
13	1 wt% MoO_x/SiO_2	0.1	723	75.2	9.0	10.2	1.0	15.0	12.2	4.0	32.1
14	5 wt% MoO_x/SiO_2	0.1	723	98.6	0	11.0	4.0	36.9	24.1	5.7	70.8
15	15 wt% MoO_x/SiO_2	0.1	723	98.2	0	8.4	4.4	42.5	27.5	6.6	81.0
16	20 wt% MoO_x/SiO_2	0.1	723	98.6	0	9.0	5.4	40.6	27.2	5.8	79.1
17	MoO_x[d]	0.1	723	99.8	0	59.6	14.3	10.5	7.2	0.9	32.9
18	SiO_2	0.1	723	33.1	10.3	3.0	0.2	1.7	1.8	2.0	5.8
19	MoO_x + SiO_2[e]	0.1	723	97.5	1.4	36.6	5.0	24.6	13.5	5.3	48.3

[a] The method for the calculation of carbon yields of different products, the compositions of gas phase products and carbon balances (see Table S2 and Table S3) were supplied in supporting information. 1,2,4-TMB: 1,2,4-trimethylbenzene. 1,2,3-TMB: 1,2,3-trimethylbenzene. [b] The experiment was carried out in nitrogen flow over the 10 wt% MoO_x/SiO_2 catalyst without the pretreatment with hydrogen flow. [c] The experiment was carried out over the reduced 10 wt% MoO_x/SiO_2 catalyst. [d] MoO_x was prepared by the thermal decomposition of ammonium molybdate at 773 K. [e] The MoO_x + SiO_2 denotes the physical mixture of MoO_x and SiO_2 which has the same chemical composition as the 15 wt% MoO_x/SiO_2 catalyst.

MoO_x/SiO_2 (see Figure S6 in supporting information), we can see that the MoO_x species on the MoO_x/SiO_2 catalyst is partially reduced under the investigated conditions. According to the XRD patterns and XPS spectra of the unreduced, reduced and spent MoO_x/SiO_2 catalysts (see Figure S7 and Figure S8 in supporting information), we can see that the valence state of the Mo species on the unreduced MoO_x/SiO_2 catalyst is about +6, while the valence state of Mo species on the reduced or spent MoO_x/SiO_2 catalyst is between +4 and +5. Therefore, we believe that the Mo species is partially reduced under the investigated reaction conditions. The partially reduced MoO_x species generated during the reaction is the active site for the conversion of isophorone to C_8-C_9 aromatic hydrocarbons. Subsequently, we studied the effect of hydrogen pressure on the catalytic performance of MoO_x/SiO_2. With the increasing of hydrogen pressure from atmosphere pressure (0.1 MPa) to 1.0 MPa, no evident change in the performance of the MoO_x/SiO_2 catalyst was observed (Table 1, entry 1 and entries 8-9). In real application, the higher reaction pressure will lead to the higher facilities cost and the higher energy consumption. Therefore, we conducted the experiments at atmosphere pressure in the following investigation.

The influence of reaction temperature on the performance of the MoO_x/SiO_2 catalyst was also investigated. From the results listed in the entry 1 and entries 10-12 of Table 1, it was found that the isophorone conversion and the carbon yield of C_8-C_9 aromatic hydrocarbons monotonously increased with the reaction temperature increasing from 623 K to 723 K, then level off with the further increase of reaction temperature to 773 K. In contrast, a volcano type relationship was observed between the carbon yield of C_9 alkenes and reaction temperature. According to this phenomenon, we speculate that the C_9 alkenes may be an intermediate between isophorone and the C_8-C_9 aromatic hydrocarbons. Besides C_9 alkenes and the C_8-C_9 aromatic hydrocarbons, 3,3,5-trimethylcyclohexanone was also identified in the liquid product obtained at low temperature (such as 623 K). Based on the above information, a three-step reaction pathway for the conversion of isophorone to C_8-C_9 aromatic hydrocarbons was proposed in Scheme 1. In the first step, the C=C group in isophorone was saturated by H_2. This reaction may be catalyzed by the partially reduced MoO_x species.[11] Subsequently, the 3,3,5-trimethylcyclohexanone generated in the first step is further hydrodeoxygenated to C_9 alkenes over the MoO_x/SiO_2. As Román-Leshkov *et al.* suggested in their recent work, such a reaction follows a Mars–van Krevelen mechanism.[12] Hydrogen is essential for the generation of oxygen vacancy sites which can remove the oxygen atoms from the ketone molecules adsorbed on the partially reduced MoO_x species. In the third step, 1,2,3-trimethylbenzene and 1,2,4-trimethylbenzene are produced by the rearrangement of the C_9 alkenes, followed by aromatization which is catalyzed by the MoO_x species.[13] As another option, *m*-xylene may also be generated by the C-C bond cleavage (or cracking)



Scheme 1. Reaction pathway for the conversion of isophorone to C_8-C_9 aromatic hydrocarbons over MoO_x/SiO_2.

followed by aromatization over the MoO_x species. Both the rearrangement and the cracking of C_9 alkenes can be promoted by acid sites. From these reactions, carbocation intermediates will be produced. Because the stability of carbocation decreases in the order of tertiary carbocation > secondary carbocation > primary carbocation, the rearrangement and cracking reaction are preferred at the carbon which is connected with two methyl groups (labelled with * in Scheme 1). For the rearrangement of methyl group, the ortho-migration is relatively easier than the meta-migration. As the result, 1,2,4-trimethylbenzene and 1,2,3-trimethylbenzene are produced as the major C_9 aromatic hydrocarbons.

The effect of MoO_x content on the performance of the MoO_x/SiO_2 catalyst was also studied. From the results illustrated in the entry 1 and entries 13-16 of Table 1, the isophorone conversion and the carbon yield of C_8-C_9 aromatic hydrocarbons increase with the increment of MoO_x content, reach the maximum when MoO_x content is about 15 wt%, then stabilize. Over the 15 wt% MoO_x/SiO_2 catalyst, the isophorone is completely converted, high carbon yield of C_8-C_9 aromatic hydrocarbons (~80%) was achieved (Table 1, entry 15).

To figure out the role of SiO_2 support in the transformation of isophorone to C_8-C_9 aromatic hydrocarbons, we also investigated the catalytic performances of the SiO_2 support and the physical mixture of MoO_x and SiO_2 (denoted as $MoO_x + SiO_2$ catalyst). To facilitate the comparison, the contents of Mo and Si in the $MoO_x + SiO_2$ catalyst were controlled the same as those in the 15 wt% MoO_x/SiO_2 catalyst. From entries 18-19 of Table 1, the SiO_2 has low activity for the conversion of isophorone to C_8-C_9 aromatic hydrocarbons. In contrast, the activity of the $MoO_x + SiO_2$ catalyst is between those of the 15 wt% MoO_x/SiO_2 and the MoO_x (or SiO_2) catalysts. Based on above results, we believe that there is synergism effect between SiO_2 and MoO_x species in the conversion of isophorone to C_8-C_9 aromatic hydrocarbons. The promotion effect of SiO_2 on the MoO_3 catalyst is not unique. As we can see from Table S4 and Table S5 in supporting information, the carbon yields of aromatic hydrocarbons over the physical mixtures of MoO_x and solid bases (such as MgO and MgAl-HT) are even lower than that over MoO_x. In contrast, higher carbon yields (49.0-61.3%) of jet fuel range C_7-C_{11} aromatic hydrocarbons can be achieved over the physical mixtures of MoO_x and solid acids (including SiO_2, acidic active carbon, H-β and H-ZSM-5) than that over MoO_x (32.9%). Compared with the physical mixture of MoO_x and weak solid acids (such as SiO_2 and acidic active carbon), higher carbon yields of toluene and C_{10}-C_{11} aromatic hydrocarbons were produced when the physical mixture of MoO_x and strong solid acids (such as H-β and H-ZSM-5) were used as the catalysts. These results further confirmed that acid sites on the supports (or catalysts) can promote the rearrangement or cracking reaction, which is beneficial for the generation of jet fuel range aromatic hydrocarbons.

Moreover, we also characterized the MoO_x and MoO_x/SiO_2 catalysts by NH_3-TPD. Before the NH_3-TPD tests, the catalysts were reduced by hydrogen at 723 K for 1 h. From the results illustrated in Table S6 in supporting information, we can see that the amounts of acid sites on the surfaces of MoO_x/SiO_2 catalysts are evidently higher than those on bulk MoO_x catalyst. This may be another reason for the higher activity of the MoO_x/SiO_2 catalysts. With the increasing of MoO_x content, the amount of acid sites over the MoO_x/SiO_2 catalyst initially increase, then stabilize when MoO_x content is greater than 15 wt%. Such a variation trend is consistent what we observed for the activity of these catalysts in the conversion of isophorone to jet fuel range aromatic hydrocarbons.

Basing on the above information, the beneficial effect of SiO_2 support can be rationalized by two reasons: 1) Dispersion effect. Such an effect will lead to the generation of more acid sites which is beneficial for the production of jet fuel range aromatic hydrocarbons. 2) As a weak solid acid, the SiO_2 support may also participate the reaction by promoting the rearrangement or cracking of C_9 alkenes which is the essential step in the conversion of isophorone to C_8-C_9 aromatic hydrocarbons.

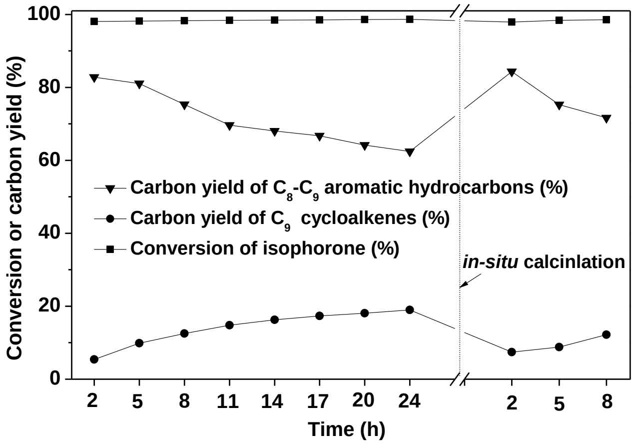


Figure 1. Isophorone conversion and carbon yields of different products over the 15 wt% MoO_x/SiO_2 catalyst as the function of reaction time. Reaction conditions: 723 K, 0.1 MPa H_2, 2.0 g catalyst, isophorone flow rate: 0.04 mL min^{-1}, hydrogen flow rate: 80 mL min^{-1}.

Finally, we also studied the stability of the MoO_x/SiO_2 catalyst in the conversion of isophorone to C_8-C_9 aromatic hydrocarbons. From the results show in Figure 1, the carbon yield of C_8-C_9 aromatic hydrocarbons over the 15 wt% MoO_x/SiO_2 catalyst decreased with the reaction time during the 24 h continuous test. The opposite trend was observed for the carbon yield of C_9 alkenes. After being *in-situ* calcined in air flow at 773 K for 3 h, the activity of the 15 wt% MoO_x/SiO_2 catalyst almost restored to its initial level. According to these results, we believe that some carbon deposition may occur during the conversion of isophorone, which leads to the deactivation of catalyst. The carbon deposited on the catalyst can be removed by calcination in air flow. As the result, the activity of the MoO_x/SiO_2 catalyst was restored to its initial value. Such a speculation was verified by the TG-MS analysis of the spent MoO_x/SiO_2 (see Figure S9 of the supporting information).

Conclusions

A new route was developed for the sustainable synthesis of jet-fuel range C_8-C_9 aromatic hydrocarbons with the isophorone which can be obtained from lignocellulose. Among the investigated catalysts, the MoO_x/SiO_2 demonstrated the best performance. The synergism effect of the partial reduced MoO_x species and SiO_2 support is important for the transformation of isophorone to C_8-C_9 aromatic hydrocarbons. This work offers a potential solution to the shortage of current bio-jet fuel at density and volumetric heating value.

Acknowledgements

This work is supported by the Natural Science Foundation of China (No. 21106143; 21277140; 21202163; 21476229) and 100-talent project of Dalian Institute of Chemical Physics (DICP).

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† Electronic Supplementary Information (ESI) available: [details information about the preparation of catalyst, activity tests, GC-MS analysis, characterization of catalysts]. See DOI: 10.1039/c000000x/

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