

New Supported [Ru₆N] Clusters as a Potential Transition Metal Nitride Catalyst

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Nitrido-ruthenium cluster [Ru₆N] catalysts were prepared by reacting [Ru₆N(CO)₁₆]⁻ cluster with MgO, K⁺-doped MgO or Cs⁺-doped MgO as a potential ruthenium nitride catalyst. The [Ru₆N] unit remained in reaction conditions, and exhibited higher activities in ammonia synthesis than conventional Ru catalysts or Ru clusters prepared from [Ru₆C(CO)₁₆Me]⁻ or [Ru₆(CO)₁₈]²⁻.

Metal clusters are expected to be effective catalysts associated with multiple metal sites. Specific activities to oxygenated compounds (MeOH, H₂CO, Me₂O) from CO + H₂ were reported on carbido-Ru clusters [Ru₆C] supported on MgO, La₂O₃, or TiO₂.¹⁻³ Reversible expansion/shrink of [Ru₆C] framework observed by EXAFS in the CO-H₂ reaction conditions facilitated the access to Ru sites and dissociation of H₂ by elongating the Ru-Ru distance.^{1,2,4} In this paper, we report the formation of new nitrido-Ru clusters [Ru₆N] on oxides and catalysis promoted by nitrido nitrogen.

[N(PPh₃)₂]⁺[Ru₆N(CO)₁₆]⁻ **1**⁵ was supported on MgO, K⁺/MgO, Cs⁺/MgO, or Al₂O₃ by reaction at 290 K (1h) in purified THF in Ar atmosphere, and the subsequent removal of THF in vacuum. The MgO (surface area 200 m²g⁻¹) was prepared from Mg(OH)₂ (99.99%) by heating at 773 K (2h) in vacuum. Water solution of Cs₂CO₃ or K₂CO₃ was impregnated on MgO, followed by treatments in O₂/H₂ at 773 K. The Al₂O₃ (aerosil C) (100 m²g⁻¹) was treated at 623 K (2h) in vacuum. The loadings of Ru were 2.5wt% for MgO, K⁺/MgO, and Cs⁺/MgO, and 1.6wt% for Al₂O₃. The supported nitrido-Ru clusters are denoted as [Ru₆N]/oxide. [N(PPh₃)₂]⁺[Ru₆C(CO)₁₆Me]⁻ or [N(PPh₃)₂]⁺[Ru₆(CO)₁₈]²⁻ **2** was supported on MgO in a similar manner to the case of **1**. These supported Ru clusters are denoted as [Ru₆C]/MgO and [Ru₆]/MgO, respectively. The conventional Ru/MgO, Ru-Cs⁺/MgO, and Ru/Al₂O₃ catalysts were prepared from Ru(NO)(NO₃)₃ (Ru 2.5 wt%).

The N₂-H₂ reactions were carried out under 101 kPa of reaction gas ($\bar{P}_{N_2}/\bar{P}_{H_2} = 1/3$) at 588 K in a flow system (flow rate 60 cm³ min⁻¹). The H₂-D₂ exchange reactions were carried out under 6.7 kPa of H₂ and 6.7 kPa of D₂ at 273 K in a closed circulating system (100 cm³). As pretreatment, incipient supported clusters were heated in vacuum at 813 K except for [Ru₆N]-Cs⁺/MgO and [Ru₆N]-K⁺/MgO (673 K), followed by treatment in H₂ (T_{H₂} = 588 - 773 K). The temperature in H₂ was specified at the end of denotation such as [Ru₆N]/MgO-588H for sample treated in H₂ at 588 K. Produced ammonia was analyzed by the decrease of electron conductivity of 0.004 - 0.002 N-H₂SO₄ solution. The observed turnover frequencies (TOF) were expressed in the unit '10⁻² min⁻¹' in the text, where all the Ru atoms were regarded as active sites except for the conventional Ru catalysts. The numbers of surface Ru atoms were estimated by the H₂-adsorption measurements for conventional catalysts. The TOF of H₂-D₂ exchange reactions on supported clusters and conventional Ru catalysts are shown in Table 1. The order was [Ru₆N]/MgO-588H (2600) > [Ru₆C]/MgO-588H (2400) > [Ru₆N]-Cs⁺/MgO-588H (1900) > [Ru₆C]/MgO-773H (700) ~

[Ru₆]/MgO-588H (700) >> [Ru₆N]/Al₂O₃-588H (34) >> conv. Ru/MgO (1.3). The supported [Ru₆N] clusters treated in H₂ at 588 K were comparable to supported [Ru₆C], and superior to supported [Ru₆] or conventional Ru catalysts for hydrogen activation.

As an example of hydrogenations, the N₂-H₂ reactions (588 K) were examined related to this hydrogen activation (Table 1). The TOF of supported nitrido-Ru cluster on MgO when treated in H₂ at 588 K (1.8) were superior to the conventional Ru/MgO (0.20) or the Ru catalysts in the literature.⁶⁻⁸ The TOF was further enhanced when nitrido-Ru cluster was supported on K⁺/MgO or Cs⁺/MgO (3.2 - 6.6). The [Ru₆N]/Al₂O₃ exhibited no activities after the H₂-treatment at 588 - 773 K though conventional Ru/Al₂O₃ produced ammonia (0.11) (Table 1).

The dependence of TOF for ammonia synthesis on the kind of precursor clusters (or Ru salt) on MgO were in the order [Ru₆N(CO)₁₆]⁻ (0.28 - 1.8) > [Ru₆C(CO)₁₆Me]⁻ (0.27 - 1.2) > [Ru₆(CO)₁₈]²⁻ (0.22) > Ru salt (0.20) (Table 1). The [Ru₆N]/MgO was superior to [Ru₆C]/MgO by 1.5 times, and superior to the others in the order in the comparison for the samples in H₂ at 588 K. It should be noted that the activities on [Ru₆N]/MgO and [Ru₆C]/MgO had strong dependence on T_{H₂}. The TOF for [Ru₆N]/MgO-773H (0.28) was only 15% of that for [Ru₆N]/MgO-588H (1.8), whereas the dependence on T_{H₂} was not observed for [Ru₆]/MgO treated in H₂ at 588 - 773 K. We studied temperature programmed reduction (TPR) in H₂ by mass spectroscopy for incipient [Ru₆N]/MgO, [Ru₆N]-Cs⁺/MgO, and [Ru₆]/MgO. These spectra had common peaks of NH₃ around 510 K, but higher temperature-peaks of NH₃ was observed around 660 K only for [Ru₆N]/MgO and [Ru₆N]-Cs⁺/MgO. As the former desorption temperature (around 510 K) coincided with the decomposition temperature of the IR peak of [N(PPh₃)₂]⁺ (cation of clusters **1** and **2**) (1117 cm⁻¹), we believe that the peak around 660 K was originated from nitrido N of **1**. The corresponding TPR in H₂ for [Ru₆C]/MgO (carbido C desorbed as CH₄) had a peak around 560 K,¹ suggesting that this cluster transformation was the cause of the TOF decrease from 1.2 (T_{H₂} = 588 K) to 0.27 (773 K) (Table 1). Based on the Ru K-edge EXAFS (KEK-PF, BL10B, proposal No. 93G010), the coordination numbers of Ru-Ru bonding (N_{Ru-Ru}) were suggested to be about four (4.0 - 4.1) for [Ru₆N]/MgO, [Ru₆N]-K⁺/MgO, and [Ru₆N]-Cs⁺/MgO after heating in vacuum (813 or 673 K) and in H₂ (588 K), similar to the value for cluster **1** (= 4), indicating that the [Ru₆N] unit remained on MgO, K⁺/MgO, and Cs⁺/MgO compared to the Ru trimers such as MgO-supported Ru₃(CO)₁₂ (in H₂ at 723 K) (N_{Ru-Ru} = 1.7)² and [Ru₆N]/Al₂O₃-588H (2.0) or aggregated clusters such as [Ru₆N]/MgO-773H (6.6) and [Ru₆]/MgO-588H (6.2). The distances of Ru-O_s (oxygen at surface) were 0.213 - 0.217 nm on MgO and 0.200 - 0.207 nm on K⁺/MgO, and Cs⁺/MgO. The [Ru₆C]/MgO lost carbido C and was transformed to [Ru₆] on MgO in H₂ at 623 - 773 K.¹ Hence, the TOF ratio of [Ru₆N] : [Ru₆C] : [Ru₆] species on MgO was 100 : 67 : 14 from Table 1. Both [Ru₆N] and [Ru₆C] were very good for the H₂ activation, especially in

Table 1. Turnover Frequencies (10^{-2} min^{-1}) of Ammonia Synthesis (588 K) and H_2 - D_2 Exchange Reactions (273 K) on Supported $[\text{Ru}_6\text{N}(\text{CO})_{16}]^-$, $[\text{Ru}_6\text{C}(\text{CO})_{16}\text{Me}]^-$, or $[\text{Ru}_6(\text{CO})_{18}]^{2-}$ Clusters, and Conventional Ru Catalysts

T_{reac}/K	588	273	
$P_{\text{N}_2}/\text{kPa}$	25.3		
$P_{\text{H}_2}/\text{kPa}$	76.0	6.7	
$P_{\text{D}_2}/\text{kPa}$		6.7	
sample	T_{H_2}/K		
$[\text{Ru}_6\text{N}(\text{CO})_{16}]^-/\text{MgO}$	588	1.8	2600
	773	0.28	970
$[\text{Ru}_6\text{N}(\text{CO})_{16}]^- \cdot \text{K}^+/\text{MgO}$	588	3.2	
$[\text{Ru}_6\text{N}(\text{CO})_{16}]^- \cdot \text{Cs}^+/\text{MgO}$	588	6.6	1900
$[\text{Ru}_6\text{C}(\text{CO})_{16}\text{Me}]^-/\text{MgO}$	588	1.2	2400
	773	0.27	700
$[\text{Ru}_6(\text{CO})_{18}]^{2-}/\text{MgO}$	588	0.22	700
	conv. Ru/MgO	773	0.20
conv. Ru- Cs^+/MgO	773	1.7	
$[\text{Ru}_6\text{N}(\text{CO})_{16}]^-/\text{Al}_2\text{O}_3$	588	0	34
	conv. Ru/ Al_2O_3	773	0.11

The dispersions of ruthenium (H/Ru) for supported cluster catalysts were assumed to be 100%.

the conditions that they kept the $[\text{Ru}_6\text{X}]$ ($\text{X} = \text{N}, \text{C}$) cluster unit. The activities of N_2 - H_2 reactions obeyed similar tendency, but the

effects of support oxides and interstitial hetero atoms (N, C, or none) as electron donor⁹ were also important, probably to the N_2 dissociation process. The detailed discussion on promoted ammonia synthesis on $[\text{Ru}_6\text{N}]$ clusters accompanied with cluster expansion/shrink ($r_{\text{Ru-Ru}} = 0.263 \pm 0.271 \text{ nm}$) will be reported in a separate paper based on EXAFS at different Ru wt% (0.48 - 3.9 wt%), *in-situ* EXAFS in H_2 or in N_2 , *in-situ* IR, and H/D inverse isotope effects.¹⁰

References and Notes

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