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Selective hydrogenation of nitroarenes to aminoarenes using MoO_x modified Ru/SiO_2 catalyst under mild conditions

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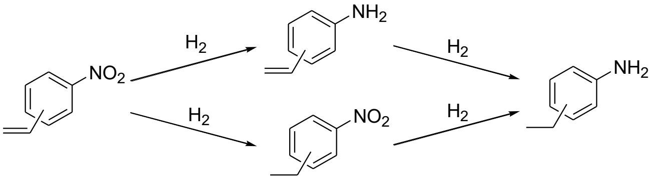
Modification of metal oxides (MoO_x, WO_x and ReO_x) with Ru/SiO_2 improved activity and selectivity in hydrogenation of 3-nitrostyrene to 3-aminostyrene under mild conditions such as 0.3 MPa H_2, 303 K and no solvent. $Ru\text{-}MoO_x/SiO_2$(Mo/Ru=1/2) catalyst was applicable to various substituted nitroarenes, providing the corresponding substituted aminoarenes in high yields (85%-99%).



Scheme 1 Hydrogenation of nitrostyrenes

Development of highly selective and active catalysts contributes to energy saving, cost reduction, and waste reduction, and supported metal catalysts will be ideal among various catalysts in terms of its reusability, durability and easy separation of products and catalysts. However, for supported metal catalysts, control of selectivity is generally difficult because of the non-uniformity of the surface active sites, and hence effective methodologies to control selectivity and activity, particularly selectivity, are quite necessary. Modification of active metal species with inorganic or organic modifiers will be one of the most promising approaches[1], however, these systems often not only require complex and tedious preparation but also decrease the activity via coverage of the active sites by modifiers[2]. Therefore, more facile, simple and effective catalyst systems enabling both high selectivity and activity are desirable to be developed from the viewpoint of green sustainable chemistry.

Selective hydrogenation of substrates having multiple different functional groups are often used as a model reaction for development of selective heterogeneous catalysts, and selective hydrogenation of functionalized nitroarenes to the corresponding aminoarenes is a useful organic reaction because the produced aminoarenes are important chemicals and intermediates for agrochemicals, pharmaceuticals polymers and pigments[1a,3]. However, for conventional hydrogenation catalysts such as noble metal supported catalysts, nonpolar functional groups such as alkenes and alkynes are thermodynamically and kinetically more subjective to hydrogenation than the nitro groups, and over-hydrogenation of the produced aminoarenes also occurs, leading to low selectivity to the aminoarenes (Scheme 1). Various effective heterogeneous catalysts for selective hydrogenation of nitrostyrene as a model reaction have been developed such as Pt-based catalysts[4], Au-based catalysts[5] and Co-based catalysts[6] and so on[7]. In particular, in spite that Pt metal originally shows higher activity to hydrogenation of alkenes than that of nitro groups, modification of Pt metal with other species[4c,e-g] or strong metal support interaction (SMSI) effect[4a,b,d,h] drastically changed the activity of Pt metal, achieving high selectivity to the target amines. Other noble metal species such as Rh, Ru and Pd also showed low selectivity[4h], however, there are few reports on activity and selectivity control of these metal species.

To date, we have developed metal-oxide-modified noble metal catalysts (noble metal: Ir, Rh and Ru; metal oxide: ReO_x, MoO_x, WO_x) for hydrogenolysis of polyols or ethers[8] and hydrogenation of carbonyl compounds such as carboxylic acids[9], aldehydes[10] and amides[11]. These studies showed that modification of noble metals with metal oxides formed active sites at the interface of noble metals and metal oxides, leading to drastic improvement of the activity and selectivity. Herein, we applied the metal-oxide-modified noble metal catalysts to selective hydrogenation of functionalized nitroarenes to the aminoarenes, showing that MoO_x-modified Ru/SiO_2 was effective for the reaction, and that modification of Ru metal with MoO_x species improved both the activity (about 5-fold) and selectivity (73% → 99%).

At first, hydrogenation of 3-nitrostyrene as a model reaction was conducted with various catalysts under mild reaction conditions such as 303 K, 0.3 MPa H_2 and no solvent (Table 1). From the results of the carbon-supported noble metal catalysts (M/C, M=Ru, Pd, Rh, Pt, entries 1-4), Ru/C provided high

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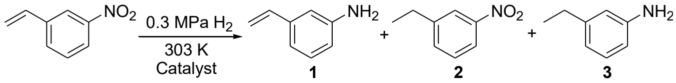
Table 1 Hydrogenation of 3-nitrostyrene using various catalysts



Entry	Catalyst	Conversion (%)	Selectivity (%)			
			1	**2**	**3**	Others
1	Ru/C*	6.2	91.2	8.3	<0.1	0.5
2	Pd/C*	90.0	<0.1	76.9	22.6	0.5
3	Rh/C*	58.3	13.6	76.0	9.2	1.2
4	Pt/C*	41.1	52.6	8.6	5.4	33.4
5	Ru/SiO_2	2.8	73.4	9.5	<0.1	17.1
6	Ru-WO_x/SiO_2	14.2	>99.9	<0.1	0.4	<0.1
7	Ru-MoO_x/SiO_2	15.3	99.5	<0.1	<0.1	0.5
8	Ru-ReO_x/SiO_2	9.9	97.9	0.9	<0.1	1.2
9	Pd/SiO_2	98.0	<0.1	70.9	28.7	0.4
10	Pd-WO_x/SiO_2	86.8	<0.1	76.2	22.4	3.6
11	Pd-MoO_x/SiO_2	92.2	<0.1	77.9	22.1	2.2
12	Pd-ReO_x/SiO_2	92.4	<0.1	75.2	24.3	9.4
13	Rh/SiO_2	73.0	0.5	96.0	3.5	<0.1
14	Rh-WO_x/SiO_2	59.9	2.0	80.2	17.7	<0.1
15	Rh-MoO_x/SiO_2	66.9	1.6	80.8	17.5	0.1
16	Rh-ReO_x/SiO_2	71.1	0.9	89.9	9.0	0.1
17	Pt/SiO_2	31.7	32.6	35.7	22.9	8.8
18	Pt-WO_x/SiO_2	38.0	11.8	56.8	26.7	4.8
19	Pt-MoO_x/SiO_2	27.9	41.9	34.6	19.2	4.3
20	Pt-ReO_x/SiO_2	38.3	20.3	54.2	12.5	13.0
21	Ir/SiO_2	30.2	32.9	47.1	11.3	8.6
22	Ir-WO_x/SiO_2	28.1	66.3	15.4	17.6	0.8
23	Ir-MoO_x/SiO_2	29.2	83.2	6.6	8.5	1.7
24	Ir-ReO_x/SiO_2	30.9	36.2	40.0	14.5	9.3

Reaction conditions: 3-nitrostyrene 3 mmol, catalyst (M'/M=1/4, M=4 wt% (*M=5 wt%), M=Ru, Pd, Rh, Pt, Ir, M'=W, Mo, Re) 30 mg, 303 K, H_2 0.3 MPa, 2 h. Others: 3-nitrosostyrene and 3-ethyl-*N*-hydroxyaniline.

selectivity (91.2%) to 3-aminostyrene (**1**), the target product, although the conversion was low. In addition, metal-oxide-modified noble metal catalysts (M-M'O_x/SiO_2 (M'/M=1/4), M=Ru, Pd, Rh, Pt, Ir, M'= W, Mo, Re) were also applied to the reaction (entries 5-24). Modification of Ru with M'O_x improved both the activity and selectivity to **1** (entries 5-8), and modification of Ir with M'O_x improved only the selectivity to **1** (entries 21-24), while modification of Pd, Rh and Pt with M'O_x showed no significant improvement of the selectivity and activity (entries 9-20). Ru-M'O_x/SiO_2 catalysts showed higher selectivity to **1** than Ir-M'O_x/SiO_2 catalysts. Therefore, Ru is a preferable noble metal for the reaction, and modification of Ru with metal oxides improved both the selectivity and activity.

In order to determine the optimal molar ratio of M'/Ru in Ru-M'O_x/SiO_2 (M'=W, Mo, Re) catalysts, hydrogenation of 3-nitrostyrene was conducted by using Ru-M'O_x/SiO_2 catalysts with various M'/Ru molar ratios (Table S1). The conversion showed volcano pattern to the M'/Ru molar ratio in all series of Ru-M'O_x/SiO_2 catalysts, and the highest conversion was obtained at M'/Ru molar ratio of 1/8. On the other hand, selectivity to **1** gradually increased with increasing the M'/Ru molar ratio. Ru-MoO_x/SiO_2(Mo/Ru=1/2), which showed high selectivity (99.5%) and about 5-fold higher activity than that of Ru/SiO_2, was selected in terms of conversion and selectivity. Ru-MoO_x/SiO_2(Mo/Ru=1/2) was reusable without loss of its catalytic performance (Table S2), and the XRD patterns and XAFS spectra were not changed after the reaction (shown later).

Various solvents were applied to the reaction using Ru-MoO_x/SiO_2(Mo/Ru=1/2) (Table S3). Water and toluene showed similar performance to that at neat condition.

Time-courses of hydrogenation of 3-nitrostyrene over Ru-MoO_x/SiO_2 and Ru/SiO_2 are shown in Figure 1. The reaction over Ru-MoO_x/SiO_2(Mo/Ru=1/2) proceeded smoothly with high selectivity to reach almost 100% at 12 h, providing **1** in 97% yield (Figure 1a). On the other hand, although the reaction over Ru/SiO_2 proceeded smoothly, the selectivity to **1** drastically decreased after 100% conversion of 3-nitrostyrene. These results suggest that over-hydrogenation of **1** was suppressed by addition of MoO_x species to Ru/SiO_2.

The scope of nitroarenes was investigated by using Ru-MoO_x/SiO_2(Mo/Ru=1/2) catalyst (Table 3). Various substituted nitrobenzenes with unsaturated functional groups were selectively converted to the corresponding anilines in high yields (entries 1-4). In addition, chloronitrobenzenes were transferred to the corresponding chloroanilines (CANs), which are typical scaffold compounds for dyes, pharmaceuticals, and agricultural chemicals[1a] (entries 5-7). Therefore, this catalyst will be practically very useful for the synthesis of various substituted anilines.

In order to clarify the catalyst structure of Ru-MoO_x/SiO_2(Mo/Ru=1/2), the catalyst was characterized by

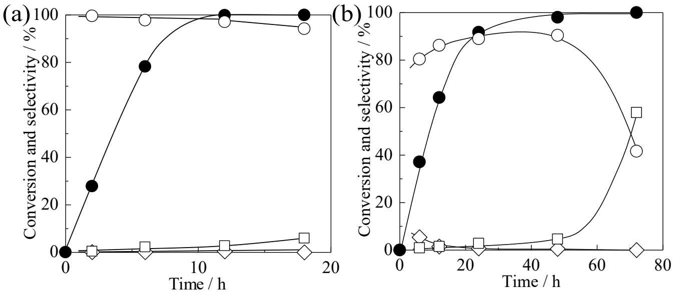
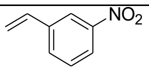
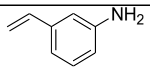
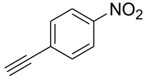
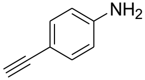
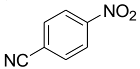
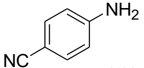
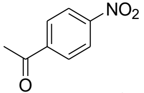
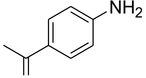
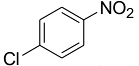
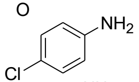
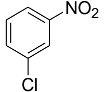
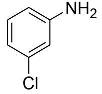
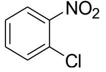
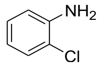


Figure 1 Time-course of hydrogenation of 3-nitrostyrene over Ru-MoO_x/SiO_2 (a) and Ru/SiO_2 (b) (●: Conversion, ○: Selectivity to **1**, ◇: selectivity to **2**, □: selectivity to **3**)
Reaction conditions: 3-nitrostyrene 3 mmol, catalyst 100 mg, 303 K, H_2 0.3 MPa.

Table 3 Scope of substrates in hydrogenation of nitroarenes over Ru-MoO_x/SiO_2(Mo/Ru=1/2) catalyst

Entry	Substrate	Product	*t* (h)	Conv. (%)	Select. (%)
1			8	97	98
2			24	96	88
3			36	>99	97
4			17	>99	99
5			4	96	>99
6			4	95	>99
7			6	96	>99

Reaction conditions: nitroarenes 3 mmol, Ru-MoO_x/SiO_2(Mo/Ru=1/2) 100 mg, toluene 3 g, 303 K, H_2 0.3 MPa.

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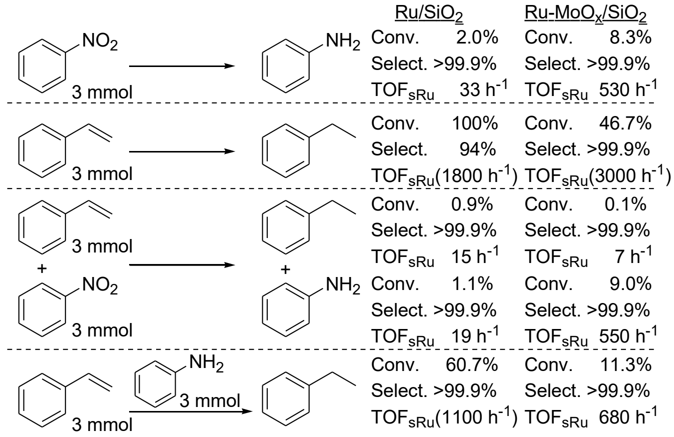
various characterization methods such as XRD, TEM, TEM-DEX, TPR, XAS and CO adsorption. XRD profiles (Figure S1) showed signals due to Ru metal in addition to those due to SiO_2, and the particle size of Ru metal was calculated to be about 5 nm on all the catalysts (Table S4). No signal due to MoO_x species was observed, implying that MoO_x species were highly dispersed or amorphous. From TEM images (Figure S2) of Ru/SiO_2 and $Ru\text{-}MoO_x/SiO_2$(Mo/Ru=1/2), the particles sizes of Ru metal over Ru/SiO_2 and $Ru\text{-}MoO_x/SiO_2$(Mo/Ru=1/2) were estimated to be 5.1 nm and 5.0 nm, respectively (Table S4), which agreed with the results of XRD. In addition, mapping analysis of metal species over $Ru\text{-}MoO_x/SiO_2$(Mo/Ru=1/2) was carried out by TEM-EDX (Figure S3). MoO_x species were dispersed on the surface of the catalyst, particularly around Ru species, suggesting that Ru metals can interact with MoO_x species. TPR profiles of Ru/SiO_2, $Ru\text{-}MoO_x/SiO_2$(Mo/Ru=1/8) and $Ru\text{-}MoO_x/SiO_2$(Mo/Ru=1/2) provided one main signal between 373 and 500 K, and the signal was shifted to higher temperature with increasing Mo/Ru molar ratio (Figure S4). No signal assignable to MoO_x species on SiO_2 support was observed. These results imply that Ru metal and MoO_x species interact with each other. From the signal intensity, the valence of Mo species over $Ru\text{-}MoO_x/SiO_2$ catalysts was calculated to be about +5 (Table S4), which is in good accordance with our previous results of $Ru\text{-}MoO_x/SiO_2$ in hydrogenation of lactic acid[9c]. XAS analyses of $Ru\text{-}MoO_x/SiO_2$(Ru/Mo=1/2) after reaction and reduction were conducted (Table S5 and Figures S5-7). From the curve fitting results of Ru *K*-edge XAFS (Table S5), the Ru-Ru (or -Mo) bond was present with the length (*R*) of 0.267 nm and the CN was about 11.6 for $Ru\text{-}MoO_x/SiO_2$ after the reduction and reaction. Ru-O and Ru-O-Ru bonds were not detected. From the Ru *K*-edge XANES results (Figure S6), the spectra of $Ru\text{-}MoO_x/SiO_2$ were similar to that of Ru powder. These results suggest that Ru species was in the metallic state, and the reduced Ru metal was maintained after the reaction, which is in agreement with the results of XRD analyses. From the Mo *K*-edge XANES results (Figure S7), the pre-edge signal due to MoO_x species with the most oxidized state (+6) was barely observed over $Ru\text{-}MoO_x/SiO_2$, suggesting that the MoO_x species on $Ru\text{-}MoO_x/SiO_2$ was reduced to some extent, and the state of MoO_x species was maintained during the reaction. This result also agrees with the results of TPR analyses. In order to estimate the surface Ru metal amount over the catalysts, CO adsorption was carried out with Ru/SiO_2 and $Ru\text{-}MoO_x/SiO_2$(Mo/Ru=1/32-1/2) (Table S4). The ratio of surface Ru metal amount to total Ru amount (CO/Ru) over Ru/SiO_2 was calculated to 0.14, and the ratios of CO/Ru over $Ru\text{-}MoO_x/SiO_2$(Mo/Ru=1/32-1/2) decreased with increasing the Mo/Ru molar ratio. This result can be interpreted by covering surface Ru metal with MoO_x species, which was not inconsistent with the results of TEM-EDX and TPR. Considering that the sizes of Ru metal particles were almost the same at all the catalysts, the decrease of CO/Ru from 0.14 over Ru/SiO_2 to 0.04 over $Ru\text{-}MoO_x/SiO_2$(Mo/Ru=1/2) means that about 70% of surface Ru metal was covered by MoO_x species.

As above, the structure of $Ru\text{-}MoO_x/SiO_2$(Mo/Ru=1/2) is as follows: Ru species are in the metallic state, and the particle size of Ru is about 5 nm. Mo species is in the oxidized state, and the valence is about +5. The Mo species are highly dispersed and partially cover Ru metal surface.

In order to elucidate the role of MoO_x species in hydrogenation of 3-nitrostyrene, the reactivities of various model substrates were compared by using Ru/SiO_2 and $Ru\text{-}MoO_x/SiO_2$(Mo/Ru=1/2), and the results and TOF per surface Ru (TOF_{sRu}) were shown in Scheme 2. The results of nitrobenzene hydrogenation showed that addition of MoO_x species increased the activity of hydrogenation of the nitro group by a factor of 15, in contrast, those of styrene hydrogenation showed that addition of MoO_x species has little influence on the activity to hydrogenation of the olefin group. Hydrogenation of styrene in the presence of the same molar amount of nitrobenzene was carried out over $Ru\text{-}MoO_x/SiO_2$, showing that nitrobenzene was hydrogenated at a similar rate of hydrogenation of only nitrobenzene, but styrene was hardly done. This suppression of olefin hydrogenation by nitro compound can explain the high selectivity to **1** in hydrogenation of 3-nitrostyrene over $Ru\text{-}MoO_x/SiO_2$. In the case of Ru/SiO_2, nitrobenzene and styrene were hydrogenated at similar rates, which agreed with the low selectivity (~70%) in hydrogenation of 3-nitrostyrene over Ru/SiO_2. In addition, hydrogenation of styrene in the presence of the same molar amount of aniline was conducted, presenting that the activity for styrene hydrogenation over $Ru\text{-}MoO_x/SiO_2$ was significantly decreased by addition of aniline, and the activity was lower than that over Ru/SiO_2, which can explain the high selectivity at high conversion level over $Ru\text{-}MoO_x/SiO_2$.

Kinetic parameters such as substrate concentration and H_2 pressure were investigated in hydrogenation of 3-nitrostyrene using Ru/SiO_2 and $Ru\text{-}MoO_x/SiO_2$. The reaction orders with respect to 3-nitrostyrene concentration over Ru/SiO_2 and $Ru\text{-}MoO_x/SiO_2$ were calculated to be 0.8 and 0.1, respectively (Figure S8a). Addition of MoO_x species to Ru/SiO_2 decreased the reaction order, which can be interpreted by strong adsorption of 3-nitrostyrene on MoO_x species. The reaction orders with respect to H_2 pressure over Ru/SiO_2 and $Ru\text{-}MoO_x/SiO_2$ were estimated to be 0.6 and 0.9, respectively (Figure S8b). Addition of MoO_x species to Ru/SiO_2 decreased the reaction order, indicating that MoO_x changed the manner of H_2 activation. According to our previous works on metal-oxide-



Scheme 2 Comparison of the reactivities of various substrates over Ru/SiO_2 and $Ru\text{-}MoO_x/SiO_2$(Mo/Ru=1/2).

Reaction conditions: substrate 3 mmol, Ru/SiO_2 or $Ru\text{-}MoO_x/SiO_2$(Mo/Ru=1/2) 30 mg, 303 K, H_2 0.3 MPa, 1 h.

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modified noble metal catalysts in hydrogenation and hydrogenolysis reactions[9c,12], the first order with respect to H_2 pressure suggests that H_2 was heterolytically dissociated to produce active hydride (H^-) and proton (H^+) and nucleophilic attack of the produced hydride species to the nitro group was the rate-determining step.

As above, the reaction proceeds via nucleophilic attack of the produced hydride species to the nitro group of adsorbed nitroarenes on MoO_x species, and the improvement of activity and selectivity can be due to strong adsorption of nitroarenes on MoO_x species and formation of hydride species at the active sites, the interface between Ru metal and MoO_x species. The hydride species are generally active for nucleophilic addition due to the anionic nature of the hydride, and also it is well-known that hydride species are effective for the hydrogenation of polarized functional groups such as carbonyl groups [13]. Therefore, the formation of the hydride species will contribute to the high activity and selectivity. Since the hydride species are considered to be formed at the interface between Ru metals and MoO_x species, the structure of MoO_x-covered Ru metals over Ru-MoO_x/SiO_2 catalyst plays an important role on the formation of the reactive hydride species. In addition, the structure of Ru-MoO_x/SiO_2 catalyst will enhance the supply of the substrate to the active site, leading to the high activity as well as the low reaction order with respect to the substrate concentration. Moreover, the structure of Ru-MoO_x/SiO_2 will decrease adsorption of the substrate on bare Ru metals and suppress the hydrogenation of the olefin group in the substrate, resulting in high selectivity.

In conclusion, Ru-MoO_x/SiO_2 catalyst acted as an effective heterogeneous catalyst for selective hydrogenation of the nitro group in functionalized nitroarenes, providing the corresponding amines in high yields (85-99%). Addition of MoO_x species to Ru/SiO_2 formed the active site at the interface between Ru metal and MoO_x species, where the substrate was strongly adsorbed on MoO_x species and active hydride species were formed on Ru metal, leading to the drastic improvement of both the activity and selectivity.

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