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Highly Efficient and Regioselective Halogenation over Well Dispersed Rhenium-Promoted Mesoporous Zirconia

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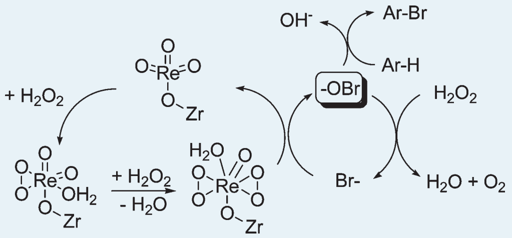
Supporting Information

ABSTRACT: Highly dispersed rhenium oxide supported on mesoporous zirconia (Re/m-ZrO_2) catalysts were prepared by a simple impregnation method, and excellent catalytic performances were obtained in liquid phase halogenation of aromatic substrates by using hydrogen peroxide and ammonium halide under mild and near neutral conditions. The para-directed selectivity in cases of bromination of aromatic substrates resulted from the stereo effect of the substrates.



KEYWORDS: Re, mesoporous zirconia, halogenation, para-selectivity

1. INTRODUCTION

Halogenated compounds have been used widely in pharmaceutical research because of their biological activity. In addition, they are versatile synthetic starting materials (in particular bromides) in carbon−carbon bond coupling reactions via Heck, Stille, and Suzuki transmetalation processes.[1] The process of bromination of aromatic substrates by the toxic elemental bromine, however, is inefficient, difficult to handle, and environmentally unfriendly. On the other hand, electrophilic halogenation in nature occurs by oxidative halogenation through the catalyzed oxidation of the halide ion to form a halogenating reagent.[2,3] The results of such a reaction have been halogenation with full halogen atom economy.[4] In recent years, there has been renewed interest in developing biomimic oxidation catalysts for the halogenation for organic substrates.[5] "Clean" oxidants for the oxidation of halides are hydrogen peroxide and oxygen. The concept was inspired by the enzymes vanadium-dependent bromoperoxidases (VBPO).[2,6] VBPO enzyme is present in most marine organisms for the synthesis of halogenated compounds from halide ion. In VBPO, its active center is an isolated vanadyl group that is attached to the protein chain via a single covalent bond.[7] Early on, there were a number of studies of biomimics of VBPO based on the peroxometallic complexes of Ti, V, Mo, and W.[8] For the homogeneous VBPO mimics, however, appreciable catalytic activities were mostly observed in strong acidic condition only.

On the other hand, new strategies based on heterogeneous catalyst in nearly neutral condition for clean bromination would be most desirable. The new generation of biomimic heterogeneous catalysts, based on supported metal oxide catalyst, often exhibit excellent activity in oxidative bromination under neutral conditions using bromide salts as a bromide source.[9−16] Easier transport and handling of the aqueous halides and dilute H_2O_2, as compared with halogens, make the process very attractive. One more "green" aspect of the heterogeneous catalyst is its ease in separation for reuse. Jacobs and co-workers found that WO_4^{2-} supported on layered double hydroxide (LDH)[10] exhibits excellent activity in oxidative bromination under nearly neutral conditions.[10,11] Previously, we have also studied the bromination reaction with tungstated zirconia (WZ) catalysts, and we have shown that the activity of phenol red bromination reaction depends directly on the dispersion of the WOx phase.[13] Walker and co-workers investigated Ti grafted on mesoporous silicate materials on catalytic peroxidative halogenation.[14]

More recently, we have investigated SBA-15 supported sulfated zirconia (SZ/SBA-15) catalysts for oxybromination of aromatic substrates using hydrogen peroxide and ammonium bromide in the aqueous phase under mild temperature and near-neutral pH conditions.[15] Good to excellent conversion and selectivity over SZ/SBA-15 were achieved. Ratnasamy and co-workers used TiO_x, VO_x, MoO_x and WO_x supported on SBA-15 exhibiting efficient catalytic activity for oxyhalogenation of aromatics with the H_2O_2−halide ion system.[16] It is suggested that a local concentration effect in mesopores giving increased encounters of reactants may be partly responsible for the improved catalysis; a similar effect was apparent in the LDH-supported catalyst designed by Sels et al.[10−12] However, the exact nature of the improvement in activity is still not clear.

Given the above progress, it is thus desirable to investigate other types of supported oxides with mesoporosity for possible better catalysts for bromination. Up to the present, heterogeneous rhenium(VII) oxide has been much less explored in this reaction. However, in the past few years, (CH_3ReO_3, MTO)[17] has showed interesting catalytic properties for activating H_2O_2 as the oxygen atom donor.[18] Accordingly, in this paper, we investigate the use of a simple impregnation technique for the preparation of a well-dispersed rhenium oxide (ReOx) catalyst

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Table 1. Phenol Red Bromination over Supported ReOx Catalysts[a]

entry	catalysts	$\nu^b \times 10^6$ (mM/s)	specific activity[c] (mmol/h·g)	surface area (m^2/g)	surface density (Re/nm^2)
1	m-630	36.5 ± 4.0^d	0.84 ± 0.09	124	
2	0.04Re/m-630	43.8	1.01	76	0.02
3	0.34Re/m-630	46.8 ± 2.5^d	1.01 ± 0.06	77	0.14
4	0.67Re/m-630	57.8	1.34	73	0.30
5	m-700	18.4 ± 0.5^d	0.42 ± 0.01	32	
6	0.05Re/m-700	23.0 ± 0.9^d	0.53 ± 0.02	35	0.05
7	0.08Re/m-700	24.6 ± 1.3^d	0.57 ± 0.03	35	0.07
8	0.46Re/m-700	33.1 ± 2.0^d	0.76 ± 0.05	47	0.32
9	0.63Re/m-700	36.1 ± 1.4^d	0.83 ± 0.03	44	0.46
10	0.37Re/m-530	5.18	0.12	167	0.07
11	0.63Re/d-500	10.0	0.23	28	0.72
12	0.6W/m-630	33.3^e	0.77	120	0.16

[a] Reaction conditions: phenol red = 0.05 mM, H_2O_2 = 10.3 mM, NH_4Br = 0.1 M, catalyst = 20 mg, 25 °C. [b] The bromination rate = the yield of bromophenol blue/reaction time. [c] Specific activity = moles of bromide oxidized per total weight of catalyst (grams) per hour. [d] Triplicates for each reaction were run. [e] Data taken from ref 13.

on mesoporous zirconia (m-ZrO_2). It is denoted hereafter as Re/m-ZrO_2. The preparation of such a catalyst with a well-dispersed active phase is highly desirable, since high dispersion of an active phase on mesoporous zirconia gives rise to not only a catalyst of high catalytic activity but also excellent product selectivity. In this paper, we present the m-ZrO_2 catalyst in the oxidative bromination of phenol red with bromide and hydrogen peroxide, and then we show the presence of Re strongly promotes the activity of this catalyst.

The design principles of the new catalyst are (1) the use of supported rhenium oxide because of the ability of the activation of H_2O_2 by a surface rhenium oxo group; (2) the use of a solid acid provides the necessary acidity in the oxyhalogenation, and thus, acidic solution can be avoided; and (3) the mesoporosity of the support facilitates the transport of reactants and products.

2. EXPERIMENTAL SECTION

2.1. Characterizations. The rhenium contents in each catalyst were determined by inductively coupled plasma atomic emission spectrometry (ICP−AES) using a Jarrel-Ash ICP 9000 instrument that is equipped with continuous wavelength detection from 170 to 800 nm. All catalysts were digested in a HNO_3/H_2SO_4/HF mixed acid and quenched by a large amount of boric acid (H_3BO_3). Ultraviolet−visible spectra (UV−vis) were taken on a Hitachi U-3310 spectrophotometer. The powder X-ray diffraction patterns were recorded on a PANalytical X'Pert PRO diffractometer using Cu Kα (λ = 0.154 nm) radiation operating at 45 kV and 40 mA. The specific surface areas were determined by N_2 adsorption−desorption isotherms performed at −196 °C with a Micromeritics ASAP 2010 instrument and were calculated according to the BET method (P/P_0 = 0.05−0.30). The extended X-ray absorption fine structure (EXAFS) spectra in our study were acquired in the Beamline 01C and 17C at NSRRC in Taiwan. The electron storage ring was operated at 1.5 GeV with a beam current of 100−200 mA. Zr−K-edge, and Re−L_{II}-edge absorbance of powder catalysts were measured in transmission geometry. The EXAFS function was derived from the raw absorption data through pre-edge and postedge background subtraction and then normalization with respect to the edge jump. After being k^3-weighted, where k is the photoelectron wavenumber, the EXAFS function was Fourier transformed from k-space to r-space. All the computer programs were implemented in the software package of UWXAFS.

2.2. Preparations of Re/ZrO_2 Catalysts. The m-ZrO_2 as template by the cationic surfactant C_{16}TAB was synthesized according to the method outlined by Ciesla et al.[19] and Waung et al.;[20] whereas zirconium hydroxide was used for the preparation of normal dense phase d-ZrO_2. For the preparation of Re/m-ZrO_2 catalyst, an impregnation method can be done simply on the as-synthesized m-ZrO_2 precursor without the need to remove the organic template. In that case, ethanol was added to the aqueous $HReO_4$ impregnation solution (C_2H_5OH/H_2O ≥ 4: 1 wt/wt). After drying the samples at 100 °C, they were calcined for 5 h at 630 and 700 °C for Re/m-ZrO_2. Specific Re/m-ZrO_2 catalysts (Table 1) used in this study were denoted as xRe/m-y, where x is the weight percent (wt %) of Re in the catalyst and y is the calcination temperature (°C).

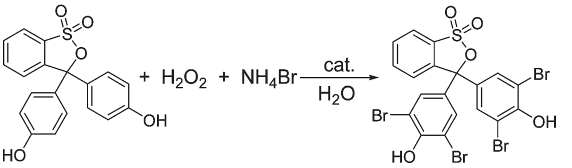
2.3. General Procedure for Bromination of Phenol Red over Re/m-ZrO_2 Catalysts. A 50 mL round-bottomed flask was charged with 32 mL of 0.05 mM phenol red (1.6 μmol) aqueous solution and 3.2 mmol NH_4X (X = Cl, Br, I), and 32 μL of 35 wt % H_2O_2 (0.33 mmol) was added to the solution. After 1 min of stirring, 20 mg of Re/m-ZrO_2 was then added to the reaction mixture, and the contents were stirred at 25 °C. Bromination of phenol red to bromophenol blue was monitored at 591 nm using UV−vis spectroscopy, and the solid catalyst was removed before each measurement.

2.4. General Procedure for Halogenation of Aromatics. A 10 mL round-bottomed flask was charged with 4.0 mmol of NH_4X (X = Cl, Br), substrate (aromatics = 0.5 mmol), and 35 wt % H_2O_2 (3.5 mmol) in acetonitrile/water mixture (v/v = 7/3). Re/m-700 (100 mg) was then added to the reaction mixture, and the contents were allowed to stir at 25 °C. After 24 h of the reaction, the catalyst was filtered, and the reaction mixture was extracted with ethyl acetate. The identification of the major products was confirmed with a Shimadzu GC (GC-17A) through a capillary column by comparison with authentic samples.

3. RESULTS AND DISCUSSION

3.1. Catalytical Bromination of Phenol Red over Re/m-ZrO_2 Catalysts. Since all the catalysts were prepared with the same mesoporous zirconia, the different impregnation/calcination reloaded catalysts possess the same morphology. The broad XRD peak at low angle (Figure S1) indicates the mesostructure of the m-ZrO_2 in the catalyst. The catalyst exhibits a wormlike mesoporous structure.[20] The high-angle regime of XRD pattern (Figure S1) indicates that m-ZrO_2 exists as the tetragonal phase.

For comparing the activities of catalytic bromination of various catalysts, we first investigated the bromination of the simple aromatic compound phenol red. Bromination of phenol red is often used as the test reaction for these biomimetic catalysts, since it can be followed easily by the UV−visible absorption technique.[8]



(1)

Table 1 summarizes the activity of phenol red bromination for selected catalysts. For the reaction in the case that 32 mL of 0.05 mM phenol red in the presence of an excess amount of bromide over 20 mg of m-630 and Re/m-630 catalysts was completed within 30 min, m-630 shows catalytic ability for bromination to similar Re/m-630, although with a much higher surface area. We also investigated the effect of the calcination temperature of the catalysts and compare their activities. It is obvious that the catalytic activity of mesoporous zirconia was decreased for samples calcined at higher temperature. It was found that Re promoted the bromination reaction, and the reaction activity of Re/m-ZrO_2 catalysts increased with increasing Re loading. For example, the catalytic activity for bromination of Re/m-700 was much improved compared with m-700. Indeed, when the loading of Re increased from 0.05 to 0.46, the bromination rate increased from 23.0×10^{-6} to 33.1×10^{-6} mM/s, resulting in a 75% yield. According to Table 1, we have an interesting finding that 0.34Re/m-630 catalyst is more active than 0.46Re/m-700 and 0.37Re/m-530 catalyst, even though the latter has a higher surface area and, thus, lower surface density of ReOx species. If ReOx is well dispersed into the mesopores of Re/m-ZrO_2 rather than localized on the external surfaces of the catalyst, then the rate of reaction for 0.67Re/m-630 catalyst (surface area = 73 m^2 g^{-1}) should be greater than the nonporous 0.63Re/d-500 catalyst (surface area = 28 m^2 g^{-1}). Indeed, the bromination rate of 0.67Re/m-630 catalyst is 6 times faster than that of 0.63Re/d-500. This suggests that ReO_x is well dispersed over the entire surfaces of Re/m-ZrO_2 catalysts. In addition, the catalyst calcined at 530 °C (0.37Re/m-530) contained micropores, and its low activity in phenol red bromination reaction may be due to the inaccessibility of the internal ReO_x sites by phenol red.

We have also tried the oxyhalogenation of phenol red over 0.02Re/m-630 using NH_4Cl and NH_4I as the halide source. We found that the catalyst was efficient only for catalyzing the iodination but failed for chlorination. It was found that the conversion (%) of phenol red to bromophenol blue was 51% in 13 min on bromination and 81% in 20 min on iodination.

We calculate the specific activity for bromination of phenol red as listed in Table 1. Compared with the specific activities reported by Sels et al.[10] for their peroxotungstates-LDH catalysts, ours activities are 5 to 10 times slower, partly because our support ZrO_2 is heavier than LDH. But compared with TS-1 or Ti-MCM-41, our catalysts are much more active.[10]

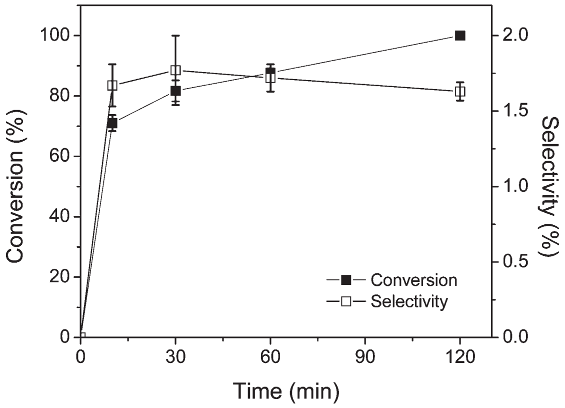


Figure 1. Catalytic profiles of Re/m-700 on bromination of aniline. The selectivity means the yield ratio of 4-bromoaniline/2-bromoaniline. Reaction conditions: aniline = 0.5 mmol, NH_4Br = 8.0 equiv, H_2O_2 = 7.0 equiv, catalyst = 50 mg 0.38Re/m-ZrO_2, solvent = acetonitrile/H_2O (7/3) at 25 °C. Triplicates for each reaction were run at each time.

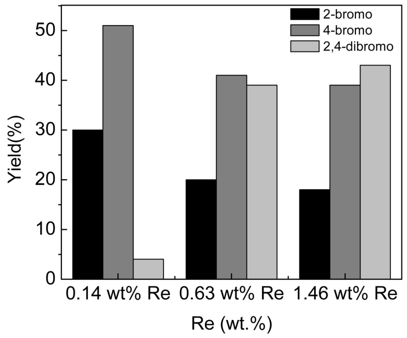
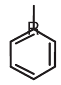
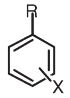
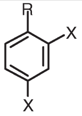
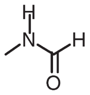


Figure 2. Bar diagram shows yields of brominated products in aniline oxybromination with various Re loading (wt %) catalysts. Reaction conditions: aniline = 0.5 mmol, NH_4Br = 8.0 equiv, H_2O_2 = 7.0 equiv, catalyst = 100 mg, solvent = acetonitrile/H_2O (7/3) at 25 °C, and reaction time = 1 h.

3.2. Catalytic Halogenation of Aromatics. Although we show Re does promote the bromination of phenol red in aqueous solution, the more interesting effect would be the bromination of other water-insoluble aromatics. The bromination with Re/m-ZrO_2 catalyst has been suggested as an electrophillic process by forming oxidized bromine intermediate in the bromination with the VBPO enzymes.[3,6,21] Accordingly, this catalyst may also be suitable for preparing simple bromoaromatics. We first demonstrate the catalytic bromination of aniline. Figure 1 shows conversion (%) of aniline and regioselectivity of monobromo product over time; for example, the yield ratio of 4-bromoaniline/2-bromoaniline. The reaction rate of aniline oxybromination was very fast: the conversion of aniline was 74% after 10 min, and aniline was consumed completely after 2 h. Monobromoaniline as well as dibromoaniline were formed. With an increase in the reaction time from 10 min to 2 h, the yield of 4-bromoaniline and 2-bromoaniline increased from 39% to 62% and from 23% to 38%, respectively. The regioselectivity is favorable toward para-selectivity, and the yield ratio of 4-bromoaniline/2-bromoaniline was found to be a constant 1.7.

Table 2. Aromatics Halogenation over Supported ReOx Catalysts[a]

entry	aromatics 	X⁻	catalyst[b]	time (h)	conversion[d] (%)	 (para/ortho) (%)[d]	 (%)[d]
1	R= NH_2	Br	0.60 Re/m-700	2	100	37/18	39
2	R= 	Br	0.60 Re/m-700[c]	4	63	63/0	0
3	R= OH	Br	0.38 Re/m-700	24	71	60/6	5
4	R= OCH_3	Br	0.38 Re/m-700	24	92	90/0	0
5	R= CH_3	Br	0.38 Re/m-700	24	0	0	0
6	R= COOH	Br	0.38 Re/m-700	24	0	0	0
7	R= OH	Cl	0.38 Re/m-700	24	31	14/10	0
8	R= OCH_3	Cl	0.38 Re/m-700	24	18	11/5	0

[a] [Aromatics] = 0.5 mmol, NH_4X = 8.0 equiv, H_2O_2 = 7.0 equiv, solvent = acetonitrile/H_2O (7/3) at 25 °C. [b] Catalyst = 100 mg. [c] Catalyst = 50 mg. [d] Determined by GC analysis with hexadecane as internal standard.

To study the effect of loadings of Re, we prepared a series of catalysts over various Re loadings ranging from 0.14 to 1.46 wt %. Figure 2 shows the yields for different wt % loadings of impregnated Re on mesoporous zirconia, as the catalysts in the bromination reaction of aniline. The conversions of aniline were 85% and 100% when 0.14 and 0.63 wt % Re/m-ZrO_2 were used as catalyst. With increasing the loading of Re, dibrominated product becomes a major product.

Then we investigated the use of different aromatic substrates in the halogenation reaction catalyzed by Re/m-700 with NH_4X and hydrogen peroxide at room temperature in acetonitrile/water mixture. The conversion of aromatic substrates and the yields of halide-substituted products obtained are shown in Table 2. For control experiments, no bromoproduct was obtained in the absence of Re/m-ZrO_2 catalyst. Neither halogen nor hypohalous acid could halogenate independently in the system. It was found that the reactivity was highest when aniline was used as a substrate. The case of phenol also shows good conversion (71%), with 66% monobrominated phenol and 5% of dibromophenol produced. The monobromophenols contain ortho/para products with the para products in large excess. Anisole converted to 4-bromoanisole as the sole product at 92% conversion. Similarly, 4-bromoformanilide was the only product from bromination of formanilide. The regioselectivity of bromination will be discussed later. Bromination products of toluene and benzoic acid were not observed under the conditions listed in Table 2, however. These indicate that oxybromination of aromatics by H_2O_2 over Re/ZrO_2 works better when aromatics bears strong electron-donating groups or base groups. Comparing of the results with other reported methods,[21] we have developed a more efficient method for heterogeneous catalytic bromination of aromatics substituted by electron-donating group in the liquid phase.

The oxychlorination of phenol and anisole over Re/m-700 were also investigated using NH_4Cl/H_2O_2 (Table 2, entries 7 and 8). It was found that the conversion of phenol and anisole in chlorination were 31% and 18%, and the ratios of 4-chloroproduct to 2-chloroproduct were 1.4 and 2.2, respectively. The results show that Re/m-700 is less efficient and shows lower para-selectivity for catalyzing the oxychlorination compared with oxybromination. Surprisingly, oxyhalogination of anisole can occur at both the ortho and para positions.

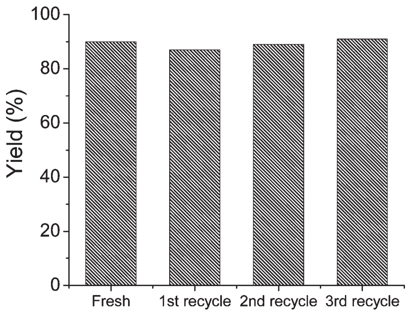
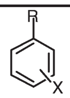
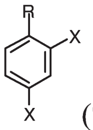
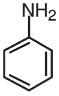
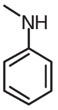
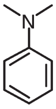


Figure 3. Recycling of Re/m-700 on bromination of anisole with H_2O_2 in aqueous solution. (Reaction conditions: anisole = 0.5 mmol, NH_4Br = 8.0 equiv, H_2O_2 = 7.0 equiv, solvent = acetonitrile/H_2O (7/3) at 25 °C, and reaction time = 2 h; GC conversion with hexadecane as internal standard.)

Bromination with H_2O_2 and bromide salt using Re/ZrOx catalyst also works for aromatics bearing bifunctional groupsm such as salicylaldehyde. Bromination takes ∼24 h to achieve 11% of conversion, and the only product is 5-bromosalicylaldehyde. Agawal et al. also reported comparable results.[22] During the reaction, OH^- is the product, and thus, one may expect an increase in the pH value. However, apparently the strong acidity in Re/ZrOx was able to neutralize the alkaline product such that little increase of pH was observed after the reaction (from 3.73 to 3.93, for example).

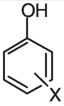
The ReOx catalysts can be easily recovered and reused after the reaction by simple filtration. To avoid a possible contribution from the leached ReOx species to the observed rate of reaction, we separated the solid catalyst by centrifugation after the first run and repeated the catalytic reaction with a fresh reactant at the same reaction time. ReOx catalyst was then reused in the

Table 3. Aromatics Bromination over Supported ReOx Catalyst[a]

entry	aniline	conversion (%)[d]	 (4-Br/2-Br) (%)[d]	 (%)[d]
1		100[b]	37/18	39
2		100[c]	69/31	0
3		100[c]	100/0	0

[a] [Aromatics] = 0.5 mmol, NH_4Br = 8.0 equiv, H_2O_2 = 7.0 equiv, solvent = acetonitrile/H_2O (7/3), catalyst = 50 mg of 0.60Re/m-700, at 25 °C. [b] Reaction time = 1 h. [c] Reaction time = 2 h. [d] GC conversion with hexadecane as internal standard.

Table 4. Bromination of Phenol over Supported Catalysts

entry	catalysts	conditions	conversion (%)	 (4-Br/2-Br)	ref
1	SiWA-impregnated ZrP	KBr/H_2O_2/AcOH	65	1.76	27
2	Modified Zeolite	KBr/H_2O_2/AcOH	70-89	1.29-2.32	25
3	TiO_2 pillared ZrP and TiP	KBr/H_2O_2/AcOH	80-85	1.47-3.0	26
4	HPA supported Zr	KBr/H_2O_2/AcOH	48-93	1.43-4.37	28
5	SZ/SBA-15	NH_4Br/H_2O_2	90	9.0	15
6	Re/m-ZrO_2	NH_4Br/H_2O_2	71	9.0	This method

bromination of aromatics. The recovered catalyst showed very high catalytic activity and selectivity after three reuses (Figure 3). In addition, there does not seem to be a significant contribution from leached catalytic species, since the supernatant solution is not catalytically active.

3.3. Regioselectivity. It is of great practical importance to study the regioselectivity in electrophilic aromatic substitution reactions. It has been recognized that para-regioselective electrophilic aromatic substitution reactions, such as nitration, alkylation, acylation, sulfonylation, and halogenation, can be achieved by carrying out reactions over solid catalysts such as zeolites.[23] Here, we use the catalyst 0.60Re/m-700 to study the regioselectivity of oxybromination of aromatics.

N-Methylaniline and *N*,*N*-dimethyl aniline were brominated, and both of them exhibited great reactivity, with 100% conversion in 2 h. The regioselectivity (4-bromo/2-bromo) in the case of secondary amine *N*-methylaniline is 2.23, but the ternary amine *N*,*N*-dimethylaniline gives 100% conversion to 4-bromo-*N*,*N*-dimethylaniline (Table 3). By comparing the result of bromination of anililne over Re/m-700 and sulfated zirconia supported on mesoporous silica (SZ/SBA-15) (Table S1), Re/m-700 is much more effective for the formation of 4-bromoaniline, which indicated better para-selectivity. In addition, 100% para-selectivity in the oxybromination of phenylether (PhOR, R = Me, Et, ^{n}Bu) over Re/m-700 was found. The high para-selectivity is due to steric hindrance at the ortho position.[24]

For the case of phenol, the situation is more interesting because the −OH group in phenol is not bulky. As mentioned before, Table 2 gives great regioselectivity on the bromination of phenol, which was almost directed to para-selectivity. The literature results are compared with the present work in Table 4. The Re/ZrOx catalyst in this work shows the highest para-selectivity, much higher than the catalyst in other heterogeneous catalysis system in the absence of acetic acid. Narender et al.

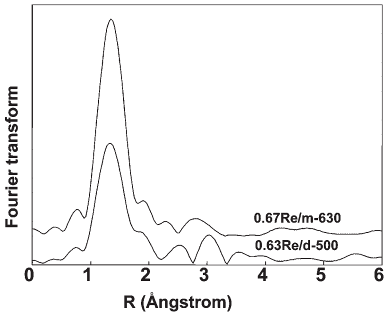


Figure 4. Fourier-transformed Re L_{II}-edge EXAFS RDF spectra of 0.67Re/m-630 and 0.63Re/d-500.

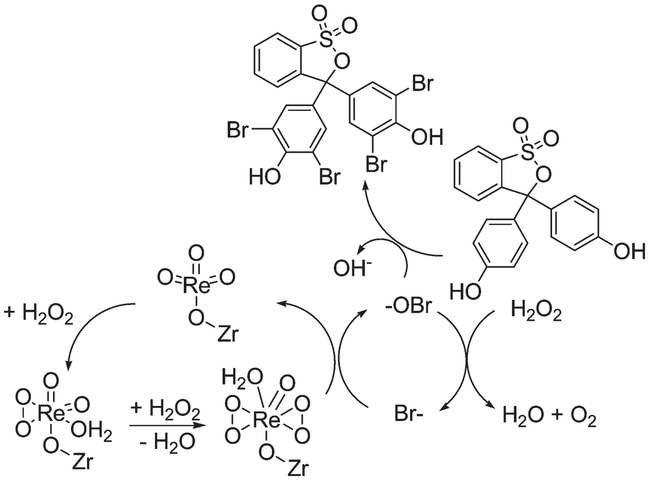
reported oxybromination of phenols catalyzed by modified zeolite as a solid acid catalyst in 70−89% of conversion and a selectivity ratio (4-bromophenol/2-bromophenol) in the range 1.29−2.32.[25]

Recently, Parida et al. also reported liquid phase bromination of phenol over heteropolyanion (HPA)-impregnated zirconium phosphate (ZrP) with 65% conversion with a selectivity ratio of 1.76.[26,27] They also reported liquid phase bromination of phenol over HPA impregnated on zirconium phosphate (ZrP) with 93% conversion and 4.37 para-selectivity.[28] Furthermore, in our previous results, mesoporous silica-supported sulfated zirconia (SZ/SBA-15) shows similar high para-selectivity (9.0) in bromination of phenol.[15] This very high para-selectivity suggested that the catalytic center resides on the interior surface of mesoporous zirconia. When phenol is adsorbed on its surface, the ortho position is partially blocked, and the catalytic Re site cannot access the ortho position of the adsorbed phenol, thus leading to high selectivity to para-bromination.

3.4. Structural Characteristics and Bromination Mechanism. Next, we would like to understand the promotional effect of ReOx species on the Re/m-ZrO_2 catalysts. To have some ideas of the distribution of ReOx species on Re/m-ZrO_2 catalysts, we employed a combination of characterization techniques. A powdered XRD technique was used to check the crystallinity of the catalysts. The broad diffraction peak at $2\theta \sim 0.87°$ (Figure S1) indicates the mesostructure of the m-ZrO_2 in the catalyst. At the high-angle regime of XRD spectra, one can see that m-ZrO_2 exists mainly as the tetragonal phase in *x*Re/m-630 catalysts. It seems that the transformation of zirconia from the tetragonal to monoclinic phase is retarded by the presence of ReOx species. This phenomenon was also observed in tungstated zirconia, such as 0.6W/m-630 catalyst.[13] Therefore, ReOx interacts effectively with the whole surfaces of m-ZrO_2, and this is an indication of good dispersion of the ReOx species.

On the other hand, when the calcination temperature is low, the channel walls of 0.37Re/m-530 remain amorphous. For dense phase zirconia, 0.63Re/d-500 has a small pore volume of ~0.03 mL g^{-1} of catalyst. The nanochannels of all *x*Re/m-630 catalysts have an average pore size of 2.8−3.0 nm and a pore volume of 0.06−0.08 mL g^{-1}. Surprisingly, 0.37Re/m-530 is microporous (pore size < 2 nm) in nature with a pore volume of 0.04 mL g^{-1}. Their surface areas are listed in Table 1. Compared with our tungstated zirconia catalyst reported previously,[13] we found that 0.67Re/m-630 catalyst has a lower surface area than 0.6W/m-630 (120 $m^2 g^{-1}$); hence, the ReOx species seem to have less thermal stabilization effect on the m-ZrO_2 structure than the WOx species. Maybe this phenomenon is related to the lesser interaction between ReOx (one Re−O−Zr bond) and the m-ZrO_2 surface compared with the interaction of WOx (>1 W−O−Zr bonds) with the zirconia surface.

Scheme 1. Plausible Mechanism of Bromination over Re/m-ZrO_2 Catalyst



The X-ray absorption technique EXAFS can provide us the radial distribution of atoms around the Re center to determine the coordination environment of Re. Figure 4 compares the EXAFS spectra of 0.67Re/m-630 and 0.63Re/d-500 catalysts. Both spectra are not corrected for phase shifts. There are two distinct differences between 0.67Re/m-630 and 0.63Re/d-500 catalysts. First, the intensity of the Re═O peak at 1.35 Å in 0.63Re/d-500 is only about half that of 0.67Re/m-630. Second, the single peak at 2.79 Å in 0.67Re/m-630 due to the Re−O−Zr bond is now split into three peaks in 0.63Re/d-500 (2.52, 3.04, and 3.56 Å). According to the EXAFS results, we can propose that the ReOx species of Re/m-ZrO_2 has three Re═O bonds and one Re−O−Zr bond, as shown in Scheme 1, whereas the species of Re/d-ZrO_2 has two Re═O and three Re−O−Zr bonds. The ReOx species of our Re/d-ZrO_2 catalyst is different from that proposed by Vuurman et al.[29,30] with one Re−O−Zr bond, since we use $Zr(OH)_4$ as the support precursor rather than using zirconia directly. Apparently, the higher density of surface Zr−OH groups can affect the nature of ReOx species formed on the Re/m-ZrO_2 catalyst as compared with Re/d-ZrO_2.

Another inference from the EXAFS spectra is the absence of Re_2O_7 in the 0.67Re/m-630 catalyst, as expected. There is no distinct peak between 3 and 4 Å which is associated with the dimeric (~3.90 Å) and polymeric (3.7−3.8 Å) Re_2O_7 species.[31] Thus, we mostly have high dispersion of Re on the surface of zirconia as isolated monomeric species. Vuurman et al. have carried out spectroscopic analysis of the nature of ReOx species on various supports.[32] They found that only one kind of ReOx species is present on silica, whereas two kinds of ReOx species are found on zirconia. Accordingly, there may be other kinds of interaction between ReOx species and zirconia in addition to the well-known condensation reaction between Re−OH and Zr−OH groups. It seems to us that the formation of the Re−O−Zr bond can occur via two routes: (a) interaction between ReO_4^- and Zr^{4+} and (b) condensation of Re−OH and Zr−OH groups.

The rhenium catalysis has some resemblance to the enzyme, vanadium-dependent bromoperoxidases, and oxybromination is through the formation of "OBr^-".[33] We propose a plausible mechanism, as shown in Scheme 1. Rhenium-oxo oxidized to rhenium peroxo by H_2O_2 is the first step. It is known that interacting with H_2O_2 is the isolated Re═O group to form an η^2-peroxointermediate. Because H_2O_2 is in excess, the bis(peroxo) Re species is major. This peroxide−rhenium adduct is an active species on oxidation catalysis. Bromide ions attack the peroxo intermediates to convert the BrO^- as the active species of bromination, and the original active site of the catalyst is regenerated concurrently. Espenson et al. have reported the kinetics modeling of the catalysis of oxidation of the bromide ion by H_2O_2 in an aqueous solution, and they suggest that the formation of BrO^- is acquired by the transfer of one oxygen from the peroxo to the bromide.[34,35] In the presence of excess H_2O_2, OBr^- records not only catalytic formation of bromopruducts but also the disproportionation of H_2O_2 in which oxygen was formed as a by-product.[36,37] The bromination reaction process can be summarized in the following scheme. Both the zirconia center and the rhenium center contributed to the catalytic oxybromination, but the Zr-supported Re center seems to be more active, and it originates from the highly oxidative capability in the multiple Re═O species.

In the future, one would like to further fine-tune the oxybromination capacity by increasing dispersion of Re over a high-area zirconia surface or in combination with sulfation of zirconia. It should be noted that other process variables, such as heating method and solvent, may also be investigated to increase the activity and selectivity of the catalytic process. For example, microwave heating[38] and supercritical CO_2[39] have been employed previously in a "green" process of oxidative bromination.

4. CONCLUSION

We have shown that an atomically and highly dispersed Re/m-ZrO_2 catalyst can be prepared by a simple impregnation technique. The mesoporous properties of its m-ZrO_2 support are largely preserved in the catalyst. The highly dispersed rhenated zirconia catalyst is effective in the halogenation of aromatics to form haloaromatics, and the catalytic activity was enhanced by 4-fold of magnitude compared with mesoporous SZ without Re. The problem of leaching of Re metal is also not severe due to the formation of a Re−O−Zr linkage. Furthermore, Re/m-ZrO_2 is very stable in reuse without loss of catalytic activity over several recyclings. In view of the heterogeneous nature and successful leaching tests and in view of the excellent activity of the catalyst under nearly neutral conditions, oxidative bromination with rhenated mesoporous zirconia may be an excellent synthetic alternative to bromination reagents such as *N*-bromo compounds.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** XRD patterns of various amounts of Re catalysts and the comparison of SZ and Re/m-ZrO_2 on catalytic bromination. This material is available free of charge via the Internet at http://pubs.acs.org.

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