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Clean Synthesis of Amides over Bifunctional Catalysts of Rhodium-Loaded Titanosilicates

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Rhodium-loaded titanosilicates were prepared and employed as efficient bifunctional catalysts in the one-pot synthesis of benzamide from benzaldehyde, hydrogen peroxide, and ammonia, which took place through a tandem reaction including ammoximation of benzaldehyde to benzaldehydeoxime and a sequential dehydration-rehydration reaction to benzamide. Various parameters that influenced the activity and product selectivity were investigated, such as crystalline topologies of the titanosilicate supports, types of transition metals, rhodium content, reaction temperature, time, solvent, and NH₃/benzaldehyde molar ratio. Ti-MWW was proved to be a suitable support for loading the Rh(OH)_x species. Rh(OH)_x/Ti-MWWgave 84.9% of benzaldehyde conversion and 86.9% of benzamide selectivity, and it was also catalytically active for the transformation of a variety of aldehydes to the corresponding amides. The reusability of the bifunctional catalyst was also investigated. The in situ FTIR technique confirmed that the one-pot reaction included Ti-catalyzed ammoximation of benzaldehyde to the benzaldehyde oxime intermediate and sequential rhodium hydroxide related dehydration-rehydration reaction of oximes to amides.

Introduction

Amides, the key intermediates for manufacturing engineering plastics in chemical industry, are also widely used in the areas of medical, agriculture, and biology,[1-3] because they participate in a variety of useful reactions including dehydration, hydrolysis, Hofmann degradation, and substitution reactions. Conventionally, amides are synthesized from the corresponding carbonyl derivatives such as nitriles.^[4–8] These manufacture processes, however, have encountered serious problems, such as using harmful acid and poisonous reactants, and coproducing a large quantity of byproducts. Such processes are thus considered to be environmentally unfriendly in terms of green and sustainable chemistry. Besides, the transformation of oximes to amides through Beckmann rearrangement is another well-known pathway for amide synthesis.^[9,10] A typical example is the manufacture of ϵ -caprolactam, the starting material for nylon-6 synthesis.^[11] The lactam is prepared by the liquidphase Beckmann rearrangement reaction of cyclohexanone oxime using a sulfuric acid catalyst, whereas the oxime is produced through noncatalytic oximation of cyclohexanone with hydroxylamine derivatives. Recently, an innovative process for lactam production has been developed by combining two zeolite-catalyzed reactions, that is, the liquid-phase ammoximation of cyclohexanone, ammonia, and hydrogen peroxide on TS-1 ti-

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tanosilicate, and the gas-phase Beckmann rearrangement on solid acid catalyst of Silicalite-1 (MFI structure).^[12]

Nevertheless, acid-catalyzed Beckmann rearrangement reactions are generally not useful for the transformation of aldoximes to primary amides.^[13, 14] Transition-metal species, such as Rh, Ru, Pd, and Ir, have been recently shown to serve as efficient catalysts for the liquid-phase transformation of aldoximes to primary amides.^[15-22] Mizuno et al. reported that the Rh(OH)_x/Al₂O₃ catalyst was capable of converting the aldoximes to the corresponding primary amides in water as a solvent without using hazardous reactants.^[23] The Rh(OH)_x/Al₂O₃ catalyst not only showed a high catalytic activity for the conversion of various aldoximes, but also exhibited a high selectivity for the desired amides and a high stability in catalytic reuse. Moreover, one-pot synthesis of amides has also been demonstrated possible from aldehydes and hydroxylamine derivatives on the Rh(OH)_x/Al₂O₃ catalyst directly.^[24] This discovery would open up the possibility of developing environmentally benign chemical processes for the production of primary amides through heterogeneous catalysis routes. Greener and more atom-efficient processes, however, are expectable if aldehydes, ammonia, and hydrogen peroxide are employed in a one-pot synthesis as reactants instead of using expensive and explosive aldoximes and sulfate or hydrochloride hydroxylamine. In this sense, it would be a desirable alternative to combine in situ hydroxylamine generation with sequential dehydration and rehydration of aldoxime, both operated with heterogeneous catalytic systems.

Titanosilicates containing tetrahedral Ti active sites in the zeolite framework, especially TS-1,^[25] Ti-MWW,^[26] and Ti-MOR,^[27,28] have been used as catalysts in the liquid-phase ammoximation of ketones or aldehydes with NH_3 and H_2O_2 ,



giving rise to the corresponding oximes. The ammoximation probably involves the formation of hydroxylamine through catalytic oxidation of NH₃ by H₂O₂ on the Ti active sites and noncatalytic oximation of ketones or aldehydes with the hydroxylamine thereof. This reaction mechanism is demonstrated on various titanosilicates irrespective of the zeolite crystalline structures. Thus, taking advantages of titanosilicates and $Rh(OH)_x$ species, a tandem catalyst would be designed to possess bifunctional properties of aldehyde ammoximation and aldoxime rearrangement. Among the crystalline titanosilicates developed so far, Ti-MWW originating from a lamellar precursor possesses a unique pore system consisting of 12-membered ring (MR) side cups and two independent interlayer and intralayer 10-MR channels, one of which contains the 12-MR supercages.^[29,30] With respect to the liquid-phase ammoximation of ketones or aldehydes, Ti-MWW was highly effective in either batchwise reactor^[26] or continuous slurry reactor.^[31,32]

Herein, $Rh(OH)_{x}/Ti-MWW$, the rhodium species supported on Ti-MWW, was successfully prepared by using $RhCl_{3}$ as the precursor and organic quaternary ammonium hydroxide as the base source, and it was employed as a bifunctional catalyst for the one-pot synthesis of primary amides from aldehydes. The reaction pathways and mechanism for the synthesis of amides were investigated.

Results and Discussion

Preparation of Rh(OH)_x/titanosilicate catalysts

We have demonstrated that Ti-MWW is a highly effective catalyst for liquid-phase ammoximation of ketones with H₂O₂ and NH₃.^[26] In the ammoximation of benzaldehyde, Ti-MWW was capable of giving a benzaldehyde conversion of 93.2% and a benzaldehyde oxime selectivity of 98.7% (see the Supporting Information, Table S1, entry 1), indicating it was also effective for the ammoximation of aldehydes. Mizuno et al. reported that the Rh(OH)_x/Al₂O₃ catalyst is capable of one-pot converting aldehydes to amides in the presence of hydroxylamine hydrochloride,^[24] in which the first step took place homogeneously through a non-catalytic route. However, if 0.2 g of Al₂O₃ was physically mixed with Ti-MWW, the benzaldehyde conversion decreased to 79.0%, whereas the H_2O_2 conversion increased to 96.5% (Table S1, entry 2). These results indicate that the Al₂O₃, characteristic of relatively strong acidity, would cause unproductive decomposition of H₂O₂, and then decrease the insitu hydroxylamine formation activity of Ti-MWW. Although Rh(OH)_x/Al₂O₃ is effective for the rearrangement of aldoximes to amides, [23, 24] the physical mixture of Ti-MWW and Rh(OH)_x/Al₂O₃ may not be the suitable catalytic system of choice for the one-pot synthesis of benzamide from benzaldehyde, as the one-pot reaction involves the ammoximation first and the oxime transformation in second step. For the one-pot synthesis of amides, a more efficient catalyst was thus expected to be designed by supporting the $Rh(OH)_x$ species on Ti-MWW.

An aqueous solution of NaOH is usually used to adjust the pH value if the $Rh(OH)_x/Al_2O_3$ catalyst was prepared by impreg-

nation.^[23,24] However, it is well known that titanosilicates could be deactivated by alkali-metal cations such as Na⁺ and K⁺.^[33,34] These cations with a high polarity impose negative effects on the titanosilicates through poisoning the Ti active sites into \equiv Si–O⁻M⁺ (M⁺ = Na⁺, K⁺, etc.). If we prepared Rh(OH)_x/Ti-MWW by impregnating the Rh(OH)_x species onto Ti-MWW using aqueous NaOH solution, the resultant catalyst showed a much lower benzaldehyde conversion (only 10.0%) along with a lower oxime selectivity (76.3%) than Ti-MWW (Table S1, entry 3). These results imply that the Na⁺ cations retarded significantly the catalytic ability of Ti-MWW in the ammoximation.

To prepare a highly effective catalyst for one-pot syntheses, a new impregnation strategy should be developed for supporting the Rh(OH), on titanosilicates. Replacing NaOH solution, we investigated impregnation of Rh(OH), with various organic quaternary ammonium hydroxides such as tetramethylammonium hydroxide (TMAOH), tetraethylammonium hydroxide (TEAOH), or tetrapropylammonium hydroxide (TPAOH). In Figure S1 in the Supporting Information, the preparation processes of Rh(OH)_x/titanosilicate catalysts by using organic quaternary ammonium hydroxides is shown graphically. The titanosilicate powders were firstly dispersed in the RhCl₃ solution, which was dirty red in color. Then, a desirable amount of organic ammonium hydroxide was added into the mixture under stirring until the pH value reached approximately 9, and the color of the mixture immediately changed to light yellow. A subsequently solid/liquid separation by filtration and drying led to a colorless filtrate and the Rh(OH)_x/titanosilicate powder in light yellow, which indicated that the Rh(OH)_x species were impregnated on the zeolite powder successfully.

The UV/vis spectra of Ti-MWW and Rh(OH)_x/Ti-MWW are shown in Figure 1. Both catalysts exhibited a strong adsorption at 220 nm assigned to the tetrahedral-framework Ti species.^[35] On the other hand, the XRD pattern of Rh(OH)_x/Ti-MWW was almost the same as that of Ti-MWW (not shown). These results verified that the loading of the Rh(OH)_x species had little influence on the coordination state of the Ti species and the crystalline structure of Ti-MWW. Nevertheless, compared with Ti-MWW, the Rh(OH)_x/Ti-MWW sample showed an additional



Figure 1. UV/vis spectra of a) Ti-MWW and b) Ti-MWW with 1.7 wt % Rh(OH)_x.

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broad band at approximately 550 nm in the UV/vis spectrum (Figure 1 b), which would be attributed to the $Rh(OH)_x$ species. In addition, $Rh(OH)_x$ /Ti-MWW exhibited Rh $3d_{5/2}$ and Rh $3d_{3/2}$ peaks at electron binding energies of 309.0 and 313.7 eV in the X-ray photoelectron spectrum, respectively, indicating that the Rh species existed in the oxidation state of +3 (Figure 2).^[36] These results further confirmed that the Rh spe-



Figure 2. Rh 3d XPS spectrum of 1.7 wt% Rh(OH)_x/Ti-MWW.

cies were loaded on Ti-MWW successfully. The Rh content of $Rh(OH)_x/Ti$ -MWW was 1.7 wt% as determined by inductively coupled plasma (ICP) analysis. Other Rh-supported titanosilicates, $Rh(OH)_x/TS$ -1, $Rh(OH)_x/Ti$ -Beta and $Rh(OH)_x/Ti$ -MOR were obtained by following the same procedures.

Catalytic properties of Rh(OH)_x/titanosilicate in one-pot synthesis of amides

Effect of different supported transition-metal species

In Table 1, the catalytic activity of $Rh(OH)_x/Ti-MWW$ are compared with the activities of $Ru(OH)_x/Ti-MWW$, $Rh_2O_3/Ti-MWW$, and $Rh(OH)_x/Al_2O_3$ in the one-pot synthesis of benzamide from benzaldehyde, H_2O_2 , and NH_3 . In addition to benzamide, benzaldehyde oxime as the intermediate and benzonitrile as the main byproduct were detected. A small amount of benzoic acid owing to deep oxidation was also de-

tected. Compared with Rh(OH)_x/Ti-MWW, Ru(OH)_x/Ti-MWW showed a lower benzaldehyde conversion and lower amide selectivity but higher benzonitrile selectivity (28.2%), indicating that rhodium was a better catalyst than ruthenium for the transformation of aldoximes (RR'C=NOH) into the corresponding N-substituted amides (RCONHR'). Rh₂O₃/Ti-MWW, prepared by incipient wetness method showed a benzaldehyde conversion of 76.6%, which was similar to that of Rh(OH)_x/Ti-MWW, but it gave only 45.5% benzamide selectivity in addition to 34.2% benzonitrile and 5.9% oxime. The observed difference in catalytic activity may be closely related to the presence or absence of hydroxyl groups in the catalysts, which might have a significant influence on the catalytic activity. Owing to the absence of Ti active sites for ammoximation, Rh(OH)_x/Al₂O₃ reasonably showed the lowest benzaldehyde conversion of 25.3%.

Effect of different titanosilicate supports

Rhodium species supported on other titanosilicates, such as TS-1, Ti-MOR, and Ti-Beta, were also prepared. The UV/vis spectra indicated that all these titanosilicates mostly contained the tetrahedrally coordinated framework Ti species (Figure S2). As reported previously, Ti-MWW, TS-1, as well as Ti-MOR were effective catalysts in the ammoximation of ketones, whereas Ti-Beta was almost inactive in this reaction. $Rh(OH)_x/Ti-MWW$ was clearly a more efficient catalyst for the one-pot synthesis of amide, compared with $Rh(OH)_x/TS-1$, $Rh(OH)_x/Ti-MOR$, and $Rh(OH)_x/Ti$ -Beta. (Table 2). The one-pot reaction consisted of titanosilicate-catalyzed ammoximation of benzaldehyde to the corresponding oxime and the rhodium-catalyzed transforma-

Table 2. One-pot synthesis of benzamide from benzaldehyde over different ${\rm Rh}({\rm OH})_{x'}$ titanosilicate catalysts. $^{[a]}$							
Catalyst ^(b)	Aldehyde conversion [%]	Nitrile selectivity [%]	Oxime selectivity [%]	Amide selectivity [%]			
Rh(OH) _x /Ti-MWW(38)	84.9	6.9	0.9	86.9			
Rh(OH) _x /TS-1(40)	74.8	16.6	4.1	70.4			
Rh(OH) _x /Ti-MOR(92)	83.1	17.1	44.4	31.2			
Rh(OH) _x /Ti-Beta(60)	40.5	17.3	40.5	21.6			
[a] Reaction conditions: see footnote in Table 1. The Rh loading was in the range of							

[a] Reaction conditions: see footnote in Table 1. The Rh loading was in the range of 1.5–1.8 wt %. [b] The number in parentheses indicates the Si/Ti ratio of titanosilicates.

Table 1. One-pot synthesis of benzamide from benzaldehyde over different catalyst. ^[a]						
Catalyst	Aldehyde conversion [%]	Nitrile selectivity [%]	Oxime selectivity [%]	Amide selectivity [%]		
Rh(OH) _x /Ti-MWW	84.9	6.9	0.9	86.9		
Ru(OH) _x /Ti-MWW	56.7	28.2	1.9	66.7		
Rh₂O₃/Ti-MWW	76.6	34.2	5.9	45.5		
Rh(OH) _x /Al ₂ O ₃	25.3	24.3	30.9	44.1		
[a] Reaction conditions: catalyst, 0.2 g; benzaldehyde, 2 mmol; solvent (water), 1.5 g;						

ammonia aqueous solution (25 wt%), 2.5 mmol; hydrogen peroxide aqueous solution (5 wt%), 2.5 mmol; hydrogen peroxide aqueous solution (5 wt%), 2.5 mmol. The reaction was performed at 343 K by feeding H_2O_2 continuously within 30 min and then stirring the mixture at 413 K for another 7 h.

tion of the oxime into amides. Rh(OH)_x/Ti-Beta reasonably exhibited the lowest activity for the one-pot reaction, because Ti-Beta was not a useful catalyst for the ammoximation as we proved before.^[26] Besides, Ti-Beta (Si/Al = 50) had both weak and strong acid sites, presumably attributed to the silanol groups at defect sites and framework Si(OH)Al groups, respectively.^[26] The hydrophilic nature of BEA* zeolite adversely influenced the impregnation of Rh species and the catalytic performance in the transformation of oxime on Rh(OH)_x/Ti-Beta. In the case of Rh(OH)_x/Ti-MOR, the benzaldehyde conver-

sion was similar to that of Rh(OH)_{*}/Ti-MWW, but the benzamide selectivity was lower. This suggests that Ti-MOR is an active ammoximation catalyst, but not a suitable support for Rh species loading. In terms of amide formation, Rh(OH)_{*}/TS-1 exhibited a better performance than Rh(OH)_{*}/Ti-MOR and Rh(OH)_{*}/Ti-Beta, but it was less effective than Rh(OH)_{*}/Ti-MWW. Considering the Rh species were probably loaded on the external surface or large pores of titanosilicate crystallites, the unique structure of MWW, especially the 12-MR supercages within the framework and the 12-MR half cups, may provide a more accessible scaffold for supporting the rhodium species.

Based on the catalytic results, the possible reaction pathways involved in the one-pot synthesis of benzamide from benzaldehyde over Rh(OH)_x/Ti-MWW was proposed (Scheme 1).



Scheme 1. Possible reaction pathways involved in the one-pot synthesis of benzamide from benzaldehyde over $Rh(OH)_{x}/titanosilicate$.

Firstly, benzaldehyde is converted to the intermediate benzaldehyde oxime, which is catalyzed by the Ti active sites of Ti-MWW through ammoximation reaction. The benzaldehyde oxime intermediate undergoes rhodium hydroxide catalyzed dehydration-rehydration reaction to form benzamide, with a small amount of benzonitrile byproduct. The oxidation of benzaldehyde and hydrolysis of benzamide may bring out benzoic acid as a byproduct, but its amount detected in the one-pot synthesis of benzamide was only trace.

Effect of various parameters on the one-pot synthesis of amide over Rh(OH),/Ti-MWW

The solvent character strongly influenced not only the activity of Rh(OH)_x/Ti-MWW but also the product distribution. In Table S2, the catalytic performances of Rh(OH)_x/Ti-MWW in the one-pot synthesis of benzamide in different solvents are compared. The most favorable solvent for Rh(OH)_x/Ti-MWW was water, which gave a benzaldehyde conversion of 84.9%, a benzamide selectivity of 86.9%, and a benzonitrile selectivity 6.9%. Although the conversion of benzaldehyde was high in tBuOH or CH₃CN, benzamide was produced at a lower selectivity (10.9–65.9%). MeOH and 1,4-dioxane were not suitable solvents for the benzamide formation, and they seemed to be also less effective for the ammoximation of benzaldehyde. The above results confirmed that water was a suitable solvent in terms of benzaldehyde conversion and benzamide selectivity.

In Figure 3, the effect of Rh loading on the one-pot synthesis of benzamide over $Rh(OH)_x/Ti$ -MWW is investigated. A series of



Figure 3. Effect of rhodium content on the one-pot synthesis of benzamide over Rh(OH)_x/Ti-MWW. Reaction conditions: see footnote in Table 1.

Rh(OH)_{*}/Ti-MWW were prepared to have a changeable Rh content (1.0–3.0 wt%). The benzaldehyde conversion maintained over 80% irrespective of the Rh content, indicating the Ti-related ammoximation was little influenced by Rh loading. The benzamide selectivity increased with increasing Rh content, and was leveled off at 1.7 wt% Rh content. On the other hand, the selectivity of benzaldehyde oxime decreased sharply with increasing Rh content, indicating it was a reaction intermediate. Thus, 1.7 wt% of Rh loading on Ti-MWW was enough to give a high amide yield in the one-pot reaction under the reaction conditions investigated.

The ammoximation of aldehyde to oxime took place effectively at a relatively low temperature (343 K), but the rearrangement of oxime to amide required relatively higher temperatures. Thus, an obvious temperature effect on the one-pot synthesis of benzamide was observed if the reaction was performed at 1.7 wt% Rh loading and by using water as the solvent (Figure 4). Rh(OH)_x/Ti-MWW exhibited almost the same benzaldehyde conversion of ca. 85% if the reaction temperature of the second step was raised from 363 K to 433 K. The benzamide selectivity reached a maximum of 85% with in-



Figure 4. Effect of the reaction temperature in the second step of the onepot synthesis of benzamide over 1.7 wt% $Rh(OH)_x/Ti-MWW$. Reaction conditions: the reaction was performed at 343 K for 0.5 h (see footnote in Table 1), and then the temperature was raised to the desired temperature for another 7 h.

creasing temperatures up to 413 K, whereas the selectivity of benzaldehyde oxime decreased to 0.5%. If the reaction temperature was varied in the range of 363 K to 433 K, the amount of benzonitrile byproduct in the reaction mixture remained almost unchanged (<10%). Therefore, it was concluded that the optimum reaction temperature for amide formation was above 413 K.

To examine the product distribution in the reaction mixture with time on stream, we conducted the one-pot reaction over $Rh(OH)_x/Ti$ -MWW at a fixed temperature from beginning to end but at a relatively low temperature (363 K) for the sake of tracking the reaction easily. As shown in Figure 5, benzalde-



Figure 5. Effect of reaction time on the one-pot synthesis of benzamide over 1.7 wt % Rh(OH), $_x$ /Ti-MWW. Reaction conditions: see Table 1 footnote expect for the second step temperature of 363 K.

hyde conversion and benzaldehyde oxime selectivity increased to maximum values (> 90%) within 1 h after feeding H_2O_2 into the reaction solution, indicating that the reaction rate of ammoximation catalyzed by the Ti active sites was extremely rapid. At the same time, trace amounts of benzamide were detected. With the reaction proceeding, the selectivity of benzaldehyde oxime dropped below 10%, whereas the selectivity of benzamide increased monotonously with reaction time. The results reflect typical phenomena of a successive reaction. The final product of amide was produced from a tandem reaction with oxime as the intermediate. The benzamide selectivity reached 82.1% after the reaction proceeded for 24 h. Meanwhile, a small amount of benzonitrile was also detected. As the mechanism proposed by Mizuno, the transformation of aldoxime to amide includes a two-step route of dehydration of aldoxime to nitrile followed by hydration of the intermediate to produce the amide.^[24] However, the selectivity of benzonitrile byproduct increased only slightly during the whole tandem reaction and remained at a low level (<10%) at 24 h. These results confirmed that the Rh(OH)_x/Ti-MWW was an effective bifunctional catalyst in the one-pot synthesis of benzamide from benzaldehyde through tandem reactions. Notably, the benzaldehyde conversion decreased by about 10% from 1 h to 24 h (Figure 5), suggesting the hydration of oxime to aldehyde could be a competitive reaction with its rearrangement to amide.

Figure S3 reveals the effect of NH₃/benzaldehyde molar ratio on the one-pot synthesis of benzamide over 1.7 wt% Rh(OH)_x/ Ti-MWW by keeping the amount of benzaldehyde constant. In general, ammoximation of benzaldehyde requires stoichiometrically equivalent moles of NH₃ and benzaldehyde, but the NH₃ is easily evacuated out of the liquid-phase reaction solution. Therefore, the reaction should be performed at NH₃/benzaldehyde > 1. As shown in Figure S2, the benzaldehyde conversion was 85% at a NH₃/benzaldehyde ratio of 1.25. Both benzaldehyde conversion and benzamide selectivity reached over 90% if the NH₃/benzaldehyde molar ratio increased from 1.25 to 1.55. Thus, an excess amount of NH₃ was beneficial to achieve a higher aldehyde conversion and a higher selectivity to amide. However, if the molar ratio further increased to 2 or 3, the benzaldehyde conversion still remained at approximately 90%, but the benzamide selectivity dropped obviously. At the same time, the unconverted intermediate benzaldehyde oxime was detected. These results indicated that a too high excess of NH₃ was no longer in favor of the one-pot reaction, especially the second step for amide formation. The XRD pattern of the used catalyst, operated at an NH₃/aldehyde molar ratio of 3.0 was almost the same as that of the fresh one, indicating the strong basic media had little negative effect on the titanosilicate support (Figure S2). On the other hand, elemental analysis showed that the content of rhodium species on the Rh(OH)_x/ Ti-MWW-3.0 catalyst decreased, indicating it was partially leached out of the titanosilicates support during the one-pot reaction (Table S3). This was probably the reason why the benzamide selectivity dropped at an NH₃/aldehyde molar ratio of 3.0. The Rh content of Rh(OH)_x/Ti-MWW-1.25 remained the same with the fresh sample, implying that the slight excess of ammonia has little negative impact on the Rh species.

One-pot synthesis of amides from various aldehydes over Rh(OH)_x/Ti-MWW

After optimizing the reaction conditions, the one-pot syntheses of amides from various aldehydes were conducted over Rh(OH)_x/Ti-MWW (Table 3). Rh(OH)_x/Ti-MWW were catalytically active for the transformation of linear and branched aldehydes to the corresponding amides (Table 3, entries 1-3). The cyclic aldehyde was converted to the amide at an aldehyde conversion of 93.9% and an amide selectivity of 91.0% (entry 4). The unsaturated aldehyde was converted to the corresponding amide without epoxidation of the C=C double bond, but at a relatively lower selectivity (61.1%) (entry 5). The conjugation of C=C and C=N bonds in the unsaturated oxime seemed to retard its rearrangement to amide. In addition to its effectiveness for the above mentioned benzaldehyde, Rh(OH),/Ti-MWW was also effective to the one-pot synthesis of various amides from other aromatic aldehydes with substituents at different positions (entries 6–11). Especially, aldehydes containing heteroatoms such as fluorine and chlorine were also readily converted to the corresponding amides over Rh(OH)_x/Ti-MWW.

The reusability of Rh(OH)_x/Ti-MWW was checked in the onepot synthesis of benzamide. The used zeolite catalysts are usually regenerated by removing the residual organic species de-

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Table 3. One-pot synthesis of amides from various aldehydes over Rh(OH) _x /Ti-MWW ^[a]								
Entry	Substrate	Aldehyde conversion [%]	Product	Amide selectivity [%]				
1	n-C₄H₀CHO	98.5	n-C ₄ H ₉ CONH ₂	85.3				
2	n-C ₁₀ H ₂₁ CHO	90.1	<i>n</i> -C ₁₀ H ₂₁ CONH ₂	53.8				
3	∕_сно	56.8		85.4				
4	СНО	93.9	CONH ₂	91.0				
5	СНО	96.7	CONH	61.6				
6	СНО	80.6	CONH ₂	93.9				
7	F CHO	88.1	F CONH ₂	87.3				
8	CHO	89.7	CONH ₂ OMe	72.4				
9	CHO OMe	85.8	CONH ₂ OMe	86.4				
10	СНО	83.4		73.2				
11	СІСНО	77.3	CI CONH ₂	73.3				
[a] Reaction conditions: see footnote in Table 1. [b] Reaction temperature for the second step, 393 K. [c] Reaction temperature for the second step, 413 K.								

posited inside the pores. To preserve the Rh(OH)_x species from dehydration, Rh(OH)_x/Ti-MWW cannot afford calcination at high temperatures. Thus, it is critical to choose a suitable calcination temperature for catalyst regeneration. As shown in Table S4, with the calcination temperature increasing from 333 K to 723 K, the benzaldehyde conversion dropped gradually, indicating the catalyst regeneration should be performed at an optimum temperature. At a lower temperature of 333 K, residual organic species was not removed completely, whereas



Figure 6. Reuse of 1.7 wt % $Rh(OH)_{x}/Ti$ -MWW calcined at 473 K. Reaction conditions: see footnote in Table 1.

at a higher temperature of 723 K, aggregation of Rh species would occur. Thus, the catalysts regenerated both showed a low selectivity for benzamide. If the used catalyst was regenerated by washing with acetone first and then by calcination at an optimum temperature of 473 K, a relatively stable benzamide selectivity was achieved.

The benzamide selectivity declined gradually with the reaction-regeneration cycles, whereas the benzaldehyde conversion was maintained at the same level (Figure 6). However, the benzaldehyde oxime selectivity increased at the same time. This suggests that the benzaldehyde oxime thus produced could not be converted into benzamide efficiently. ICP analysis indicated that a part of the Rh species was leached during repeated reaction, which may account for the decrease in amide selectivity.

Reaction mechanism of the one-pot synthesis of benzamide over $Rh(OH)_x/Ti-MWW$

The reaction behaviors mentioned above implied that the onepot reaction mostly consisted of the ammoximation of benzaldehyde and the formation of benzamide through a sequential dehydration-rehydration reaction. To further confirm the reaction mechanism, we investigated the process of the one-pot synthesis of benzamide by using IR spectroscopy. The Rh(OH),/ Ti-MWW catalyst was punched into tablet and pre-evacuated in a guartz IR cell to remove adsorbed water and other species, and then one drop of substance was added onto the sample. As shown in Figure S5a, the adsorption of benzaldehyde on pre-evacuated Rh(OH)_x/Ti-MWW gave the characteristic band of C=O stretching at 1700 cm⁻¹. The band at 871 cm⁻¹ assigned to the N-O stretching was observed if the pre-evacuated sample was adsorbed with benzaldehyde oxime (Figure S5b). In addition, after one drop of benzamide was added to the pre-evacuated sample, a sharp adsorption band at 1660 cm⁻¹owing to C=O stretching together with a broad band at 1400 cm⁻¹ assigned to the overlapped stretching of C-N and N-H bond were observed (Figure S5 c). In the case of benzonitrile, a band at 2229 cm⁻¹ formed, which was caused by the C \equiv N stretching (Figure S5 d).

In Figure 7 a the IR spectrum of benzaldehyde adsorbed on pre-evacuated Rh(OH)_x/Ti-MWW is shown. Then, the sample was exposed to NH_3 for 15 min followed by introduction of one drop of 50 wt % H₂O₂ at 343 K, and a new band developed at 871 cm^{-1} together with the disappearance of the C=O stretching at 1700 cm⁻¹ (Figure 7 b). As mentioned in Figure S3b, the new band was assigned to the N-O stretching, indicating the formation of the intermediate benzaldehyde oxime. After the sample was heated at 423 K for 3 h and then cooled to room temperature, the N-O stretching band of the intermediate at 871 cm⁻¹ disappeared and a strong band at 1660 cm^{-1} assigned to C=O stretching of benzamide formed. Besides, a broad band at 1400 cm⁻¹ attributable to the overlapped stretchings of C-N and N-H appeared (Figure 7 c). These results indicate that the intermediate benzaldehyde oxime thus formed was converted to benzamide. In addition, a weak band attributable to the C \equiv N stretching at 2229 cm⁻¹



Figure 7. FTIR spectra of a) benzaldehyde, b) benzaldehyde oxime formation, and c) benzamide formation on 1.7 wt % $Rh(OH)_x/Ti-MWW$ (c).

formed, implying that the byproduct benzonitrile was also formed during the reaction process. This result further confirmed that benzonitrile was produced as the intermediate of aldoxime hydration and rehydration to form amide.

Water played an important role during the formation of benzamide. We have investigated the role of water in the second step of the one-pot reaction with FTIR technique. The FTIR spectra of the formation of benzamide directly from benzaldehyde oxime without or with water addition are shown in Figure 8b and 8c, respectively. Compared to the spectrum of



Figure 8. FTIR spectra of the a) one-pot formation of benzamide on 1.7 wt.% Rh(OH)_x/Ti-MWW; b, c) formation of benzamide directly from benzaldehyde oxime without or with water addition on 1.7 wt% Rh(OH)_x/Ti-MWW, respectively; and d) formation of benzamide directly from benzaldehyde oxime with water addition on Rh-free Ti-MWW.

one-pot formation of benzamide from benzaldehyde, ammonia, and hydrogen peroxide (Figure 8a), Figure 8b exhibited a more intensive band at 1700 cm⁻¹, assigned to the C=O stretching of benzaldehyde, but a weaker band at 1660 cm⁻¹ attributed to the C=O stretching of benzamide. This indicated that the benzaldehyde oxime was rearranged to the amide not effectively, but underwent decomposition partially to benzaldehyde. However, in the presence of water, a stronger band at 1660 cm⁻¹ attributed to the C=O stretching of benzamide developed (Figure 8c), suggesting benzaldehyde oxime preferred to transform into benzamide in the presence of water. For a control, if the direct rearrangement of benzaldehyde oxime was performed in the presence of water but over Rh-free Ti-MWW, a strong band at 1700 cm⁻¹ attributed to the C=O stretching of benzaldehyde was observed (Figure 8 d). This means that the catalytic transformation of benzaldehyde oxime to amide hardly occurred in the absence of Rh species, but the hydration of the oxime to benzaldehyde turned to be the main reaction.

In Scheme 2, the one-pot synthesis of amide is summarized graphically. The Ti active sites located in the Ti-MWW frame-



Scheme 2. Graphic illustration of the reaction mechanism of the one-pot synthesis of amide from aldehyde, ammonia, and $\rm H_2O_2$ over $\rm Rh(OH)_{s}/\rm Ti-MWW.$

work catalyze the ammoximation of benzaldehyde in the presence of H_2O_2 and NH_3 to produce benzaldehyde oxime. The ammoximation probably involves hydroxylamine as an intermediate. Diffusing to the Rh active sites located at the exterior of Ti-MWW, the oxime is then converted to benzamide through hydration and rehydration reactions.

Conclusions

Bifunctional catalysts that possess the ability for both aldehyde ammoximation and aldoxime rearrangement can be designed and synthesized by supporting rhodium hydroxide onto titanosilicate crystallites. Using organic bases of quaternary ammonium hydroxides instead of NaOH solution generated the Rh(OH)_x species but without poisoning the Ti active sites. Ti-MWW supported Rh species, Rh(OH)_x/Ti-MWW, was an efficient catalyst in the one-pot preparation of benzamide from benzaldehyde. The investigation with FTIR spectroscopy revealed that the one-pot synthesis of amide needed the cooperation of Ti-catalyzed ammoximation of aldehydes to aldoximes and Rh-related rearrangement of oximes to amides. Rh(OH)_x/Ti-MWW tended to lose the amide selectivity gradually in catalytic reuse, mostly because of a partial leaching of Rh active sites. This implies that more useful ways for stabilizing the $Rh(OH)_x$ species should be found, which would improve the reusability of titanosilicate-supported Rh catalysts.

Experimental Section

Synthesis of titanosilicates

Titanosilicates with different zeolite topologies (MWW, MFI, MOR, BEA*), that is, Ti-MWW,^[29,30] TS-1,^[37] Ti-MOR,^[27] and Ti-Beta,^[38,39] were synthesized by either direct hydrothermal synthesis or a post-synthesis method following the procedures reported previously.

Preparation of Rh(OH)_x/titanosilicate catalysts

Rhodium-loaded titanosilicates were prepared by modifying the procedures previously adopted for synthesizing Rh(OH)_x/Al₂O₃.^[23,24] In a typical preparation for Rh(OH),/Ti-MWW, Ti-MWW zeolite (1 g) was dispersed in an aqueous solution (30 mL) containing a desired amount of RhCl₃. The mixture was subjected to vigorous stirring for 3 h at RT, and then the solution color changed from red to orange. Thereafter, a desirable amount of organic guaternary ammonium hydroxide (1 M, TMAOH, TEAOH, or TPAOH) was added dropwise to the mixture under continuous stirring until the pH value reached approximately 9.After further stirring at ambient temperature for 24 h, the product was collected by filtration and washed repeatedly with ethanol. Then, the sample was vacuumdried at 333 K to remove the solvent, which resulted in Rh(OH),/Ti-MWW catalyst. For control experiments, Rh(OH),/TS-1, Rh(OH),/Ti-MOR, and Rh(OH)_x/Ti-Beta were prepared by the same procedure. Ru(OH)_x/Ti-MWW was also prepared by the above mentioned method but replacing RhCl₃ with RuCl₃. Rhodium oxide supported Ti-MWW, Rh₂O₃/Ti-MWW, was obtained by the incipient wetness impregnation method followed by calcination at 773 K in air.

Characterization methods

XRD patterns were recorded on a Bruker D8 ADVANCE diffractometer (CuK_a) to check the crystallinity of the samples. The amounts of Si, Ti, Ru, and Rh were quantified by ICP analysis on a Thermo IRIS Intrepid II XSP atomic emission spectrometer. The UV/vis diffuse reflectance spectra were recorded on a Shimadzu UV-2550 spectrophotometer by using BaSO₄ as a reference. XPS spectra were recorded with a PHI Quantum 2000 Scanning ESCA Microprobe equipment by using monochromatic AIK_{α} radiation. The IR spectra were collected on NicoletNexus 670 FTIR spectrometer in absorbance mode at a spectral resolution of 2 cm⁻¹. For in situ IR measurements, the sample was pressed into a self-supported wafer of 4.8 mg cm⁻² thickness. The wafer was set in a guartz IRcell that was sealed with CaF₂ windows and connected to a vacuum system. After the sample was evacuated at 423 K for 2 h to remove adsorbed water and then cooled down to RT, one drop of benzaldehyde was added onto the sample. Then the sample was exposed to NH₃ at 343 K for 15 min followed by introducing one drop of H_2O_2 (50 wt %) onto the sample. Furthermore, the IR cell was heated at 423 K for 3 h. After cooling down to RT, the IR spectra were finally recorded.

Catalytic reactions

The liquid-phase ammoximation of benzaldehyde with H_2O_2 and NH_3 was performed in a 20 mL batch reactor. The mixture containing catalyst (50 mg), H_2O (5 g), benzaldehyde (10 mmol), and am-

monia (12 mmol) of a 25 wt% ammonia solution was stirred vigorously at 343 K. H₂O₂ (12 mmol) was continuously added to start the reaction at a constant rate with a micropump for 1 h. Then, the mixture was left to react for another 0.5 h. The liquid-phase one-pot synthesis of benzamide was performed in a 25 mL Teflonlined autoclave with a magnetic stirrer. For a typical reaction, a desired amount of catalyst, solvent (1.5 g), benzaldehyde (2 mmol), ammonia (2.5 mmol) of a 25 wt % ammonia aqueous solution were charged into the reactor and heated under stirring at 343 K. H₂O₂ (12 mmol) of a 5 wt% H₂O₂ aqueous solution was added continuously within 0.5 h to start the reaction. The reaction temperature was then raised to the desired temperature, at which the reaction mixture was stirred for 0.5-23.5 h. The one-pot synthesis of amides from other aldehydes was performed by using the same procedures. The reactant conversion and product selectivity were determined on a gas chromatograph (Shimadzu 14B, FID detector) equipped with a 30 m DB-WAX capillary column. Ethanol (10 mL) was added to homogenize the reaction mixture, and the catalyst powder was removed by centrifugation. The products were identified with authentic substances or with GC-MS (Agilent-6890GC/ 5973MS). Unconverted H₂O₂ was determined by iodometric titration.

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