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Al-containing mesoporous carbon as effective catalysts for the chemoselective reduction of carbon–carbon double bonds in nitrostilbene derivatives

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ABSTRACT

A series of Al, Mn, Cu and Fe metal-containing mesoporous carbon catalysts were synthesized for catalyzing selective reduction of carbon–carbon double bond in 4-nitrostilbene analogs bearing nitro group with hydrazine hydrate. The results indicated that the reduction reaction was able to be achieved successfully between carbon–carbon double bond and nitro group. The efficient method has been developed for the reduction of C═C double bonds with diimide, catalytically generated in situ from hydrazine hydrate by the synthesized catalysts. The 0.15Al–MC1 as heterogeneous catalyst exhibited the highest catalysis activity and chemoselectivity in all synthesized catalysts. In the presence of 0.15Al–MC1, the reduction of carbon–carbon double bond in 4-nitrostilbene derivatives was up to 99% yield and >99% chemoselectivity at 70 °C in ethanol. On the other hand, the high selective reduction of nitro group in 4-nitrostilbenes was also facile to be achieved with hydrazine hydrate, active carbon and $FeCl_3 \cdot 6H_2O$ under inert atmosphere.

1. Introduction

The reduction of carbon–carbon double bonds is a very important process in organic synthesis, which is normally accomplished by hydrogen gas in the presence of nobler transition metal catalysts. These catalysts can be in either a hetero [1] or a homogeneous fashion [2], such as Rh/C, Pd/C, Nickel Raney, PtO_2, hetero rhodium complex [3,4], or Wilkinson's catalyst, homogeneous rhodium complex. Although these hydrogenations with metal catalysts often proceed efficiently, there are important limitations for high pressures, expensive catalysts, toxicity and heavy metal pollution. Carreira and co-workers reported a new catalyst system for the enantioselective reduction of nitroalkenes utilizing Cu species and bis-phosphine ligand JOSIPHOS [5,6]. However, these hydrogenations are problematic when several functional groups such as nitro group, benzylic ketone, aryl halide and other unsaturated bond exist in the same molecule because they are rapidly reduced or isomerized.

One of the few alternatives is the use of diimide (diazene, HN═NH), generated in situ from hydrazine or its derivatives [7]. Experimentally, the use of diimide as reducing agent has the advantage of avoiding flammable gases and that no noble metal catalysts are needed. This reduction process of using diimide is environmentally benign since nitrogen gas is the sole waste product. It is generally accepted that diimide reduce nonpolarized double bonds via a cycloaddition mechanism [8]. Therefore hydrogenolysis, reduction of polarized bonds, or isomerization does not take place. However, diimide itself is unstable and facile to produce nitrogen and hydrazine. Therefore a large number of methods for its in situ generation have been reported including the base-induced elimination of substituted hydrazines [9] and the oxidation of hydrazine hydrate [10]. The catalytic oxidation of hydrazine using oxygen or air, which would be the ideal method for generating diimide [11,12], also remains problematic from the point of view of green chemistry since a great excess of hydrazine (10 to >400 equiv.) is required to achieve this [13–15]. Recently, Imada's group and Minnaard's group reported the generation of diimide from hydrazine hydrate and oxygen/air using flavin-type compounds as organocatalysts, respectively [7,10]. Remarkably, a large excess of hydrazine hydrate was not needed. These systems do not give double bond isomerization, and it is a valuable alternative when metal-catalyzed hydrogenations are problematic. Very recently, Imada's group further extended the potential of flavin catalysts with the development of a two-phase system allowing

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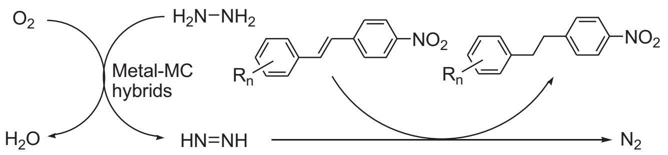


Scheme 1. The reduction of C=C in stilbene derivatives with hydrazine hydrate in the presence of metal–MC hybrids.

the recycling of their catalysts [16]. Although their catalysis system could afford a high yields in the reduction of terminal and disubstituted alkenes, tetra-substituted double bonds and stilbene were not reduced at all. Thus, introduction of new efficient methodologies for the reduction of various carbon–carbon double bonds is still in strong demand. In our efforts to develop mesoporous carbon (MC) materials for clean heterogenous catalysts, we have successfully prepared MC materials with high specific surface area and uniform mesoporous structure [17–19], and introduced organic functional groups on the surface of pore channels of synthesized MC material to yield a surface modified MC materials for catalyzing some organic reactions [20]. Considering the generation of diimide in situ from hydrazine hydrate and oxygen/air needs the presence of appropriate catalysts, and MC and its metal-containing hybrids with high specific surface area and uniform mesoporous structure have attracted considerable attention in catalysis area [21,22], we attempt to support some cheap metal species, possessing an ability for the activation of molecular oxygen, on MC materials as catalysts in the generation of diimide in situ. With this strategy, the selective reduction of C=C bond in stilbene analogs bearing nitro group was carried out (Scheme 1). Herein, we report the highly chemoselective catalytic reduction of carbon–carbon double bond or nitro group in nitrostilbene derivatives with hydrazine hydrate.

2. Experimental

2.1. Materials and chemicals

All reagents materials were obtained from commercial sources and used without any further purification. 50% aqueous solution of $Mn(NO_3)_2$ was used of commercially available reagent. The 4-nitrostilbene derivatives were prepared from aromatic aldehyde and 4-nitrotoluene using our published procedure [23].

2.2. Preparation of Al-containing MC1 and MC1

Al-containing MC1 and MC1 were synthesized by multi-component co-assembly strategy associated with a direct carbonization process. In a typical synthesis, 25.0 g F127 was dissolved absolutely in 140.0 g of ethanol/water (1/1 vol.) solution under stirring at room temperature. And 16.5 g resorcinol (R) was added into the solution (signed A). An appropriate amount of hydrated $AlCl_3$ corresponding to Al/R (molar ratio) equal to 0.15, 0.25, 0.60 was dissolved in 70.0 g of ethanol/water (1/1, v/v) solution (signed B). Solution B was dropped into solution A when the color of solution A turned to be a light brown. The pH value was adjusted to 2 with 37% HCl. After stirring for 2 h, 23.0 mL of formaldehyde (F) (37%) was subsequently dropped into the above solution. The mixture was kept stirring until it turned cloudy and began to separate into two layers. The upper layer was discarded, after this two phase mixture was further kept aging for 60 h. The lower polymer-rich phase was formed to a stick monolith. The monolith was dried at 85 °C for 24 h and carbonized under N_2 atmosphere. The carbonized process was programmed with heating ramps of 1 °C/min from 25 to 400 °C and 5 °C/min from 400 to 800 °C and kept at 800 °C for 2 h. After that, the furnace was naturally cooled to room temperature under N_2 atmosphere. X-ray photoelectron spectra (XPS) was recorded on a Kratos Analytical Ltd. AXIS ULTRA X-ray photoelectron spectrometer using monochromatized Al Kα X-ray (1486.6 eV) as the excitation source. The binding energy (BE) of the spectra was calibrated by referring to carbon 1s peak located at 284.8 eV. The resulting catalysts are designated as *x*Al–MC1, *x* denotes the molar ratio of Al ion to R at the beginning of polymerization (e.g. 0.15Al–MC1 show that the Al-containing mesoporous carbon was prepared from 0.15 molar ratio of Al ion to R at the beginning of polymerization mixture).

The same procedures were carried out for the preparation of $0.25Al(NO_3)_3$–MC1, $0.4Al(NO_3)_3$–MC1 and $0.6Al(NO_3)_3$–MC1, except that the different amount of $Al(NO_3)_3$ was used as aluminum source. Pure mesoporous carbon MC1 was prepared by the similar method except for adding aluminum salt.

2.3. Preparation of Cu, Mn and Fe-containing MC1

The same procedures were carried out for the preparation of 0.15Cu–MC1, 0.15Mn–MC1, 0.15Cu–Mn–MC1 and 0.15Fe–MC1, except that the corresponding metal salts $Cu(NO_3)_2{\cdot}3H_2O$, 50% solution of $Mn(NO_3)_2$, and $Fe(NO_3)_3{\cdot}9H_2O$ were used, respectively.

2.4. Preparation of 0.25Cu–MC2 and 0.25Mn–MC2

2.4.1. Preparation of resol precursor

The resol precursor was prepared by using phenol and formaldehyde in a base-catalyzed process according to the reported method [24]. 20.0 g (212.5 mmol) of phenol was melted at 40–42 °C and 4.26 g of 20 wt% NaOH (21.3 mmol) aqueous solution was added slowly under stirring. After 10 min, 35.4 g (436.2 mmol) of formalin (37 wt% formaldehyde) was added dropwise, and the mixture was then heated up to 70–75 °C and stirred for another 60 min at this temperature. Upon cooling down to room temperature, the pH value was adjusted to about 6.0 by 2.0 M HCl solution. Subsequently, the solution was evaporated at 50 °C under reduced pressure to remove water. The resultant product was re-dissolved in ethanol to form a 20 wt% ethanolic solution; thereby separating sodium chloride as a precipitate at the same time.

2.4.2. Preparation of 0.25Cu–MC2 and 0.25Mn–MC2

0.25Cu–MC2 was synthesized from prepared resol, tetraethyl orthosilicate and F127, followed by carbonization and silica removal with NaOH solution. In a typical preparation, 3.2 g (0.26 mmol) of block copolymer F127 and 0.50 g of $Cu(NO_3)_2{\cdot}3H_2O$ (2.07 mmol) were dissolved in 16.0 g of ethanol with 2.0 g of 0.2 M HCl. Then, 4.16 g (19.9 mmol) of TEOS and 10.0 g 20 wt% ethanol solution of resol were mixed in sequence. After stirring for 2 h at 40 °C, the solution was transferred into dishes and kept at room temperature for 5–8 h to remove ethanol. After ethanol was evaporated, the dishes were put into an oven at 100 °C for thermopolymerization for 24 h. The product was scraped from the dishes, pyrolyzed at 700 °C for 2 h with a ramping rate of 2 °C/min under nitrogen flow. The silica component was removed by stirring the resulted mixture in 60 g of 1.0 M NaOH solution at 80 °C for 24 h. The obtained product was designated as 0.25Cu–MC2, 0.25 denotes that 0.25 g of $Cu(NO_3)_2{\cdot}3H_2O$ was applied to per 1.0 g of resol.

The same procedures were carried out for the preparation of sample 0.25Mn–MC2, except using 1.0 g of 50% $Mn(NO_3)_2$ aqueous solution instead of $Cu(NO_3)_2{\cdot}3H_2O$.

2.5. Preparation of 0.62Al–MC1–I and 0.62Mn–MC1–I

0.62Al–MC1–I and 0.62Mn–MC1–I were prepared by a conventional wet impregnation method. In a typical preparation of 0.62Al–MC1–I, 2.5 g of MC1 was added to a beaker containing 8 mL of deionized water. 0.58 g (1.56 mmol) $Al(NO_3)_3 \cdot 9H_2O$ was added to the above-mentioned solution under vigorous stirring. The mixture was further stirred for 3 h, and allowed to stand for 8 h under ambient condition. The 0.62Al–MC1–I was obtained by heating at 100 °C overnight to evaporate water and incubating in a N_2 atmosphere at 600 °C for 6 h. 0.62 denotes that 0.62 mmol of $Al(NO_3)_3 \cdot 9H_2O$ was applied to per 1.0 g of MC1.

The same procedures were carried out for the preparation of sample 0.62Mn–MC1–I, except using 0.56 g (1.56 mmol) of 50% $Mn(NO_3)_2$ aqueous solution instead of $Al(NO_3)_3 \cdot 9H_2O$.

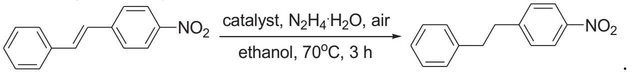
2.6. Characterization methods

N_2 adsorption isotherms were measured using a Micromeritics ASAP 2020 nitrogen adsorption apparatus (USA). All the samples were degassed at 260 °C for 6 h prior to Brunauer–Emmett–Teller (BET) measurements. The BET surface area was calculated using the BET method based on adsorption data in the relative pressure (P/P_0) range 0.05–0.3, the total pore volume (V_{tot}) was determined based on the amount of the N_2 adsorbed at a relative pressure of 0.992 (P/P_0). The pore size distribution (D_{pore}) was derived from desorption isotherm by using the Barrett–Joyner–Halenda (BJH) model. The powder XRD patterns were recorded on a Rigaku D/Max-3c diffractometer equipped with a Cu Kα radiation ($\lambda = 0.154$ nm) beam operating at 40 kV and 40 mA. Data were obtained in the 2θ range of 0–80° at a scanning rate of 8°/min. SEM image and EDX were recorded using a Quanta 200 environmental scanning electron microscope. Sample was mounted using conductive carbon double-sided sticky tape. TEM experiment was conducted on a JEM 2100 electron microscope operating at 200 kV. ^1H NMR, ^{13}C NMR spectra were recorded using $CDCl_3$ as a solvent on a Bruker Avance 400 MHz spectrometer. Chemical shifts (δ) are reported in parts per million, and coupling constants (J) are in hertz, using TMS as an internal standard. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Elemental analyses were performed on a Vario EL III elemental analyzer. GC and GCMS analyses were performed on Shimadzu GCMS-QP2010 apparatus with RTX-1MS capillary column (30 m × 0.25 mm × 0.25 μm).

2.7. Catalytic reductions

To a 10 mL two neck flask were added 100 mg of catalyst, 7 mL of ethanol, 1.0 mmol of the corresponding substrate and the 4 equiv. of 80% hydrazine hydrate. The reaction mixture was stirred at 70 °C under air environment for required time. Samples were taken at regular intervals to analyze by GC using diphenylmethanol as internal standard for calculation the yields of target products and the conversions of substrates. The final mixture was filtered and the filtrate was concentrated under reduced pressure to afford crude product which was purified by recrystallization with the mixture solvent of ethanol and water.

Table 1
Screening the catalyst for the reduction of C=C double bonds of 4-nitrostibene.[a]

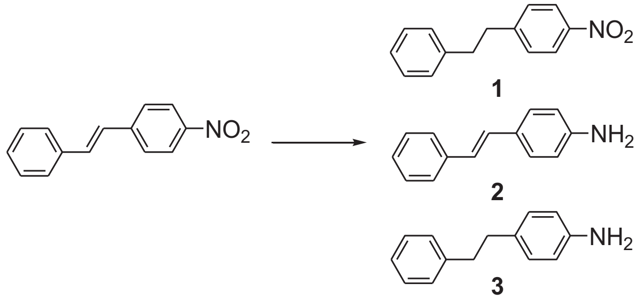


Entry	Catalyst	Yield[b] (%)	Selectivity (%)
1	–	34	72
2	0.15Mn–MC1	64	91
3	0.15Cu–MC1	46	71
4	0.15Cu–0.15Mn–MC1	62	90
5	0.15Fe–MC1	58	61
6	0.15Al–MC1	80	95
7	0.25Cu–MC2	6	6
8	0.25Mn–MC2	23	47
9	0.62Mn–MC1–I	62	84

[a] The reaction conditions: 4-nitrostilbene (0.22 g, 1.0 mmol), catalyst (100 mg), 80% hydrazine hydrate (0.60 g, 4 equiv.), ethanol (7 mL), 70 °C, 3 h under air.
[b] Determined by GC using diphenylmethanol as internal standard.

3. Results and discussion

Considering that Cu [25,26], Mn [27,28], Fe [29,30] and Al [31] complexes, metal nanoparticle, alloys and metal–organic frameworks (MOFs) have been used as catalysts to activate molecular oxygen for the oxidation of organic substrates or the reduction of carbon–carbon double bonds with hydrazine hydrate, we used multi-component co-assembly strategy associated with a direct carbonization process to yield several metal-containing MC catalysts, such as 0.15Mn–MC1, 0.15Cu–MC1, 0.15Cu–0.15Mn–MC1, 0.15Fe–MC1 and 0.15Al–MC1 in modified method [32]. 0.25Cu–MC2 and 0.25Mn–MC2 were synthesized by triconstituent co-assembly of prepared resol, tetraethyl orthosilicate (TEOS) and F127, followed by carbonization and silica removal [24]. Meanwhile pure mesoporous carbon MC1 was prepared by the similar method with that of to 0.15Al–MC1 method except for adding metal salt, and Mn-containing mesoporous carbon hybrid 0.62Mn–MC1–I was prepared with impregnating method [33] from MC1 and $Mn(NO_3)_2$. With these catalysts, we used 4-nitrostilbene as a model substrate to investigate the chemoselective reduction of carbon–carbon double bonds with hydrazine hydrate in ethanol under air atmosphere. As shown in Table 1, in the control experiment the desired product was obtained in low yield (34%) and selectivity (72%) in the absence of catalyst (entry 1 in Table 1). Mn, Cu, Fe and Al supported on MC exhibited certain catalytic activity to the reduction of C=C double bonds (entries 2–6 in Table 1). 0.25Mn–MC2 presented negative activity (entry 8 in Table 1) compared with the control experiment (Fig. 1 in S1), although Mn-containing catalysts 0.15Mn–MC1 and 0.62Mn–MC1–I exhibited moderate activity (entries 2 and 9 in Table 1). It was worthy to note that 0.15Cu–MC1 exhibited low catalytic activity in the reaction (entry 3 in Table 1), in contrast, 0.25Cu–MC2 possessed obvious inhibition effect on the reaction (entry 7 in Table 1 and Fig. 2A in S1). The constituents of reaction mixtures in the presence of 0.15Cu–MC1 and 0.25Cu–MC2 were determined by GC analysis when reactions were prolonged to 7 h (see Fig. 2B in S1). Although the higher conversions of 4-nitrostilbene were obtained at 7 h in the presence of 0.15Cu–MC1 and 0.25Cu–MC2, (88% and 99%) respectively, 1-nitro-4-phenethylbenzene (**1**), 4-styrylaniline (**2**) and 4-phenethylaniline (**3**) were found in these two reaction mixtures. The results suggested that three different reduction reactions as Scheme 2 occurred competitively at the same time, and the Cu-containing MC showed lower chemoselective reductions especially in the presence of 0.25Cu–MC2. These results indicated that the chemoselective reduction of C=C double bond or nitro group in 4-nitrostilbene is a key problem, and Cu-containing MC



Scheme 2. Various reduction of 4-nitrostilbene.

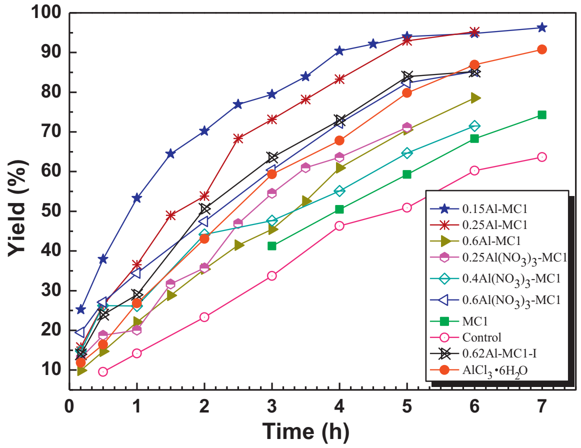


Fig. 1. The catalytic effects of Al-containing MCs on the chemoselective reduction of C=C bond in 4-nitrostilbene. *Reaction condition*: 4-nitrostilbene (0.22 g, 1.0 mmol), catalyst (100 mg), 80% hydrazine hydrate (0.60 g, 4 equiv.), ethanol (7 mL), 70 °C under air atmosphere.

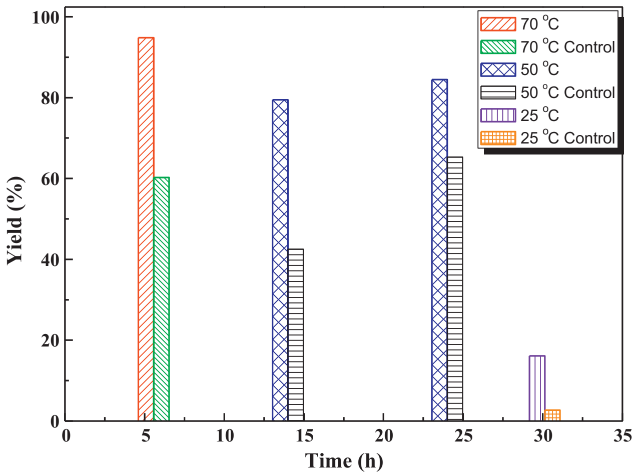


Fig. 2. The yields of 1-nitro-4-phenethylbenzene from 4-nitrostilbene in the presence of 0.15Al–MC1 at different temperatures.

is not suitable to chemoselectively reduce C—C double bonds. The reaction in the presence of 0.15Fe–MC1 has middle chemoselectivity (61%) with 96% conversion of 4-nitrostilbene at 3 h. To our delight, 80% yield and 95% selectivity was achieved in the presence of 0.15Al–MC1 (entry 6 in Table 1). It might imply that Al supported on MC1 as catalyst prefer to the selective catalytic reduction of C—C double bond in 4-nitrostilbene. All the results indicated that the activity of these materials depend closely on metal species, the amount of metal loading and the synthesis procedure of catalyst.

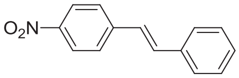
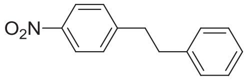
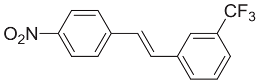
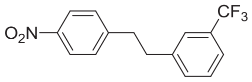
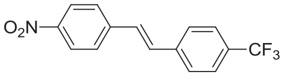
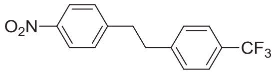
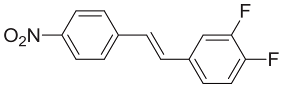
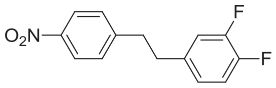
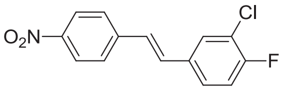
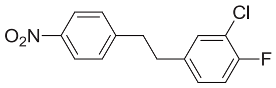
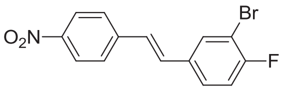
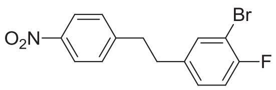
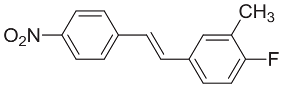
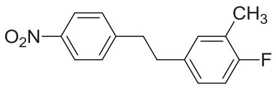
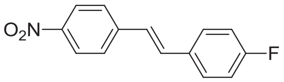
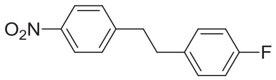
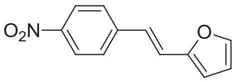
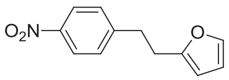
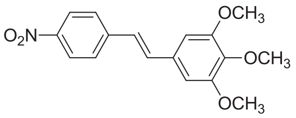
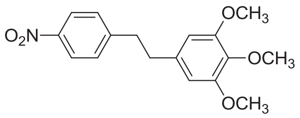
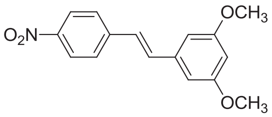
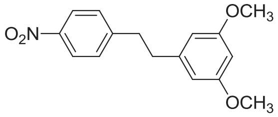
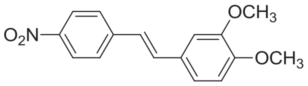
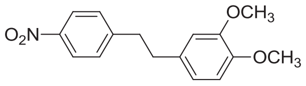
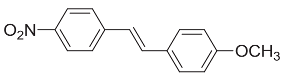
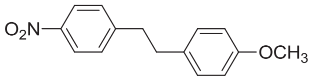
To further investigate the catalytic effect of Al-containing MCs, other six Al-containing MCs were evaluated in the reduction of C=C bond under the same condition. As shown in Fig. 1, 0.15Al–MC1 exhibited the highest activity in all tested catalysts. With prolongation of reaction time from 10 min to 5 h, the yield of target product 1-nitro-4-phenethylbenzene increased rapidly from 25% to 94% with 98% selectivity. Subsequently from 5 h to 7 h, the yield increased slowly to 98%. Apparently an excellent result was achieved at 5 h under the catalysis of 0.15Al–MC1. Fig. 1 also showed that support MC1 itself presented catalytic activity comparing with control experiment, but its activity is lower clearly than that of 0.15Al–MC1. It is obvious that this excellent result contribute to the synergetic effect of Al specie with MC, and the technological process of catalyst preparation. This result inspirited us to further optimize the reaction conditions using 0.15Al–MC1 as catalyst.

The reaction temperature was investigated in the presence of 0.15Al–MC1 at 25, 50, 70 °C, respectively. The yields of target product were increased with the extension of reaction time and increase of temperature (Fig. 2). At 25 °C, the reduction reaction occurred very slowly, and gave low yields whatever in the presence or absent of catalyst. Only 16% yield of product was obtained in the presence of catalyst, even if prolonging reaction time to 30 h. The results indicate that the reduction of C—C double bonds is hard to carry out at lower temperature. Increasing reaction temperature to 50 °C, the yield of target product sharply increased to 79% at 14 h in the presence of 0.15Al–MC1. But little increase in yield was only observed when reaction was prolonged from 14 to 24 h at 50 °C. However, further increasing temperature to 70 °C, an excellence yield (95%) could be obtained at 6 h. These results indicated the 70 °C is optimum temperature. To further investigate the temperature effect on the catalytic reaction, acetonitrile with higher boiling point was selected as solvent to replace of ethanol. At 70 °C, the slightly different result was observed under the same reaction condition (Fig. 3 in S1). When the reaction temperature was increased to 80 °C in acetonitrile, the selectivity of reduction on C=C bond became lower, and 4-phenethylaniline was detected in the reaction system. The result indicated that higher reaction temperature does not fit to the selective reduction of C=C bond. In fact, higher temperature such as 100 °C will result in the decomposition of hydrazine hydrate to N_2, NH_3 and H_2. Therefore considering the selectivity of reaction and toxicity of acetonitrile, ethanol was selected as the ultimate solvent. On the basis of above results, the optimized catalyst and reaction condition were obtained as 4-nitrostilbene (0.22 g, 1.0 mmol), 80% hydrazine hydrate (0.60 g, 4 equiv.) in ethanol (7 mL), at 70 °C under air in the presence of 0.15Al–MC1 (100 mg) for 5 h.

In order to investigate the key role of oxygen in the reduction, an oxygen-free experiment was investigated in the presence of 0.15Al–MC1 in optimized reaction condition under N_2 atmosphere. A few of target product (<10% yield) was found under N_2 atmosphere despite in the presence of 0.15Al–MC1 (Fig. 4 in S1) after 5 h. In contrast, the certain 4-styrylaniline was found in the reaction mixture. These results further suggest the oxygen is essential in the formation of diimide from hydrazine with catalyst (Scheme 1). To the best of our knowledge, the hydrazine produces H_2 at higher temperature in the presence of Fe^{3+} and active carbon to reduce nitro group in organic compounds [34]. Thus, the chemoselectivity reduction of nitro group in 4-nitrostilbene was also investigated using hydrazine hydrate with $FeCl_3$ and active carbon in ethanol at 70 °C under the protection-free from inert gases. 77% of yield of 4-styrylaniline from 4-nitrostilbene and 98% of conversion were obtained after 10 min, while about 17% of 4-phenethylaniline was determined in this reaction. The generation of 4-phenethylaniline should attribute to the presence of air. Thus as the expectation, an improved yield (93%) of 4-styrylaniline was obtained after 10 min under N_2 atmosphere (Fig. 5 in S1). These experiment facts obviously indicated that when hydrazine hydrate was used as reducing agent, diimide was generated for the reduction of C—C double bonds in the presence of oxygen, while in air-free condition it preferred to the reduction of nitro group. So far, an excellent method has been achieved successfully for the chemoselective reduction of C—C double bond or nitro group in 4-nitrostilbene.

The catalyst 0.15Al–MC1 should also be able to chemoselectively catalyze the reduction of C—C double bonds in other stilbene analogs. We expanded reaction to the reduction of various substituted stilbenes under the optimized condition. It can be seen from Table 2 that all the nitrostilbenes with electron-withdrawing or electron-donating groups afford high yields and chemoselectivity of C—C double bond reduction except for 3′,5′-dimethoxyl

Table 2
The selective reduction of C—C double bonds in stilbenes bearing nitro group with hydrazine hydrate in the presence of 0.15Al–MC1 catalyst in ethanol.[a]

Entry	Substrate	Product	Yield[b] (%)	Selectivity[b] (%)	Time (h)
1			98	98	7
2			92	97	10
3			96	97	8
4			94	95	11
5			92	>99	9
6			99	>99	11
7			94	99	7
8			91	96	7
9			73	96	10
10			89	92	14
11			53	65	7
12			68	93	10
13			89	92	14

[a] The reaction conditions: substrate (1.0 mmol), 0.15Al–MC1 (100 mg), 80% hydrazine hydrate (4 equiv.), ethanol (7 mL), 70 °C under air.

[b] Determined by GC. Yields were calculated using diphenylmethanol as internal standard.

-4-nitrostilbene and 3′,4′-dimethoxyl-4-nitrostilbene (entries 11 and 12 in Table 2). The electron-withdrawing groups in nitrostilbene derivatives did not affect the yield of the C—C double bond reduction, and the reactions exhibit high selectivity (>91%). Compounds with electron-donating groups such as methoxyl gave lower yields than compounds with electron-withdrawing groups.

An excellent catalyst 0.15Al–MC1 has been obtained for the chemoselective catalytic reduction of C—C double bond in nitrostilbene analogs with hydrazine hydrate. In order to further explore the relationship between catalyst structure and catalytic activity, the structures of some prepared catalysts were characterized by N_2 adsorption, powder wide-angle X-ray diffraction (WAXD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) imaging techniques. The nitrogen adsorption isotherms of the four catalysts, MC1, 0.15Al–MC1, 0.25Al–MC1 and 0.6Al–MC1 and their corresponding BJH (Barrett–Joyner–Halenda) pore size distribution are shown in Fig. 3. These samples show type IV isotherms with a quite obvious H2-type hysteresis loop at relative pressure, which is a characteristic of mesoporous structure [35]. As presented in Table 3, their specific surface areas closely depend on the molar ratio of Al ion to resorcinol in their preparation process. Their catalysis activities for the reduction of C—C double bond (Fig. 1) are consistent with their specific surface areas. Except MC1, catalyst 0.15Al–MC1 possesses the highest specific surface area (493 m^2/g) in three catalysts prepared from $AlCl_3$ as aluminum source and it also exhibits the best catalytic activity with TOF

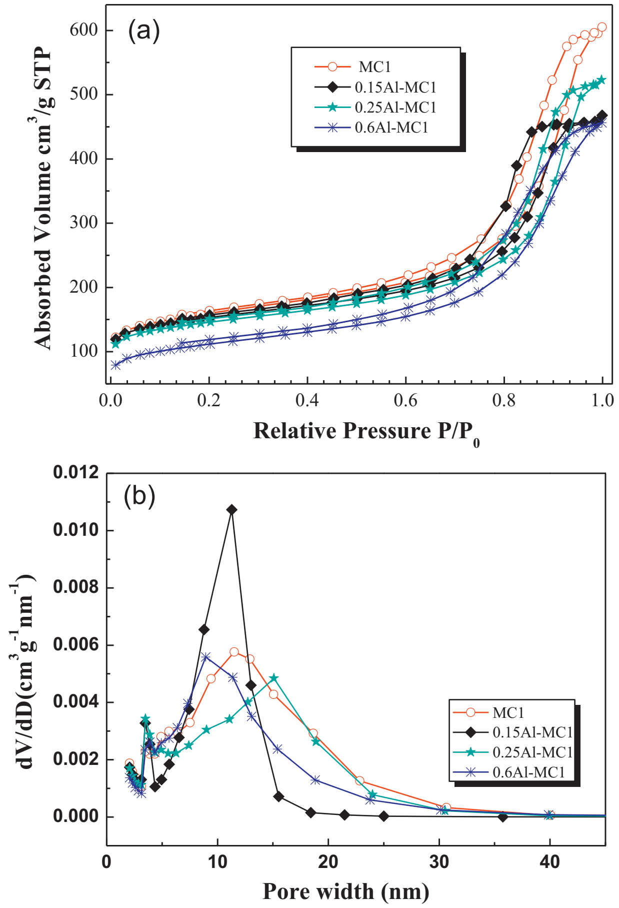


Fig. 3. N_2 adsorption isotherms (a) and corresponding pore size distribution curves (b) of MC1; 0.15Al–MC1; 0.25Al–MC1; 0.6Al–MC1. Pore size distributions were evaluated from desorption branches of N_2 isotherms using the BJH model.

Table 3
Textual parameters of several catalysts.[a]

Sample	S_{BET} (m^2/g)	V_{tot} (cm^3/g)	D_{pore} (nm)	TOF[b]
MC1	518	0.94	10.5	2.653
0.15Al–MC1	493	0.72	8.6	5.372
0.25Al–MC1	470	0.81	10.3	5.188
0.6Al–MC1	370	0.71	9.4	4.085

[a] S_{BET}, apparent surface area calculated by BET method; V_{tot}, total pore volume at $P/P_0 = 0.99$; D_{pore}, pore sizes calculated from desorption branches of N_2 isotherms using the BJH model.

[b] TOF = mmol product formed per unit specific surface area per hour ($\times 10^{-3}$ mmol/m^2 h^{-1}).

of 5.372×10^{-3} mmol/m^2 h^{-1}. Meanwhile 0.25Al–MC1 presents slight lower catalysis activity (TOF: 5.188×10^{-3} mmol/m^2 h^{-1}) than 0.15Al–MC1, consenting with that 0.25Al–MC1 possessing slight lower specific surface area than 0.15Al–MC1. These facts indicated that in our established containing Al–MCs catalysis system the specific surface area of these mesoporous catalysts is an important factor for their catalytic activity, and the ratio of Al ion to R in the preparing process of catalysts affected obviously on the specific surface area of catalysts. On the other hand, the pure mesoporous carbon material MC1 with the biggest surface area exhibited the lowest TOF value. It suggests that the Al play a key role in the catalyst.

Nevertheless, it is difficult to characterize the structure only with the N_2 sorption measurement. To further obtain structure evidence of the porous catalyst 0.15Al–MC1 with the best catalysis activity, we observed its optical impression by TEM. Fig. 4a reveals the existence of the evidently disordered but uniform-size wormlike pore channels in 0.15Al–MC1. The surface morphology of catalyst 0.15Al–MC1 was shown by the SEM image in Fig. 4b. Since the samples were crushed for SEM analysis, 0.15Al–MC1 demonstrates largely smooth granular carpolite-like morphology with particle size up to the micrometer scale. The aluminum including in catalyst 0.15Al–MC1 is affirmed by energy dispersive X-ray spectroscopy (EDX) (Fig. 6 in S2). Approximately 0.4 wt% of aluminum species is enchased in the mesoporous frame of carbon. The Al state in Al–MC1 catalysts is major in Al_2O_3 form deduced from the peak at 73.8 eV [36] in the XPS of 0.6 Al–MC1 (Fig. 7 in S2). In the Al 2p spectrum, another littler peak at 76.5 eV could be assigned to Al^{3+} in $AlCl_3$ and imply small amount $AlCl_3$ also exist in the catalyst. In the O 1s spectrum, the peak at 531.6 eV assigned to oxygen in Al_2O_3 [37], consistent with the observation in the Al 2p spectrum. However, no diffraction peak of any Al species was observed in XRD spectrum of 0.15Al–MC1 (Fig. 8b in S2), and two broad diffraction peaks of all the tested samples centered at 23° and 44° of 2θ in wide angle region (Fig. 8 in S2), which can be generally indexed to (0 0 2), (1 0 1) diffraction for glass-like carbons bearing graphitic characteristic [38]. These imply that Al species is very equably disperse and not to form crystal in carbon matrix.

4. Conclusion

We reported a simple method to prepare Al-containing mesoporous carbon catalysts by multi-component co-assembly strategy associated with a direct carbonization process from resorcinol, formaldehyde, triblock copolymer F127 and corresponding metal salt. When these heterogeneous catalysts were used to the chemoselective reduction of C—C double bond in nitrostilbene derivatives

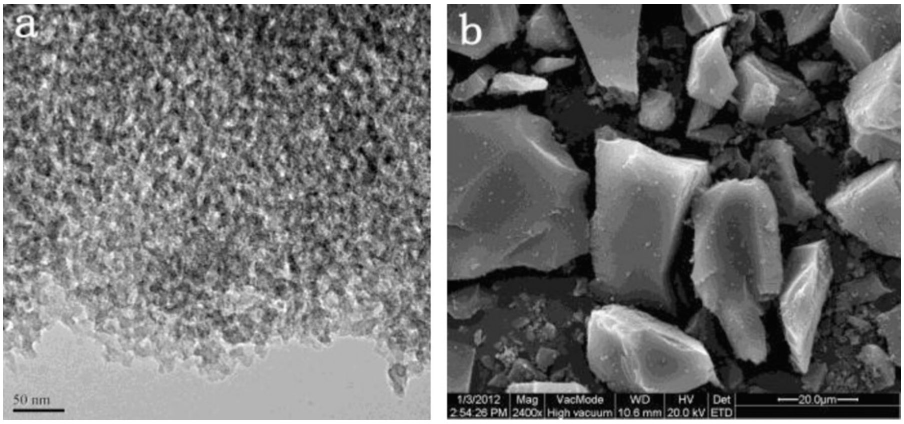


Fig. 4. TEM (a) and SEM (b) images of 0.15Al–MC1.

with hydrazine hydrate as reducing agent under air atmosphere, 0.15Al–MC1 exhibited the best catalysis activity (up to 99% yield and >99% selectivity) in all the tested catalysts. Meanwhile the nitro group in nitrostilbene derivatives can also chemoselective reduced with hydrazine hydrate under inert atmosphere. These protocols were preformed under relatively mild reaction conditions, and will attract considerable attention because of low cost, high efficiency and low environmental impact.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2013.01.040.

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