Asian Journal of Chemistry; Vol. 27, No. 10 (2015), 3555-3558

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.18827

Selective Oxidation of Alkylbenzenes to Aryl Ketones with Polymer-Supported Molybdenum Catalyst

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Received: 29 October 2014; *Accepted*: 13 January 2015; *Published online*: 22 June 2015; AJC-17301

A new polymer-supported molybdenum-3,5-dimethyl pyrazole catalyst was synthesized and the structure was characterized by FT-IR and SEM. The resulting catalyst presented high activity for selective oxidation of alkyl aromatics to benzylic ketones with *tert*-butyl hydroperoxide and could be reused at least five times without loss of activity.

Keywords: Polymer-supported, *tert*-Butyl hydroperoxide, Alkyl aromatics, Oxidation.

INTRODUCTION

Aromatic ketone compounds are not only important chemical raw materials, but also they are intermediates for the generation of the useful primary, special chemicals and high economic value fine chemicals, agrochemicals, pharmaceutical and perfumes industry[1]. Many studies have been reported about selective oxidation of alkyl aromatics to corresponding benzylic ketones with O_2[2-5], H_2O_2[6-8], *tert*-butyl hydroperoxide (TBHP)[9,10] and $KMnO_4$[11]. Habibi and coworkers[4] reported the aerobic oxidation of ethyl benzene, cyclohexene and oximes catalyzed by a SiO_2/Al_2O_3-supported manganese catalyst and NHPI. The reactions showed higher yields. Velusamy and Punniyamurthy[8] reported the oxidation of alkylbenzenes to the corresponding ketones with copper(II) complex in the presence of 30 % H_2O_2 with conversion higher than 80 %. Arshadi and coworkers[9] reported the oxidation of ethyl benzene to acetophenone with Co(II)-Schiff base complex in the presence of *tert*-butyl hydroperoxide with conversion of 86 % and selectivity of 99 %. And the following catalyst systems were used for the alkyl aromatics to ketones, such as metalloporphyrins[12], metal phthalocyanine[13], metal complexes[14], transition metal[15], Schiff base complexes[16], heteropoly acid[6], *etc*.

In order to meet the demand of aromatic ketone compounds, the new eco-friendly technique of the catalytic oxidation of alkyl aromatics to ketones under mild conditions has been the focus of researchers. Green oxidants such as hydrogen peroxide, alkyl hydroperoxides and molecular oxygen were used. Transition metal complex can selectively oxidize organic compounds under mild conditions[17], but the problem of reusability limits their application. Hence many researchers are constantly trying to find a suitable heterogeneous catalytic system for the oxidation of alkyl aromatics.

In this work, a recyclable polymer-supported molybdenum-3,5-dimethyl pyrazole catalyst was synthesized in order to solve the problem of resources waste. *tert*-Butyl hydroperoxide is a kind of alkyl organic peroxide of hydrogen. This study reported one catalytic system based on alkyl aromatics-catalyst-*tert*-butyl hydroperoxide for alkyl aromatics oxidation. The high conversion and selectivity were obtained under optimal conditions.

EXPERIMENTAL

Chloromethylated polystyrene and ethyl benzene derivatives were purchased from Aladdin. Other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. and used without further purification. The constituents were confirmed based on GC analysis. Gas chromatography (GC) analysis was performed on an Agilent GC-6820 equipped with a 30 m × 0.32 mm × 0.5 µm HP-Innowax capillary column and a flame ionization detector. Fourier transform infrared spectra (FT-IR) were recorded on NICOLET NEXUS870. Scanning electron micrographs (SEM) of the samples were taken with ZEISS-DSM 960A microscope with attached camera.

Preparation of polymer-supported 3,5-dimethyl pyrazole catalyst [PS-DVB(dmpz)][18]: Chloromethylated polystyrene (2.0 g) was allowed to swell in acetonitrile (10 mL) for 2 h. A solution of 3,5-dimethyl pyrazole (3.05 g, 31.8 mmol) was prepared in acetonitrile in the presence of equivalent amount of KI (5.28 g, 31.8 mmol) and triethylamine (3 mL). This solution was added to the above suspension and the reaction mixture was heated at 90 °C for 24 h with stirring. After cooling to room temperature, the brown resins were separated, washed several times with hot acetonitrile and dried in air oven at 110 °C.

Synthesis of polymer-supported molybdenum-dmpz catalyst PS-DVB[$MoO(O_2)_2(dmpz)_2$][19]: The polymer-anchored 3,5-dimethylpyrazole PS-DVB (dmpz) (2.5 g) was allowed to swell in DMF (10 mL) for 2 h. MoO_3 (3.8 g, 26.5 mmol) was dissolved in 30 % H_2O_2 (265 mmol). The solution was cooled in an ice-bath and then this solution was added in PS-DVB (dmpz). A red suspension was obtained at this stage which was stirred for 1 h and then left overnight at about 4 °C to afford a lemon yellow coloured microcrystalline complex.

Oxidation of alkyl aromatics: In a typical procedure, to a mixture of catalyst (0.5 mmol), acetonitrile (10 mL) and alkyl aromatics (5 mmol) were added *tert*-butyl hydroperoxide (15 mmol) in turn. Samples were withdrawn periodically. After required hours, the reaction mixture was cooled to room temperature.

RESULTS AND DISCUSSION

Scheme-I shows the sequence of events in the functionalization of PS-DVB with 3,5-dimethyl pyrazole and MoO_3. First, PS-DVB was allowed to swell in acetonitrile that can be used in activating groups. It is easier to combine the secondary nitrogen on 3,5-dimethyl pyrazole with -CH_2Cl on PS-DVB in the absence of KI and triethylamine. The brown resins (**Scheme I**-2) were obtained. The second step, MoO_3 dissolved in aqueous H_2O_2 and reacted with the appropriate stoichiometric quantities of the brown resins (**Scheme I**-2), then coordination polymer was isolated. Coordination polymer (**Scheme-I**) was formed through coordination bond between the imine on dmpz with Mo. The unsupported catalyst was not considered because it can't be reused.

Fourier-transform infrared (FT-IR) spectra analysis of unsupported catalyst and the polymer-supported molybdenum-dmpz catalyst were reported in Fig. 1. An absorption band at about 2920 cm^{-1} attributed to the stretching vibrations of C-H groups. Band at 1600 cm^{-1} was assigned to C-N stretching vibration. Band at 941 cm^{-1} was assigned to Mo=O stretching vibration. Band at 796 cm^{-1} was assigned to O-O stretching vibration. In the spectra of unsupported catalyst [Fig. 1(a)], the absorptions at 3318 cm^{-1} was N-H group. In the spectra of the polymer-supported molybdenum-dmpz catalyst [Fig. 1(b)], the band at 3318 cm^{-1} upon N-H disappeared, which indicated substitution reaction of -CH_2Cl with -NH.

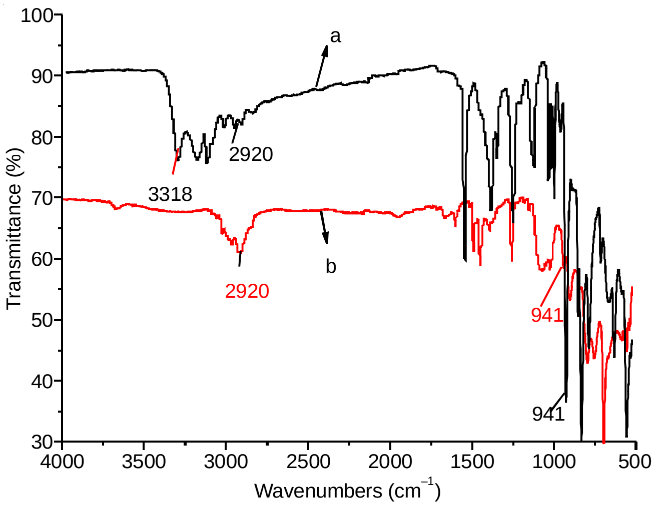


Fig. 1. FT-IR spectra of (a) unsupported molybdenum-dmpz catalyst and (b) the polymer-supported molybdenum-dmpz catalyst

To further characterize the catalyst, SEM images were obtained as shown in Fig. 2. It can be clearly shown that the pure polymer beads have a smooth, flat surface and particle diameter is also homogeneous in Fig. 2(a). The morphological change in the polymer-anchored ligands and immobilized Mo complexes is quite evident from Fig. 2(b). The image of the metal complex shows blocky shapes, which may be due to interaction of the Mo metal with the ligand changed the fixed geometry of the complex.

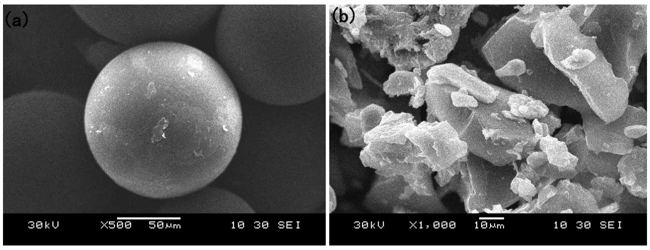
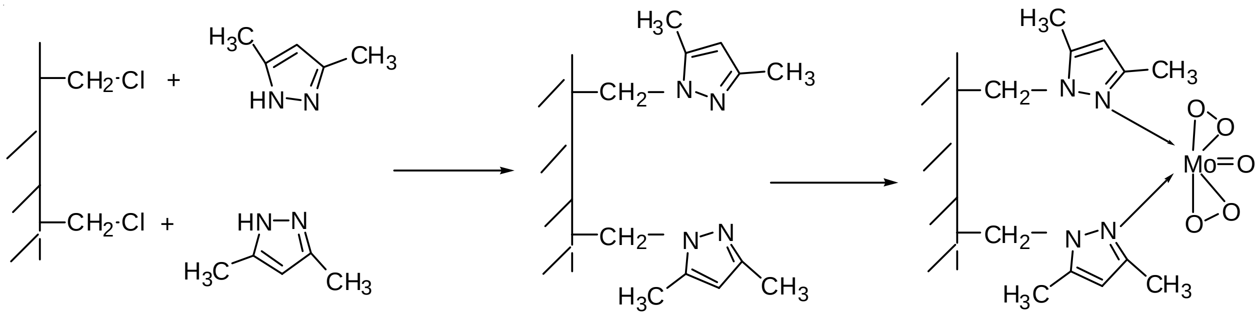


Fig. 2. SEM image of PS-DVB and PS-DVB[$MoO(O_2)_2(dmpz)_2$]

Ethyl benzene was selected as a model. The activities of the catalytic system were measured at different molar ratio of



1 2 3

Scheme-I: Preparation of PS-DVB[$MoO(O_2)_2(dmpz)_2$]

ETB:catalyst:TBHP and the results were shown in Table-1. The tests with catalyst were better in conversion compared to blank test. With increased amount of *tert*-butyl hydroperoxide, the conversion of ethyl benzene was enhanced (Table-1, entries 3-6). However, more by-products are produced such as PEA and BA because of over-oxidation. The separation difficulties and the cost of experiments are increased. With double amount of catalyst, AcPO was not easy to be produced at lower temperature. Instead, more by-products are produced. With prolonging of the reaction time, conversion of ethyl benzene and selectivity of AcPO were increased at 80 °C (Table-1, entries 7-10). So, with a molar ratio of ETB:catalyst:TBHP at 1:0.2:3, 94 % selectivity of acetophenone and 99 % conversion of ethyl benzene were obtained at 80 °C for 36 h.

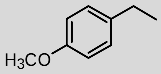
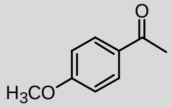
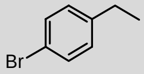
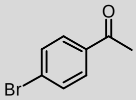
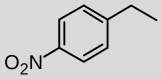
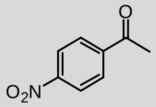
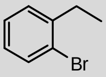
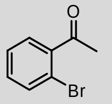
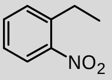
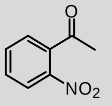
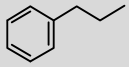
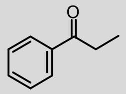
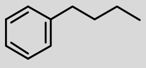
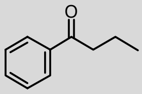
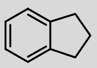
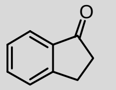
Table-2 summarized the reaction of alkyl aromatics in the presence of the prepared catalyst, alkyl aromatics were oxidized to their corresponding ketones under mild conditions. As can be seen in Table-2, the oxidations of some ethyl benzene derivatives proceed smoothly and show good selectivity to acetophenone. Significantly, an electron donating substituent (*e.g.* methoxy group, entry 1) at the *para*-position of ethyl benzene has a positive effect on the oxidation yield while an

TABLE-1
EFFECT OF AMOUNT OF *tert*-BUTYLHYDROPEROXIDE AND CATALYST ON ETHYL BENZENE OXIDATION[a]

Entry	Ethyl benzene:Catalyst:Oxidant	Temp. (°C)	Time (h)	Conversion (%)[b]	Selectivity (%)[b]		
					AcPO	PEA	Others
Blank	1:0:3	80	24	51	37	21	42
1	1:0.1:3	80	24	89	96	2	2
2	1:0.1:3	80	36	88	95	2	3
3	1:0.1:4.5	70	24	87	77	10	13
4	1:0.1:4.5	70	36	93	84	5	11
5	1:0.1:4.5	80	24	95	89	1	10
6	1:0.1:4.5	80	36	96	92	1	7
7	1:0.2:3	70	24	87	70	14	16
8	1:0.2:3	70	36	92	87	7	6
9	1:0.2:3	80	24	94	93	4	3
10	1:0.2:3	80	36	99	94	3	3

[a]Reaction conditions: ethyl benzene (5 mmol), acetonitrile (5 mL).
[b]Determined by GC and GC-MS analysis based on the internal standard (*n*-decane).

TABLE-2
OXIDATION OF VARIOUS ALKYL AROMATICS CATALYZED BY PS-DVB[$MoO(O_2)_2(dmpz)_2$] UNDER THE INVESTIGATED CONDITIONS[a]

Entry	Substrate	Conversion (%)[b]	Selectivity (%)[b]	Product
1		94	94	
2		75	89	
3		78	89	
4		68	80	
5		65	79	
6		92	87	
7		87	85	
8		75	81	

[a]Reaction conditions: substrate (5 mmol), *tert*-butylhydroperoxide (50 mmol), catalyst (1 mmol), acetonitrile (5 mL), 80 °C, 24 h.
[b]Determined by GC and GC-MS analysis based on the internal standard (*n*-decane).

electron withdrawing substituent including the NO_2 or Br group at the *para*-position suppresses the oxidation (entries 2, 3). Due to steric effects, all substituents at *ortho*-position have a negative effect on the oxidation reaction (entries 4, 5). Alkyl benzenes containing open chain alkyl group such as *n*-propyl benzene and *n*-butyl benzene underwent the reaction with 92 and 87 % conversion providing corresponding benzylic ketones with 87 and 85 % selectivity (entries 6, 7). Indane is oxidized to 1-indanone effectively and selectively, which gives 75 % conversion and 81 % selectivity (entry 8). These results show the substrate compatibility of this protocol.

PS-DVB[$MoO(O_2)_2(dmpz)_2$] is slightly soluble. The catalyst was separated simply by filtering and the resulting clear supernatant can be decanted. After being washed by methanol, it was subjected to another reaction with identical substrate. In this experiment, the supported catalyst can be reused for at least 5 times at the same reaction conditions without loss of activity (Fig. 3).

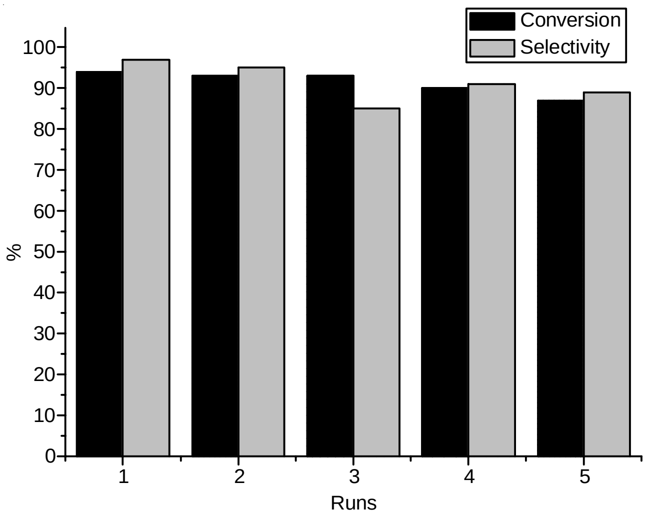


Fig. 3. Recycling study of PS-DVB[$MoO(O_2)_2(dmpz)_2$]

Conclusion

The prepared catalyst PS-DVB[$MoO(O_2)_2(dmpz)_2$] showed highly activity for the oxidation of ethyl benzene and other alkyl aromatics to the corresponding ketones under mild conditions. As a supported catalyst, it is environmentally friendly and reusable.

ACKNOWLEDGEMENTS

This project is funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

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