Cobalt Catalyst Heterogenized on SBA-15 for *p*-Xylene Oxidation

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Cobalt(III) complex has been heterogenized onto a mesoporous material SBA-15 and successfully applied to the liquid phase oxidation of *p*-xylene in spite of not using either a solvent or bromide ion.

Oxidation of alkylaromatics to the corresponding carboxylic acids has been considered as an important reaction in industry, particularly *p*-xylene into terephthalic acid for the production of fibrous materials.[1] Cobalt based homogeneous catalytic systems are widely used for this reaction.[2] However these catalytic processes suffer from serious drawbacks due to the use of acetic acid and bromide ion. Although the problem deserves to attract more attention for the development of more cost effective and environmentally benign processes, the contribution towards heterogeneous systems has been very limited while most of the reported work in this field has devoted to the development of homogeneous catalysts and optimum reaction conditions.[3,4] Clark[5] also immobilized the Co(III) in a porous silica material to study the oxidation and epoxidation reactions, but it seems that the adjustment of support material is to be the basis for the further development of the catalyst. The SBA-15 is known to be robust thermally and hydro-thermally and also diffusion free due to thicker pore walls and larger pore size respectively. The pore wall thickness (31–64 Å) and pore size (260–300 Å) of SBA-15[7] are much larger than those of MCM-41[6] (10–15 Å and 20–30 Å, respectively), which has been most commonly used as a mesoporous silica. These advantages paved us to Co(III) heterogenized on the SBA-15. Designing a solid catalyst with similar catalytic properties of homogeneous catalyst is known to be a tough challenging task. In this work, a novel mesoporous SBA-15 material containing cobalt complex (CoSBA-15) has eventually been designed, prepared and applied to the oxidation of *p*-xylene with/without solvent and bromide comparing with the conventional homogenous catalytic system and it has been found that its catalytic activity in terms of turnover number is much higher than the conventional homogeneous catalyst in spite of not using either a solvent, free radical initiator or bromide.

A mesoporous silica SBA-15 containing carboxylic acid group has been synthesized via modification of the procedure described elsewhere.[7] In typical batch, 20 g of Pluronic P123 triblock polymer (EO$_{20}$PO$_{70}$EO$_{20}$, M_{av} = 5800, Aldrich) was dissolved in a mixture of 465 g of deionized water and 137.5 g of hydrochloric acid (HCl, 35%, Oriental Chemical Industries). To this polymer solution, a mixture 39.6 g of tetraethyl orthosilicate (TEOS, 96%, Show) and 4.88 g of 4-trietoxysilylbutyronitrile (TESBN, 98%, Aldrich) was quickly added with vigorous magnetic stirring. The resulting gel mixture was stirred for 1 day at 313 K and subsequently heated for 1 day at 373 K in an oven to increase the degree of silanol group condensation. The solid product was filtered and dried at 353 K in a vacuum oven overnight. The product was then slurried in ethanol under reflux condition, filtered, washed with ethanol and dried at 393 K in an oven. The washing resulted in the removal of more than 95% of the polymer, which was confirmed by IR absorption spectroscopy and TGA analysis. The solid product containing CN group (SBA-15-CN) was treated with hot aqueous sulfuric acid so as to hydrolyze the -CN in to -COOH.[5] The SBA-15 containing COOH group (SBA-15-COOH) thus obtained was dispersed in distilled water and an aqueous solution of cobalt nitrate and sodium acetate and pyridine were added to this mixture. The mixture was heated to 373 K and subsequently dilute hydrogen peroxide was added drop by drop over 8 h. The solid was filtered, washed, dried and used as catalyst. Elemental analysis of the CoSBA-15 using ICP gave 7.3 wt% loading of cobalt. The performance of the CoSBA-15 was tested for the oxidation of *p*-xylene in a 150 ml autoclave at different temperatures and pressures in the presence of molecular oxygen admixture with nitrogen. After the reaction, the resulted mixture separated into solid and liquid. The solid products were esterified with methanol and analyzed by a GC quipped with DB-1 capillary column and FID. The products were confirmed by GC/MS.

Figure 1 shows powder X-ray diffraction (XRD) patterns for SBA-15 materials. All exhibit XRD patterns with a very intense diffraction peak and two weak peaks, which are characteristic of 2-d hexagonal (*P6mm*) structure with excellent textural uniformity.[7–9] There were no significant changes upon washing with EtOH, oxidation of CN group and cobalt immobilization except for the expected change in XRD peak intensity. It was confirmed that the nitrogen adsorption isotherms are of Type IV in nature and exhibited H1 hysteresis loop, which is typical of mesoporous solids. The adsorption isotherms show a sharp inflection at
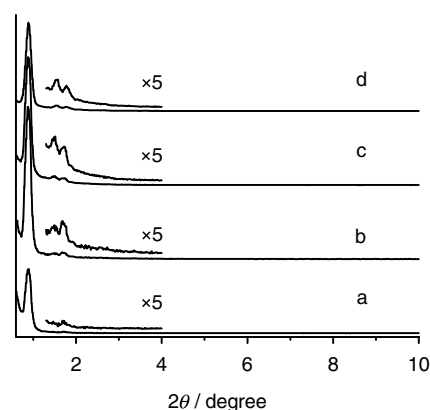
Figure 1. XRD patterns for the SBA-15 materials: (a) as-made SBA-15-CN, (b) washed SBA-15-CN, (c) SBA-15-COOH and (d) CoSBA-15.

relative pressure of 0.65–0.85, which is a characteristic of capillary condensation within uniform mesopores.[10] Pore sizes are 8.2 nm and 8.1 nm and BET surface areas are 684 $m^2 \cdot g^{-1}$ to 454 $m^2 \cdot g^{-1}$ for the SBA-15-COOH and CoSBA-15, respectively. These indicate that the immobilization of cobalt does not affect on the pore structures of the SBA-15 material and cause the decrease of surface area that is consistent with cobalt loading. TG-DTA studies on the SBA-15-COOH and the CoSBA-15 reveal that the organic moieties begin to be decomposed above 573 K, which means the catalysts are stable at reaction temperature. IR spectra show CN stretch band at 2248 cm^{-1} for SBA-15-CN material and C=O absorption band at 1711 cm^{-1} for SBA-15-COOH material. This indicates that CN groups are completely converted to COOH by oxidation using sulfuric acid, which can be also confirmed by 13C MAS solid NMR experiments.

The remarkable activity of the CoSBA-15 catalyst can be seen from the Table 1. The CoSBA-15 catalyst (Run Nos. 1 and 4) has shown considerable activity in the absence of solvent. Although the conversions were lower than the homogeneous systems (Run Nos. 3 and 5), it showed very high turnover numbers considering the amount of reactant used. A key factor in achieving higher catalytic performance of a CoSBA-15 material is due to stabilization of Co(III) on the support. It is reported that the higher oxidation state of Co is desirable for the high activity of the oxidation catalyst.[11] Initially the cobalt ion exists as Co(II) in cobalt nitrate, the oxidation state of which is raised to Co(III) during immobilization in the support and the higher oxidation state is stabilized by pyridine ligands.[5] The comparison of the oxidations using cobalt bromide (Run No. 5) and cobalt acetate (Run No. 6) at 403 K and 20 atm elucidates the role of bromide ion in the homogeneous system. The conversion was observed to

Table 1. Oxidations of p-xylene with the heterogenized catalyst and soluble catalysts.

Run No.	1[a*]	2[a]	3[b]	4[a*]	5[c]	6[d]	7[a]	8[b]
Temp./K	403	403	403	403	403	403	463	463
Time/h	16	16	16	3	3	3	3	3
P_{total}/atm	2	2	2	20	20	20	20	20
P_{O2}/atm	1	1	1	5	5	5	5	5
Conv./mol%	27.4	95.1	98.8	50.6	88.1	9.0	95.2	94.0
Yield/mol%								
TA	20.1	62.6	76.6	36.1	57.3	3.6	76.6	3.8
TPA	0.1	12.6	12.6	5.3	19.1	0	14.2	82.7
TALD	7.0	1.0	1.1	4.1	2.5	3.8	0.4	0.1
MBAL	0	0.5	0.1	3.6	0	0	0.2	0
TPAD	0.1	10.7	1.1	0.5	0.1	1.1	1.0	0.6
MBAC	0.2	2.0	0.7	0.2	0.2	0.5	0.2	0.1
Others	0	5.9	6.7	1.2	9.0	0	2.7	6.8

Reaction conditions: p-xylene = 48.6 mmol (*244 mmol for solvent-free system), acetic acid (25.26 g), [a]CoSBA-15 (0.2 g cat. = 0.255 mmol of Co), [b]CoBr$_2$/Mn(OAc)$_2$, (0.541 mmol/ 0.647 mmol), [c]CoBr$_2$ (0.541 mmol), [d]Co(OAc)$_2$ (0.541 mmol). TA: p-toluic acid, TPA: terephthalic acid, TALD: p-tolualdehyde, MBAL: p-methylbenzyl alcohol, TPAD: terephthaldehyde, MBAC: p-methylbenzyl acetate.

be very low and terephthalic acid was not detected on cobalt acetate contrary to cobalt bromide. The bromide ion acts as a promoter as well as free radical initiator. It was reported that the addition of bromide ion and manganese to the cobalt catalyst, its activity was increased by 16 times and long induction periods were absent.[1] In the recent times there were some reports regarding non-bromide systems, but peroxides were used for the substitution of bromide ion.[4] It seems that it is impossible to eliminate the bromide ion activator from the homogeneous catalytic system unless and otherwise substituted by the free radical initiators (peroxides).[4] Although the bromide ion is the most important component of the oxidation catalyst, a non-bromide CoSBA-15 solid catalyst was equally active when compared to the bromide systems under the specified reaction conditions. Our results reveal that neither the bromide ion nor the free radical initiator is necessary for the oxidation of p-xylene. It should be noted that the catalytic activity of the CoSBA-15 catalyst (Run No. 2) is comparable with the existing industrial homogeneous catalyst (Run No. 3) at the low pressure.

However, at higher temperature, the catalytic activity of CoSBA-15 (Run No. 7) was inferior to that of CoBr$_2$/Mn(OAC)$_2$ (Run No. 8), which is probably due to the loss of pyridine from the catalyst at elevated temperatures, as confirmed by DTA and CHN elemental analysis. The catalyst can be easily rejuvenated by the addition of pyridine. However, different approaches are under investigation to stabilize the CoSBA-15 catalyst even at elevated temperatures.

In conclusion, highly active CoSBA-15 solid catalyst for the oxidation of p-xylene in the absence of solvent exhibited an excellent performance even at the low pressure and also its activity is very high even without a solvent or bromide. The results suggest that there is a bright possibility to develop a bromide-free and solvent-free catalytic system for the liquid phase oxidation of alkylaromatics.

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